BOOK OF ABSTRACTS

(as of 23 August 2010)

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The European Corrosion Congress

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THE EUROPEAN CORROSION CONGRESS

From the Earth's Depths to Space Heights

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As of 23 August 2010

О КОМПАНИИ TOKYO BOEKI

Японская фирма TOKYO BOEKI была основана в октябре 1947 года и, в настоящее время, объединяет 20 дочерних компаний, действующих по всему миру: в Японии, США, Австралии, Корее, Китае, России и некоторых других странах. В октябре 2009 года компания отмечала 50-летие Московского представительства.

Будучи одной из самых стабильных и надежных японских торговых компаний, работающих в России, TOKYO BOEKI, прежде всего, известна как официальный представитель ведущих японских производителей научно-аналитического и промышленного оборудования: JEOL (электронные микроскопы, системы микроанализа, приборы для обработки и анализа поверхности, системы пробоподготовки), NIKON (промышленное оптическое оборудование, лазерная конфокальная и световая микроскопия, инспекционное оборудование), RIGAKU (рентгеновские дифрактометры, рентгенофлюоресцентные элементные анализаторы, промышленное оборудование для неразрушающего контроля), фирмы YAMATO SCIENTIFIC (лабораторное оборудование, промышленная рентгеновская томография), SPSS SYNTEX (исследовательское и промышленное оборудование для искрового плазменного спекания), ULVAC – вакуумные печи, системы нанесения покрытий, DENYO – сварочное оборудование, KIP – инженерные системы.

Кроме того, фирма поставляет в Россию оборудование английских, американских и немецких компаний, таких, как OXFORD INSTRUMENTS ANALYTICAL (системы для микроанализа), GATAN (приставки к электронным микроскопам, системы пробоподготовки) и др.

Мы предоставляем нашим заказчикам весь спектр услуг: поставка оборудования, гарантийное и послегарантийное обслуживание, поставка запчастей, обучение персонала и т. п. Со многими нашими клиентами мы продолжаем сотрудничать на постоянной основе уже более 50 лет.

Для того, чтобы обеспечить наших клиентов качественным гарантийным и послегарантийным сервисным обслуживанием, TOKYO BOEKI совместно с производителями организовывает сервисные службы по всем видам поставляемого оборудования: заводская сервисная служба JEOL в Москве, где работают несколько японских и российских сервисных инженеров, заводская сервисная служба OXFORD INSTRUMENTS в Москве по обслуживанию систем микроанализа, установленных на приборы JEOL. TOKYO BOEKI, имеет свой штат инженеров, сертифицированных производителями оборудования (RIGAKU, NIKON и др.).

TOKYO BOEKI постоянно стремится максимально полно и всесторонне соответствовать требованиям наших заказчиков. Российское подразделение компании - ООО «Токио Боэки (РУС)» берет на себя весь комплекс работ по импорту продукции в Россию, ее таможенной очистке, сертификации и т.п.

Мы всегда готовы к взаимовыгодному сотрудничеству!

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Workshop on Nanotechnologies

Invited Plenary Lectures

Progress in Corrosion Inhibition and Modification of Protective Nanolayers on Metals

Yu. I. Kuznetsov
A.N. Frumkin Institute of Physical Chemistry and Electrochemistry of Russian Academy of Science, Moscow, Russia
E-mail: kuznetsov@ipc.rssi.ru

Nowadays the methods of corrosion inhibition continue to be developed very intensively. It is precisely corrosion inhibitors (CI) are often capable forming the ultrathin (nanosize) layers at metals, which could be successfully used for corrosion control. The utmost layers are formed as the result of the adsorption of CI or CI reaction with the cations of the metal to be protected. The ellipsometric investigations of adsorption of various CI allow~~s~~ an understanding of the adsorption («oxide-free») passivation of iron by sodium phenylanthranilate (SPA), which was discovered in the mid 1970s. Enhancement of the efficiency of adsorption passivation is demonstrated through the use of more hydrophobic substituted SPA. For example, adsorption of sodium fluphenaminate (SFP) begins at concentrations six exponents lower if compared to SPA. It is described by the Temkin isotherm with ΔG^0_A = 56.5 kJ/mol, which is 3.6 times higher than the ΔG^0_A estimated for SPA. Of even greater importance is the fact that compositions on their base are more effective CI than substituted SPA itself. It is often associated with the ability of one component of mixture to initiate the adsorption of the other one. The above said became the reason for the research of adsorption films design under the conditions of the successive adsorption of CI components. It was shown that preliminary chemisorption of some CI can stimulate an increase in ΔG^0_A for many other CIs. Examples are presented of the positive impact of purposeful change of design of protective films of organic CIs on the protective capability of these CI, e.g. in moist atmosphere. The conclusion of this work is that using passivating treatment of metal surface by “layer by layer” method can provide the best protection against atmospheric corrosion. Progress in developing the aqueous non-toxic composition to obtain conversion coatings and their passivation are discussed. The new methods of metal passivation offer wide possibilities of very effective anti-corrosion protection in prolonged storage, in technological fluids, etc.

In other part of lecture the state-of-the-art of research dealing with the development and perfection of complex-forming CI is analyzed. Attention is focused on two main mechanisms of action of CI. The first of them is related with the ability of many CIs (azoles, phosphonates, etc.) to form insoluble complexes with cations of metal being protected. The second mechanism is more complex, but it can provide very effective protection of metal. It involves not only adsorption but also surface reactions of the electrophilic substitution of complex-forming cations, deposition of barely soluble hydroxides and formation of hetero- and polynuclear complexes. Ways of creating mixed effective CI and other possibilities of application of complex formation (e.g. antagonism of action of two depassivators) are considered.

Progress in protection of metals with the volatile CIs is briefly demonstrated. It is noted that they can not only protect various metals under intense moisture condensation conditions, often in the presence of H_2S and CO_2, but also increase protective action of conversion coatings. Combination of CIs with other means and methods of metal protection from corrosion is one of their promising applications. Some examples of applying such combined protection of metals are analyzed.

Study on the Current Fluctuations during the Early Stage of Pitting Corrosion

Yu Zuo, Yuming Tang
School of Materials Science and Engineering
Beijing University of Chemical Technology, Beijing 100029, China
E-mail: zuoy@mail.buct.edu.cn

Electrochemical noises are observed during the early stage of pitting corrosion in many metal/solution systems. Generally the electrochemical noises are considered as the results of early stage of pitting corrosion, or metastable pitting, and reflect the nucleation, growth and repassivation of metastable pits on materials surface. Hence the electrochemical noises are closely related to the stable pitting corrosion and may provide information not only on the mechanism of early stage of pitting but on the prediction of pitting tendency in the system. In this paper, the current fluctuations of stainless steels, carbon steels and pure iron during metastable pitting in chloride containing solutions were analyzed and the purpose of the work was to find the relationships between the metastable pitting parameters and stable pitting tendency. Following results were observed:

1. Many current fluctuations were observed for 316L stainless steel in chloride solution at constant potentials below the pitting potential. When current record was divided into several time intervals, the maximum peak currents in different time intervals during potentiostatic test followed extreme distribution. The extreme distribution changed with changes of potential and chloride concentration in the solution.
2. The relationship between peak current and average growth rate of metastable pits on 316L stainless steel was analyzed. The peak currents of metastable pits did not increase simply with increase of the propagation rate. A middle growth rate range was beneficial for formation of relatively larger metastable pits. This middle growth rate range was consistent with the growth rates of stable pits under the same condition. As the solution chloride concentration increased, the growth rate range which is suitable for growth of metastable pits moved in increased direction.
3. For carbon steels and pure iron, the pit size distribution calculated from the current fluctuations was very close to that observed with SEM, indicating good correlation between current fluctuations and growth process of metastable pits. A bigger pit may be composed of several smaller pits, and several local dissolution events around a certain active site caused accumulated corrosion damage. Corrosion products may pile up at pit mouth and lead the pit to an occluded state, thus metastable pitting process was replaced by stable pitting.

The above results show that it is possible to trace the early pitting process and to predict pitting tendency and possible pitting rate in certain environment by analyzing the current fluctuations during metastable pitting process.

The effects of air pollution and climate on materials including cultural heritage

Johan Tidblad (johan.tidblad@swerea.se)
Swerea KIMAB AB, Drottning Kristinas väg 48, SE-11428 Stockholm, Sweden

Abstract

Atmospheric corrosion was during the 20th century marked by the industrial revolution and the increasing emissions from coal burning and SO_2 was seen as the most important pollutant that accelerates atmospheric corrosion of materials. Knowledge of atmospheric corrosion processes was mainly developed in industrial countries for technical materials in the temperate zone and the effect of climate was seen as a constant background on top of which the effect of pollutants and other aggressive substances was added. During the end of the 20th century to today several trends are emerging that changes our view of atmospheric corrosion.

In many industrialised countries SO_2 levels are today very low and corrosion is no longer decreasing in urban areas even if the corrosion levels can be more than twice of that in surrounding rural areas. In order to assess the total corrosion, several individual contributions must be considered and thus the term “multi-pollutant situation” was coined. Technical constructions are still suffering but the loss of our cultural heritage is a new major concern.

SO_2 levels in many tropical and subtropical countries are still high and show no substantial decreasing trend. Knowledge derived from field exposures in the temperate climate are in many cases useful to predict corrosion but can also be misleading. Corrosion can under some circumstances be very high in these countries and this has lead to the proposal of an extra class above C5 in the present revision of ISO 9223 (Corrosion of metals and alloys - Corrosivity of atmospheres - Classification).

Further reducing air pollutants are one of the more effective ways of compensating for increased risk of corrosion due to climate change. However, the mitigation strategies for climate change are not necessarily reducing the corrosivity of atmospheres. There is therefore a risk of increased corrosion in the future, depending on the location, both due to changes in the climatic situation and due to changes in the pollution situation optimised only for the benefit of reducing effects of climate change.

Atmospheric corrosion is not untouched by the computer technology and increased availability of information. Dose-response functions relating corrosion to the environment are no longer of only academic interest. The use of GIS software and availability of environmental data makes the manufacturing of colourful maps of corrosion a relatively simple process. These maps are very powerful when communicating results, inviting for use and abuse by people outside the corrosion community.

Composite Polymer Protective Coatings for Use in Aggressive Media

V.A. Golovin
Russian Academy of Science, N.A.Frumkin Institute of Physical Chemistry and Electrochemistry, Moscow, Russia, golovin@rocor.ru

Polymers serve as a basis for developing composite materials with outstanding properties for a variety of technological applications. It appears advisable to adopt this approach in order to develop state-of-the-art polymer protective coatings for use in a wide range of aggressive media.

This report looks at the principal physical and chemical processes on which the operational capability of composite polymer protective coatings depends, insofar as these apply to coatings designed for use in highly aggressive media and under stringent operating conditions.

Special attention is paid to mass transfer processes occurring in aggressive media, notably to sorption, diffusion and possibility of a selective binding of the medium by a polymer or by special additives. Methods for studying diffusion and sorption in aggressive media are considered. Integrated data are provided on profiles of aggressive media concentration in anticorrosive polymers and on anticipated rates of aggressive component penetration through the coating to the protected substrate. Attempts to develop polymer coatings acting as a total diffusion barrier similar to metal or glass enamel coatings are shown to lack feasibility. Potential for using a protective polymer coating as a selectively permeable layer is considered.

The principal types of coating faults are considered, as well as their contribution to mass transfer processes and initiation of coating disintegration. A mechanical stability model for spot adhesion faults in thick linings has been developed, integrating the fault size with the in-service tolerance for adhesion and internal stress.

In order to enhance the operational capability of coatings in aggressive environments a concept of sandwich construction has been proposed that would ensure an optimal arrangement of linings with diverse physical and chemical properties and features.

The impact of a multilayered coating construction on coating properties is considered. It is shown that optimizing a multilayered structure dramatically reduces permeability to highly aggressive media, eases the overall internal stress, and reduces stress localization in dangerous spots of both coating and substrate.

The concept of a multilayered coating construction makes it possible to build up a special layer that adheres to metal and is supposed not only to possess a certain mix of mechanical properties but also to ensure the required, preferably constant, adhesion strength under the impact of penetrating medium. In particular, this adhesion layer is an ideal place for putting corrosion inhibitors and protective additives to work, provided that overlying linings prevent inhibitor washout and reduce the inflow of aggressive medium, thus enhancing the impact of protective additives.

Controlled diffusion properties make the concept of a multilayered coating construction especially useful for the development of environmentally friendly coatings.

Based on the proposed concept, examples are given of development of certain state-of-the-art polymer coatings for a variety of critical applications.

Lecture Programme

Automotive Corrosion

Recent trends of surface coated steel for automotive panels

*Jongsang Kim, Yonkyun Song, Sang-Keol Noh, Changhoon Choi, Jaedong Choi,
Yonho Kim, Changgyun Jung and Jongki Oh*

POSCO Technical Research Laboratories, 699, Gumho-dong,
Gwangyang-si, Jeonnam, 545-090, Korea
E-mail: petersong@posco.com

Corrosion protection of steel has been a major concern to researchers in steel industry. Metallic, inorganic and organic coating technologies have been employed to enhance corrosion resistance. Technical issues of steel industry change along with other industrial progresses. Recently, requirements for steel have become more diversified. More various surface and material properties are required from different field of applications.

Naturally, functional surface coating has become one of the most studied areas in steel industry to open a new next generation steel market. For functional surface coating, various process technologies and coating products are investigated. Nano and UV technology are employed to give various functions. In terms of automotive industry, The hot dip galvanized

(HGI), galva-annealed steel (HGA) and electroplated zinc (EG) steel have been used for the base material for automotive panels. Many efforts to apply Al-alloy and Mg sheet have been done to reduce the weight auto-body.

Lubricant GI and GA are introduced to avoid galling effect during press forming. The lubricant lacquer and coating technique on HGI and HGA would be main technologies to improve competitiveness. Resin coated Zn-Ni is competitive with plastic for fuel tank. As bio fuels are expected to replace conventional fossil fuels, corrosion troubles by the degradation of bio-fuels and condensed water which has never been experienced would be a key factor to determine the fuel tank material.

In this article, recent trends of functional coating technologies for automotive panels and general purpose are introduced with brief technical descriptions of representative coating products.

Corrosion resistance of hot-stamping Usibor steels for automobile light-weighting

L. Dosdat, O. Clauzeau, J. Petitjean, T. Vietoris
ArcelorMittal Global R&D Maizières Automotive Products, France

Abstract

In order to meet the environmental requirements concerning the automotive industry, a lot of efforts are put into weight reduction of car components. The hot stamping of very high strength steels makes this goal possible: their use to produce structure and safety parts showing exceptional mechanical properties can lead to weight savings up to 50% compared to standard high yield strength steel. The direct hot-stamping process consists in austenitizing blanks in the heat treatment oven, then in stamping these hot blanks in a press and in water-quenching in the tool. On the other hand the indirect hot stamping demands a cold pre-forming step but can produce more complicated geometries.

ArcelorMittal's Usibor AluSi is a steel for direct hot stamping with an ultimate tensile strength of about 1500 MPa. The boron steel substrate 22MnB5 is pre-coated by a continuous hot-dip aluminum-based metallic coating, changing to a multilayer Al-Si-Fe coating during the hot-stamping process. This coating allows the highest hot stamping robustness, with lower cost. However, ArcelorMittal also developed zinc-based solutions offering sacrificial protection: galvanized Usibor GI which requires an indirect hot stamping, and galvannealed Usibor GA which is more cost effective since it can be used as well with direct process.

The corrosion resistance of all these press-hardened coated steels, including the bare 22MnB5, was evaluated and compared to the one of a standard galvanized mild steel reference, using the cyclic test VDA 621-415.

After 10 weeks, the measurement of creepback from scribe lines done on e-coated parts formed in laboratory reveals that Usibor GA and Usibor GI have better cosmetic corrosion resistance compared to Usibor AluSi. However, the red rusting developed on shear-cut edges gives a quite different positioning of the various materials in terms of cut-edge corrosion resistance, seeing that Usibor AluSi is much closer to Usibor GA and Usibor GI, all of them better than bare 22MnB5. Standard galvanized steel – which is not heat-treated, so has no iron in the coating after stamping – is the only material showing white rust.

Moreover, cross-section examinations and quantification of attack depths on walls of hot stamped parts after 15 weeks of the accelerated corrosion test indicate a similar very good perforating corrosion resistance of all coated Usibor products (lots of residual coating, very limited pitting in base metal). They behave at least as good as standard galvanized reference (not heat-treated), and much better than bare 22MnB5. These results have been confirmed with other accelerated corrosion tests (KWT-D Daimler test, GMW test), showing the great potential of hot stamped coated steel.

ROLE OF ALLOYING ELEMENTS FOR IMPROVED CORROSION RESISTANCE OF ZN-AL-MG COATINGS ON STEEL

Polina Volovitch[1], Christian Allely[2], Alsayed A. Aal[1,3], G. Lefevre[1], Kevin Ogle[1]

[1]LPCS, CNRS UMR7045, Ecole Nationale Supérieure de Chimie de Paris, 11 rue Pierre et Marie Curie, 75231 Paris Cedex 05, France
E-mail: polina-volovitch@chimie-paristech.fr
[2] ArcelorMittal Research SA, 57283 Maizières-lès-Metz, France
[3] Surface Protection & Corrosion Control Lab, Central Metallurgical Research & Development Institute (CMRDI), P.O. 87 Hellwan, Cairo, Egypt

The corrosion resistance of hot dip Zn-Al-Mg coated steels is much higher than that of conventional zinc coated steels. In the present work the corrosion inhibitive role of Mg and Al in Zn-Al-Mg coatings is considered for both early and later stages of corrosion. Corrosion product characterization was carried out using X-ray diffraction, infra-red spectroscopy, scanning electron microscopy with X-ray microanalysis on technical Zn-Al-Mg coatings after various exposure times in cyclic corrosion tests with NaCl or Na_2SO_4 containing atmosphere. The results are compared with thermodynamic modeling and electrochemical measurements as well as in-situ atomic emission spectroelectrochemistry, and point out the predominant effect of magnesium. The improved corrosion resistance of Zn-Al-Mg alloys compared with Zn-Al alloys in the early stages of corrosion is indeed correlated with the stabilization of the crystalline forms of basic zinc salts (like simonkolleite, hydrozincite etc.) in presence of Mg^{2+} against their transformation into smithonite ($ZnCO_3$), amorphous hydrozincite and zincite (ZnO) during ageing cycles in presence of CO_2. At this stage, Al remains on the coating in an insoluble form because of the nearly neutral pH. This is in accordance with the absence of an Al rich corrosion product on the surface of the corroded samples. Further evidence for this mechanism comes from in-situ atomic emission spectroelectrochemical experiments showing a strong preferential dissolution of Zn and Mg in the early stages of exposure to the electrolyte. At more advanced stages, the pH of the system increases sufficiently for Al dissolution to occur. The presence of Al3+ in the solution inhibits corrosion by two different mechanisms: (1) by buffering the pH of the electrolyte around 9.2 due to the precipitation of $Al(OH)_3$ thereby preventing the dissolution of zinc based corrosion products into soluble hydroxide complexes and promoting the formation of simonkolleite in place of zincite (ZnO); and (2) by promoting the formation of double based salts (layered double hydroxides, LDH) which seem to have interesting properties for corrosion protection. The protective action of different corrosion products is discussed in terms of their physical - chemical properties and their crystallographic structures.

New Applications Outlook for Magnesium Alloys

Prof. Vladimir Kechin, Vladimir State University,
87 Gorky St., 600000 Vladimir, Russia
Prof. Efim Lyublinski, Northern Technologies International Corporation
23205 Mercantile Rd., Beachwood, OH 44122, USA

Abstract

A wide range of industrial applications of magnesium and its alloys is well-known. Magnesium alloys have excellent mechanical properties. They are highly-durable and posess the ability to absorb shock and vibrating loadings. Magnesium alloys have a low density and are convenient for cutting.

In a number of applications, magnesium alloys are the most cost-effective metals. At the same time, in many industrial conditions, magnesium alloys cannot be recommended due to their inherent susceptibility to corrosion in aggressive environemnts. This paper summarizes the data of corrosion resistance of magnesium and magnesium alloys in different industrial environments. Results that show the ability to increase the corrosion resistance of magnesium and magnesium alloys, by using special heat treatment technologies and applying nanocoatings, are discussed.

Keywords: magnesium, alloys, environment, corrosion, heat treatment, nanocoatings.

Influence of Microstructure on the Corrosion performance of Dual Phase steels

D. FARIAS[1,2], F.HANNOUR[3], J.M.C. MOL[2], H. TERRYN[1,4], J.H.W. de WIT[1,2]

[1]Materials innovation institute M2i, Mekelweg 2, 2628CD, Delft, The Netherlands
[2]Delft University of Technology, Department of Materials Science and Engineering, Mekelweg 2, 2628CD Delft, The Netherlands (d.e.fariasmoreno@tudelft.nl)
[3]Vrije Universiteit Brussel, Research Group Electrochemistry and Surface Engineering, Pleinlaan 2, B-1050 Brussels, Belgium
[4]Corus Research, Development and Technology, PO Box 10.000, 1970 CA IJmuiden, The Netherlands

The development of new grades of (ultra) high strength steels in the automotive industry, with attractive combinations of strength and manufacturability will contribute to achieve significant weight reduction with a minimum impact on structural integrity and cost.

Dual Phase (DP) steels have a microstructure of mainly soft ferrite, with islands of hard martensite dispersed throughout. The strength level of these grades is primarily related to the amount and distribution of martensite in the microstructure. DP steels have a high work hardening rate, with a typical yield strength-to-tensile strength ratio of about 0.5-0.6. These DP steels have been designed and optimized for improved mechanical behaviour and therefore normally have a poorer or at least not well documented and understood corrosion resistance.

In the present research, the microstructure of a commercial grade DP600 is modified by different heat treatment regimes in order to create phase ratios ranging from nearly fully ferritic to fully martensitic. The effect of the individual and combined ferrite and martensite phases on the corrosion performance and electrochemical behaviour is investigated. The effect of the chloride concentration and the presence or absence of a carbonate buffer solution in the electrolyte is studied. For this purpose, an approach is followed based on the use of macro electrochemical techniques (exposed area of working electrode greater that 1cm^2), as well as microscopical analysis. Open circuit potential, potentiodynamic and potentiostatic polarization measurements have been performed, analyzed and compared for a variety of model DP steels. The influence of both the individual and relative amounts of ferrite and martensite as well as the morphology and refinement of the phase constituents on the electrochemical response of model DP steels is discussed.

Key Words: Potentiodynamic curves, Ferrite, Martensite, Dual Phase Steel

Corrosion performance and mechanical properties of joined materials used in the automotive industry

Nathalie LeBozec, Anne LeGac and Dominique Thierry
French Corrosion Institute, Brest, France

The automotive industry envisions that an optimized vehicle in terms of performance and cost can be achieved only by using different materials at different vehicle locations in order to utilize the materials' functionalities to a full extend (weigh reduction, optimization of properties…). Currently, steel and aluminum are the most important construction materials for the mass production of automotive structure. However, other materials such as magnesium alloys and stainless steel are also used. The use of dissymmetric assemblies of materials in the automotive industry has also led to the development of joining technologies other than spot welding and arc welding such as clinching, adhesives, laser welding and MIG brazing. However, and despite the development of these new joining technologies, there are still important gaps of knowledge with regards to the corrosion performance of different joint populations using dissymmetric and symmetric materials.

Materials commonly used in the automotive industry were assembled with different combinations using various joining techniques in order to evaluate their corrosion performance as well their mechanical properties. Steel based materials included carbon steel, high strength carbon steel, zinc coated steel and stainless steels. Light alloys covering different aluminium alloys and magnesium alloy were selected. Joining techniques integrated spot welding, laser welding, arc welding, MIG brazing, clinching and adhesive bonding with epoxy.

The behaviour of the different assemblies in terms of mechanical properties and corrosion aspect was assessed after cyclic accelerated corrosion tests. The results indicated a relationship between the corrosion inside the confined joint and the decrease of the mechanical properties of the assemblies.

Synergistic corrosion inhibition in multi-metal systems

M.L. Zheludkevich, S. Kallip, A.C. Bastos, J. Tedim, M.G.S. Ferreira

DECV/CICECO, Universidade de Aveiro, 3810-193 Aveiro, Portugal

New strategies of "light car" and "green aircraft" promoted in Europe are based on significant weight reduction of future vehicles aiming in the lower fuel consumption and consequently in the reduction of carbon dioxide emission.

The light car design is grounded on use of new grades of high strength steels instead of mild steel and on application of other alternative materials with comparable mechanical properties and lower weight. Thus Mg alloys, Al alloys and carbon fiber reinforced plastics (CFRP) are considered by car producers for different structural parts of car body. These materials play an increasing role in construction of new aircrafts as well. However the galvanic corrosion can become a limiting factor for different multi-material applications in corrosive environments. The current anti-corrosion approaches are mainly suitable for single-material structures. Therefore the need of development of the new strategies of active and passive corrosion protection for the multi-material applications is evident.

In the present work we have tested number of organic and inorganic inhibitors for different galvanic couples of industrial relevance such as Al-Mg, Fe-Mg, Zn-Fe, Fe-Al and others. Conventional integral electrochemical techniques as well as novel micro-electrode multi-metal array cells combined with Scanning Vibrating Electrode Technique (SVET) were employed to study the kinetics and inhibiting efficiency. It was found for several systems that inhibition efficiency of the mixture of inhibitors confers an important synergistic effect being more effective than additive inhibiting action of individual inhibitors. The explored combinations of inhibiting compounds can be used in active corrosion protection coatings being added to the polymer formulations directly or in form of nanocontainers.

Influence of Heating and Cooling Cycles on Automotive Exhaust Corrosion

Muhammad Yasir*, Gregor Mori*, Andreas kalytta**, Armin Reller**, Helmut Wieser***

***** Christian Doppler Laboratory of Localized Corrosion, University of Leoben, Austria
****** Department of Physics, University of Augsburg, Germany
*** EMCON Technologies GmbH, Germany

Abstract

Corrosion in automotive exhaust components is one of the major problems due to which failures occur even after a very short period of time. A large number of high alloyed ferritic and austenitic stainless steels are commonly used for exhaust systems in the automotive industry in order to achieve reasonable lifetimes of such components. It is a common concept that lifetime of a component is directly related to performance of steel against corrosion. Interactions of salt solution from outside and acidic condensate from inside are some of the critical factors that affect the performance of steels. The effect of sensitization in stainless steels on rate of corrosion is well understood from literature. Exhaust systems have to withstand cyclic heating and cooling phases.

The objective of this study was to develop a basic understanding that can determine the combined effect of wet corrosion with systematic heat treatments of some commercial grades of stainless steel. Corrosion resistance to chloride attack is characterized with different heat treatments. It was found that there is a high impact of heating cycles on acceleration of corrosion. Results show a relative big difference in amount of pits and of pit depths between initially heated and periodically heated samples. A fundamental understanding on the interaction of sensitization, heat impacts and aqueous corrosion is presented in the paper.

Keywords: Stainless steels, aqueous corrosion, high temperature corrosion, pitting corrosion, sensitization.

Electrochemical Measurements for the Examination of the Corrosion Behaviours of Stainless Steels in Automotive Exhaust Systems

C. Hoffmann, P. Gümpel

Konstanz University of Applied Sciences/D, choffman@htwg-konstanz.de, guempel@htwg-konstnaz.de

Abstract:
The corrosion resistance of different stainless steel candidate grades for the automotive exhaust systems: austenitic types with and without molybdenum, ferritics with different contents of chromium and molybdenum and manganese austenitic types has been assayed in different laboratory tests. These tests simulate the special corrosion conditions in these systems. They comprise the impact of acidic chloride bearing media, the alternating wet-dry conditions and the influence of the soot particles.

Parallel to the laboratory tests the influence of the active carbon, simulating the soot particles, has been investigated in electrochemically measurements. A new preparation of the samples has been assessed, which eliminates the edge effects and also permits the placement of the active carbon on the metallic surface of the samples so that the results from these measurements reflect just the corrosion attack on the defined surface under the influence of the electrolyte and the soot particles. The different morphology of the pits on the samples with and without active carbon was observed under the microscope and the depth of the pits was measured with a special microscope.

In these laboratory tests the influence of the soot particles on the corrosion resistance of the stainless steels in an automotive exhaust system was considered and its influence was investigated for the first time. The active carbon is decisively intensifying the corrosion attack.

Monitoring the road environment for on-vehicle testing

Martin Jönsson[1] *Bo Rendahl, Ingegerd Annergren*

SWEREA KIMAB, Drottning Kristinas väg 48, SE-114 28 Stockholm, Sweden

ABSTRACT

Accelerated corrosion tests, such as cyclic corrosion tests and proving ground tests, is commonly used by the industry to test automotive material. However the corrosion test that best mimic the real life conditions for automotive materials is of course on-vehicle exposure in authentic road environment. The microenvironment on-vehicle is complex with a number of parameters that influence the corrosion rate such as the relative humidity, temperature and particle emissions. In this work a measurement package has been put together that can withstand the harsh environment that exists on-vehicle measurements. The measurement package includes measurements of relative humidity, temperature (air temperature, surface temperature and dew point) collectors for road mud (anions, cations, pH), corrosion panels (zink, carbon steel and crevice samples). The results from the measurement package have been compiled with an interval of two months. Hence variation in corrosion rate and climate parameters during the duration of a year for on-vehicle testing has been recorded and is discussed.

Keywords: Field exposure, Automotive corrosion

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[1] martin.jonsson@swerea.se tel: +46 8 674 17 86

MULTI-LEVEL PROTECTION OF MATERIALS FOR VEHICLES BY “SMART” NANOCONTAINERS - *M U S T*

M.L. ZHELUDKEVICH*[1], T. HACK[2], C. SIMON[3]

[1] University of Aveiro, CICECO, Department of Ceramics and Glass Engineering,

3810-193 Aveiro, Portugal

[2] EADS Deutschland GmbH, EADS Innovation Works, 81663 Munich, Germany

[3] SINTEF, P.O. Box 124, Blindern, 0314 Oslo, Norway

*** Corresponding author: +351234370255, mzheludkevich@ua.pt**

This paper describes briefly the concept of the FP7 Project “MUST” aiming at development of next generation of protective coatings for transport industry. The main vision of the project is to develop new coating technologies based on active multi-level protective systems for future vehicle materials in automotive, aerospace and marine industry. This particular paper reviews part of the work where automotive applications are particularly concerned.

The main objective of the project covers design, development, testing and application of novel multi-level protection systems as coated materials for future vehicles radically improving long-term performance of metallic substrates. On the other hand metallic or hybrid joints bonded by adhesives containing intelligent release systems are expected to show improved durability and protection against corrosive disbonding.

The multi-level protection is established by the novel self-healing concepts employing various active mechanisms. New self-healing coatings and adhesives will be based on “smart” release nanocontainers incorporated in commercial paints, lacquers and adhesive formulations. A multi-level self-healing approach will combine - in one same system - several damage prevention and reparation mechanisms, which will be activated in response to environmental conditions.

The perspectives, challenges and limitations of application of the self-healing coatings and adhesives in the future car designs will be discussed in the present paper.

Evaluation of durability of nano-silica containing clear coats for automotive applications

E. Scrinzi[1], S. Rossi[1], P. Kamarchik[2], F. Deflorian[1]

[1] *Department of Materials Engineering and Industrial Technology*
University of Trento, Via Mesiano 77, 38123 Trento, Italy

[2] *PPG Research Centre, Allison Park, PA, USA*

In automotive application, multilayer coating systems are typically used to guarantee protection from corrosion phenomena and aesthetic properties. A coating system's appearance and its durability is becoming increasingly important for automotive original equipment manufacturers. Clear coats are required to maintain long term aesthetic appearance, colour and gloss stability to weathering and mechanical damage. One key property is scratch and mar resistance. The use of nano-fillers is a promising strategy to increase the abrasion resistance without affecting the optical clarity of high gloss coatings.

In this work, the influence of nano-silica particles on properties of clear coats has been studied. Three different 2 component isocyanate/polyol clear coats were chosen: one without any fillers, and two with nano-silica particles disposed in the surface layer of the coating. One of these at a normal crosslinker level and one with enhanced crosslinking. The samples were exposed to natural and artificial weathering. The stability of clear coats was evaluated by colour and gloss measurements to evaluate aesthetic changes, by FTIR analysis to determine any degradation of the polymer bonds, by electrochemical impedance spectroscopy measurements to verify the protection properties of the multilayer coating systems.

Taber test and falling abrasive test have been used to simulate coating abrasion and erosion respectively. Gloss retention was measured for the different clear coats. Environmental scanning electron microscopy has been used to study the surface morphology after the damage.

Artificial weathering (UV radiation and salt spray chamber) and abrasion tests were combined to investigate the influence of weathering on mar resistance of the clear coatings.

PRE-COATED STEEL FOR IMPROVED CORROSION PROTECTION AT CUT-EDGE, STONE CHIP AND IN MIXED METAL CONSTRUCTIONS.

Dr. Marcel Roth, Manager Organic Coatings, Henkel Adhesive Technologies,
marcel.roth@henkel.com
Alexey Smirnov, Technical Sales Specialist, Henkel Adhesives/ATM division, Henkel Rus ltd., Alexey.Smirnov@ru.henkel.com

New developments of weldable primers for car manufacturing from Henkel stand in the focus of the present publication. In addition to the most important feature of enhanced corrosion protection the new products offer a high potential of additional values such as improved stamping with no or low oil load, a clean and reliable production process via defined surfaces for bonding and painting, more freedom for design and construction e.g. for aluminum/steel constructions as well as improved cut edge corrosion protection. It will be elucidated how the new technology of organic coatings can contribute to a higher quality, total-cost reduction and process-reliability.

Weldable primers have to provide several properties such as spot weldability, E-coatability, corrosion protection, alkaline stability, paint adhesion during stamping and compatibility with structural adhesives. The focus of the 1st generation was set on corrosion protection in flanges and cavities. The goal of the development for the next generation was to expand the performance on cut-edge corrosion protection, significantly reduced creepage at stone chips and prohibition of corrosion in mixed metal constructions by disactivation of galvanic couples via insulation and barrier functions. By using self lubricating pigmentations it is also possible to enhance the stamping properties of pre-coated steel compared to uncoated substrates. Using these coatings in combination with conventional oil load, the working window for stamping is significantly increased. Even without oiling the stamping process is possible. Lower curing temperatures of the new coatings provide compatibility with bake hardening steel. While the 1st Generation protects 10 weeks against red rust corrosion in flanges during VDA test, the next Generation protects for 20 weeks. A challenge for the developments was the protection against cut-edge corrosion. The electrochemical potential between the Zn-layer and the iron causes a dissolution of the Zn based sacrificial anode. This galvanic corrosion occurs at scribes, cut edges and stone chip and is driven thermodynamically. A novel pretreatment which deposits traces of iron on top of the Zn-layer reduces this effect by reducing the electrochemical potential at the borderline Zn/Fe as shown by Kelvin probe measurements. Corrosion tests prove the extraordinary corrosion protection at scribe, cut edge and stone chip. The dissolution of the sacrificial anode and the paints flaking off is completely inhibited. The coatings will also be a key technology for light weight constructions using aluminum parts.

Mixed metal constructions show enhanced corrosion which is driven by galvanic corrosion between aluminum and steel. Organic coatings act as insulating layers and barriers against oxygen and humidity. The ongoing developments comprise further optimization of the technology package “organic coatings and new 1step pretreatments” to provide a superior technology for corrosion protection and additional multifunctional properties.

Ionic Liquids as lubricants in industrial applications – new solutions for special applications

M. Ramunno[1], B. Pohrer[1], N. Ebel[1], P. Wasserscheid[2], E. Schlücker[1],
1 Institute of Process Machinery and Systems Engineering,
2 Institute of Chemical Reaction Engineering,
University Erlangen-Nuremberg,
Cauerstrasse 4, 91058 Erlangen/Germany

Ionic Liquids represent a novel and innovative substance family. They consist of complex ions which mostly show two or more asymmetric long side chains so that their possibility to form a crystal structure is reduced. Hence Ionic Liquids are salts being liquid at room temperature or below 100 °C. About 10^{18} possibilities to combine different ions to get so called "Taylor made Ionic Liquids" are provided in literature. Because of their salt characteristics Ionic Liquids have nearly no vapour pressure, they are not flammable and most of them are non toxic. Some Ionic Liquids are nearly as incompressible as water and have good requirements as lubricants[1]. These properties make them interesting as media for chemical and engineering applications. For instance Ionic Liquids offer several options for optimization of process machines like diaphragm pumps. Using these new materials offers high potential in performance increase as well as in savings concerning the investment and operating costs [2].

Within different research projects the Institute of Process Machinery and Systems Engineering has gathered experiences in using Ionic Liquids as process liquid in various fields. In particular the Ionic Liquids show potential as lubricants for bearings in vacuum applications, in pumps and for example wind energy plants. Due to their thermal stability up to 300°C they also suit for high temperature employments and of cause in combustion engines where piston rings have to be lubricated. Lubrication is additionally feasible in applications where up to now no liquid could be used. For example concerning the compression of oxygen it is state of the art to work with dry working machinery. These dry machines are fragile and have no long life expectations. With one really inert Ionic Liquid it was possible to run a lubricated screw compressor in order to produce 3 MPa pure oxygen.

In every application using bearings, the lubrication medium is in contact to a multiplicity of materials. The bearing itself may consist of different materials like steel, brass or plastics. There are sealings in every application made of elastomerics or soft metals. Especially to copper and brass Ionic Liquids are extreme corrosive. Under high temperature and pressure they can even be corrosive even to steel. It is an important aim to reduce corrosion problems in order to make Ionic Liquids available for more processes. The corrosiveness against different materials like stainless steel, steel, aluminium, copper, brass and different elastomeric materials is investigated. With a new experimental setup it is possible to research corrosion under different atmospheric conditions (e.g. nitrogen, wet air or air). Thus there are great prospects in finding background information of the corrosion mechanisms. Some Ionic Liquids show lower friction forces as even the best highly additivated engine oils which where tested. But of cause there are again problems with corrosion like tribocorrosion in this case, which is difficult to deal with. For that it is essential to search for additives to solve these problems. Another fact that makes present research activities confident about the great advantages of Ionic Liquids for special applications is that the one used in the oxygen compressor doesn’t show any signs of aging after having run the system for about 8000 hours[3].

There is also great potential in the field of automotive lubrication. Thus in some experiments it was possible to reduce fuel consumption about 8 percent just by replacing the oil with an Ionic Liquid. Ionic Liquids therefore have great promise to save energy in numerous industrial applications.

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Numerical Analysis on Galvanic Corrosion of Galvanized Steel Sheet

Masamitsu Matsumoto, Nobuhiro Okada, Katsuhiro Nishihara and Takeo Kudo
Corporate Research & Development Labs., Sumitomo Metal Industries, Ltd.

1. Introduction

Zinc and zinc alloy coated steel sheet are applied for automotive body for corrosion protection. The corrosion environmental variation that an automotive body encounters has been expanding as its market expands. We have been developing a numerical analysis model based on basic equations that is useful as a numerical experimental tool.

2. Mathematical model

The input data for the numerical analysis model are geometry data shown in Fig. 1, ion concentrations in the solution and polarization curves as a boundary condition. The calculation procedure is as follows: calculate conductivity of the solution, potential and current density, molecule migration, electro neutrality, and chemical reactions.

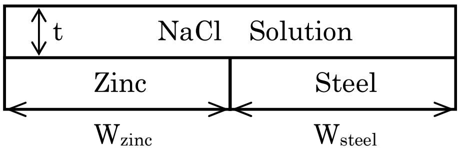

Fig.1 Schematic diagram of Zn/Steel galvanic couple for numerical analysis.

3. Results

Figure 2 shows the protection distance of zinc coating is decreased as NaCl concentration is decreasing and as the water film thickness is decreasing.

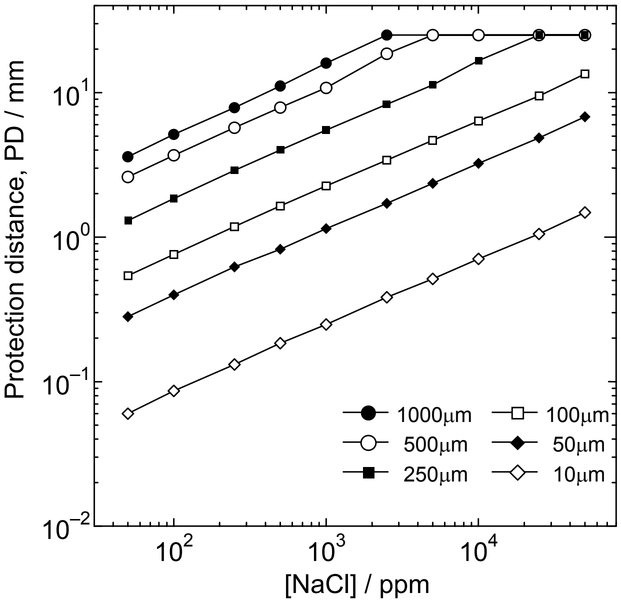

Fig. 2 Numerical analysis result of the protection distance in various thickness and concentration of NaCl solution film.

4. Summary

The numerical analysis model that simulates the galvanic corrosion of galvanized steel sheet has been developed. The effects of the concentration of various anion and cation on the corrosion products distribution and the defect of ED coating on the under-film corrosion are published. The progress of the numerical analysis technology for automotive corrosion is expected and our model is applicable for automotive corrosion.

EVALUATION OF THE CORROSION PROTECTION OF COOLANTS FOR COMBUSTION ENGINES AT ELEVATED TEMPERATURES VIA ELECTROCHEMICAL METHODS

Torsten TROSSMANN[1], **Georg ANDERSOHN**[2], **Klaus EPPEL**[3], **Christina BERGER**[4]

[1] *Technische Universität Darmstadt, Germany, trossmann@mpa-ifw.tu-darmstadt.de*
[2] *Technische Universität Darmstadt, Germany, andersohn@mpa-ifw.tu-darmstadt.de*
[3] *Technische Universität Darmstadt, Germany, eppel@mpa-ifw.tu-darmstadt.de*
[4] *Technische Universität Darmstadt, Germany, berger@mpa-ifw.tu-darmstadt.de*

To achieve a sustainable reduction of CO_2-emissions caused by the global passenger and freight traffic, more efficient or new propulsion technologies are required. However, in the medium-term the combustion engine will not be replaced, e.g. for trucks, but it will be often used in a parallel-hybrid vehicles or as a range-extender for passenger cars. Besides the further electrification of the propulsion chain the future combustion engine will have a smaller swept volume and a reduced number of cylinders. The optimization of the thermal management of the whole cooling system offers an opportunity to decrease fuel consumption and CO_2-emissions, however results in a major challenge from the viewpoint of corrosion engineering.

Measures to reduce friction, like temporally deactivating the coolant pump, to optimize the combustion process, like embedding a load-depending cooling, or to reduce weight by reducing the coolant volume have a positive effect on fuel consumption and power density, but induce higher thermal loads on the materials and the coolant, which is also responsible for corrosion protection of all wetted metals. Higher temperature levels and higher heat fluxes have a direct influence on the damaging process. Research is needed regarding the corrosion protection offered by the coolants. Therefore, an adequate corrosion protection is not necessarily guaranteed after implementation of the proposed measures. Fleet tests, system checks on engine test benches or sophisticated test methods, like modular hot test apparatus (MHTA) according to FVV guideline R530-2005, simulate service like stresses, but offer no fundamental evaluation of the causal corrosion processes. Electrochemical methods can be applied to clarify these test results and to understand the formation and degradation of protective films. Based on the results using cyclic current potential curves and impedance spectroscopy it is feasible to differentiate the corrosion protection effect depending on the material-coolant combination. In addition, direct dependency between the corrosion protection and the temperature of the selected coolant or material sample can be identified. As a result statements can be mentioned about the corrosion system at a certain temperature level.

Analysis of the reliability of the sea water acidified accelerated test (SWAAT) for aluminium brazing sheet

F. Norouzi Afshar[1, 2], *E. Szala*[3], *A. Wittebrood*[3], *J.M.C.Mol*[2], *H.Terryn*[1, 4] *and J.H.W. de Wit*[2]

1. *Materials Innovation Institute M2i*, Mekelweg 2, 2628 CD Delft, the Netherlands.
F.Norouzi-Afshar@m2i.nl
2. Delft University of Technology (TU Delft), *Department of Materials Science and Engineering, Mekelweg 2, 2628 CD Delft, The Netherlands.*
J.M.C.Mol@tudelft.nl, J.H.W.deWit@tudelft.nl
3. *Corus Research Development & technology,*
elizabeth.szala@corusgroup.com, aad.wittebrood@corusgroup.com
4. *Vrije Universiteit Brussel (VUB), hterryn@vub.ac.be*

Abstract

Aluminium brazing sheet is a sandwich material made out of two aluminium alloys. The 4xxx type alloy allows joining of complex shaped automotive heat exchangers while the 3xxx alloy supplies the necessary strength to the component.

This paper is part of a work dedicated to a research to enhance corrosion protection by microstructural control of aluminium brazing sheet.

The most common accelerated corrosion test used for aluminium brazing sheet or its components is the Sea Water Acidified Accelerated Test (SWAAT) [1]. A two hours cycle consisting of 30 minutes spray followed by 90 minutes soak at above 98% humidity is applied [2]. It is reported in literature that the SWAAT test provides similar corrosion attack and morphology within a few days representative of several years of service life [3]. However, still some ambiguity exists, indicating that the test suffers from significant scattering of the results [1,4]. As the test is also used for research purposes a fundamental and detailed understanding and interpretation of the results is necessary. Therefore, the objective of this work is to understand the reason for the variability of accelerated corrosion test results for brazing sheet.

This reliability study aims to elucidate whether the variation of the test results are caused by experimental variations (i.e. specifications of the accelerated test chamber, sample preparation…) or correlate to actual fundamental differences in the corrosion properties of the aluminium alloys (i.e. intrinsic properties of the alloy as the composition and the distribution of the various phases).

A number of parameters have been investigated that potentially could influence the outcome of the SWAAT test. The most dominant parameters are screened and examined according to industrial experiences. The results are used to narrow the operation window of the test and making it more reproducible and reliable in its correlation with practical operating conditions.

Key words: aluminium brazing sheet, accelerated corrosion test

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Comparison of the performance of standardized accelerated tests used or in development in the automotive industry

A. LeGac and N. LeBozec,
French Corrosion Institute, 220 rue Pierre Rivoalon, 29200 Brest, France.

Corrosion resistance is an important requirement for materials used in the automotive industry particularly for vehicles that operate on roads treated with de-icing salts. Field testing, including stationary and mobile exposures is the most reliable way to evaluate the corrosion properties of the materials but they are costly and time consuming. Since the 80’s, the automotive manufacturers have developed a large number of testing procedures which alternate between pollution phase and wet/dry periods dedicated to the cosmetic corrosion of precoated materials. The German vehicle producers have referred to the VDA 621-415 standard to develop and qualify new corrosion resistant products and to select materials. However, this test fails in simulating on vehicle situations. Thus, to better simulate natural exposure of automotive substrates, a new accelerated corrosion test in replacement of the VDA 621-415 standard is currently in development by a working group of the VDA (German vehicle producers association) and the VDEh (German steel producers association). The present study compared the corrosion performance of the standardized and the newly developed test towards cosmetic, crevice and galvanic corrosion using a large number of materials with low and high durability coating systems. The influence of the mode of application of the salt solution during the new corrosion test was also evaluated. The behaviour of materials exposed both in the accelerated corrosion tests and on-vehicle in areas where de-icing salts are applied was compared as well.

From field monitoring with risk management decision: Improvement of ENA NOCS technique using artificial neural network approach served for corrosion detection.

M. Halama[1], *D. Jerolitsch*[2], *P. Linhardt*[2], *J. Zilkova*[3], *R. Dzedzina*[1]

[1]*Technical University of Košice, Faculty of Metallurgy, CCL, Letná 9, 042 00 Košice,*
Slovakia, maros.halama@tuke.sk
[2] *Vienna University of Technology, Institute of Chemical Technologies and Analytics,*
Getreidemarkt 9/164ec, A-1060 Wien, Austria
[3]*Technical University of Košice, Faculty of Electrical Engineering, Košice, Slovakia*

Abstract

The problem deals with developing of reliable method based on short-time monitoring using electrochemical noise analysis with NOCS setup (No Contact to Substrate).

First ENA experiments using portable system composed of mini laptop, digital multimeter 6 ½ digits and amplifier LPMH07 were performed on both artificially pre-corroded and naturally exposed HDG and Al/Zn alloy coated steels under atmospheric conditions. Microstructures of the coatings were determined using SEM followed by EDX analysis.

We have spent the majority of time by measuring on well defined surfaces; nevertheless we wanted to take a closer look at random samples to study the ability of the system to assess the corrosion stability of different coatings. The chosen setup could prove its stability and reliability during these tests but we have observed strong dependence of stability of NOCS setup on size of sensor cells.

Therefore we decided to continue in verifying the technique under laboratory conditions on realistic samples obtained from suppliers to the automotive industry – (pre-corroded hot dip galvanized steel samples with and without application of cathaphoretic paints and/or different primers after salt spray cabin tests). To complete the feasibility study, the large set of data obtained during measurements in labs was used to train an artificial neural network. The application of first models on samples with an unknown level of corrosive degradation showed promising results. For the moment, "under development" monitoring system allows detecting between 5 levels (very active/active/medium/passive/very passive) state on Zn based coated steel.

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Cathodic Protection

Cathodic Protection Effectiveness Assessment by Determining the Soil Corrosivity

Maud BARBALAT[1], Lise LANARDE[1], Didier CARON[1], Michel MEYER[1], Philippe REFAIT[2], Sylvain FONTAINE[3], Jean VITTONATO[4], François CASTILLON[5]

[1] GDF Suez, La Plaine Saint-Denis, France, [2] LEMMA, La Rochelle, France, [3] GRT Gaz, Compiègne, France, [4] TOTAL, La Défense, France, [5] TIGF, Pau, France

Buried gas transmission lines are protected against external corrosion by organic coatings. Cathodic protection (CP) is designed and operated with the aim to mitigate corrosion, where coating is faulty. Basically, pipe potential is lowered, at least to a value, the protection potential, such that residual corrosion rate is practically negligible. The NF EN ISO 12954 : 2001 standard specifies reference values of the protection potentials, according to soil conditions.

Practical background showed that intrinsic soil corrosivity is one of the main factors determining the protection potential values. However, in some kind of soils, protection potentials recommended by the ISO standard are overestimated. In other cases, where soil resistivity is very high, recommended protection potentials cannot be applied on pipelines. But, such noncompliance doesn't necessarily generate damage on the pipes.

In order to improve this situation, a laboratory study has been initiated by GDF Suez and TOTAL, with the general aim to improve guidance on cathodic protection criteria and develop new tools and new methods to identify the "just necessary and sufficient" conditions to guaranty a practically negligible corrosion rate and improve buried pipelines CP control.

The first step of this study deals with prediction of the intrinsic soil corrosivity towards steel, under free corrosion condition, as a function of the main soil physico-chemical properties.

Some short and mid-term gravimetric corrosion tests were made on steel samples, buried in soil boxes, and freely exposed to corrosion. The soil boxes are filled with simulated soil media, under static conditions representative of "real" field situations. The principal soil factors, namely, soil texture, pH, conductivity of aqueous extract, humidity level, soil resistivity, redox potential are carefully controlled. In parallel, by means of electrochemical measures (steel samples free potential evolution, electrochemical impedance and linear polarization resistances measurements as well as plot of polarization curves, at different terms during tests) and their interpretations, in the framework of electrochemical process modeling, theoretical corrosion rates have been determined. Comparison, for different kind of soils, between theoretical and gravimetric corrosion rate allows to appreciate electrochemical models aptitude to predict actual corrosion rate.

Thanks to this comparison, and expressing the corrosion rate measurements results through the traditional "proportionality coefficient" (B coefficient) between the average corrosion current i_{corr} (Faraday equivalent current) and the inverse of the linear polarization resistance, for different soil conditions, some B coefficients reference values were tabulated, according to main physico-chemical factors (resistivity, humidity level, pH, redox potential and temperature), providing a prediction tool of intrinsic soil corrosivity, first step in development of new tools and new methods for diagnosing CP effectiveness and improving CP protection criteria.

Methodology for evaluation of soil corrosivity in buried pipelines for different regions of Rio de Janeiro

Denise S. Freitas[1], Simone L. D. C. Brasil[2], J. Fernando P. Coelho[3], João Hipólito L. Oliver[4], Felicle del Valle L. Araujo[5], Lisiane G. Lima[5]

Buried structures are subject to corrosion processes, whose intensity is related to the severity of the soil. The physical-chemical and biological properties of the soil characterize their specific severity, and external factors determine their relative severity. As external factors, it is possible to mention potential leakage currents generated by cathodic protection and direct current traction systems. Local properties, such as resistivity, pH, water retention capacity and the presence of soluble salts are features that indicate the specific severity of a soil with relation to the metallic structures. In this work, several experimental techniques were used for evaluation soil corrosivity from different regions of Rio de Janeiro, considering mountain and industrial features The laboratory tests consisted of chemical, physical-chemical and electrochemical analyses, besides gravimetric testing. Qualitative and semi-quantitative analyses of the insoluble constituents were carried out through X-Ray Fluorescence Spectroscopy (FRX) and the soluble constituents were evaluated quantitatively through aqueous extracts with FRX and the spectrophotometer in the visible range of light. Concerning the physical-chemical parameters, the pH values, resistivity versus degree of moisture and water retention capacity were determined. Carbon steel specimens were exposed to samples of soils with degrees of moistures varying between 5% and 30%, corrosion potentials were monitored and polarization curves were obtained.. The corrosion rates were also determined under these same moisture conditions. After 30 days of exposure, surface analyses of the specimens were carried out to determine the morphology of the corrosion process, being possible to identify the presence of pittings in some specific moisture conditions. With these analyses, it was possible to characterize the corrosiveness of these grounds, which will allow their use in studies of cathodic protection parameters in controlled field.

[1] PhD., DCOR/National Institute of Tecnology – INT, Brazil
[2] DSc., School of Chemistry/Federal University of Rio de Janeiro, Brazil
[3] Engineer, PETROBRAS, Brazil
[4] Engineer,TRANSPETRO/PETROBRAS, Brazil
[5] DCOR/National Institute of Tecnology – INT, Brazil

New methods of ensuring integrity of TNK-BP field pipelines

***Sergey Kichenko*[1], Maksim Petrunin[2], Andrey Marshakov[2]**
[1]*OJSC TNK-BP, Russia, e-mail: sbkichenko@tnk-bp.com*
[2] *A. N. Frumkin Institute of Physical Chemistry and Electrochemistry, RAS, Russia,*
E-mail maxim@ipc.rssi.ru; mar@ipc.rssi.ru

The significance of corrosion protection in oil industry has always been very high. The reason is that corrosion often results in pipeline failure leading to oil spill and environmental damage. Wide application of inhibitor protection in TNK-BP in the recent years allowed to suppress internal corrosion to a great degree. At the same time, the problem of external corrosion of TNK-BP field pipelines remains acute. The situation is worsened by complexity of corrosion protection and absence of reliable methods to assess the corrosion of pipelines beyond design life. Traditional methods of inspection in the pits enable to evaluate selectively thickness of pipe wall and calculate the probabilistic remaining service life but they do not reflect real corrosion condition of pipeline especially in case of local corrosion which is the main cause of accidents.

During this study over than 20 different field pipelines were inspected. The factors of intensive (3-5 mm/year) local corrosion of steel were identified and comprehensive ground instrument-aided corrosion inspection scheme was proposed. This scheme allows to identify sections of pipelines which are subject to pitting corrosion most of all.

Inspection scheme consists of three stages: 1) analysis of design and service documentation for identification of pipeline sections for instrumental inspection; 2) instrumental "surface" inspection for localization of potentially dangerous sections which includes measurement of coating resistance, detection of coating holidays, analysis of chemical composition of soil (pH, chloride-, nitrate-, sulphide-, calcium and magnesium ions), express measurement of steel corrosion rate, identification of corrosion macro-couples; 3) corrosion monitoring at selected sections using corrosion indicators. Based on the results of measurement of general and local corrosion rates, pipeline sections with high corrosion risk are defined and recommendations on application of urgent anti-corrosion measures are provided.

A low-cost but efficient method of local sacrificial anode protection was proposed based on the results of this work. This method ensures higher integrity of field pipelines by applying selective protection only to sections with corrosion risk.

Proposed instrumental inspection methodology and local sacrificial anode protection method were successfully tested in 2006-2008 in TNK-BP and were applied to 57 pipelines of Orenburgneft allowing to reduce number of failure in these pipeline in several times.

Combined Close Interval Potential Surveys and Direct Current Voltage Surveys for Increased Pipeline Integrity

Peter Nicholson
NACE Accredited Senior Corrosion Technologist
Managing Director
Cathodic Technology Limited
15-1 Marconi Court
Bolton, Ontario, Canada, L7E 1E2

Abstract

With today's electronic instrumentation, it is possible to combine close interval potential surveys (CIPS) with direct current voltage gradient surveys (DCVG) of buried and underwater pipelines for improved accuracy in assessing the level of cathodic protection combined with locating coating defects without spatial errors. Modern electronic survey instruments are capable of stamping each reading with the time, date and sub-metre GPS coordinates. This provides information for accurate mapping of the pipeline location, current state of the cathodic protection system, and further allows personnel to accurately locate areas requiring excavation for coating repair. This paper will show by example how combined CIPS and DCVG surveys undertaken to NACE standards are of benefit to pipeline operators in ensuring cost- and time-effective integrity management of their pipeline systems.

THE EFFICIENCY UPGRADING OF THE PIPELINES' CATHODIC PROTECTION

N.P. Glazov, *CJSC VNIIST, Moscow, Russia,* ***K.L. Shamshetdinov,*** *CJSC VNIIST, Moscow, Russia,* ***N.N. Glazov*** *LLC "Gazprom VNIIGAZ", Moscow, Russia****, A.V. Goncharov*** *LLC "Gazprom VNIIGAZ", Moscow, Russia*

Nowadays all buried steel pipelines should be obligatory protected with the help of the complex protection against the corrosion by the isolation coatings and cathodic polarization (CP). The efficiency of the cathodic protection is defined by the required lowering of the corrosion rate for the support of the trouble free operation of pipelines within the preseted period of the operation with minimal costs on CP.

With the increasing of the original quality of the isolation coating the corrosion rate is increasing especially within the effect of stray currents. It needs the hardening of the time of bringing into action the CP means and supporting the continuous cathodic polarization.

The reducing of the CP efficiency by electric installations' earthings arranged on the pipeline is considerably balanced by the performance of these earthings from the zinc rolled.

The method of calculation and protecting means against the corrosion effect of the alternating currents of the high-voltage power lines.

In high resistivity soils the extended anodic grounbeds made a good showing especially in rocky soils within their arrangement in one trench with the pipeline.

Some theoretical and practical developments in cathodic protection of underground municipal pipelines

E.G. Kuznetsova
Academy of Municipal Economy after K.D. Panfilov, Moscow, Russia.

Some aspects of corrosion and electrochemical protection of underground steel pipelines were studied.

Experimental and mathematical modeling corrosion macrocells (CMCs) on pipeline in different grounds was carried out. Reasons of origination of various CMCs along pipelines and the degree of their corrosion danger were determinated.

During cathodic polarization the cathodically induced passivation of steel is possible in enough dry grounds. During the pauses in cathodic protection dangerous CMCs, suppressed by the cathodic polarization, may regenerate and some new CMCs may originate due to the cathodically induced passivation of steel.

The cells which form (during pauses in the cathodic protection) due to the difference in the protective potentials along the pipeline, i.e., from −1,1 V to −0,85 V (vs a saturated $Cu/CuSO_4$ reference electrode) within the protection zone, are not dangerous, because the more negative the polarization potential, the higher the degree of the cathodically induced passivity of the metal. The less passivated electrode soon becomes an anode in such CMC. In a week (or more) it may become active and the cell may transform into a dangerous CMC if the cathode is still passive.

These results served as the scientific base for developing the requirements on the admissible duration of pauses in the operation of cathodic protection (to 14 days per year). It was included in technical standards.

Investigations of influence of alternating current on corrosion of steel in different grounds were performed. In sounds and clays the corrosion rate of steel increases when alternative current density is ≥ 3 mA/sm^2, and corrosion of steel in clays becomes local. Cathodic protection is achieved at cathodic current densities more than densities in absence of alternating current.

The method determining dangerous influence alternating current on underground pipelines was advanced.

CATHODIC DELAMINATION: MECHANISMS, MATERIALS AND TESTING PROTOCOLS

Z./Makama*, J.R. Smith, I.B.Beech, M.Webb[‡], I.Doble[‡], D.Nicolson[‡] and S.A. Campbell

Applied Electrochemistry and Microbiology Group, School of Pharmacy & Biomedical Sciences, University of Portsmouth, St. Michael's Building, White Swan Road, Portsmouth PO1 2DT, U.K.
zakari.makama@port.ac.uk

[‡]*PDM Neptec Ltd., Omega Business Park, Alton, GU34 2YU, UK.*

Increased activity in the offshore oil and gas, submarine and telecom industries require the use of autonomous under water vehicles and other remotely operate equipments due to very hash environmental conditions. This equipment requires the use of electrical assemblies and harnesses, which incorporate underwater connectors, encapsulated sensors and transducer arrays, cable bend control systems and polyurethane moulding equipment and supplies. Cable connector assemblies destined for employment in underwater or harsh environments must be sealed, most critically at the metal connector-to-cable interface. This is achieved by using a polyurethane moulding which bonds between the metal connector back-shell and the cable. In environments where sacrificial anodes are used to provide specific corrosion protection, cable assemblies can become be prone to a phenomenon known as cathodic delamination, which can compromise polyurethane-to-metal bonds, which results in cable assembly failure.

This communication addresses the problems related to materials selection given the new legislation (REACH) restricting the future use of many substances used in the production of cable connectors and other related products. For example, the problems related to the reduced levels of mercury as a catalyst in the synthesis of polyurethane and the resultant variation in their properties and handling.

One of the major barriers to the use of new materials is the lack of short-term laboratory or *in-situ* test methods for making accurate and reliable predictions of their long-term performance. Because cable connector assemblies must perform in hash, complex physical environments which are characterised by multiple variables with non-linear relationships, Engineers are couscous to ensure that empirical data (if any) are validated with tests which are representative of the actual service conditions. The development of design methodologies and/or short-term testing protocols to simulate the long-term service requirements and stability of these assemblies based on the Arrhenius theory and the ASTM test method for cathodic delamination will also be discussed.

EVALUATION AND MITIGATION OF AC INTERFERENCE IN DENSE RIGHT OF WAYS: A PEMEX EXPERIENCE

Ing. Julio César Sánchez Torres
+ Petróleos Mexicanos- Dirección Corporativa de Ingeniería y Desarrollo de Proyectos/
Subdirección de Operaciones de Proyectos/ Gerencia de Ingeniería Especializada
Tel. +52 55 19442500, Ext.38742, e-mail : julio.cesar.sanchez@pemex.com and
jcemperador7@gmail.com

ABSTRACT

Petroleos Mexicanos is the biggest enterprise in Mexico and Latin America as well as one of the few oil companies in the world that develops all the productive chain of the industry, upstream, downstream and final product commercialization.

PEMEX Refinación (Refining), one of the four subsidiary entities of Petroleos Mexicanos, processes, transports and markets a wide range of products derived from crude oil. Oil products are transported and distributed to Mexico City thanks to the Tuxpan – Poza Rica – Cima de Togo – Azcapotzalco pipeline system. The 70 MBD (Million Barrels per Day) capacity for gasoline being too limited for the expected demand growth, the addition of a new 18” line in the Right Of Way (ROW) Cima de Togo – Venta de Carpio was studied in order to reach 140 MBD.

The corporate entity named Dirección Corporativa de Ingeniería y Desarrollo de Proyectos (DCIDP), responsible of the project management of the major projects for the subsidiary entities of PEMEX, led this study. One of the major complexities of this project lies in the mitigation of interferences due to the influence of several HVAC power lines in a ROW that already includes several pipelines.

In this paper, a simulation software suite will be presented that is able to model both resistive (“close field”) as inductive (“far field”) interference in ROW’s with pipeline and power transmission networks of any complexity. Practical results of simulations will be presented as well as the resulting recommendations towards security of workers at the time of installation of the pipeline and its maintenance.

Cathodic protection of LPG mounded vessels – Specific solutions for particular problems

O. Fumei, Isproma, Rome ,Italy
L. Di Biase, Isproma, Rome, Italy
R. Cigna, Isproma, Rome, Italy
A. Al Humaid, GASCO, Riyadh, Saudi Arabia
Y. I. M. Riad, GASCO, Riyadh, Saudi Arabia

Corrosion of LPG Tanks is, among others, a long term risk for safety. Apart the many rules implemented, also by learned lessons from past accidents, corrosion protection of LPG Tanks is quite a special application. Our experience in new large capacity Mounded GPL Systems has led to focus specific ”HOT SPOTS” in the various phases of design, installation, commissioning and operation of such systems. In order to be successful, the design, materials selection, site erection procedures and operation of a Cathodic Protection system should come alongside the above said phases, thus making aware the CP specialists of the peculiarities that can influence the implementation of such type of installation.

The complex various phases of site erection of two 2000 m^3 LPG mounded tanks in Madinah (KSA) area, and the subsequent positive commissioning results, together with the development of a new modular CP Equipment devoted to such type of Complex Structures, including an “in-built” specific Monitoring System are presented and discussed.

The implementation of the CP System involved many kind of specific competences in various fields such as mechanical installation, choice of soil and proper compaction, careful verification of coating damages and the relevant repair, design of the installation of groundbeds and permanent reference electrodes, wiring of the whole system up to the Control Room.

Commissioning has confirmed that in such complex structure the unavoidable presence of hidden “hot spots” can be healed thanks to the preventative measures taken in the various phases of the CP design and installation.

LIGHTNING PROTECTION FOR PETROLEUM AND GAS PLANTS - NEW EMC SYSTEM SOLUTIONS

Daniel Soleil, *EMCS Engineering, 13560 Senas (F).*
E-mai : daniel.soleil@wanadoo.fr http://pro.wanadoo.fr/geniecem
Alain Alcaras, *Thales Communications, 49-Cholet (F)*
E-mai : alain.alcaras@fr.thalesgroup.com
Philippe Le Hô, *CCTA, 31500 Toulouse (F) - E-mail* contact@ccta.fr
George Zeigler, *SPGS, Inc - Mansfield, Ohio 44906 – (USA).*
E-mail: gzeigler@spgs-ground.com www.spgs-ground.com
Patrick Lambert, TRAPIL, 75 Paris (F) – E-mail: plambert@trapil.com

1- Abstract : This paper presents an example of a petroleum station where are developed typical innovated protections about the application of a new EMC concept on the electromagnetic compatibility studies and protections for systems. This concept specifically adapted on the field of large and complex sensitive installations is called the “zero method”. It uses an accessible and easy process to control what happen inside of the electrical and electronical systems and consequently how to protect them. This new approach is agreed by international IEC standards particularly 62 305 -1 to 4, and applied in hospitals and research buildings, computer centers - hydroelectrical power plants, gas and petroleum plants etc …to find quickly economic and technical performing solutions against damages caused by lightning and industrial parasitic currents effects.

3. Petroleum and Gas plants

Petroleum and gas plants are known as specially sensitive because of Cathodic Protection which multiply separated earthings. The domain of Cathodic Protection uses special dissociations between the bonding to the earth of the buried metallic elements carried with a negative potential compared to the positive potential of the soil polarised by the anodes electrodes. Frequent errors of installations are caused by the amalgam existing between the terms «Earthing and Grounding». Bonding is relating to the protection of the persons and goods facing the danger introduced by electric currents and the protection against the lightning needs direct Earthing, avoiding bonding. Some new particular components had been designed to answer at the Zero Method criterions.

4. Conclusions

The efficiency of these solutions is confirmed along more than ten years of operation. This approach improves electricians, facility safety and provides light costs.

NEW ASPECTS OF EXPANDED CONSTRUCTIONS CATHODIC PROTECTION

Timonin A.V, Sinko V.F, Timonin V.A.
OAO All-Russia Scientific and Research Institute of Corrosion
Russia 105318, Moscow, Scherbakovskaya, 3;
e-mail: rcnt1@yandex.ru

Cathodic protection of internal surface of long-line construction and elements, cracks and gaps is a very serious problem. It is generally accepted that the long-range action of pipes internal surface cathodic protection is only several diameters. When the protective current flows through narrow electrolytes sections, considerable voltage drop occurs and as a result there is no protection potential on metal surface. The scales on the pipelines internal surface seriously decrease pipeline transmission capacity up to line complete shut down. At the same time the known deposition of corrosion products and insoluble salts on cathodic areas could be used to augment corrosion protection range.

During deposition regulated by cathodic current density, pH, well environment and flow rate the compact screening layers with high electric resistance that will allow to significantly raise long-range action of one anode could be formed. Concurrently during cathodic reaction of oxygen depolarization the oxygen level in the environment as well as its corrosivity declines. The results related to the research of kinetics of corrosion and protection layers formation modes during cathodic polarization are presented. Corrosion protection of pipeline internal surface has been carried out on 2 facilities (water line Nebit-Dag iodine plant, Turkmenistan, and main water line Astrakhan- Mangyshlak, Russia – Kazakhstan).

CORROSION BEHAVIOR AND MECHANICAL PROPERTIES OF 316 STAINLESS STEEL UNDER CATHODIC PROTECTION IN 3.5% NaCl SOLUTION

Fr. Hedaiat[1], T. Shahrabi[2]

[1] Department of Materials Science, Faculty of Engineering, Azad University, Branch of Behbahan,P.O. Box 63617, Behbahan, Khuzestan, Iran, fa_hedaiat@yahoo.com
[2]Department of Materials Science, Faculty of Engineering, Tarbiat Modarres University, P.O. Box 14115-143,Tehran, Iran, tshahrabi34@modares.ac.ir

Austenitic stainless steels such as STS 316 and 304 are frequently used as corrosion resistant materials in aqueous solutions. If the material is exposed to severely chloride-containing environments, including seawater, it should be protected from localized corrosion using appropriate methods because the passive film tends to dissolve. Cathodic protection is a widely used method for corrosion prevention and protection of marine and submarine structures. The application of cathodic polarisation suppresses the metal dissolution and pit formation, thus reduces the possibility of localized corrosion at the surface of metals. In this study, zinc and mild steel sacrificial anodes were used to prevent pitting and crevice corrosion of 316 stainless steels. Results showed that protection potential more negative than -600mV (SCE)$-600mV(SCE)$ prevent crevice and pitting corrosion. The required average current density for protection was about 80-120mA/m^2$80-120\ mA/m2$. The crevice former was MCA washer according to ASTM-78-95.

Erosion–corrosion tests showed that at a constant wearing load, cathodic protection could significantly decrease E-C rate but the cathodic protection effect reduced when the applied cathodic potential exceeded a certain value. Furthermore, under relatively low loads, with increasing cathodic potential, the protection efficiency increased. Protection potential more negative than -1150mV (SCE)$-1150mV(SCE)$ deteriorated the surface of 316SS due to hydrogen embrittlement and enhanced wear loss. A rotating disk with four specimen holders on its edge was used for erosion-corrosion test, and it was modified in a manner that it allows electrochemical measurement to be done. Results of microhardness measurements showed that cathodic protection increased specimen's hardness.

Finally, the corrosion fatigue performance of samples was investigated by conducting a series of rotary bending, corrosion fatigue tests at 90Hz$90Hz$. It was found that increasing the applied polarization potential from -650mV$-650mV$ to -1000mV (SCE) improved the corrosion fatigue life$-1000\ mV(SCE)$. On the other hand, over-cathodic protection above -1300mV (SCE)$-1300\ mV(SCE)$ reduced the corrosion fatigue life of samples due to hydrogen embrittlement.

Modern conception of the complex corrosion diagnostics for underground pipelines and tanks

RANS Academician, professor V.V. Pritula
JSC VNIIST, Moscow, Russia

Some different technologies of corrosion diagnostics exist now. These technologies are directed to receiving of the following information:

- about the corrosion aggressiveness of soil;
- about the dangerous stray current presence;
- about the object insulation coating condition;
- about the object electrochemical protection condition;
- about the object protection level provided by electrochemical protection means;
- about the corrosion condition of object.

In these cases the final object of every corrosion diagnostics technologies is the evaluation of remain resource for each object at real corrosion situation with the system of anticorrosion protection which exist at such object.

No one from numbered information fields separately can not provide the achievement of set aim. In connection with it the modern science based conception affirmed the necessity of complex corrosion diagnostics. This technology include harmoniously all pointed up types of diagnostic works. In result, there is comprehensive and reliable evaluation of remain resource not only, but and prognosis of the risks of probably happened corrosion refusals together for diagnosed objects. The foundation of such new result are:

- the integral evaluation of corrosion dangerous of ground environment according to criterion of free corrosion speed rate for object without anticorrosion protection;
- the discret (till to each individual tube section) evaluation of damage degree and electrical resistance value of insulation coating on pipeline;
- the individual evaluation of capacity for work to existing and acting means of electrochemical protection;
- the probably evaluation of solidity reserve for corrosion damaged object with the exist anticorrosion protection according to criterions of remain corrosion speed rate and the limit state of construction solidity of diagnostic object.

The Data Base «Corrosion» which is formed by such way with the utilization of the complex corrosion diagnostics permit to reduce the optimum volume and the terms of repair-restoring works and to cut the expenditures to support of longevity, durability and capacity for work to pipelines and tanks.

The Influence of Cathodic Protection Time Gaps on Pipe Wall of Gas Main Corrosion Condition Under Insulating Coating Disbondment

N.K. Shamshetdinova («Gazprom VNIIGAZ, Ltd.», Moscow oblast, Leninsky rayon, pos. Razvilka),
N.A. Petrov («Gazprom Gaznadzor, Ltd.», Moscow, Vernadskogo prospect, d.41, bldg.1)

The insulating coating becomes deteriorated due to variuos reasons in course of pipeline operation. Nowadays corrosion under insulation (so called «underfilm corrosion») along with SCC is major cause of large diameter pipe mains corrosion faults.

In laboratory conditions original electrochemical cell was set-up, physically modelling gas pipeline insulation disbondment, similar to disbonment in natural conditions. It was resumed, that voltage potentials of electrodes in crevice increase along with the total polarization current on its opening. To achieve protective voltage shift of metal in deeper parts of disbondment significantly less current density is required, than for metal near opening. Quantitively difference between applied current densities for 20 cm long crevice near opening and at the end can achieve one decade. Consequently, the farther from the opening is protected surface, the less current density is enough to establish protection potential. Comparing the intensities (absolute values of derivatives with length) potential shift and current density variations along the disbondment, we resume, that current density along the crevice reduces much more intensively. Thus, protection under the disbondment with opening is possible at certain increase of protective potential at opening with respect to normative.

During investigation of cathodic polarization time gaps on steel corrosion under disbondment it was resumed: the farther depolarized segment from opening of the disbondment, the slower process of depolarization takes place and the greater is polarization current at the beginning of disbondment, the faster disbondment polarization as a whole proceeds. If electrodes are considered as segments of disbondment polarized to various potentials and taking into account, that polarization of the openning is always higher, than of deeper segment, then duration of transition process after switching protective current off and possible duration of corrosion macrocell operation (CMC) can be determined. Comparison of depolarization chronograms of the first and the sixth model electrodes shows, that during polarization process potentials become equal approximately in 4 minutes, following by CMC functioning nearly 1 hour, where deeper segment of disbondment is anode.

Investigation results allows to recommend to harden requirements on keeping cathodic polarization uninterrupted for buried pipelines with coating corrugation in open holidays zones. On sections of high corrosion risk in emergency it is recommended to use automatic powering on of reserve current source, that must be realized not later than corrosion macrocell initiation.

X100 Field Trial – Evaluation of Mainline and Field Joint Coatings

Dr. A. N. K. Jadoon*
BP, Exploration and Production Technology, Chertsey Road, Sunbury TW16-7LN, U.K
Dr. I. Thompson
GL Industrial Services UK, Holywell Park, Loughborough LE11-3GR, U.K
*corresponding author

Operating and distribution companies are potentially interested in the use of high and ultra-high strength steels for the transportation of high pressure gas. The ultra-high strength X100 grade steel was commercially developed as a potential option. In addition to proven operational performance, a better understanding of the coating application temperatures impact on the mechanical properties and performance of the X100 remains.

BP carried out a 2 year field trial to demonstrate the operational capacity and integrity of a large diameter (48 inch) high pressure pipeline constructed from X100 grade steel. The 800m pipeline was buried in a clay backfill and exposed to natural weathering associated with the North of England. Flow pressure cycling was carried out to simulate 40 years of operational service.

The mainline and field joint coatings employed were fusion bonded epoxy (FBE). These were applied at a lower application temperature of 220°C compared to the typical 230-240°C. The lower application temperature was within the manufacturers approved application and curing temperature range. The lower temperature was used to assess the ultimate performance properties of the mainline and field joint FBE coatings. A higher application temperature could potentially have detrimental effects on the mechanical properties and performance of the X100.

A 200m section of the pipeline was exposed to three different potential (cathodic protection) levels for the duration of the trial:

i. Free potential (no cathodic protection)
ii. Intermediate potential of -850 to -950mV
iii. High potential of -1200 to -1300mV

Mainline and field joint coating samples were taken from the three different potential zones and extensive testing carried out. This paper presents and discusses the results of the testing.

It was found that the different levels of cathodic protection had negligible effect on the properties of the mainline and field joint coatings.

The post-field trial properties of the mainline coatings were unaltered (i.e. same as pre-field trial) despite natural weathering for over 2 years.

Although the mechanical properties (flexibility and impact resistance) of the field joint coatings were acceptable, the coatings water soak and cathodic disbonding resistance were far inferior to those of the mainline coating.

Evaluation and Modeling of Cathodic Disbonding of High Solid Thick Polyurethane Pipeline using Electrochemical Impedance Spectroscopy(EIS)

J. Neshati [a,*] *, J. Mofidi* [b] *, F. Akvan* [b]
[a] *Corrosion Department, Research Institute of Petroleum Industry(RIPI), Tehran, Iran*
[b] *Faculty of Chemistry, North Tehran Branch, Islamic Azad University, Tehran, Iran.*

Abstract

Cathodic disbonding is one of the main problems in coated pipelines under cathodic protection.
In this research,tested parameters included the coating thickness, the artificial holiday (defect) and electrolyte type were investigated according to ASTM G8 using Electrochemical Impedance Spectroscopy (EIS).A double electrochemical cell has been used in order to separate the measurements of cathodic disbonding process from the influence of the impedance of an artificial defect . Artificial holidays diameters were selected as 3, 6 and 9 mm . Experiments were done in 3.5 % NaCl, KCl and $CaCl_2$ solutions at room temperature with different coating thicknesses (354,483,1014µm) . Immersion time was 28 days and during the immersion cathodic potential of -1.5 V(vs.SCE)was applied ,but the EIS measurements were done in open circuit potential(OCP). Parameters properties were evaluated by analyzing electrochemical impedance data obtained in the two parts of the cell.
Investigations showed above parameters under over protection conditions were efficacious in cathodic disbonding coating process, but with no logical correlations between each parameter and any disbonded area individually. Model was introduced based on the phase shifts obtained from EIS curves using the break point frequencies and the parameters mentioned above. This model can predict the disbonded areas for electrolytes with a 1:1 cation/anion relationship. Electrolytes showed anions diffusion plays an important role in the case of positive ions diffusing through the coating that it was justified by limit equivalent conductance

Keywords:
Cathodic disbonding, Modeling, Cathodic protection, Polyurethane coating ,Electrochemical impedance spectroscopy(EIS),Pipeline.

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[*] Corresponding author: neshatyj@ripi.ir

Design of a Cathodic Protection System for a Refurbished Jetty

Abstract: The construction of a new LNG receiving terminal project included an effort to extend the life of a very large existing jetty structure and associated berths. The jetty was originally constructed in the 1970's and included a mix of pre-stressed concrete piles, partially coated steel piles and concrete support structures located in and above the splash-zone. In an effort to extend the life of the structure for future service, the piles and other support structures were retrofitted with impressed current cathodic protection. Use of impressed current required addressing significant design challenges including avoidance of hydrogen effects on pre-stressed tendons, and the monitoring and protection of hundreds of submerged piles and atmospheric zones.

Numerical Evaluation of Chloride Migration Caused by Cathodic Protection of RC-Structures

Authors: C. Helm; M. Raupach; C. Wolf

In the recent years cathodic protection (CP) has become a well known and generally accepted repair method for reinforced concrete structures affected by chloride induced corrosion. Surface applied anode systems are usually installed at the concrete surface closest to the corroding rebar. In some cases this setup is inapplicable. For example, if the surface is not accessible (e.g. outer side of a tunnel shell), or the application of the anode system would cause unacceptable traffic digestions (e.g. highway bridge deck). In these cases it could be beneficial, to apply the anode system on the rear surface of the structure.

To determine, whether a sufficient protection of the corroding rebar layer can be achieved, without an overprotection of the rebar next to the anode system, a research project has been initiated. Within this project “Numerical Simulation of the Cathodic Protection Applied to Protect the Rear Reinforcement of RC-Structures”, founded by the German Research Foundation (DFG), a 3-dimensional numerical model has been created, to predict the current and potential distribution within the structure. The geometry, the resistivity of the concrete, as well as the polarisation behaviour of the active and passive rebar and the impressed current anode system are taken into account by the model. The accuracy of the model has been shown in a comparative study on laboratory results.

Current research activities deal with the integration of time dependent processes into the model. The migration of chloride ions towards the impressed current anode causes a drop of the chloride content in the vicinity of the rebar and therefore has a beneficial effect on the polarization behaviour on the long term. A first approach has been made by implementing the Nernst-Planck equation into the model to calculate chloride migration along the electrical field created by the cp.

In this paper, the basics of the applied model are presented. The results of the model are verified by comparison with laboratory results. Therefore 24 disc like specimens (2% chloride/cem), where exposed to current densities ranging from 2 – 100 mA/m² with respect to the concrete surface. After 28, 56 and 90 days of exposure chloride profiles are determined to assess the shift of the profiles due to the cp. These profiles will then be compared with those obtained by numerical simulation to assess the accuracy of the model. Finally parametric studies are presented, to evaluate the decrease of the chloride content in the vicinity of the rebar, which can be achieved during the service-life of a cp system under several practical conditions.

Investigating the effect of Interrupted Cathodic Protection on reinforced concrete structures

Christian Christodoulou, AECOM Europe, Birmingham, U.K.
Dr. Gareth Glass, AECOM Europe, Birmingham, U.K.
John Webb, AECOM Europe, Birmingham, U.K.
Prof. Simon Austin, Loughborough University, Loughborough, U.K.
Dr. Chris Goodier, Loughborough University, Loughborough, U.K.

Impressed Current Cathodic Protection (ICCP) has been one of the major components of the repair and maintenance strategy on many motorway structures in the U.K. It has hlped to prolong the life of more than 700 structures, in a significantly sustainable manner, by reducing the need to remove chloride contamnated but otherwise sound concrete. The study was initiated after identifying that some of the CP systems were reaching the end of their design life and required a significant level of maintenance (including anode replacement) to operate in accordance with the latest codes of practice. In addition, there were a number of field applications where the application of ICCP has been interrupted due to severe anode deterioration or vandalism.

The objective of this work was to collate evidence from field structures to support preliminary laboratory results that the application of cathodic protection to a reinforced concrete structure over a period of time can transform the protective environment around the reinforcement.

This experimental field study interrupted the current to ten structures which had been protected with ICCP for a period of time between 16 and 5 years and corrosion rates were monitored to determine when reinforcement corrosion will initiate again.

It was found that after 5 or more years of ICCP, the steel remained passive for at least 24 months after interrupting the protective current, despite the presence of chloride contamination representing a substantial corrosion risk. In some cases, severe anode deterioration meant that the current was interrupted at an unknown point in time prior to the initiation of the scheme.

Four main conclusions are drawn about this approach. It can give an indication of when repairs to ICCP systems are likely to be critical; provide new evidence for the design lives attributed to systems using lower cost anodes; reduce the requirement to replace systems at the end of their functional lives; and the interval between planned maintenance of existing systems may be extended with corresponding reduction in monitoring frequency.

Sacrificial Galvanic Coating for Corrosion Protection of Metal Reinforcement Embedded in Concrete

Andrea Hansen, Alla Furman, Marlin Hansen, Angel Green,
Cortec Corporation, White Bear Lake, MN/USA

Objective

The goal of this study was to optimize the corrosion protection of a sacrificial galvanic coating by adjusting its formulation and installation techniques. A number of electrochemical techniques were utilized for measuring parameters of the Galvanic Coating. These laboratory and field studies include electrochemical potential, electric resistance, corrosion current, and others.

Significance of Work

Sacrificial coatings provide a barrier between concrete and its surrounding environment and in addition they protect reinforcement by allowing corrosion of the sacrificial metal and preventing corrosion of the actual structural steel embedded in the concrete. The development of an easy to apply Galvanic Coating would be a breakthrough technology having great commercial value for the following industries: Transportation, Infrastructure, Marine Infrastructure, Civil Engineering, and Construction, where costs of corrosion and repair are very high.

Laboratory Test Results

Susceptibility of the Galvanic Coating to electrochemical anodic reaction was evaluated by weight change in salt water. The change in weight showed that anodic reaction was occurring.

The Galvanic Coating was applied onto concrete samples with embedded rebar. Electrochemical potential, current flow and ‘instant off’ were measured. The Galvanic Coating meets the criteria for evaluation of affective cathodic protection, including an ‘instant off’ potential more negative than -850mV and at least -100mV shift of potential on the rebar

Concrete blocks were monitored for the level of electrochemical potential with a Cu/$CuSO_4$ electrode during 1700 hours in humidity cabinet. While the control blocks stayed in corrosion range o -300mV to -330 mV, rebars connected to Galvanic Coating were -700mV to -1100mV.

Field Trials

GalvaPulse measurements of the rebar in the bridge showed a range of 19.7-42.9μm/yr (average of 31.3μm/yr) on the side protected by the Galvanic Coating versus a range on the control side of 40.6-227μm/yr (average of 96.3μm/yr.) The rebars protected with the Galvanic Coating average three times lower corrosion rate.

Conclusion

Extensive formulation work has resulted in a system that provides the needed polarization for cathodic protection of reinforcing steel embedded in concrete for a variety of structure environments. Laboratory and field measurements show that the formulated Galvanic Coating was easy to apply and conforms to performance criteria of sacrificial anodes.

Coatings

PHOSPHATING
The status and perspectives of development in Russia

T. Vagramyan, N. Grigoryan, E. Akimova, A. Abrashov
D. Mendeleyev University of Chemical Technology of Russia, Moscow, Russia

Phosphating processes have been in active industrial use for over than 100 years and even though a lot has been done to improve these processes, the works on developing of the new directions are conducted till today. The quality requirements of the phosphate coatings and technologies of their application, including economic and ecological aspects, have recently been considerably raised. Main directions in perfecting the phosphating processes are improvement of protective and other functional properties of coatings, decrease in concentration of solutions, temperature and processing time, simplification of correction, decrease in ecological danger, unification of phosphating solutions, etc.

One of the problems that the motor industry has been facing in the recent years is the necessity of simultaneous phosphating of steel, zincked steel and aluminum surfaces.

This problem resolution is complicated by the use in the modern motor industry of rather difficult in operation so-called tri-cation phosphating solutions containing ions of zinc, manganese and nickel. Phosphatic layers, suitable for further cataphoretic painting, are formed in this solutions.

The development of universal phosphating solution is complicated due to the components used in the solution for activation of aluminum surfaces, that also cause the zincked steel to overpickle. Our researches have shown that the easiest resolution of this issue is simultaneous infusion into the phosphating solution of free **fluoride**- and complex **hexafluorosilicate**- ions in certain proportions. This causes some insignificant changes in components proportion in the phosphating solutions used in practice. Correction of such solutions becomes somewhat more complicated because two different solutions must be used.

The other important aspect is toxicity and cost reduction of phosphating solutions. As it is known, the majority of modern phosphating solutions contains nickel ions. Especially in the recent years, the use of nickel salts does not only cause high toxicity of solutions but also leads to a considerable increase in cost of phosphating processes. The possibility of replacement of nickel salts with those of copper is stated in literary reviews. However, due a number of reasons, including copper contact isolation, this possibility was not investigated further. Our investigations have shown a possibility of replacing the nickel salts with copper ions in crystalline phosphating solutions that are widely used in Russia, the process shows no significant changes in characteristics of processes and quality of coatings.

A specific feature of using liquid phosphating concentrates delivered from manufacturers in Russia, is the difficulty in their long-distance transportation during winter time. Liquid concentrates freeze and partially lose their properties after defrosting. We have developed a dry composition designed for amorphous phosphating and correction of the phosphating solution. Effects that the accelerators have on the process of forming of coatings have been investigated and a number of appropriateness was found.

Electrochemical fabrication of oriented ZnO crystallites on TiO_2 nanotubes.

Marielle Eyraud[a], G. Jimenez-Cadena[b], C. Chassigneux[a], E. Comini[b], G. Sberveglieri[b], T. Djenizian[a]

a. Universités d'Aix-Marseille I, II et III-CNRS, UMR 6264: Laboratoire Chimie Provence, Equipe: Electrochimie des Matériaux, Centre Saint Jérôme 13397 Marseille Cedex 20,
*marielle.eyraud@univ-provence.fr

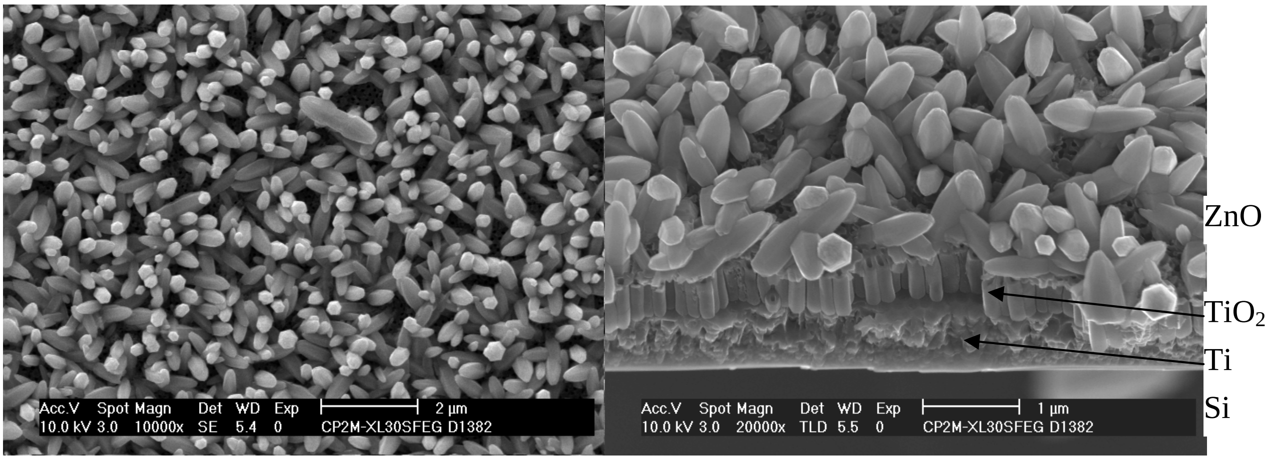
b. INFM-CNR SENSOR Lab and University of Brescia, Via Valotti 9, 25133 Brescia, Italy

Composite electrodes such as ZnO/TiO_2 can be alternative materials to improve the efficiency of sensitized solar cell [1, 2]. These materials can be obtained separately using several methods included CVD, PVD, hydrothermal and electrochemical methods. However, electrochemical approach has never been reported to produce oriented ZnO crystallites on TiO_2 nanotube layers.

In this paper we firstly focused on the anodization conditions to produce TiO_2 nanotube thin films grown from a 1,5 µm thick Ti layer sputtered onto Si. Here, highly-organized titania nanotubes were obtained in glycerol viscous electrolyte (NH_4F+ H_2O + glycerol). The influence of cell voltage, anodization time and acid treatment on the morphology of TiO_2 nanotubes have also been studied.

ZnO crystals were cathodically deposited from a zinc nitrate bath at 70°C. SEM and XRD diagrams were carried out to study the influence of the electrochemical parameters (applied potential, deposition time, and bath composition) on the ZnO nanostructures.

Oriented ZnO wire-covered TiO_2 nanotubes composite electrodes were finally electrochemically grown from a Ti thin film sputtered on silicon.



Top view and cross sectional SEM images of ZnO crystals on TiO_2 nanotubes obtained from the anodization of a Ti thin film on Si substrate

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CHARACTERISATION OF NANOTUBULAR TiO_2 FILMS ON TI-6AL-4V ALLOY FOR BIOMEDICAL APPLICATIONS

E. Matykina[1], J. M. Hernandez-López[2], A. Conde[1], J.J. de Damborenea[1], M.A. Arenas[1]

[1] *Centro Nacional de Investigaciones Metalúrgicas (CSIC), Avda. Gregorio del Amo, 8, 28040 Madrid, Spain, e.matykina@cenim.csic.es*
[2] *Facultad de Química, UNAM, C.P. 04510, México D.F.*

TiO_2 nanotube films are of increasing interest for biomedical implant applications as an alternative to surface treatments with micrometer-scale topography. As studies on titanium show, TiO_2 nanotube films offer enhanced cell interactions and possibility of controlled drug loading and delivery for stimulation of bone growth [1]. The majority of TiO_2 nanotube research has been done on c.p. titanium. On the other hand, formation of titanium oxide nanotubes on high strength titanium alloys used for load-bearing prosthetic applications has been far less studied. In these applications the reduction of the probability of infection during surgery and healing process is one of the primary goals. In the last years ion incorporation into titanium surface has been considered of interest in order to provide antibacterial properties to the surface [2]. In the present work fluorine incorporation from the bath utilised to grow the self-organised TiO_2 nanotubes was investigated on Ti-6Al-4V alloy. Two types of oxide films with a diameter of 20 and 100 nm and thickness of ~100 and 350 nm were grown in acidic fluorine containing solution at 20 V under DC control for 5 and 60 min at 20°C. The morphology, stoichiometry and microstructure of the obtained nanotubes were characterised by scanning electron, transmission electron microscopy, energy-dispersive X-ray spectrometry, X-ray fluorescence spectrometry, and Rutherford backscattering analysis. The electrochemical stability and corrosion mechanism of the nanotube oxide films were investigated using cyclic potentiodynamic polarisation and electrochemical impedance spectroscopy during immersion in phosphate buffer solution at 37 ± 1 °C up to 3 weeks. Fluorine content, nanotube morphology, microstructure and corrosion resistance are discussed with respect to their optimisation for potential antibacterial coatings.

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SYNTHESIS OF COATINGS IN MOLTEN SALTS FOR CREATION OF FUNCTIONAL MATERIALS

Sergey KUZNETSOV

I.V. Tananaev Institute of Chemistry, Kola Science Centre RAS, 26a Akademgorodok, 184209 Apatity, Murmansk region, Russia, E-mail: kuznet@chemy.kolasc.net.ru

Extreme conditions of articles exploitation cause utilization of expensive refractory metals and alloys ensuring their adequate performance. The problem can be approached by depositing coatings on the surface of units and mechanisms, i.e. creating composite materials. In this case, the substrate material provides the strength and electric characteristics while the coatings realize the necessary surface properties.

Nowadays coatings are mostly produced by CVD, PVD methods, plasma and detonation spraying. At the same time, using ionic melts for deposition coatings is highly attractive. Molten salts provide the production of coatings by electrochemical synthesis, precise surface alloying, by employing the reaction of disproportionation and currentless transfer.

This study presents our findings in the area resulting in the production of different functional coatings that can be conventionally split into the following groups:

1. Corrosion-resistant coatings: from hafnium, niobium and tantalum obtained by stationary, non- stationary and pulse electrolysis.
2. Heat-resistant coatings: from hafnium and niobium-hafnium alloy on borosiliconizing graphite, diboride of hafnium.
3. Multifunctional coatings: carbides, borides and silicides of refractory metals.
4. Catalytic coatings: carbides of molybdenum on molybdenum substrate.
5. Barrier coatings: titanium and niobium coatings on glass-ceramic shells for hot isostatic pressing.

Modified anodising processes for light metals based on the incorporation of nanoparticles or nanocapsules

W. Fürbeth, D. Tabatabai, B. Tigges, S.K. Weidmann

DECHEMA e.V., Karl-Winnacker-Institut, Theodor-Heuss-Allee 25,
60486 Frankfurt am Main, Germany, fuerbeth@dechema.de

Anodising is a well established method for the corrosion protection of Al and Mg alloys. However, nowadays some anodising procedures should be replaced due to environmental conflicts. For example, chromic acid anodising is based on Cr(VI) compounds which have been banned from many applications, yet. Other anodising treatments, as e.g. hard anodising or plasma-electrolytic methods, need very high amounts of energy and are therefore not very cost-efficient.

As for some of these methods no generally accepted replacements have been developed, yet, there is a need for research on alternative anodising strategies using non harmful substances and less amounts of energy. In this presentation preliminary results of three running projects on modified anodising processes will be summarised. They have in common that chemical nanotechnology is used to improve the corrosion, adhesion or wear properties of the anodic oxide layers.

Phosphoric acid anodizing is frequently used to achieve good adhesion properties. Unfortunately, open porous layers do not exhibit sufficient corrosion resistance, however, the common sealing by hydration is not successful in this case. Moreover, such sealing process closes the pores completely and leads consequently to the loss of the good adhesion properties. An alternative approach could be a modified phosphoric acid anodising process (MPAA) to form oxide layers with large open pores followed by an incorporation of oxidic nanoparticles into the pores but preserving some of the porous structure in the surface region for adhesion promotion. Oxide layer structures with pore diameters up to 100 nm were achieved. SiO_2-particles were incorporated into the pores without closing them completely. The electrochemical behaviour is investigated in view of the corrosion performance of this novel surface modification process on AA1050. The results are discussed in comparison with non-impregnated MPAA-layers and CAA-layers.

Hard anodising is used to obtain corrosion and wear resistant aluminium surfaces, however, high amounts of energy are needed to obtain dense oxide layers. Therefore the aim of the second project presented is to obtain sufficient corrosion and wear resistance consuming less energy. This should be reached by pulse anodisation in sulphuric acid combined with an incorporation of hard oxidic nanoparticles increasing wear resistance as well as inhibitor-filled nanoparticles or nanocapsules providing self-healing properties. First results on the combined anodising process and the resulting oxide layer properties will be shown.

Also on AZ31 Mg alloys new anodising coatings should be developed which are generated at low voltages without the use of hazardous substances but still deliver comparably good corrosion protection. This shall be accomplished by electrophoretically incorporating mesoporous nanoparticles containing corrosion inhibiting substances into the growing anodising layer. Ultrasonic treatment should be used to support the oxide growth. First results on anodising methods at low voltage, the unfluence of ultrasound, the incorporation of nanoparticles and the corrosion properties will be presented.

A composite coating for corrosion protection of AM60B magnesium alloy

M. Bestetti, A. Da Forno, Politecnico di Milano/I; A Mandelli, S.P. Trasatti,
M. Trueba, Università degli Studi di Milano/I

Oxide films have been produced on AM60B magnesium alloy using micro-arc oxidation process in an environmentally friendly alkaline solution with and without addition of titania nanoparticles. The surface morphology and cross-section of anodized samples were analyzed by Scanning Electron Microscopy (SEM) coupled with EDS and the phase composition was investigated by X-ray Diffraction (XRD). Hardness tests were performed by means of a micro-hardness tester. Electrochemical polarization tests and wear tests were performed to evaluate the corrosion resistance behaviour and the wear resistance of the coated magnesium alloys. Addition of titania nanoparticles does not affect corrosion resistance significantly, but the oxide films produced in titania-containing solution are denser, thicker and have more uniform morphology than those produced in titania free solution. In the oxides achieved at 130V-140V in presence of titania (4g/l) a spinel phase ($MgAl_2O_4$) was observed. Spinel increases the hardness up to 550 HV (10mN, 10 s). The addition of titania nanoparticles in the solution represents an interesting way to synthesize hard coatings on magnesium alloy AM60B by micro-arc oxidation in a short process time (10 minutes).

Optical and electrochemical measurement of the thickness of anodic thin films on titanium

Maria Vittoria Diamanti, Marco Ormellese, Barbara Del Curto, MariaPia Pedeferri,
Politecnico di Milano, Milan/Italy; presenting author: MariaPia Pedeferri

Anodic oxidation of titanium has been widely addressed in several research articles, since the properties of the so formed oxide layer are of particular interest in several fields. Its applications range from the creation of photocatalytic devices, to the improvement of biomedical implants characteristics, to architectural and design applications that exploit the chromatic properties conferred to the oxides by interference phenomena.

The research work here presented is aimed at providing a better understanding of the oxide growth process in diluted sulphuric acid media, with specific reference to the influence of applied voltage, through the determination of its thickness, as well as its colour, morphology and structure. In particular, attention was focused on the thickness of the anodic oxides, which was cross-investigated by means of spectrophotometric measurements and by elaborating galvanostatic polarization data. Comparisons will be displayed between commercial purity titanium and Ti6Al4V alloy.

Spectrophotometry also provided information about the oxide chromatic properties. its structure was investigated by means of X-Ray Diffraction measurements, while the surface morphology was observed with Scanning Electron Microscopy.

The oxides were proved to have amorphous structure up to a threshold applied voltage, where spark deposition phenomena occurred and crystallization in the form of anatase began. As for the oxide thickness, a linear dependence of thickness on applied voltage is frequently reported in literature, since the range of analysis is usually limited. Nevertheless, two separate growth rates were detected: 2.1 to 2.4 nm/V, depending on material and electrolyte, at applied voltage higher than 10 V, and an almost doubled growth rate at lower voltages. This was ascribed to the lower resistance to oxidation demonstrated by the substrate before the generation of a sufficiently thick barrier film.

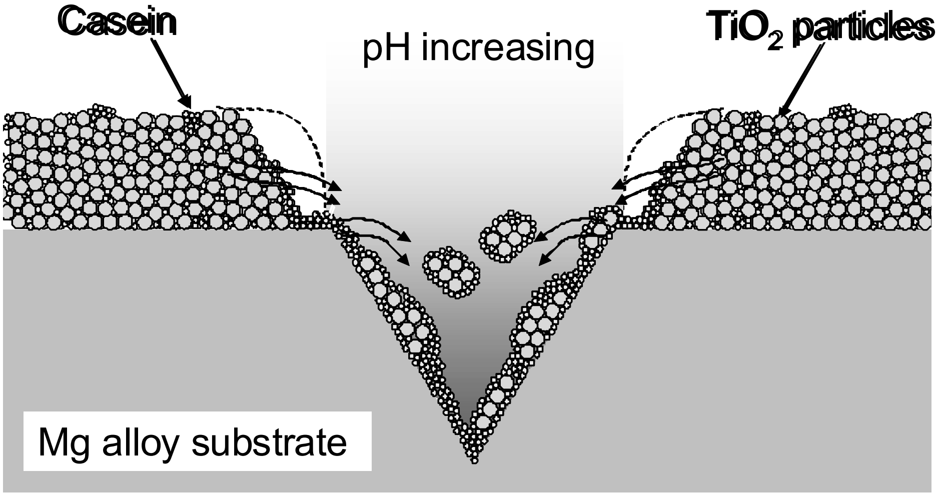
Self-Healing Corrosion Protective Coatings by Oxide Particles and a pH-Sensitive Organic Agent on a Magnesium Alloy

Akihiro Yabuki, Hiroshima University, Higashi-Hiroshima, JAPAN;
Mariko Sakai, Hiroshima University, Higashi-Hiroshima, JAPAN

Keywords: chrome-free, coatings, magnesium, partciles, self-healing

Abstract

Magnesium and its alloys have many excellent properties, such as the lowest density of industrial metals. Poor resistance to corrosion, however, limits the application of these materials in corrosive environments. Thus, protective coatings are needed for improved resistance. In this study, a self-healing corrosion protective coating was developed using environmentally friendly material for magnesium alloy AZ31. The coating uses TiO_2 oxide particles and casein as a pH-sensitive organic agent. A film made up of TiO_2 particles was formed on a magnesium alloy plate by dip coating, which was then immersed in a casein solution of pH12 to be inserted into the particle film. An acid solution was then added to adjust the pH of the casein solution and fix the casein in the TiO_2 film. After using a knife-edge to create an artificial defect in the coating, a corrosion test was carried out in a NaCl solution at a temperature of 35 °C. Self-healing properties were evaluated by monitoring the polarization resistance of the scratched specimen in the corrosive solution and observing the surface appearance of the specimen after the corrosion test. After changing the pH of the solution from 12 to 5, casein 3-4 μm in mean diameter were observed on the surface of the TiO_2 film. The polarization resistance of the scratched specimen in the corrosive solution was increased with testing time, and a deposited film consisting of TiO_2 particles and casein was observed after the test. Thus, it was confirmed that the coating had self-healing properties. The self-healing effect of the coating appeared to be due to the release of casein micelles and TiO_2 particles as a result of the pH increase caused by the cathodic reaction in the corrosion process, and by the formation of a film on the defect (Figure).



Thin, Nanoparticulate Coatings for the Improvement of the Corrosion and Passivation Behavior of AZ Magnesium Alloys

Florian Feil, Wolfram Fürbeth, Karl-Winnacker-Institute, DECHEMA e.V, Frankfurt am Main /Germany;

The advantage of magnesium as lightest construction metal is often overshadowed by its high reactivity and poor corrosion performance. In contrast to aluminium based materials, magnesium alloys do not form a stable, self-protective oxide layer at pH values lower than 12. Therefore for most fields of application, magnesium based devices require appropriate protective coatings.

We recently developed a procedure to apply thin (usually less than 1 µm thick) coatings based on aqueous silica nanoparticle dispersions and sol-gel sealings onto AZ magnesium alloys.[1] These purely inorganic, multilayered coatings could offer a higher thermal and mechanical stability than most organic or hybrid coatings. Compared to their limited thickness, these coatings offer decent protective properties. However, even if these coatings are crack- and defect-free, they do not isolate the substrate completely from environmental influences. During corrosion tests in different electrolytes, a passivation process can be observed. The order of passivation seems to depend on coating thickness, porosity and composition, as well as the electrolyte. Especially the addition of rare earth compounds to the coating materials seems to improve the passivation process and the long-term stability.

We compared the passivation behaviour of different coated samples (coatings based on aqueous dispersions, sol-gel sealed samples and multilayer coatings) in various electrolytes. Observations from time dependent EIS experiments were correlated with results from complementary techniques like electron microprobe analysis, electron microscopy, AFM, Kelvin microprobe analysis, AAS and salt spray tests. Electron microprobe analysis of the corroded areas reveals the deposition of corrosion products under the intact coatings. This shows that electrolyte diffusion thru pores in the coating limits the protective properties and corrosion appears.

Depending on the electrolyte used during electrochemical investigation a more or less stable layer composed of corrosion products is formed under the coating, increasing the coating resistance. The inorganic coating helps to improve the passivation behaviour by keeping the corrosion products together. We also observe an increase of the aluminium content in the deposited corrosion products under the coating compared to the base alloy. This indicates depletion of Mg^{2+} ions into the electrolyte.

Currently we are trying to use this occurrence as advantage. By using adequate electrolytes for immersion of the coated samples we selectively try to deposit stable, insoluble compounds under the coating. The accumulation of aluminium salts could also help to form a more stable, better protective oxide skin than normally formed on AZ alloys. While keeping the smooth surface and the transparent appearance of the nanoparticle based coatings, this process could be promising to improve the protective properties and to form a visually appealing, purely inorganic corrosion protection system for magnesium alloys.

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GLASS-LIKE ENVIRONMENTALLY FRIENDLY SOL-GEL COATINGS FOR CORROSION PROTECTION OF METALS

Rosero-Navarro N.C., Castro Y., Aparicio M., Durán A.
Ceramic and Glass Institute (CSIC), Spain, karolrosero@icv.csic.es

Metal substrates such as aluminium, magnesium and their alloys present good mechanical properties, high conductivity and easy machining, but suffer localized corrosion when they are exposed to aggressive environments limiting their applications in different fields. Thus, active protection is strongly necessary to prevent the corrosion as well as any minor damage incurred in service. At present, the most efficient protection systems are chromium based coatings, like Chromium Conversion Coatings (CCC) and Chromium Acid Anodised (CAA), which offer a self-healing protection. However, chromates are considered as potential lung carcinogen responsible for DNA damage and make them environmentally hostile. A lot of research has been focused on the use of rare-earth metal compounds as an alternative for chromates.

In this work, we present a new type of CexOy glass-like coatings produced from cerium nitrate and using different complexing compounds: citric acid, acetic acid and diethano-amine and surfactants1. The surfactant plays a critical role in the synthesis of homogeneous and adherent coatings on different substrates. The characterization of the coatings includes FTIR-ATR, TEM, SEM, GDOES, polarisation curves and electrochemical impedance spectroscopy (EIS) as well as standard test. Transparent and yellowish coatings were obtained by dipping with thickness up to 500 nm. GDOES revealed a shifting of the cerium signal to the interface region between coating and substrate compared with the cerium signal in the profiles recorded before immersion. The EIS results show an increase in the protective properties of the coatings with a rise of $|Z|$ and phase angle with the immersion time. These CexOy glass-like coatings have demonstrated their suitability to substitute current conversion coatings and produced in different substrates including aluminium and magnesium alloy.

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1 N. C. Rosero-Navarro, Y. Castro, M. Aparicio, A. Durán, Spanish and PCT patents. Ref. P200930982

Protective enamel coatings deposited on steel

S. Rossi, *E. Scrinzi*

Department of Materials Engineering and Industrial Technologies, University of Trento,
Via Mesiano 77, 38123 Trento, Italy

Enamelling is one of the oldest techniques to protect metallic substrates from corrosive phenomena and to improve the aesthetic aspects.

In this work, the durability and the change in the surface properties of different types of enamels are investigated. Low–carbon steel panels were coated with different types of vitreous enamel applied by two different methods: wet dip coating and electrostatic powder coating. The protection system consisted of two protective layers with a total thickness between 115 μm and 370 μm.

The abrasion resistance of the enamel coatings was evaluated through falling abrasive test using Ottawa sand as abrasive agent. Gloss measurements were used to quantify the loss of aesthetic properties. To evaluate the decrease of protection properties against corrosive phenomena, electrochemical impedance spectroscopy was used in 5 %NaCl solution simulating an aggressive environment. The electrochemical impedance measurements were carried out step by step every 2 litres increments of fallen abrasive amount. Coating resistance of 10^6 Ωcm^2 was considered as the threshold for the loss of protective protection properties of the enamel layers.

In order to highlight the morphology of the damage and correlate it to the changes in the gloss and protective properties, the damaged surfaces were observed using optical and electronic microscopes.

The erosion of the coating uncovered the porosity present inside the enamel, causing an increase of the surface roughness and a consequent reduction of gloss. For the samples studied, the corrosion protection properties were similar. The enamel coating protected the substrate as a barrier effect. To lose the protection properties, it was necessary to have a substantial reduction in the thickness or the formation of cracks.

To investigate the influence of the environment on the aesthetic-perceptive and protective properties of the enamel coatings, the samples were exposed to UV radiation for 1000 hours.

The changes of aesthetic properties were evaluated through colour change measurements. The samples showed a high resistance to UV radiation due to the inorganic nature of the used pigments and of this kind of coating. Nevertheless, some samples showed a slight reduction of gloss and a colour change.

Anticorrosive properties of coatings based on aqueous materials

***S.A. Nenakhov*, V.P. Pimenova**
NPP "Teplohim", Moscow, Russia

Water-based coatings in recent years rapidly replacing paints on organic solvents. The only area where, so far beyond the competition are solvent-based materials, is to protect metals from corrosion. Skepticism of experts to protect against corrosion on the anticorrosive properties of aqueous coatings, though diminished by some success in the area of protecting metals from corrosion by water-based coatings in atmospheric conditions, but still not cleared especially for corrosion protection of responsible products, respectively.

The report attempts to review the current state of the problem anticorrosive properties of coatings from water-based materials in terms of modern physico-chemical concepts on the functioning of protective coatings and electrochemical measurements on these coatings formed from typical water-based materials, and ways to further improve the anticorrosive properties of coatings based on aqueous materials. On the basis of electrochemical measurements (electrical resistance, capacitance, electrode potential , the corrosion current) systems with different types of coatings showed that water paints with different nature of film-forming can be divided into two groups.

Coatings of the first group - coatings based on dispersed film-forming agents - have very low electrical resistance, higher capacity, the potential of near-cue to the potential of the metal and sufficiently high currents of corrosion. Coating of the second group - on the basis of film-forming emulsion of different nature - have a fairly high resistance (tens of kilohms), low capacity, a more positive potential (rather than the protected metal) and small currents of corrosion and they also show some diffusion resistance.

The hypothesis that the observed difference is due mainly to the character of pores (cross-cutting and closed) and the concentration of pores formed in the coatings based on dispersed and emulsion film-forming agents. The data show promising directions for further efforts on the emulsion and water-soluble paints. They also show that in the study and development of low-resistivity water materials can be successfully used the method of chronopotentiometry. It is conjectured that it was the second group of coatings to enhance their electrochemical resistance can be successfully applied methods are widely used in anticorrosion practice (inhibition, sacrificial anode and passivating effect).

Fluoropolymer anticorrosion coatings

Eliana Ieva[2], Fabio Polastri[1],Tiziana Poggio[2], Shiow Lin[3], Valery Kapeliouchko[2]

[1] Solvay Solexis, Bollate, Italy
[2] Solvay Solexis, Spinetta Marengo,Italy
[3] Solvay Solexis, West Deptford, US

In the field of anticorrosion coatings, fluoropolymers play a fundamental role due to their impressive properties guarantee from the out standing chemical structure. High chemical and thermal resistances permit to protect items from corrosion in very aggressive environments.

Two fluoroplastics have been considered as successful choice in anticorrosion coating field. Partially fluorinated Halar® ECTFE polymer (EP1281730) can be applied with electrostatic powder coating or with spray coating in the slurry formulation. The processing results very simple and high thickness coating could be obtained with very good performances of chemical protection.

Perfluorinated Hyflon® PFA and MFA polymers are normally applied with EPC to generate coatings with higher temperature and chemical resistance.

In the present work coating technology, processing conditions and coatings properties have been analyzed. Results on permeation, surface properties and adhesion will be presented in comparison to other coating materials.

Application examples in anticorrosion fields, mainly focused on Chemical processing, Semiconductor and Oil&Gas Industries, will be illustrated to show the excellent performances of our fluoropolymers.

Effect of temperature on the impedance behaviour of coated mild steel in 3% sodium chloride solution.

J.M. Sykes, Z. Sharer Sahir

Department of Materials, University of Oxford, Parks Rd, Oxford OX1 3PH, UK

Mild steel panels coated with epoxy-phenolic and polyamide cured-epoxy paints have been exposed to 3% sodium chloride solution at 50°C and tested by electrochemical impedance spectroscopy (EIS) across a range of temperatures. High temperature exposure coupled with EIS has been shown to be a useful way to accelerate testing (Walter). More recently, EIS and temperature cycling has been used by Bierwagen to further speed up coating deterioration. Tests by Ochs and Vogelsang using another technique called 'relaxation voltammetry' at different temperatures have leads to the conclusion that the processes controlling coating resistance exhibits high activation energy.

In the present study, fitting of the EIS response to a model circuit was used to determine the film resistance and the charge transfer resistance for the corrosion reaction as a function of test temperature. The activation energy determined from these values is low for film resistance (typical of ion transport), but very often much higher for the charge transfer resistance. The most likely explanation is that the corrosion reaction is not controlled by the coating film resistance.

A combined macroscopic adhesion and interfacial bonding study of epoxy coatings on pretreated AA 2024-T3

Ö. Özkanat[1,2], B. Salgın[3], M. Rohwerder[3], J.M.C. Mol[2], H. Terryn[1,4], J.H.W. de Wit[2]

[1] Materials innovation institute (M2i),
Mekelweg 2, 2628 CD Delft, The Netherlands, o.ozkanat@m2i.nl
[2] Delft University of Technology, Department of Materials Science and Engineering,
Mekelweg 2, 2628 CD Delft, The Netherlands
[3] Max-Planck-Institut für Eisenforschung GmbH, Max-Planck-Straße 1,
40237 Dusseldorf, Germany
[4] Vrije University Brussels, Research Group Electrochemical and Surface Engineering
Pleinlaan 2, B-1050 Brussels, Belgium

In the aerospace industry, there is an increasing demand towards aluminium alloys owing to their lightweight and low cost properties. These alloys, prone to corrosion-induced degradation, are generally in need of a protection by organic coatings. Nevertheless, even such composite systems might become ineffective over the long service period due to the loss of adhesion at the polymer/(hydr)oxide/aluminium interface. Therefore, the achievement of the long-term stability of these systems requires the control and the understanding of the phenomena that originate at these interfaces.

In this work, AA 2024-T3 and bisphenol-A based epoxy coatings have been selected as a model system. The effects of surface pretreatments on the polymer/(hydr)oxide/aluminium interface have been studied by investigating two aspects: the molecular bonding mechanism and the macroscopic adhesion properties. The molecular bonding mechanism of functional groups -which are the representative interfacial adhesive molecules of the epoxy coating- has been investigated by utilizing grazing angle Fourier Transform Infrared Spectroscopy (FTIR). As a result of different surface pretreatments, bonding mechanisms (bridging bidentate and/or unidentate) of the representative molecules have been revealed. In order to investigate the adhesion forces at a macroscale, lap-shear (Universal Tensile Testing Machine) and scratch (Micro Scratch Tester – CSM Instruments) tests have been performed on differently pretreated surfaces. The same investigation has also been carried out as a function of three different coating compositions. Results have shown that both surface pretreatments and the chemical composition of the coating significantly affect the structural bond strength, as well as the failure type (adhesive and/or cohesive). Furthermore, in order to link the macroscopic adhesion forces to chemical properties of the buried interface, Scanning Kelvin Probe (SKP) measurements are being carried out.

On the Joining of Metal and Plastic: Structuring, Coating, Corrosion, and Water Permeability

Allan H. Holm[1], Jeppe Byskov-Nielsen[2], Rune Hoejsholt[3], Jens V. Boll[3], Pedro Sá[3], Peter Balling[2].

[1]*Grundfos Management A/S, Research Department, Poul Due Jensens Vej 7, DK-8850 Bjerringbro, Denmark, ahholm@grundfos.com*
[2]*Aarhus University, Department of Physics and Astronomy, DK-8000 Aarhus C, Denmark*
[3] *Grundfos Management A/S, Poul Due Jensens Vej 7, DK-8850 Bjerringbro, Denmark*

Laser surface structuring has been employed to create new and interesting composite materials. Joints between metallic and polymeric have been made with exceptionally high joint strength.[1] In this communication we elaborate on the concerns regarding corrosion resistance of the joints and the possible protection by the use of extremely thin organic coatings. Unfortunately, the laser surface structuring apparently leads to recasted metal that has a lower corrosion resistance than the starting material. For many applications the joints absolutely need to minimize the water permeability going through the bulk material and also the metal-polymer interface. Leak test at a range of temperatures have been performed and evidence that it, in our hands, is not possible to produce a "perfect item" in that the mass transport is controlled by pore transport. The diffusion through the compact material represents only a fraction of the overall water permeability.

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Electrochemical Studies of Electroactive Conducting Polymers Containing Corrosion Inhibiting Ions

Christopher A. Vetter, Maocheng Yan, Victoria Johnston Gelling

A polypyrrole/aluminum flake composite pigment was synthesized via an aqueous chemical oxidation process. The pigments were doped with sulfate, molybdate, vanadate, or phosphate during the synthesis procedure. Epoxy primers containing 35% by volume of the different polypyrrole composite pigments were drawn down onto aluminum 2024 T3 panels and then studied with SVET and coupling current measurements. It is evident from the coupling current results that the dopant has a large affect on the coupling between the coating and the aluminum 2024 substrate. While the primer doped with sulfate exhibits a large coupling current in the presence of nitrogen, in the presence of air it does not couple with the substrate. The primer doped with molybdate however, exhibits very low coupling current in the presence of nitrogen and a high amount of coupling in the presence of air. In all cases of coupling the PPY composite acts as the anode in the electrochemical cell indicating that the PPY may be activating the aluminum flake towards anodic activity. These results highlight the important role of oxygen in the galvanic coupling between PPY coatings and active metal substrates. The SVET results show that while the primers doped with sulfate and phosphate do not inhibit corrosion to any large extent in defect areas, the primers doped with vanadate and molybdate do inhibit corrosion in defect areas. This behavior could be due to dopant release from the polypyrrole films.

Smart functionalized polymer dispersions for effective mapping of heterogeneous metal surfaces: New concepts for corrosion protection

Sergej Toews[1], Wolfgang Bremser[1,]* Horst Hintze-Bruening[2], Michael Dornbusch[2]

[1]Universität Paderborn, Coating and Surface Technology, Warburgerstrasse 100, 33098 Paderborn, Germany;
Phone +49 5251 60 3876
*Corresponding Author, Email: wolfgang.bremser@tc.uni-paderborn.de

[2]BASF Coatings GmbH, Glasuritstrasse 1, 48165 Muenster, Germany

The development of environmental friendly coatings for corrosion protection of steel continues to attract a great deal of attention. Within this paper we present a new concept for corrosion protection based on functionalised water borne latexes and their application to heterogeneous metal surfaces such as hot dip galvanized (HDG) steel.

It is well known that industrial HDG steel samples show a heterogeneous surface. In the first part of this paper we characterised the different surface chemistry. The characterisation of the surface was performed with a high lateral resolution on a nanometre scale by Scanning Auger Microscopy (SAM) and Energy Dispersive X-Ray Spectroscopy (EDX) attached to an ultra high resolution Field Emission Scanning Electron Microscopy (FESEM). The electrochemical mapping was obtained by a micro Scanning Capillary Cell (SCC) and Scanning Kelvin Probe – Force Microscopy (SKP-FM).

In the work for the second part of this paper, we synthesized water borne polymer dispersions with different functional anchoring groups on the surface of the dispersion particles and investigated the adsorption of these latexes to the HDG steel surface during a dip coating process. It was possible to design polymer particles, able to map the heterogeneous substrate surface effectively.

The combined micro-electrochemical investigations and the synthetic approach, designing latexes for very selective surface adaptation, could provide a new route to “smart coatings” adapted to the very specific heterogeneous chemical and electrochemical properties of industrial surfaces.

HYBRID COATINGS BASED ON CONDUCTING POLYMERS AND POLYSILOXANES

Monica Trueba, Stefano P. TRASATTI

Dept. of Physical Chemistry and Electrochemistry, Università degli Studi di Milano,
Via Golgi 19, 20133 Milan,Italy
Email address: monica.trueba@unimi.it, stefano.trasatti@unimi.it

One of the challenges in developing polypyrrole coatings for efficient corrosion protection is to overcome processability difficulties and to improve adhesion onto active metals. On the other hand, silane-based treatments, which are very attractive for simple application, improved adhesion and outstanding corrosion protection, act essentially as a physical barrier. Doping with small amounts of chemicals having corrosion inhibiting properties is needed for these films to acquire active protection.

We have developed a new approach leading to obtain a composite film containing polypyrrole units and polysiloxane linkages in a simple way using a pyrrolil silicon compound as a primer on as-received wrought Al alloys [1]. The outstanding corrosion protection, with respect to classical organofunctional silanes and polypyrrole films, was attributed to: (i) higher degree of compactness and thickness, resulting from the primer molecule crosslinking via silanol groups condensation and pyrrole ring couplings; (ii) improved adhesion due to preferential adsorption of silanol groups and condensation at the metal/film interface; (iii) mixed protection in terms of passive (barrier) and active (anodic) actions provided by polysiloxane and polypyrrole chains within the composite network, respectively.

Further confirmation of the validity of this approach as applied to low carbon and hot-deep galvanized steels was obtained by different corrosion tests in correlation with spectroscopic characterization techniques, when compared to control coatings of poly-2H-imidazole-silane (PImSi) and polyoctylsilane (POSi).

In order to get further insight into mechanistic aspects of the coating deposition on the substrate surface and its corrosion performance, we are currently working on aniline- and thiophene-silicon molecules.

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Appraised Dry Film Thickness - new concept for the interpretation of DFT data collected from coated structures

Łukasz Augustyński, M.SC, Road and Bridge Research Institute
Agnieszka Królikowska, Ph. D., Road and Bridge Research Institute

Dry Film Thickness of a coating onto steel structure is one of the three major factors influencing the durability of anti-corrosion protection (DFT, shape, environment).
The assessment of DFT might be an useful tool to forecast the performance of the coating of a structure aimed to be exposed to a natural environment.
If the structure is build with a complex geometry, the coating thickness will have different values in scattered locations. Recording all thickness data distribution from all elements of a huge structure (e.g. a bridge structure) is expensive, complicated and consequently is usually neglected by the owner.
On the other hand the owner is particularly interested in assessment of the structure's condition in such a way as to allow the durability of a structure to be evaluated as far as possible.

In this paper the introduction of a new concept: *Appraised Dry Film Thickness (ADFT)* is proposed, being a function of local DFT data gathered from all elements of the structure. This value is a characteristic parameter for any complex structure and will help to forecast the durability of a coating system.
The algorithm proposed for Appraised Dry Film Thickness assessment is a development of the method mentioned in ISO 19840.

Actual DFT data collected from steel structures by authors as well as results of their own laboratory investigations of durability of paint systems depending on ADFT's value in different environments were used.

A COATING COMBINATION OF SELF-HEALING POLYMERS AND CORROSION INHIBITORS FOR ACTIVE CORROSION PROTECTION OF METALS

I. DE GRAEVE[1], G. VAN ASSCHE[2], G. SCHELTJENS[2], J.-B. JORCIN[1], E. TOURWE[1], Y. VAN INGELHEM[1], A. HUBIN[1], B. VAN MELE[2], Y. GONZALEZ-GARCIA[3]; J.M.C MOL[3]; H. TERRYN[1]
Vrije Universiteit Brussel
[1] Group of Electrochemical and Surface Engineering
[2] Group of Physical and Polymer Science
Pleinlaan 2, 1050 Brussels, Belgium
[3] Delft University of Technology, Department of Materials Science and Engineering, Mekelweg 2, 2628CD Delft, The Netherlands
Corresponding author: Y.GonzalezGarcia@tudelft.nl

Abstract

A polyurethane (PU) based segmented block copolymer with polyester (PCL) soft blocks was deposited as a coating. This physically crosslinked polymer system shows a self-healing ability based on the fracture and reformation of thermally reversible physical bonds in the polymer matrix. Because heat is necessary to trigger and assist the healing process, these materials are classified as non-autonomic healing polymers. The investigated polymer system is generally not used for coating of metals, hence its potential as a coating material was explored. Additionally cerium nitrate was added to the coating formulation as corrosion inhibitor. As such a multiple action self-healing coating system was created based, on the one hand, on the inhibitor passivating the metal when the coating is damaged and the metal exposed to a corrosive environment, and on the other hand, on the ability of the coating material itself to physically heal a sustained local damage resulting in the repair of the barrier properties. The healing ability of this combined polymer system was studied in bulk and as a coating using various thermomechanical analyses and Electrochemical Impedance Spectroscopy (EIS). First results indicate that when the coatings are locally damaged by scratching, a thermal treatment to a temperature above the melting point of the soft PCL phase in the block copolymer and below the melting point of the hard PU phase, results in coating repair as observed using AFM and in a regaining of its barrier properties as observed with EIS.

Self-healing anticorrosive organic coating based on the release of a reactive Silyl Ester

S.J. Garcia[1], H.R. Fischer[2], P.A. White[3], J. Mardel[3], A.E. Hughes[3], J.M.C. Mol[4]

[1] Delft University of Technology, Department of Aerospace Materials and Manufacturing, Kluyverweg 1, 2629 HS, Delft, The Netherlands
[2] TNO Industry and Technology, Materials Performance, De Rondom 1, 5612 AP, Eindhoven, The Netherlands
[3] CSIRO Materials Science & Engineering, Clayton South MDC, Clayton, 3169, Australia
[4] Delft University of Technology, Department of Materials Science and Engineering, Mekelweg 2, 2628 CD, Delft, The Netherlands

The easiest and mostly applied method to protect and to reduce corrosion rates of metals is the use of organic coatings which offer protection by active pigment release and passive barrier mechanisms. However, when these systems suffer any kind of damage the passive protection is no longer there and the metal substrate is directly exposed to the corrosive environment. Under these conditions, corrosion inhibitors, of which the most used and efficient ones are chromate-based pigments, are leached out from the coating and act at the metallic substrate. This mechanism is known as self-healing (SH) mechanism by inhibitor release. Intrinsic to this approach is that the pigment in the coating is released without control until there is no more pigment left in the coating. This leaves a depletion zone in the coating that does not allow further protection.

During the last decade, a different active SH mechanism based on the sealing of the crack-damage has been described and implemented to anticorrosive organic coatings. This second approach proposes the recovery of the barrier protection by the reaction of chemical species that are released from the coating or by the use of expandable phases which will close the crack. One of the problems of this approach is that the sealing of the crack can entrap water and corrosive agents between the newly created barrier system and the metal thus impelling undercoating corrosion processes.

A possible solution to these problems would be the use of a system that protects the metallic surface by reaction with water at the metallic surface creating a passive layer on top of the metal. In this work a new organic-based healing agent based on a silyl ester is presented and its synthesis and performance is described. The silyl ester was first tested as a repairing agent (assisted healing) and secondly encapsulated and incorporated into an organic matrix to study the autonomic self-healing properties of the complete system. A new high-throughput technique for healing agents' evaluation named multiwell was employed to determine the minimum amount of agent to heal a crack. In order to evaluate the healing ability of the silyl ester, Electrochemical Impedance Spectroscopy (EIS) is used and identified to be a key technique for the development and performance evaluation of self-healing anticorrosive organic coatings.

Study of the effect of mechanical treated cerium (IV) oxides on the corrosion protection of painted galvanized steel

M. Fedel, F. Deflorian, S. Rossi
University of Trento, Department of Materials Engineering and Industrial Technologies,
Via Mesiano 77, 38123, Trento, Italy

The potential of cerium (IV) oxides as active pigments to provide corrosion inhibition was investigated by a few authors. However, the effectiveness of these inorganic pigments and their protection mechanism is not completely understood. In this work, the effectiveness of mechanically treated CeO_2 nanoparticles as active filler into an organic coating was investigated. For this purpose, different cerium (IV) oxide nanoparticles were added to the polymeric matrix: mechanically treated CeO_2 nanoparticles, mechanically treated CeO_2/SiO_2 nanoparticles and mechanically treated SiO_2 nanoparticles (used for comparison). The nanoparticles were dispersed into the polymeric matrix and HDG steel panels were coated with the different paints. The painting systems containing the different nanoparticles were characterized using electrochemical techniques, such as electrochemical impedance spectroscopy (EIS) and cathodic polarization and exposure in the salt spray chamber (NSST). A Cr^{6+} pre-treated sample was used as a reference to compare the performances of the other samples. The NSST results (considering both scratched and intact samples) proved the good performances of the coating containing the CeO_2/SiO_2 mixed nanoparticles. The paint containing only the mechanically treated SiO_2 nanoparticles showed a fairly good resistance in the salt spray chamber considering the scratched samples. However, the corresponding intact samples showed a great extent of blistering formation (after 1000h of exposure in the salt spray chamber).

The EIS measurements evidenced the low corrosion protection properties of the paints containing only the mechanically treated CeO_2 and SiO_2, respectively. After about 1250 hours of immersion in 0.1M NaCl solution, the chrome control sample showed a very good corrosion protection level, proved by the value of the low frequency impedance in the order of $10^{10}\Omega cm^2$, while the samples containing the mix of mechanically treated CeO_2/SiO_2 nanoparticles showed a decrease of this value, related to a decrease of the protection properties of this coating. In particular, after the 1250h of exposure, the paint containing the mix of mechanically treated CeO_2/SiO_2 nanoparticles showed total impedance value in the order of $10^9\ \Omega cm^2$.

The cathodic polarization tests (-1.6V vs Ag/AgCl, 5 cycles of 30 minutes) evidenced the low extent of detachment of the coating containing the mix of mechanically treated CeO_2/SiO_2 nanoparticles.

The electrochemical characterization and neutral salt spray test results proved the effectiveness of the mechanical treated cerium (IV) oxides treated together with SiO_2 as active pigments to improve the corrosion protection of the substrate. In addition, it was evidenced that the paint containing only the CeO_2 nanoparticles or only the SiO_2 nanoparticles is not able to ensure good corrosion protection of the substrate.

Interaction of carboxylic acid groups with zinc surfaces

P. Taheri[1,2], *J.M.C. Mol*[2], *H. Terryn*[1,3], *J.H.W. de Wit*[2], *J.R. Flores*[4],
F. Hannour[4]

1 Materials Innovation Institute (M2i), Mekelweg 2, 2628 CD Delft, The Netherlands,
P.Taheri@tudelft.nl
2 Delft University of Technology, Department of Materials Science and Engineering,
Mekelweg 2, 2628 CD Delft, The Netherlands,
J.M.C.Mol@tudelft.nl, J.H.W.dewit@tudelft.nl
3 Vrije Universiteit Brussel, Department of Electrochemical and Surface Engineering,
Pleinlaan 2, B-1050 Brussels, Belgium,
hterryn@vub.ac.be
4 Corus Research, Development and Technology, PO Box 10.000, 1970 CA
IJmuiden, The Netherlands,
jose.flores@corusgroup.com, fouzia.hannour@corusgroup.com

The present paper investigates the interfacial bonding properties of copolymerized polyolefin coating on pure zinc substrate as a function of surface composition. Galvanized steel has been used for over one century, as the zinc based coating that effectively and economically can protect underlying steel parts from corrosion. Additionally, the surface of galvanized steel is often painted to provide a superior corrosion resistance as well as an asthetic look. Consequently, the bonding characteristic of the paint is one of the most important factors affecting the final corrosion properties. It is known that the surface composition significantly affects the bonding characteristics. Conversion coatings are an alternative way to modify the surface composition and consequently the bonding characteristics of the polymer coating to the surface. For this reason, it is crucial to understand the surface composition of different treated samples which in turn control the de-adhesion and delamination of the organic coating. The localized acid-base properties of the treated surfaces have been evaluated with X-ray photoelectron spectroscopy (XPS). However, studying the bonding characteristics of the polymeric coating to the metal surface at the buried interface is challenging from an experimental perspective. For that reason, the functional groups of the polymer coating can be simplified to model the bonding functionality. Since the copolymerized polyolefin coatings were found to chemisorb and form carboxylate groups, succinic acid was selected to model the used coatings and self-assembling monolayers. The mechanism of bonding interaction between succinic acid and differently pretreated Zn-based surfaces was studied in detail by FTIR-RAS. The results show a clear correlation on the hydroxyl fraction and the number of adsorbed molecules to the surfaces.

NEW NON-TOXIC PRETREATMENT AND WATER BASED WASH PRIMER FOR THE AIRCRAFT INDUSTRY

M. Kharsan, Angel Green, Cortec Corporation, White Bear Lake, MN/ USA

Today's Department of Defense is charged with the pursuit of environmentally preferable alternatives to products and processes traditionally used. The highly specialized coating process of the military aircraft is one area where such an initiative is underway. NASA, in coordination with the Tri-Services is actively seeking greener alternatives to chromate coatings.

This abstract will discuss the development of a non-toxic, non-hazardous, self-healing pretreatment as well as a low VOC, water based wash primer. The products will undergo both real world evaluations in a salt water environment, as well as in-depth laboratory testing.

OBJECTIVE

To prove that the products will pass the required 3000 hours of salt spray testing in accordance with the military specification. Two competitive pretreatments and a competitive urethane topcoat were evaluated with the newly developed pretreatment and wash primer.

Another objective was to see if one of the products in the 3-step coating process could be eliminated thus reducing the over all cost of coating aircrafts as well as providing the same corrosion protection of the existing coating system.

RESULTS

The data showed the compatibility of the available pretreatments and the developed pretreatment with the developed water based wash primer.

The test concluded that the new wash primer was most compatible with one of the competitive pretreatments as well as the developed pretreatment. The pretreatment and the wash primer passed the required 3000 hours of salt spray testing.

Further test results showed that having just a pretreatment and a topcoat would pass the 3,000 hours of salt spray testing. The results that were found were that the developed pretreatment with the competitive urethane topcoat passed the 3,000 hours of salt spray testing. Also the developed pretreatment with a developed moisture cure urethane passed the required 3000 hours of salt spray testing as well.

CONCLUSION

Extensive formulation work has resulted in a new non-toxic pretreatment and wash primer that provides the corrosion protection required for NASA and the US Air force. The benefits of this new coating system are that it provides the same amount of corrosion protection for aluminum substrates as the currently used chrome based pretreatment systems.

Another benefit of the coating system is that the second step in the process, the wash primer, may be able to be eliminated, and a pretreatment and topcoat could be all that is needed to meet the aerospace industries requirements.

Electrochemical behaviour of ZrO_2 sol-gel pre-treatments doped with cerium nitrate on AA 6060 aluminium alloy

L. Paussa[1], N.C. Rosero Navarro[2], F. Andreatta[1], D. Bravin[1],Y. Castro[2], M. Aparicio[2], A. Duran[2], L.Fedrizzi[1]

[1] Department of Chemical Science and Technology, University of Udine, Italy;
[2] Instituto de Cerámica y Vidrio (CSIC), Campus de Cantoblanco, Spain;

Aluminum alloys are widely employed in many industrial and building applications due to good combination of mechanical properties and low density. In particular, alloys of the 6xxx series like AA 6060 are extensively employed in rolled and extruded products. Sol-gel coatings represent an alternative corrosion protection method to chromate based systems, which must be replaced. Recently, it was shown that ZrO_2 based sol-gel coatings deposited on AA 6060 can provide good corrosion protection to AA 6060. However, ZrO_2 based sol-gel systems cannot provide self-healing effect, which is a peculiar property of chromate conversion coatings. Indeed, the structure of the zirconium oxide does not contain species able to restore barrier properties when defects or damage impairs coating protection.

In this work, ZrO_2 based sol-gel coatings doped with cerium nitrate were produced in order to evaluate the inhibition effect of cerium ions for aluminum alloys coated with sol-gel films. The cerium nitrate was added to the solution containing the zirconium alkoxide precursor. Three types of samples were produced: a non inhibited type consisting of 3 layers of ZrO_2, an inhibited system consisting of two layers of ZrO_2 with an intermediate layer doped with cerium nitrate and an inhibited system consisting of two layers containing cerium nitrate with a top layer of ZrO_2.

The electrochemical behaviour of the three ZrO_2 based sol-gel systems – non inhibited and inhibited ones – was studied by means of open circuit potential measurements, potentiodynamic polarization and electrochemical impedance spectroscopy. The surface morphology and coating homogeneity were investigated by means of scanning electron microscopy.

Effect of different surface preparations prior to painting on the corrosion behaviour and surface activity of mild steel

D. J. Mills, S. S. Jamali

School of Science and Technology, University of Northampton,
St George's Avenue, Northampton, NN2 6JD, UK
Tel 0044 1604 893005/3213
E-mail: douglas.mills@Northampton.ac.uk

Abstract:
Previous work in our laboratory (1) showed that the type of surface preparation of the steel prior to coating had a dramatic effect on the subsequent corrosion protection afforded in immersion tests and in salt spray testing. Particularly water jetting led to better performance. It is generally accepted that factors such as removal of impurities and introducing surface roughness to steel to obtain better adhesion through the mechanical interlocking of polymeric structure and the metal surface play a part. However it is postulated that the ease of breakdown of the oxide film is also critically important and varies between surface preparations. This was investigated in the present study where 5 different surface preparation methods (abrasive blasting, water-jetting, abrasion, acid pickling and degreasing) were applied to the mild steel surface and each resultant surface was characterised using electrochemical methods. The Scanning vibrating electrode technique (SVET) was performed in dilute saline water to detect anodic and cathodic sites on the surface and also to determine the intensity of electrochemical activity at these sites. Scanning electron microscope (SEM) together with energy dispersive X-ray spectroscopy (EDX) was used to characterise the surface structure and its chemical composition. Changes in open circuit potential have been monitored during the time of exposure to electrolyte in order to investigate the general surface activity. The corrosion rate and active/passive behaviour has been studied by means of linear polarisation method and consequently electrochemical impedance spectroscopy (EIS) was employed to analyse the charge transfer situation on the metal surface. Results using these techniques will be presented and discussed. An anticipated outcome from this work is development of a simple electrochemical method to assess that a metal surface is in a condition suitable for coating. This could also be used as a way of checking that standard pretreatments had been effective and assist in the development of new ones.

Keywords: surface pre-treatment, SVET, surface activity, electrochemical characterisation

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The protective conversion coatings on AA 7075 aluminum alloy, obtained in alkaline converting solutions

Yury KUZENKOV

A.N. Frumkin Institute of physical chemistry and electrochemistry Russian Academy of Science, Moscow, Russia

High-strength V95 aluminum alloy (Russian analogue of AA 7075 alloy) belongs to Al-Mg-Cu-Zn system. These alloys possess low corrosion resistance in atmospheric and water environments. The application of molybdate solutions for chemical oxidizing of aluminum alloys is one of perspective trends of chromateless converting formulations development. It has been shown earlier, that it is possible to obtain the chromateless conversion coatings on aluminum-magnesian alloys and aluminum-copper alloys of Al-Mg-Cu system in alkaline molybdate formulations modified by various oxidizers and corrosion inhibitors. The coatings with high protective properties formed in the investigated converting formulations. In this connection, a study of chemical oxidizing in such converting formulations of V95 aluminum alloy with various heat treatments seemed interesting.

The kinetics of conversion coatings formation on V95 alloy with various heat treatments in alkaline molibdate-borate converting formulations and their protective properties in chloride solutions were investigated by corrosion and electrochemical methods. The regularities of influence of the developed chromateless converting formulation IFHANAL-3 components on the protective properties and structure of conversion coatings on V95 alloy are revealed with the use of x-ray spectral microanalysis methods. It is shown, that low corrosion resistance to local anode activation in chloride solutions of coatings on alloy V95 is connected with their enrichment with zinc and copper oxides. The filling of the obtained conversion coatings in a solution of IFHAN-25 inhibitor increases their protective properties to chromate coatings' level due to the adsorption inhibitor film formation on a coating surface. The tests of such coatings in the salt fog chamber have shown that their corrosion resistance exceeds 168 hours.

Aluminium corrosion protection by silane-zeolite composite coatings

Calabrese L., Bonaccorsi L., Proverbio E., University of Messina, Dep. Industrial Chemistry and Materials Engineering, Messina, Italy

The use of silanes as adhesion promoters and as protective layers for metal substrates is very attractive for industrial application because of their high durability, good adhesion and easy deposition procedures.

Organosilane compounds have a general formula $R_n SiX_{4-n}$ (where X is the hydrolysable group). When they are hydrolysed to silanols, $R_n Si(OH)_{4-n}$, it is possible to create a good interaction between the polymeric film and the metallic substrate by forming a complex interface region, containing strong -Si-O-M covalent bonds. After curing, the silane layer acquire anti-corrosive coating properties.

Silane coatings act mainly as barrier coatings and they do not have any active electrochemical behaviour. The addition of a component particles as zeolite Y, allows to obtain a more durable and protective barrier film.

Zeolite high thermal and chemical resistance allows coatings to be used in various aggressive environments and operating conditions. The intrinsic non-toxicity of the coating components, which could constitute an interesting alternative to chromium-based surface treatment, extends the applicability of zeolitic coatings to food and pharmaceutical industries. Certainly the characteristic that most enhances the coating potentiality is the possibility to use the nano-porous structure to selectively incorporate specific molecules or ions [1] such as chemicals or corrosion inhibitor which can be then gradually released during coating service life. Such “smart coatings“ could be able to adapt to changes in the environmental conditions in which structures operate [1-3].

In this work the electrochemical behaviour of Aluminium 6010 coated with different zeolite Y - trimethoxy(propyl)silane composite films was investigated. Electrochemical tests were performed in 3,5 percent by weight NaCl solutions. Both single and bi-layered coating was prepared. In particular the bi-layered coatings were characterised by an external silane-zeolite composite film, prepared by using different concentrations of zeolite nano-particles (1000, 2000, 4000 ppm) in the hydrolysis solution; the interface layer was instead without zeolite particles.

The electrochemical behaviour of coated aluminium samples was assessed by electrochemical impedance spectroscopy (EIS) and potentiodynamic polarisation tests; SEM analysis was used to verify the deposited film homogeneity and to allow us to identify the correlation between properties and structure of the composite coating. The experimental results evidenced a good coverage of the coating on the aluminium substrate. The polarisation curves evidenced an improvement of the aluminium substrate corrosion resistance when zeolite particles were added to the silane film

Further experimental investigations will be carried out in the future to validate the obtained results and to deepen the knowledge on the anti-corrosion behaviour of these composite coatings.

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Electrodeposited sol-gel coatings containing Ce-Ti nanocontainers loaded with inhibitors for the corrosion protection of AA 2024-T3

Evaggelos MEKERIDIS , *George KORDAS*

Sol-Gel Laboratory, IMS, NCSR 'DEMOKRITOS', 15310 Aghia Paraskevi Attikis, Greece, emekeridis@ims.demokritos.gr

Abstract

Silane and silicone based sol-gel coatings were grown on Al-2024/T3 substrates under electrochemical regimes and the dip-coating method, using cerium nitrate as the electrolyte. Cerium-titanium oxide nanoparticle reservoirs loaded with 2-mercaptobenzothiazole (2-MB) and 8-hydroxyquinoline (8-HQ) were incorporated into the sol-gel matrix in order to improve the corrosion protection. This deposition technique provides coatings with high cerium concentrations as the cerium salt act not only as inhibitor but also as the electrolyte during deposition. The silane 3-Glycidopropyltrimethoxysilane (GPTMS), silicones Diethoxydimethylsilane (DEDMOS) Trimethoxymethylsilane (TMOMS) were used as precursors. The electrodeposited coatings were compared to coatings developed by dip coating method. A temperature range was studied, in which the organic inhibitors are not decomposed. Impedance measurements were carried out in order to evaluate the corrosion protection properties of the films in 0.05 M NaCl aqueous solution and the inhibitor release of the nanocontainers. SEM/EDAX measurements were employed for the characterization of the morphology of the coatings. It was found that GPTMS based films provided better protection against corrosion. The presence of the nanocontainers improved the corrosion protection. The prolonged release of inhibitor provides long term corrosion protection of the aluminium alloy 2024 compared to the un-doped coating with impedance values one order of magnitude higher comparing to the bare substrate after 72 hours in NaCl solution.

Influence of the Nanocontainer Distribution and Loading on the Performance of the Nanocontainer-Based Self-Healing Coatings

Dmitry G. Shchukin
Department of Interfaces, Max-Planck Institute of Colloids and Interfaces, D14424 Golm/Potsdam, Germany. E-mail: dmitry.shchukin@mpikg.mpg.de

The new multifunctional coatings should combine passive components inherited from "classical" coatings and active components, which provide fast response of the coating properties to changes occurring either in the matrix of multifunctional coatings (e.g., cracks, local pH change) or in the local environment (temperature, humidity). Recent level of the surface science shows new opportunities for fabrication of active feedback coatings through the integration of nanoscale containers or continuous networks loaded with the inhibitor into coating matrix thus designing completely new coating of the "passive" host - "active" guest structure.[1-4] The main idea here is to use nanocontainers (networks) with a shell possessing controlled permeability properties. As a result, nanocontainers are distributed in the passive matrix keeping active material in "trapped" state. When the corrosion process is started inside the coating, nanocontainers respond and release encapsulated active material. This means that loaded containers present in “non-active” state when no corrosion exist and become “active” only after beginning of the corrosion and formation of the crack releasing the encapsulated inhibitor or sealing agent into corroded area.

Despite the high level of success achieved in the field of nanocontainer-based coatings during the last few years, there still exist some, more fundamental, problems on the mixing nanocontainers with the coating material, effective loading of the nanocontainers with the inhibitor and nanocontainer distribution inside the coating matrix. More detailed, these problems involve the answers for the following questions: (i) How to avoid the agglomeration of the nanocontainers; (ii) What should be the optimal loading capacity and (iii) What should be the optimal container content and distribution inside the coating, which, actually, depends on the coating thickness and barrier properties.

The answers to these questions can be found in the presented report, where we apply both theoretical and practical approaches for investigation of the nanocontainer behaviour inside the coatings (both water- and oil-based) and elaboration of the nanocontainer distribution-coating thickness dependencies for designing the nanocontainer-based coatings with “the best” self-healing and barrier properties. The novel optimized protection coatings exhibit very high corrosion protection because of nature of the incorporated containers.

The anticorrosion and self-healing properties were demonstrated on steel and aluminium alloy AA2024 substrates and for organic and sol-gel coatings.

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Self-healing protection of coatings with inhibitor-loaded mesoporous SiO_2 nanoparticles

D. de la Fuente, J.M. Vega, B. Chico, N. Granizo and M. Morcillo.
Materials Engineering, Degradation and Durability Department
National Center for Metallurgical Research (CENIM-CSIC),
Avda. Gregorio del Amo 8
28040 Madrid/Spain.
Tel. +34 915538900, E-mail. delafuente@cenim.csic.es

Incorporation of nanocontainers loaded with corrosion inhibitor into coatings could provide a self-healing effect during the corrosion process. The self-healing ability occurs due to release of entrapped corrosion inhibitors in response to pH changes produced at the anodic and/or cathodic areas during the corrosion process. However, to successfully achieve this behavior the nanocontainers should be homogeneously distributed in the coating and should possess controlled and corrosion-stimulated inhibitor release to heal the defects.

In the present work, mesoporous silica particles have been employed as a carrier of four different corrosion inhibitors: cerium(III) nitrate, sodium phosphomolybdate, sodium vanadate and zinc cromate. The latest was considered only as a reference for comparison purposes. To improve controlled released, a multilayer shell was then assembled on the inhibitor-loaded silica nanoparticles by the layer-by-layer (LbL) technology with electrostatic assembly of oppositely charged species. A reference coating, as polyvinyl butyral (PVB), has been used for the incorporation of the prepared encapsulated loaded nanoparticles.

The corrosion behavior and self healing ability of the coatings have been studied by means of Electrochemical Impedance Spectroscopy (EIS) and Scanning Kelvin Probe (SKP). The obtained results have stated the importance of encapsulation for corrosion inhibitor release. On the other hand, in most of the cases a successfully self healing of the artificially prepared defects has been observed.

In-situ ATR-FTIR and EIS studies of hidden aluminium / polymer interfaces with an intermediate silane film upon exposure to water and electrolyte

Maria Öhman and Dan Persson

Swerea-KIMAB, Drottning Kristinas väg 48, 114 28 Stockholm, Sweden,
maria.ohman@swerea.se

Summary

Alterations at the interface between aluminium, coated with a silane film, and a polymer coating were analysed *in situ* during exposure to an electrolyte solution using ATR-FTIR and EIS. By using substrates with thin vacuum evaporated aluminium films, the ATR-FTIR technique in the Kretschmann configuration allows interfacial analysis from the metal surface and less than 1 µm into the bulk polymer. Additional characterisation of the silane film applied to the aluminium was performed by ATR-FTIR and IRRAS-FTIR, and water induced alterations where followed upon exposure. The studies provided information from the hidden interface, such as the transport of water through the polymer film, corrosion processes, water induced alterations of the silane film, and possible interactions between the silane film and the polymer coating.

A prospect for using mesoporous particles in corrosion protection

Magdalena Walczak, School of Engineering, Pontificia Universidad Católica de Chile, Santiago/Chile

Michael Rohwerder, Max-Planck Institut für Eisenforschung, Düsseldorf, Germany

Frank Marlow, Max-Planck Institut für Kohlenforschung, Mülheim an der Ruhr, Germany

The continuous search for improved performance of protective coatings motivates the application of advanced materials and technologies in the coating formulation. In particular, the feature of enhancing the level of protection as a reaction to the less or more abrupt changes in the surrounding environment, i.e. the ability to self-repair, has been made available. One of approaches to implement this feature is by incorporation of functional particles. Such particles can act as a corrosion inhibitor or a curing agent themselves or serve as carriers for delivery of suitable functional molecules.

The present investigation deals with delivery kinetics of molecules stored in the carrier particles. The objective is to identify the release mechanism and the relevant release parameters, which are then to be used for tailoring the release rates. The use of mesoporous material, rather than a balloon-like microcapsule, is motivated by the ease of manufacturing and the prospect of prolonged delivery times. Mesoporous silica, an amorphous material with well defined and often well ordered pores, is selected because of its variety of shapes and structures as well as suitability for large-scale processing. In the first approach, a model system is studied: SBA-3-type of silica particles loaded with an organic dye. The dye is chosen for a convenience in detection, so that spectroscopic and optical methods can be applied to the same system. Release from individual particles is studied using a light microscope, whereas UV-Vis spectrometer is used for studying release from particle assemblies. The obtained information on release kinetics is further subject to curve analysis in order to specify diffusion coefficient inside the particle(s). In addition, the contribution of surface diffusion barrier to the release times is demonstrated [1]. The presence and modification of the surface diffusion barrier is exploited for modification of release times without the necessity of changing the porosity [2]. The modified release times range from a minute to few hours.

Applicability of the studied model system for corrosion protection is demonstrated by exchanging the dye molecules for corrosion inhibitors (either chromates or molybdates). Also the type of the particles is changed to allow for spherical morphology. The obtained effective diffusion coefficients and surface mass transfer coefficients differ from those of the model system the release times remain in the same order of magnitude and are equally subject to modification by surface diffusion barrier. Suitability of the particles for enabling self-healing is demonstrated by experimenting release into environments of specific characteristics.

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The effect of thermally interdiffused magnesium and aluminum on the kinetics of organic coating cathodic delamination from zinc (galvanized steel)

H. Neil McMurray , Zak Barrett and Geraint Williams
Materials Research Centre, School of Engineering, Swansea University
Singleton Park, Swansea, SA2 8PP, United Kingdom.

PVD is used to deposit thin layers of magnesium or aluminium onto the zinc surface of hot dip galvanized steel. A digitally controlled sliding shutter apparatus is used to produce Mg and Al layers of continually varying thickness, typically ranging from a few hundred nanometers to zero, on a single substrate. The coated substrate is then heated under an inert atmosphere to produce a thermal interdiffusion of metals. After interdiffusion the modified substrate is overcoated with a clear organic lacquer – polyvinylbutyral (PVB). Aqueous sodium chloride is then introduced through a penetrative defect in the PVB coating so as to produce a cathodic delamination (of PVB) which propagates in a direction normal to the original direction of Mg or Al layer thickness variation. The progress of cathodic delamination over the whole experimental surface is followed using a scanning Kelvin probe (SKP) apparatus. In this way the kinetics of cathodic delamination may be characterised simultainously for portions of the zinc surface containing systematically varied quantities of interdiffused metal. The distance over which cathodic delamination has occurred may be estimated from the position of the time-dependent inflection in potential-distance profiles. Mechanistic inferences regarding how Al and Mg act to strongly inhibit the process of cathodic disbondment may be drawn from the characteristic potentials associated with different portions of the potential-distance profile. The effect of magnesium on profiles is illustrated in Fig 1. Our approach may be though of as being combinatorial in that a library of Mg/Zn/Al combinations is first generated and then rapidly evaluated using parallel and automated methodologies.

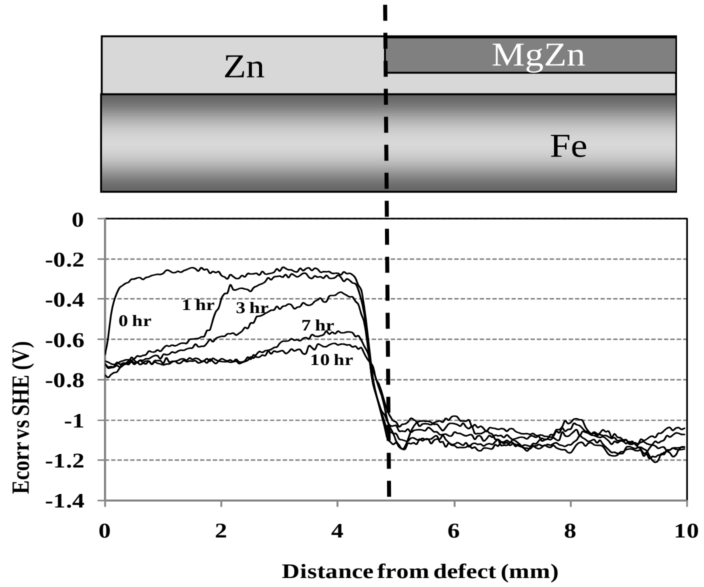

Fig. 1 ***Upper:*** Schematic illustration of galvanized steel substrate partially modified by thermally interdiffused Mg. ***Lower:*** Corresponding time-dependent potential (Ecorr) profiles when the PVB coated substrate undergoes cathodic delamination

Corrosion and mechanical behavior of mono- and multi-layer Al-based PVD coatings in NaCl solution

A. Perez[1]*, A. Billard*[2]*, S. Touzain*[1]*, J. Creus*[1]

[1] *LEMMA , Université de La Rochelle, Av. Michel Crépeau, F-17042 La Rochelle cedex 1, France.*
[2] *LERMPS , Univ. Technologique de Belfort Montbéliard, F-90010 Belfort, France.*

Abstract

Aluminum-based coatings deposited by dc magnetron sputtering Physical Vapor Deposition (PVD) are known as an alternative friendly solution to pollutant corrosion protection systems. In order to improve the sacrificial effect with regards to steel, Zn, Y or Mg can be added to the PVD coating formulation. Moreover, a multilayer structure including hardener elements (Mo, Mn) can also be proposed as a way to improve mechanical resistance.

The first objective of this work is to study different Al-Zn, Al-Y and Al-Mg compositions and their corrosion behavior for an immersion test in NaCl 5 wt.% solution. The results show that depending on the alloying element content, pitting or uniform corrosion behaviors are obtained. For the samples showing a uniform corrosion, the immersion test reveals that they provide a good protection to steel during the immersion period. Secondly, multilayer PVD systems were designed in order to associate good corrosion performances with better mechanical properties: Al-Zn/Al-Mo and Al-Y/Al-Mn were tested. The results are discussed in terms of microstructure, corrosion potential and mechanical resistance.

Chemical Vapor Deposition of Aluminum as a Widely Applicable Technique for Corrosion Protection

S. Oberhauser[1], B. Kuzmanović[2], I. Sieber[1], J. Heller[1], A. Luttmer[2], M. Zeitler[2], C. Strobl[3]

Aluminum can be deposited on steel or other metallic substrates by controlled thermal decomposition of aluminumorganic compounds at temperatures below 400 °C under atmospheric pressure. The process is based on the Chemical Vapor Deposition (CVD) technique with higher deposition rates than typically achieved by conventional galvanic deposition of aluminum from aprotic solvents. The aluminization by means of Metal Organic Chemical Vapor Deposition (MOCVD) procedures does not involve significant environmental hazards as well as comprising any persistent organic or toxic chemicals.

In this work we demonstrated that the MOCVD technique is suitable for coil coating lines as well as for coating of multiple smaller parts. Furthermore, inner surfaces of hollow parts or tubes can be reached easily by the precursor and hence properly coated. The resulting Al-layers are closed and show a very even thickness distribution. Such layers provide a good corrosion resistance in neutral media containing chlorides. The determined corrosion rates of the Al-MOCVD coatings in these electrolytes are significantly lower compared to the widely used Zn-galvanic layers. To further improve the overall corrosion resistance, the Al-MOCVD coatings could be additional passivated either applying Cr(VI)-free or Cr-free layers.

Hardness and overall corrosion resistance of the Al-MOCVD coatings can be even further enhanced by involving other elements like Zn in the generated coating. In this way corrosion attack at the locations where defects are present in the Al-coating can be eliminated. Such defects may come from cutting or even stone-chipping. To emphasize, as already indicated earlier, for producing such Al-Zn-coatings the temperature of deposition by the described technique is much lower compared to the hot dip deposition of Al-Zn-layers.

Finally, we have shown that by thermal treatment it is possible to transform the pure Al-layers to very stable aluminides with a high-melting point. Such aluminides are known from turbine applications and exhibit high corrosion protection against exhaust-gases even at high temperatures.

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[1] InnCoa GmbH, Neustadt / Donau, Germany
[2] AkzoNobel, Deventer, The Netherlands
[3] University of Applied Sciences Ingolstadt, Ingolstadt, Germany

AN INVESTIGATION INTO THE SACRIFICIAL CORROSION PROTECTION OF STEEL SUBSTRATES BY THERMALLY SPRAYED ALLOY COATINGS

Oliver LEWIS[1], **Hywel JONES**[2], **Angela HARDMAN**[3], **Chris WHEATLEY**[4]

[1] *Sheffield Hallam University, UK, o.lewis@shu.ac.uk*
[2] *Sheffield Hallam University, UK, a.h.jones@shu.ac.uk*
[3] *London and Scandinavian Metallurgical Ltd, UK, ahardman@lsm.co.uk*
[4] *CJ Wiretech Ltd, UK, chris@cjwiretech.co.uk*

The in-service degradation of steel artefacts and structures by corrosive attack can lead to costly and potentially dangerous failures. Aluminium coatings are therefore frequently applied to protect steel substrates and hence prolong service life. When the coating is scratched or damaged, exposing the underlying steel, the resulting galvanic couple leads to preferential corrosion of the aluminium, thus protecting the substrate. Thermal spraying can be used to apply such coatings, as the technique is capable of depositing thick coatings which can also be applied in-situ.

While aluminium coatings are effective in certain circumstances, there are situations in which a passive oxide film may form on the surface of the coating, negating its ability to provide sacrificial corrosion protection to the substrate. For that reason, alloying elements may be added to the coating to ensure that it actively corrodes under a greater range of environments.

The research presented here has examined the performance of a new range of thermally sprayed aluminium alloy coatings in different chloride environments, with tests also performed on aluminium coatings for comparison. Electrochemical measurements have included galvanic corrosion tests using a zero-resistance ammeter (ZRA) over extended time periods, while accelerated environmental corrosion tests have also been performed on coatings with artificially generated defects. The appearance and composition of the coatings before and after corrosion testing has also been studied using scanning electron microscopy (SEM) and X-ray diffraction (XRD).

CORROSION OF TANTALUM COATED CONSTRUCTIONS MATERIALS FOR WATER ELECTROLYZERS IN CONCENTRATED PHOSPHORIC ACID

Milan KOUŘIL[1], Erik CHRISTENSEN[2], Søren ERIKSEN[3], Bo GILLESBERG[3]

[1]Institute of Chemical Technology, Prague, Czech Republic, kourilm@vscht.cz
2Technical University of Denmark, Denmark, erc@kemi.dtu.dk
3Tantaline, Denmark, se@tantaline.com

Suitable materials for a construction of a new water electrolyzer had to be chosen. The metallic parts will be exposed to concentrated phosphoric acid at high pressure and temperature. In the case of electrodes, intensive anodic polarization must be also considered. The corrosion tests evaluated the efficiency of tantalum coating on basic materials for electrode protection. The electrodes have to be resistant to a concentrated phosphoric acid, even under anodic polarization up to 2.5 V. Other metallic parts of the electrolyzer have to be phosphoric acid resistant at normal and also at increased temperature. Number of materials was tested, including different grades of stainless steels, tantalum, niobium, titanium and nickel alloys. These were treated in dilute and concentrated phosphoric acid up to 150 °C. Corrosion rate was determined from a weight loss, polarization resistance measurement or determination of metal content in phosphoric acid by ICP-OES analysis. The only corrosion resistant material in 85 % phosphoric acid at 150 °C and polarization of 2.5 V was tantalum. The construction of whole electrodes of tantalum is though economically unacceptable. Therefore corrosion testing was applied on stainless steel AISI 316 and titanium with coherent tantalum coating. The tantalum coating on a titanium sample, where a profile analysis showed a structured interface between the coating and the titanium surface, approved excellent protective properties of a substrate under the coating. A weight loss was caused only by a corrosion of tantalum, which was 4 $\mu m.a^{-1}$. On the other hand, the tantalum coated stainless steel, where the profile analysis showed a sharp interface between the coating and the steel surface, the steel under the coating was dissolved. Moreover, defects of the tantalum coating were detected with a microscope. Analogously to the tantalum coated titanium is probable that enrichment of the surface of the stainless steel with the tantalum before the tantalum coating process increases the quality of the tantalum coating. That might lead to another increase of the protective ability of the coating.

For a construction of other parts of the electrolyzer exposed in a cold phosphoric acid without a polarization, stainless steel AISI 304 or AISI 316 is sufficient from the corrosion resistance point of view. Hastelloy B-3 or tantalum coated steel is recommended for parts exposed to the phosphoric acid at the temperature up to 150 °C.

Corrosion resistance of Zn/Co alloy coated carbon steel

J. M. Falcón[1], A. C. Neiva[1] I. V. Aoki[1].

[1] *Chemical Engineering Department – Polytechnic School – University of São Paulo*
Av. Prof. Luciano Gualberto, travessa 3, n0. 380 – CEP 05508-010 - São Paulo –
Brazil. E-mail: idavaoki@usp.br

Abstract

During the last years, efforts for obtaining zinc-based coatings based with additional corrosion resistance made researchers review the requirements of protection and look for alternative layers, giving rise to new types of coatings made of zinc alloys with metals as Fe, Ni and Co. Furthermore, these alloys were developed to replace the cadmium coatings, which was extensively used as barrier and sacrificial coating in the automotive and aerospace industry because of its excellent corrosion resistance and mechanical properties but was prohibited because of its toxicity and severe environmental regulations. The development of Zn-Co alloy coatings appeared as an alternative for obtaining layers with more resistance that the conventional zinc and with a lower additional cost. The aim of this work is to study the electrodeposition of the Zn-Co alloy on carbon steel by cyclic voltammetry using potentiostatic and galvanostatic techniques and to evaluate the corrosion resistance of coated samples. The composition of the bath was: $ZnCl_2$=138g/L; $CoCl_2.6H_2O$=28g/L; KCl=220g/L; H_3BO_3=22g/L, ratio of $[Zn^{2+}]/[Co^{2+}]$ = 9:1, pH=4,5±0,1.The cyclic voltammetry was accomplished with scan rate of 100 mV.s^{-1}, an electrode of Ag/AgCl/KCl$_{sat}$ used as reference, a Pt foil or a zinc anode as counter electrode and vitreous carbon and carbon steel as working electrodes (substrates). Before each experiment the solutions were deaerated by bubbling nitrogen for 15min. The corrosion resistance of the coated samples was evaluated in naturally aerated 0,1 M NaCl by open circuit potential, electrochemical impedance spectroscopy, linear polarization resistance and potentiodynamic polarization curves. The potentials applied for the potentiostatic depositions were -1300 mV, -1375 mV and -1450 mV, whereas for the galvanostatic depositions the cathodic current densities applied were 5 mAcm^{-2}, 15 mAcm^{-2} and 30 mAcm^{-2}for 3 minutes. The voltammograms showed two anodic peaks located at -0,65 V vs. Ag/AgCl/KCl$_{sat}$ and -0,35 V vs. Ag/AgCl/KCl$_{sat}$ attributed to dissolution of zinc rich phases and cobalt, respectively, and a current density peak in the cathodic scan was related to alloy deposition. Scanning electron microscopy (SEM) showed that the electrodeposits obtained at a potential of -1450 mV for potentiostatic deposition or, at 100 mAcm^{-2}, in the case of galvanostatic deposition were more homogeneous and compact. Zn/Co coated samples obtained potentiostatically at -1450 mV vs. Ag/AgCl/KCl$_{sat}$ showed better grain refinement and anticorrosion properties compared to pure zinc. Structural and chemical characterization of coatings was accomplished by XRD and XRF.

Influence of silicon and magnesium on the corrosion behaviour of hot dip aluminium coatings on steel

Ine Schoukens, Research Group Electrochemical and Surface engineering – vrije Universiteit Brussel, Pleinlaan 2, 1050 Brussel, Belgium
Iris De Graeve, Research Group Electrochemical and Surface engineering – vrije Universiteit Brussel, Pleinlaan 2, 1050 Brussel, Belgium
Franz Horzenberger, OCAS, Pres. J. F. Kennedylaan 3, 9060 Zelzate, Belgium
Herman Terryn, Research Group Electrochemical and Surface engineering – vrije Universiteit Brussel, Pleinlaan 2, 1050 Brussel, Belgium

Galvanised steel is a common form of steel used in transport and construction applications. A zinc layer acts as a sacrificial anode and protects the underlying steel against corrosion. An alternative to this product is the use of aluminized steel in which the aluminium layer gives improved functional properties, such as a higher thermal stability and the possibility of having a more decorative surface appearance.

For aluminium as a bulk product it is known that a compact, inert and passivating layer is formed spontaneously at the surface, giving inherent good corrosion properties to the metal. However, the object of this study is a thin (20-30 µm) hot dipped aluminium layer formed on top of a steel substrate. This layer contains Al-Fe, Al-Fe-Si and/or Mg-Si precipitates (depending on the aluminium hot dip bath formulation) and consists of several sublayers: an interdiffusion layer between the steel and the aluminium, an aluminium alloy layer and an oxide layer. The properties and behaviour of such layers have been only fragmentarily studied.

In the present work the influence of silicon and magnesium on the corrosion behaviour of hot dip aluminium coatings on steel is investigated. Therefore, open circuit potential measurements as a function of time and potentiodynamic polarisation measurements in 1M NaCl are recorded on three different types of hot dip aluminium coatings on steel: a pure aluminium coating, aluminium-silicon coatings and an aluminium-silicon-magnesium coating. Classical rolled bulk aluminium alloys (AA1050 and AA4045) are used as reference material.

An increase of the amount of silicon from 0 to 7wt% in the molten aluminium bath leads to an increase of silicon in the coating surface. This enrichment does not have an influence on the OCP of the coating: the OCP is stable and has a similar value as the pure aluminium coatings and the bulk material. When also magnesium is added to the molten aluminium bath the coating becomes more reactive.

In the potentiodynamic polarisation curves (scanning from -1V vs. OCP to +1V vs. OCP) the influence of silicon is clearly visible. In accordance with what can be seen on the bulk material, an increase in silicon at the surface leads to a cathodically less active surface. Also in the anodic part of the curve a difference in corrosion behaviour is seen between the coatings with a low (0 or 1%) and a high (3 or 7%) amount of silicon: the coatings with high silicon content tend to pit immediately while the coatings with lower silicon content show a passivation plateau before pitting starts. This might be explained by the higher cathodic activity of these surfaces which leads to the formation of passivating cathodic reaction products. Confirmation can be found in potentiodynamic anodic polarisation measurements where all coatings pit immediately. Potentiodynamic cathodic polarisation measurements under ambient atmosphere and under nitrogen atmosphere are being performed in order to have a better understanding of the cathodic behaviour.

Electrochemical preparation and characterization of Ni/Al_2O_3 functionally graded coatings

E. García-Lecina, I. García-Urrutia, J.A. Díez, CIDETEC, San Sebastián/Spain; F. Smeacetto, Politecnico di Torino, Torino/Italy; G. Gautier, CNRS-ISTEC, Torino/Italy*
**egarcia@cidetec.es*

Composite electroplating is a method of codepositing fine particles of metallic, non-metallic compounds or polymers in an electrodeposited metal matrix in order to improve material properties such as wear resistance, lubrication, or corrosion resistance. Traditional composite coatings consist on homogenous materials having the same properties in all the directions. However, there is another possibility: to obtain composite coatings functionally graded, characterized by posses composition and structure gradients that provoke changes in the material properties.

In this sense, the aim of this study is to obtain Ni/Al_2O_3 functionally graded coatings with different content of Al_2O_3 particles in order to obtain high-performance materials for specific applications. Ni/Al_2O_3 functionally graded coatings on steel have been obtained by electrodepositing different layers of Ni/Al_2O_3 composite coatings from nickel Watts baths with different content of Al_2O_3 particles. Characterization of the graded coatings has shown a good adhesion among the layers and a continuous distribution of Al_2O_3 particles in the nickel matrix. Further analysis has shown that not only composition but also texture, hardness and Young modulus changed in a gradual way. Moreover, the functionally graded Ni/Al_2O_3 coatings have similar corrosion resistance and better wear resistance than nickel.

Corrosion resistance of Ni/SiC and Ni/Al_2O_3 nanocomposites electrodeposited under ultrasonic vibrations

C.Zanella, M. Lekka, P.L. Bonora, S. Rossi
Department of Materials Engineering and Industrial Technologies, University of Trento, Italy

The interest in the electrocodeposition has been revived due the development of new nanotechnology methods for the production of nano-particles. The codeposition of nanoparticles might enhance the mechanical properties of composite deposits without penalizing the corrosion resistance and avoid the formation of an abrasive third body during the wear process. On the other hand, the volume fraction of codeposited nano-particles is generally low and usually inversely proportional to their size. Many efforts have been done in order to improve the codeposition rate of nanoparticles.

Most of the research on Ni composites is focused on the electrodeposition process or on the mechanical and wear properties rather than on the corrosion resistance.

In this work, the protective properties of nickel matrix nanocomposite coatings have been studied by means of potentiodynamic curves and electrochemical impedance spectroscopy. Two different nanopowders, i.e. silicon carbide and alumina, were added to a Watts type galvanic bath in order to deposit the nanocomposites coatings on steel substrate. Ultrasonic vibrations have been considered as new process parameter to improve the dispersion of the powder into both the plating bath and metal matrix coating and to substitute pitting control agents for the production of defect-free coatings.

Unique, functional properties of composite coatings are derived not only from the presence of the particles dispersed in the bulk of the metallic matrix but also on the matrix microstructural changes induced by the interaction between particles and electrocrystallization process. Therefore the microstructure of all type of coatings haves been analyzed by SEM on the cross-section and the agglomeration of the powder have been observed by light optical microscope (LOM) in case of Ni/Al_2O_3 and by TEM in case of Ni/SiC.

It has been demonstrated that the codeposition of the SiC particles induces an important microstructural refinement. On the contrary the Al_2O_3 powder is strongly agglomerated and only under ultrasonic vibrations can be dispersed and change the field oriented columnar structure of the nickel matrix to un-oriented fine grained.

Ultrasound revealed to have a positive effect not only in avoiding the porosity but also in dispersing the ceramic powder and increasing the codeposition rate leading thus to the production of protective and very refined coatings. Moreover, the better dispersed powder induces an improvement also in the corrosion protection leading to the formation of a more stable and resistant passive nickel oxide.

All these interactions between ultrasounds, nanopowders and electrocrystallization process lead to improved mechanical properties and the enhancement is proportional both to the powder content and the dispersion degree.

Nanocomposites, Ni/SiC, Ni/Al_2O_3, sono-electrodeposition

CURRENT TRANSIENTS AT POTENTIOSTATIC NUCLEATION

Y. D. GAMBURG
A.N. Frumkin Institute of physical chemistry and electrochemistry, Russian Academy of Sciences, Moscow, Russia

At electrochemical nucleation a distinction is usually made between the two types of transient I – t curves: for instantaneous and for progressive nucleation. The characteristic features of the corresponding functions are well-known. Both functions pass maxima at a definite time depending on nucleation rate J (or overall nuclei number N) and diffusion coefficient D. The values of maximum current I_{max} and the correspondent time t_{max} allow to calculate the quantities J and N. But the computed number differs essentially from the observed amount of growing clusters. It is connected with catastrophic defect of the existing models residing in arbitrary choice of initial and transitive modes of growth.

Alternative model is developed which differs by taking into account sufficiently more parameters of the actual process. It is noticed than the newly arisen nuclei at the first stage grow with the minimum rate determined only by exchange current density up to the moment when their radii grow up to about four-fold critical one. Then during the definite period there takes place the growth in a mode of mixed kinetics, the diffusion limitations being initially week but gradually arise. The purely diffusion regime may be established only at a last period of growth, and this fact shows that the correct solution of the problem of transition I – t curve must contain the values of electrochemical data, namely exchange current and transfer coefficient.

Analytical solutions are derived for independent growth of the array of clusters initiated at different moments and growing simultaneously; the solution describes the transition from a kinetic mode to diffusion one. It is taken into account that in the case of parallel growth there exist the clusters having different stages of their individual growth. Further transition to the flat diffusion stage characterized by Cottrell diffusion law (after overlapping of diffusion-diluted zones) is considered from the point of view of the two consecutive processes having their own diffusion resistances. First of these resistances is that for hemispherical diffusion to each cluster; it gradually falls to zero, resulting in the growth of the total current. The second one is the resistance for the flat diffusion front is gradually included according to a degree of overlapping of diffusion zones to each cluster; correspondingly, its total current falls. As a result of summation these two resistances the resulting current for consecutive stages passes through its maximum. But neither the value of this current nor its time can be used as diagnostic criteria for the character of nucleation and growth. The shape of the transition curve is not uniquely determined by instantaneous or progressive type of nucleation. However the course of the curve gives a possibility to find the exchange current density, nucleation rate and the total number of clusters for comparison with independent experimental data.

Tantalum surface alloys: Next generation of corrosion protection.

Søren Eriksen, Tantaline A/S, Nordborgvej 81, DK-6430 Nordborg, Denmark

The need for corrosion-resistant materials is continuing to grow as engineers push their existing processes harder to gain more efficient production and as new next-generation processes, which are far more demanding, come online. These processes push conventional materials and specialty alloys beyond their limits, creating a strong need for new material solutions.

The Tantalum vapor surface alloying technology takes advantage of the superior corrosion resistance properties of tantalum. In a furnace heated to 700-900°C tantalum metal is chemically deposited. The tantalum diffuses into the substrate, typically stainless steel, creating a surface alloy. The gaseous tantalum atmosphere is maintained in the furnace so that a dense layer of pure tantalum grows on the surface of the part over the diffusion layer to a thickness of 50µm.

The Tantaline treated part has its original part size and shape, but has the same chemical properties and corrosion resistance as pure tantalum metal.

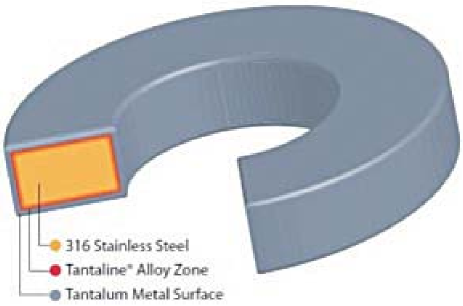

Figure 1. Schematic cross section of a treated stainless steel washer showing the surface alloy diffusion zone and pure tantalum metal surface.

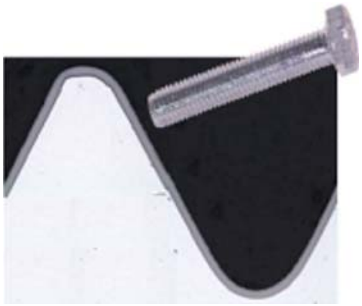

Figure 2. Micrograph showing cross section of Tantaline treated Fastener. Original profile is preserved.

The result is a product with the corrosion resistance of tantalum metal, at costs competitive with specialty alloys like Hastelloy® C276 and with the commercial availability of stainless steel.

Tantalum Surface Alloy properties and testing

Corrosion testing in hot hydrochloric acid and sulfuric acid, both concentrated at 75ºC, has verified that the treated parts show no corrosion after 1 month as expected for tantalum. Reference samples of high nickel alloys, titanium and stainless steels all had severe corrosion attacks.

Thermal cycling between 300ºC and room temperature, cooling by water quench, has demonstrated good resistance to thermal shock. After 100 quench cycles still no corrosion was seen in hot hydrochloric acid and metallographic sectioning showed no signs of deterioration.

The mechanical ruggedness of the surface alloy was tested. Samples were indented with a Rockwell C cone indenter at the midpoint and U-bent 180° over a mandrel before testing in boiling 37% hydrochloric acid for 24 hours. All the samples survived with no signs of corrosion.

The conclusion is that because of the tantalum surface alloy that is formed, Tantaline products are extremely rugged and durable compared to typical coatings where bonding is primarily mechanical.

Corrosion and Corrosion Protection of Drinking Water Systems

Influence of drinking water treatment processes on the pitting corrosion of copper pipes in domestic installations

Timo Jentzsch, Angelika Becker, Ute Ruhrberg,
IWW Water Centre, Muelheim an der Ruhr, Germany

Partially massive problems with pitting corrosion in domestic copper installations have occurred in some supply areas. Type and extent of corrosion is influenced by material, manufacturing, service and drinking water conditions in a complex way. Experience indicates that damage only occurs with the combination of several unfavourable conditions.

It is important to obtain a better understanding of the limiting conditions of drinking water for the initiation, stabilisation and repassivation of pitting because not all of these conditions are known completely yet. This especially applies to the activation of repassivated pits in aged copper pipes when the drinking water quality is changed significantly, for example by the optimisation or deconstruction of water treatment plants or by changing the technology of treatment. For this case there is a lack of reliable indicators to evaluate which change of water parameters can lead to a stabilisation of pit growth up to the perforation of the pipe wall.

Additionally more information is needed to know under which conditions (in which waters) damages caused by pitting corrosion can be minimised or sanitised using water-related measures, for example treatment with phosphate- and/or silicate-based corrosion inhibitors, or – in the case of a change in water quality – can be prevented in advance.

This poster introduces test methods to investigate the likelihood of pitting corrosion in the case of a significant water quality change and to set up corrosion prevention measures according to the results of these investigations. It also gives an outlook at the development of a new test method for the evaluation of the influence of the drinking water quality on the pitting corrosion of copper.

Development of a test method for a fast and reproducible proof of the corrosion resistance of stainless steels in drinking water

R. Feser, St. Pückel, University of Applied Science, Iserlohn, Germany

An easy testing procedure should be developed, which allows to ensure a comparable corrosion behaviour of new stainless steels to the approved stainless steel 1.4401 in drinking water.

Usually the equivalence of stainless steels for drinking water applications is proofed by the electrochemical determination of pitting potential of the various steels in neutral salt solutions. To perform the electrochemical testing an adequate testing equipment and qualified operators are necessary to analyse the data.

Because of this it could be useful to develop a more simple test method, which gives fast information for manufacturers. An easy exposure tests connected with microscopic analysis, could provide fast clarification of the equivalence of stainless steels.

Stainless steel obtain its corrosion resistance mainly from the formation of passive films which consist of chromium and iron oxides.

Chlorides are present in drinking water, destroy the passive film and initiate pitting corrosion. Therefore the quality of the passive film determines the corrosion resistance against pitting corrosion.

By means of exposure tests in solutions with a redox system and a significant chloride concentration, test conditions could be defined under which clear differences between various steels could be found. The chloride concentration, which has been used was 250 mg/L, which is appropriate to the limits in drinking water. The testing time is 24 – 72 h.

First results will be presented for several stainless steels, redox systems and chloride concentrations.

Investigation of an electrochemical non destructive technique to control the degradation of reinforced concrete pipes in drinking water distribution systems

C. Marconnet[1], M. Djafer[1], Y. Gourbeyre[2], J-M. Lucatelli[3], S. Buttoudin[1], V. Heim[4]

1 Veolia Water, 6, Esplanade Charles de Gaulle, 92751 Nanterre Cedex, France
2 Anjou Recherche, Chemin de la digue, BP 76, 78603 Maisons-Laffitte Cedex, France
3 CAE Laboratoire Matériaux, 40, avenue de la première armée française, 14000 Caen, France
4 Syndicat des Eaux d'Ile de France, 14, rue Saint Benoît, 75006 Paris, France

Steel core reinforced concrete pipes represent only a small amount of the whole French drinking water distribution system but are particularly strategic (feeders with a nominal diameter superior to 400 mm). They represent 80 % of the length of the drinking water feeder network on the territory of the Syndicat des Eaux d'Ile de France (suburbs of Paris, France). The ageing of these pipes can lead to corrosion of the steel core and then to leaks or, occasionally, to a burst of the pipe which can cause important damage. The improvement of the pipe renewal program needs the development of non destructive control methods to assess the steel core degradation.

In these pipes the steel core located between two concrete layers is covered by a protective oxide layer called passive film. The presence of aggressive elements within the soil (like chloride ions) can lead to corrosion of the steel core by locally attacking and dissolving the passive layer.

An electrochemical method called APVG (*Anodic Polarisation Voltage Gradient*) was tested to control on site the corrosion state of the steel core. This method consists in an anodic polarization of the steel core generating current leaks through the isolation defects of the passive layer and potential gradients in the soil. Such gradients can be detected and measured by moving two $Cu/CuSO_4$ reference electrodes on the ground along the pipe. The aim is to locate and evaluate the dimensions of the defects, from the ground, without excavation works and service disruption (no need to empty the pipe), so as to estimate the degradation of the pipe steel core.

This paper describes the principle of the APVG method. The challenge was in the determination of the accurate experimental conditions (potential/current/time) to detect a defect without accelerating the steel core corrosion, and also in the application of this new technique to real cases of differently-degraded pipes.

On the whole the first results obtained in this study are rather optimistic on the feasibility of the APVG method on site.

Galvanic Corrosion of Lead Pipe after Partial Lead Line Replacements

Jie Hu[1], Faculty of Civil Engineering and Geosciences, Department Materials and Environment, Delft University of Technology, Stevinweg 1, 2628 CN, Delft, The Netherlands
Fuxing Gan[2], Department of Environmental Engineering, School of Resource and Environmental Science, Wuhan University, Wuhan 430072, China
Caroline Nguyen[3], Marc Edwards[3], Department of Civil and Environmental Engineering, Virginia Polytechnic Institute and State University, Blacksburg, VA 24060 USA

Partial replacement of lead drinking water pipe in U.S. results in a galvanic connection of lead and copper pipe. To test the galvanic effect between lead pipe and copper pipe, a series of experiments were conducted with different water conditions (different Cl^- to SO_4^{2-} Mass Ratio (CSMR) and disinfectants) under stagnant situation.

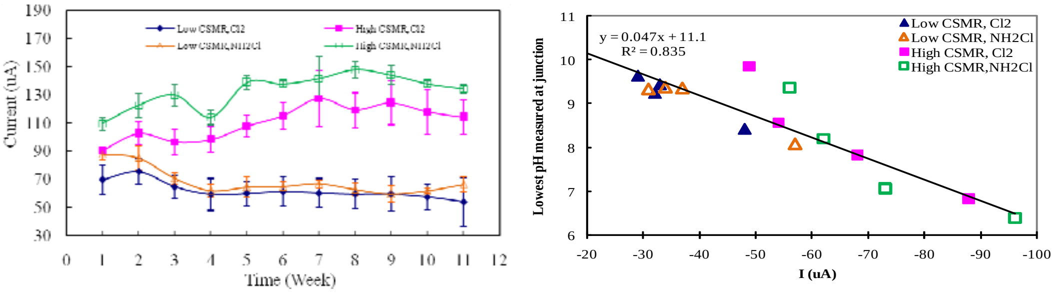

Fig 1 Galvanic current and relationship with pH at junction

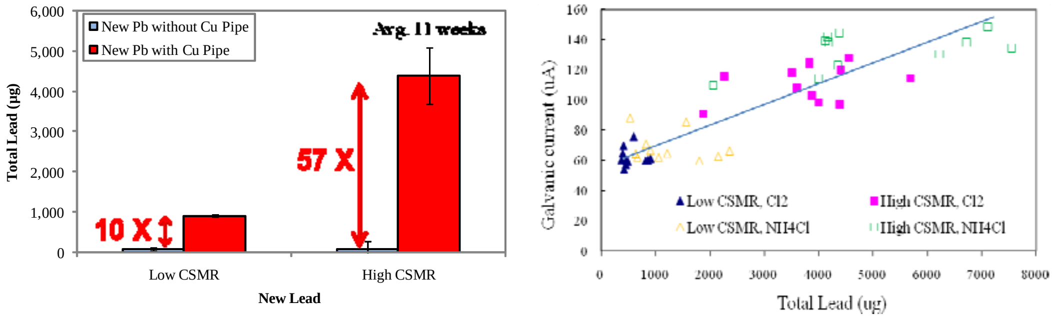

Fig 2 Total lead amount in test water and relationship with galvanic current

During an 11 weeks experiment period, high galvanic current was observed, and CSMR of drinking water is an important factor which can influence the galvanic corrosion rate. The higher the CSMR is, the higher the corrosion rate of lead pipe is. Fig 1 also shows there is a linear relation between galvanic current and the pH at the lead and copper junction, consistent with the Lewis acidity of release Pb^{+2} at the anode. The total lead in water dramatically increased when lead pipe was connected with copper pipe (Fig 2). With low CSMR, the lead was 10 times more when lead pipe was connected with copper pipe; with high CSMR, the lead amount was even 57 times more when lead pipe was connected with copper pipe. There is also a linear relation between total lead amount in the water and galvanic current. The results indicate that the partial lead line replacement can cause galvanic corrosion of lead pipe and increase the likelihood of lead contamination from drinking water.

Corrosion and Scale Inhibition

X-RAY ELECTRON SPECTROSCOPY AND ADSORPTION OF HETEROCYCLIC MOLECULES ON METALLIC SURFACES

Leonid P. Kazansky, Institute of physical chemistry and electrochemistry, Russian Academy of Sciences, Moscow Russian Federation

It is well known that the reliable protection of metals may be ensured by corrosion inhibitors that form very thin (nanosized) films. Information concerning the qualitative and quantitative composition of the surface layers formed on a metal by organic molecules is of great importance for understanding corrosion inhibition. Because the interaction of organic molecules with the surface metal atoms occurs at the atomic level the X –ray photoelectron spectroscopy (XPS) is one of the most powerful methods for studying the utmost surface layers which thickness may be less than 3λ (λ is escape depth of the ejected electrons that depends on different parameters and may vary from 0.7 to 4 nm). The easiest part of the study is the qualitative analysis that permits to determine practically all elements by their characteristic peaks. The second part, more difficult, is the quantitative analysis, especially when the surface film is not homogeneous. In this report we pay attention namely to the quantitative analysis that may be accomplished with the help the MultiQuant software [1] taking into account the intensity of the XPS peaks of all atoms of adsorbate and substrate. The inhibitors belong to the class of azoles, which are considered as very efficient corrosion inhibitors for different metals.

For example the XPS study of the adsorption of benzotriazole (BTA) on the mild steel surface has shown that in borate buffer solution the surface is covered by a film consisting of BTA and thickness of this rather protective film does not exceed 3 nm. [2] However this film is not so protective against of pitting corrosion. On the other hand 5-phenyl tetrazole (PTA) substantially shifts the pitting potential but does not chemisorb on the surface, but if added to the BTA solution benefits to protective properties of the formed films despite less thickness (<2 nm) [3]. However the more efficient was proved 8- hydroxyquinoline (HQ) that at concentration of 2.5 mM forms the surface films of 6 nm thick consisting of the iron chelate complex that completely passivates mild steel even in solution containing 3% NaCl. [4]

Similar complex formation occurs on copper surfaces when treated in acidic, neutral and alkaline phosphate solutions both in the presence of 4,5-dinitrobenzimidazole (DNBI) and PTA. In both cases the XPS evidences phosphate is not incorporated in the films and oxidation state of copper is +1. Using analysis of Auger CuLMM peaks the thickness of the formed films is calculated. It was shown that in a case of DNBI it is supposed that the first stage is fixation on DNBI molecules by azole nitrogen and on this monomolecular layer precipitates polymeric complex, which thickness reaches 4 nm. The thickness of these films depends on the DNBI concentration in solution. On the other hand adsorption of PTA on copper differs from the previous one. Up to concentration ~0.7 mM PTA does not adsorb on copper and increasing the PTA concentration result in formation of rather thick layer (6-8 nm).

Some examples of additional information using angle resolved XPS studies are given.

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METAL PASSIVATION BY PHOSPHOROUS-CONTAINING INHIBITORS

A.A. Chirkunov
Institute of Physical Chemistry and Electrochemistry
Russian Academy of Sciences, Moscow, Russia

Passivity of metals is an important property at corrosion protection. Passive state can be achieved not only by formation of stable oxide film or barely-soluble substances, but also due to the adsorption of organic compounds. Adsorption plays the main role at formation of passive layers by inhibitors; however it often accompanied by chemisorption.

In present paper the passivation properties of some organic phosphorous-containing inhibitors are evaluated. Phosphonates must be considered in the first place. The most of them are well known as inhibitors in neutral aqueous solutions and widely used for water treatment in cooling systems. Their protective action is linked, mainly, with deposition of sparingly soluble hydroxides and polynuclear complexes. Mechanism of inhibition action of phosphonates allows expecting their ability to passivate metal surface.

It was shown that phosphonate inhibitors form a stable thin film on steel surface which prevent a damp atmospheric corrosion. Protective action of phosphonates can be enhanced by combination with some other inhibitors, such as carboxylate or heterocyclic compounds.

Monophosphonates with formula $C_nH_{2n+1}PO_3Na_2$, where n = 7 – 11 are also investigated. They are able to pasivate mild steel in neutral borate buffer solution containing 0.01 M NaCl but weakly prevent the depassivation. Adsorption of them was evaluated ellipsometrically.

Another class of organic phosphorous-containing inhibitors are the ethers of phosphoric acid, such as octylphosphate, bis-(2-ethyl)-hexylphosphate or dialkyl-polyethyleneglycolephosphate. Along with ability to cause the spontaneous passivation of steel they prevent its local depassivation.

The work is partly supported by the Russian Foundation of Basic Research

Synergistic improvement of the inhibitory activity of dicarboxylates in preventing mild steel corrosion in neutral aqueous solution

Driss LAHEM[1], *Mireille Poelman*[1], *Marjorie Olivier*[1,2],

[1] *Materia Nova ASBL, Rue de l'Epargne 56, 7000-Mons, Belgium,*

Driss.Lahem@umons.ac.be, Mireille.Poelman@umons.ac.be

[2] *Université de Mons (UMONS), Service de Science des Matériaux, 20, Place du Parc, 7000-Mons, Belgium, Marjorie.Olivier@umons.ac.be*

Abstract

Mild steel has wide range of applications. However, corrosion is a severe problem for mild steel in aqueous media. Currently, widely used corrosion control technologies include protective coatings, anodic and cathodic protection, corrosion inhibitors, polymers, and corrosion resistant metals and alloys. Among them only the use of passivating inhibitors is convenient and economic for controlling aqueous corrosion of steel.

In this paper, the efficiency of dicarboxylates corrosion inhibitors for mild steel in near neutral sodium chloride solution was studied using electrochemical methods as open circuit potential (OCP), potentiodynamic polarization curves and electrochemical impedance spectroscopy (EIS). Surface analysis (SEM, XPS) were carried out to determine the kind of protection afforded by these inhibitors and to establish the mechanism of corrosion inhibition of the substrate in neutral media.

Performances of a series of dicarboxylates inhibitors were tested separately and in combination with neutral organic inhibitors (such as benzotriazole) under static conditions and at room temperature.

Dicarboxylates inhibitors show very high efficiency and may in some cases lead to the passivation of steel. Furthermore, it was shown that the mixtures of inhibitors are even more promising in terms of steel protection. A synergistic effect may be observed leading to inhibition properties that far exceed the effectiveness of a single compound. Optimal proportions of the compounds in the mixture were determined.

Reduction of copper loss in potable water in domestic installations by water treatment (decarbonisation, corrosion inhibitors)

Angelika Becker, Ute Ruhrberg, Timo Jentzsch
IWW Water Centre, Muelheim an der Ruhr, Germany

In the scope of examinations for water supply companies in Germany, the effects of water treatment processes (decarbonisation, dosage of corrosion inhibitors (phosphate, silicate)) on the corrosion behaviour of materials which are used for water distribution (unalloyed steel, cast iron) and house installations (galvanized steel, copper) were tested in test rigs. In addition to the measurements of copper concentration in drinking water, a special point of view was the estimation of the copper load in sewage sludge caused by house installations made of copper.
For this special investigations, experimental studies have been made with specimen columns which were assembled from weighed copper ring specimens (see figure 1).

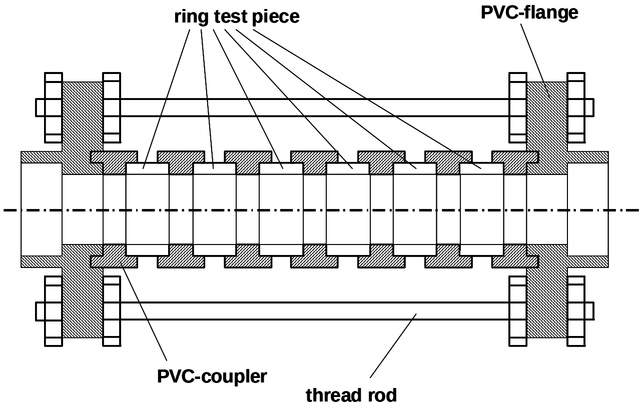

Figure 1: Specimen column

Copper specimens taken at different testing times have been investigated with respect to mass loss measurements. Additional analysis of the inner copper surface gave information about the type of corrosion and the development of the surface.
The testing conditions will be described and the dominant influences of water characteristics with respect to water treatment processes will be discussed. Results of both types of measurements - copper concentration and copper load - will be presented.

INHIBITION AND STIMULATION OF THE ANODIC DISSOLUTION OF HETEROGENEOUS BINARY ALLOYS IN NEUTRAL MEDIA

V.V.Ekilik, A.G.Berezhnaya
Southern Federal University, Rostov-na-Donu, Russia

The anodic behavior of passivated Sn-Zn, Sn-Cd, Bi-Sn, and Cd-Bi alloys has been studied compared to pure metals in sulphate, borate, sulphate-borate, and chloride- borate solutions by transient electrochemical methods. Some azoles, potassium oleate, potassium chloride, and tetraalkyl ammonium chlorides have been used as regulators of the anodic process.

The peaks formation on forward and reverse anodic and cathodic polarization curves was found to be caused by the formation and dissolution of tin hydrides, passivation of alloy components, the selective alloy dissolution, as well as the reduction of passive films.

On eutectic and hypoeutectic Sn-Cd alloys benzotriazole (BTA) inhibits the alloy dissolution at all the potentials in sulphate media but influences weakly passivating oxide quantity. Contrary to alloys, in the case of pure tin metal BTA accelerates the dissolution process above the potentials region of the second peak formation.

Increasing the Cd content in the alloy changes the action of potassium oleate (PO) from stimulation to inhibition in the secondary repassivation region, the amount of passivating oxide being decreased.

PO inhibits tin and Sn-Zn alloy dissolution in borate buffer.

The effects of potassium chloride and tetraalkyl ammonium chlorides on passivation and local depassivation of Sn-Cd eutectic composition alloy have been compared.

PO retards effectively the selective dissolution of eutectic Bi-Sn alloy at high sodium sulphate concentration $C_{Na_2SO_4}$, while benzimidazole and BTA initiate this process. For intermediate $C_{Na_2SO_4}$ all additives suppress repassivation during tin dissolution from the alloy. PO retards the selective alloy dissolution preferentially due to protect film formation. At low $C_{Na_2SO_4}$ PO reduces values of current in hundreds times, especially on reveres curves.

The difference in influence of additives on anodic behavior of homogeneous and heterogeneous binary alloys is determined by the selective dissolution features. In the case of homogeneous alloys a selective dissolution is rapidly finished, the alloy dissolution as well as additives effectivity being defined by noble alloy component. In the case of heterogeneous alloys the less noble alloy component dissolution is removed to pores and is retarded to a lesser degree. The difference in the anodic behavior of both alloy components is diminished under repassivation conditions. Kinetics of the anodic process and additives effectivity depend on the less noble alloy component to a more degree.

APPLICATION OF THE CYCLIC POLARISATION TECHNIQUE FOR MEASURING THE PERFORMANCE OF INDUSTRIAL LOCALISED CORROSION INHIBITORS

Edouard RENY[1]

[1]Nalco Europe BV, The Netherlands, ereny@nalco.com

It is well known that the most damaging form of localised corrosion in recirculating cooling systems is pitting corrosion. If localised corrosion occurs on the heat exchanger plate, it is likely that in absence of proper treatment, pits will drill right through the plates leading to a general failure of the cooling system. The consequent costs and demand on non-renewable resources associated with premature asset replacement can be very significant.

Traditional strategies to control general corrosion are well known and very effective. On the other hand, chemical technologies aimed at protecting mild steel surfaces against pitting corrosion in aqueous environments and that exhibit an undeniable effectiveness, have yet to be discovered.

This paper outlines a new methodology to evaluate the performance of various compounds in terms of localised corrosion inhibition. The electrochemical technique used is cyclic polarisation applied to a 3-electrode cell. The data collected allow the calculation of Electrochemical Key Performance Indicators (EKPIs) that represent respectively, the fraction of corrosion current due to non–repassivated pits; the normalized integration of this fraction; and the position of the re-passivation potential in regards to the rest potential.

This method was used to screen localised corrosion inhibition properties of compounds that are already industrially available. The EKPIs collected were validated by visual observations. This work was performed using one-litre Greene cells linked to a potentiostat piloted by a computer. From this study, a programme that showed some promise was identified. Further characterisation of this programme was carried out using a pre-pilot system consisting also of 3-electrodes immersed in 10 litres of electrolyte for a duration equivalent to the Holding Time Index (HTI) of a typical open recirculating cooling system. Again, strong correlations between the EKPIs and observational parameters such as pit density, and average and maximal pit depths, illustrate how this methodology can be used to evaluate the impact of future inhibitors on the qualitative and quantitative character of localised corrosion.

Inhibiting the acidic corrosion of metals: surface and bulk effects

S.M. RESHETNIKOV, M.A. PLETNEV, I.B.SHIROBOKOV
UDMURT STATE UNIVERSUTY, RUSSIA

Quaternary ammonium salts as a model of the acidic corrosion are unable to block the active surface sites of the metal (typically, surface defects). They inhibit the cathodic and anodic reactions primarily due to the changes in the structure of water near the electrode. Insofar as the changes are not restricted to a monolayer, but involve some bulk of electrolyte near the phase boundary, such an inhibiting effect can conditionally be referred to as "bulk". Onium compounds of the elements of the third and forth periods of the V and VI groups also inhibit the acidic corrosion of metals. However, along with the considered ways of the deceleration of the electrode reactions typical of ammonium salts, phosphonium, arsonium, and sulfonium can be cathodically split. Being split concurrently with the hydrogen reduction , phosphonium, arsonium, and sulfonium cations act as additional cathodic depolarizers. Besides that, the surface products of reactions are much more hydrophobic than the original cations and can specifically adsorb on the metal due to the electrondonor properties of the central atoms. As the result, both cathodic and anodic processes are decelerated due to the adsorption of the original (or primary, following Horner) inhibitor and the newly formed secondary inhibitor . During the adsorption of inhibitors, not only the adsorbate, but also an adsorbent changes. A wide usage of tunnel scanning microscopy allowed people to reveal the reconstruction of the metal surface upon the adsorption of nucleophilic particles. Therefore, one should not neglect the effect of the chemisorbed inhibitor particles on the corrosion reactions of a metal via the reconstruction of the surface as well. This peculiarity may probably predetermine the similarity of the effect of iodid-ion on the cathodic hydrogen evolution and the anodic iron dissolution. Thus, analyzing the mechanism of the protective effect of inhibitors, one should differentially take into account their electrode and near electrode effects. The near electrode effects involve: changes in the structure of a solvent near the electrode and the resulting change in the conditions of proton transfer; changes in the parameters of the translation motion of the solvent molecules near the electrode and changes in the composition of the first coordination shell of the depolarizer. Besides adsorption, the electrode effects involve changes in the chemical nature of the inhibitor during the corrosion-electrochemical process, a change in the Fermi level of a metal due to the adsorption of the nucleophilic inhibitors ,and a reconstruction of the metal surface upon the adsorption of inhibitors.

Application Experience and New Approaches for Volatile Corrosion Inhibitors

Prof. Efim Lyublinski, Patrick Lynch, Eng. Irina Roytman,
Northern Technologies International Corporation
23205 Mercantile Rd., Beachwood, OH 44122, USA
Tatiana Yakubovskaya, ZAO MostNIC-Zerust
Profsouznaya street, 93a, Office 528/503
Moscow, 117279, Russia

Abstract

The efficiency and service life of a wide range of volatile corrosion inhibitors (VCIs) are summarized and discussed. Important data, related to application experience of these VCIs, during last 10 years is presented. It is shown that, in most, cases ferrous, non-ferrous, and multimodal VCI films, capsules, pipe strips, make it possible to achieve a high efficiency of corrosion protection of metal parts and equipment during storage, shipping, and application of a wide range of spare parts and equipment in various industries. The existing and new VCI systems presented in this paper allow us to select the most effective type of metal preservation, based on different application conditions with required service life.

New methods allow for a range of VCI applications to be reliably extended into new areas of applications, which are described. These existing and new technologies increase efficiency and service life and decrease the total cost of corrosion protection in Oil & Gas, Military, Automotive, Electronic, Electrical, and other sectors.

Keywords: Corrosion, inhibitors, VCI, films, capsules, efficiency, service life, ferrous, nonferrous metals.

Inhibitors of iron acid corrosion on the basis of unsaturated organic compounds

Yaroslav AVDEEV
A.N.Frumkin Institute of Physical Chemistry and Electrochemistry of Russian Academy of Sciences, Moscow, Russia

Unlimited compounds (UC): some acetylene compounds, α,β-unlimited aldehydes and azomethins were investigated as inhibitors of iron acid corrosion. It was established that high protective properties of UC on steel corrosion are the consequences of their polymerization on the surface of the metal with the formation of hydrophobic protective film. Unhydrogenating UC are not able for polymerization and formation of protective film of polymers. As a rule the rise of unsaturation of UC increases their protective action.

UC, with their high efficiency in HCl often turn out to be low-efficient or stimulate steel corrosion in the solutions of mineral acids (H_2SO_4, H_3PO_4, $HClO_4$) with hydrophilic anions (HA). This effect is a consequence of cathodic hydrogenation of UC, which flows most effectively in the solutions of mineral acids with HA. Adding of such acids additives to the solution, suppressing cathodic discharge of hydrogene, sufficiently increases the efficiency of UC. It is shown that when hydrophobic anions (I^-, CNS^-, diethyldithiourethane) are present, azomethins in sulfuric solutions turn out to be not stimulators of corrosion but inhibitors, providing $Z \geq 99\%$.

UC depending from their structure, composition of corrosion medium and conditions of corrosion flowing can change the mechanism of their action from adsorptive, which is the most universal but the least effective, to adsorptive-polymermaking, providing the highest coefficient of inhibition. The reason for such action of UC is the dependence of the direction of dominating chemical inhibitor changing from the corrosion conditions. The following changings of UC are possible:

1) *cathodic UC restoration*, accelerating cathodic reaction and provoking the inhibitor expenditure;
2) *UC volume polarization*, making the inhibitor go out from the corrosion medium;
3) *the formation of the protective polymer film on the metal surface,* which is firmly connected with the steel surface. It is formed through the stage of the formation of complexes of surface atoms with UC molecules and changes its structure in the course of time.

The examples of the protective films formation by some UC, their inhibition of steel corrosion and effects of protective aftereffect are considered.

THE PROTECTIVE PROPERTIES OF SOME PRIMARILY ADSORBED SURFACTANTS DISPLAYED IN THE CORROSION OF A NUMBER OF METALS ACCOMPANIED BY HYDROGEN AND METAL DEPOLARIZATION

Grigoriev Valentin P., *author & ed.*, ***Shpan'ko Svetlana P.***, *co-author*, ***Plekhanova Elizaveta V.***, *co-author*, ***Boginskaya Vera V.,*** *co-author*,
Burlov Alexander.S., *co-author, Southern Federal University*
Rostov-na-Donu, Russia

The object of the study is the corrosion-electrochemical behavior of some metals (Fe, Ni, Zn, Al, Cu, Ag) with different surface charges that have been pre-processed in various surfactant solutions.

The study determines empirical correlations between a decrease in the protective properties of primarily adsorbed surfactants and the duration of their protective effect as a function of solution temperature, surfactant concentration and the characteristics of their molecular structure.

A decrease in the concentration of surfactants desorbed from the surface of a metal is investigated in its dependence on the temperature and the duration of the metal's immersion in an uninhibited solution. This relation complies with the transient diffusion equation.

Constituents of the coefficient of corrosion inhibition, which in these conditions are determined by the surface blocking and the change in the Ψ'- potential, are calculated.

In the process of surfactant desorption effective corrosion activation energies are determined.

The possibilities to increase the duration of the protective effect exerted by primarily adsorbed surfactants with the addition of various mineral salts are investigated in terms of linear Gibbs energy relations and the HSAB concept.

Primarily adsorbed surfactants lead to a rapid reduction in the rate of corrosion with metal depolarization (contact exchange) in the first seconds of this process.

The surfactants that are introduced into process solution slow down the contact plating less effectively than the surfactants applied primarily to an electrode and then transferred to the surfactant-free process solution.

A mathematical interpretation of the determined dependencies in the protective effect of primarily adsorbed surfactants is proposed.

Complex approach to the estimation of copper pitting corrosion inhibition by benzotriazole in alkaline media under different temperatures

Svetlana Kaluzhina, Ekaterina Skrypnikova, Voronezh State, Russia,

The problem of copper and it's allows pitting corrosion (PC) is still one of the most actual problems. Variety of pitting initiation mechanisms acquires special approaches to select rational methods of protection, among which inhibition plays significant role. This direction development assumes not only new inhibitors synthesis, but also revealing specific properties of traditional inhibitors, that appears possible under modern tool methods using.

At the present work the decision of last problem is presented on an example of research of the copper PC in alkaline solutions with Cl^- and SO_4^{2-} - ions additives under different temperatures and varying benzotriazole (BTAH) concentration from 10^{-7} to 10^{-3} M. The chosen objects of research essentially differs on the pitting initiation mechanism and temperature effects. To obtain authentic data about the copper pitting initiation mechanism BTAH inhibitive action, along with electrochemical methods have been used IR-spectroscopy, optical and scanning electronic microscopy and X-ray analysis methods. Interpretation of obtained results was made on the basis of modern theories of pitting initiation (nucleophilic substitution, point defects and halide nucleation models) involving the phenomena of adsorption, complexing and "hard and soft acids and bases" principle.

Under quantitative estimation of BTAH protective action have been used the pitting initiation induction period, pitting initiation potential shift and polarizing resistance in systems with and without inhibitor. Correlation between the last confirms reliability of the received data about BTAH high inhibitor activity. The obtained results have shown, that BTAH is effective copper PC inhibitor, and its activity sharply increases under temperature rise. Full protection of copper against PC takes place under C(BTAH) = 4×10^{-5} M (20^0C) and C(BTAH) = 2×10^{-7} M (60^0C) at chloride-containing mediums; C(BTAH) = 8×10^{-4} M (20^0C) and C(BTAH) = 5×10^{-7} M (60^0C) at sulphate-containing solutions. Under set temperature BTAH shows the greatest effect in the presence of chlorides-ions that corresponds to known differences in the copper PC mechanism in the studied electrolytes.

Acknowledgement

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MASS-SPECTROMETRY FOR CORROSION PROCESSES AND CORROSION INHIBITORS INVESTIGATION

Aleksey K. Buryak, Tat´yana M. Serdyuk, Aleksey V. Uleanov
Establishment of Russian Academy of science
A.N.Frumkin Institute of physical chemistry and electrochemistry, Moscow, Russia.

Termo-desorption mass-spectrometry (TDMS), chromato-mass-spectrometry (CMS), matrix-assisted laser desorption/ionization (MALDI), surface-assisted laser desorption/ionization (SALDI) are the most popular mass-spectrometry methods in research of corrosion processes.

TDMS makes possible to study important characteristics of corrosion systems: accumulation gases in metals and alloys, formation of corrosion products and transformation of inhibitors. TDMS allows study substances, which desorbing from surface or evaporating from volume without decomposition and to establish composition of substances, which isolate when heated corrosion products and electrical precipitation coverings. Corrosion products adsorbed and chemosorbed inhibitors and products of their destruction can be identificate by the method of TDMS.

CMS is one of the most rapid and informative methods of analysis of organic compounds. After appropriate sample preparation the method can be widely used for analysis of different classes of inhibitors and products of their transformation in corrosion processes.

MALDI and SALDI are the modern methods of mass-spectrometry analysis. These methods have gained wide distribution for analysis of high – molecular and unstable compounds. Important advantage of these methods is a possibility for direct surface analysis without preliminary sample preparation. MALDI and SALDI mass-spectrums of corrosion products, organic and inorganic inhibitors in pure state and on different surfaces are examined. Examples of investigation of behaviour of inhibitors and the composition of corrosion products on the surfaces of construction materials used in space technology are presented in this work.

Inhibition effect of novel nonionic surfactants on the corrosion of carbon steel in acidic medium

M.A. Hegazy, Egyptian Petroleum Research Institute, Cairo/ET

The inhibition effect of novel nonionic surfactants on the corrosion of carbon steel (CS) in 1 M HCl was studied at different temperatures (20–60 ^{o}C) by weight loss, electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization methods. The CS surface morphology was investigated by SEM. The obtained results showed that the prepared nonionic surfactants are excellent inhibitor in 1 M HCl, and the inhibition efficiency (η) increases with the inhibitor concentration and temperature increasing. The adsorption of inhibitors on the CS surface obeys the Langmuir adsorption isotherm equation. Thermodynamic parameters have been obtained by adsorption theory. Polarization curves show that the synthesized inhibitors are mixed-type inhibitors in hydrochloric acid.

SVET screening of corrosion inhibitors using multi-metal electrode approach

Silvar Kallip, Alexandre C. Bastos, João Tedim, Mikhail L. Zheludkevich, Mario G.S. Ferreira

CICECO, Department of Ceramics and Glass Engineering, University of Aveiro, Campus de Santiago, 3810-193 Aveiro, Portugal

The need for active corrosion protection of different metallic structures calls for the development of new more efficient corrosion inhibitors. The most recent trend is to introduce the corrosion inhibitors into the protective polymer coatings aiming in active self-healing functionality [1]. The inhibitors available up to now are often incompatible with polymer coatings or have important environmental restrictions. Nowadays the corrosion protection of multi-metal structures becomes also an issue. Therefore inhibitors efficient for different metals used in the same structure are of great interest.

Given the high number of alloys and metal combinations used in the different areas of engineering and the nearly unlimited number of possible corrosion inhibitors, the selection process for the best inhibitors to each alloy, along with the conditions for best performance, can be tedious and repetitive.

The SVET (*Scanning Vibrating Electrode Technique*) combined with developed multi-electrode cells has been used to screen the possible inhibitor systems. The idea is to have different metals or alloys in one multi-electrode cell with the testing taking place simultaneously in the same measurement using SVET, which allows to estimate accurately the local anodic and cathodic corrosion activities. It has the advantage of reducing time and saving the amount of materials needed for measurement. Also the conditions of the SVET experiments are close to the undisturbed environment since the corrosion processes are not stimulated by any applied polarisation. Another advantage of using the multi-electrodes allows to simulate the real galvanic corrosion processes in combined material constructions and intermetallic phases of metal alloys.

Preliminary studies (Fig.1) have shown usability of presented method for rapid screening of different inhibitor systems ($Ce(NO_3)_3$, $CeCl_3$, $NaNO_3$ and 1,2,3-Benzotriazole) for different metals. Also the corrosion protection efficiency of different inhibitor filled nanocontainer systems (Layered Double Hydroxide nanocontainers (LDH) loaded with MoO_4^{2-}, NO_3^- and VO_x anions) has been tested.

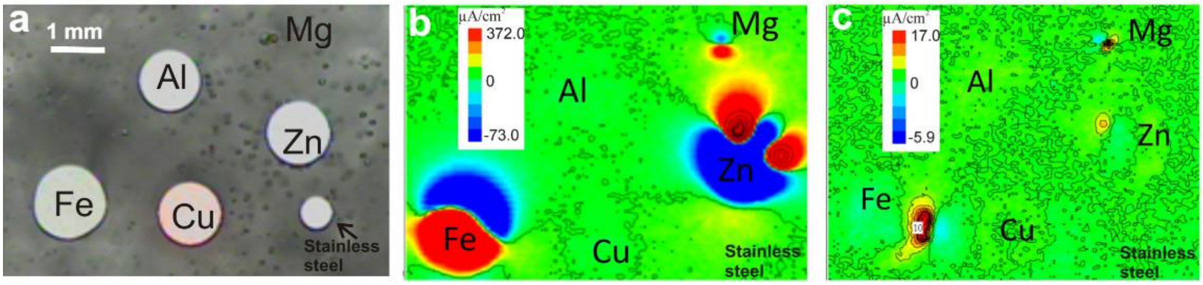

Fig. 1. The photograph (a) and SVET maps in pure corrosive media 0.05M NaCl (b) and with 10 mM addition of inhibitor $Ce(NO_3)_3$ (c) of multi-electrode test cell.

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ELECTROCHEMICAL AND QUANTUM CHEMICAL STUDIES OF SOME CROWN ETHERS AS CORROSION INHIBITORS FOR CARBON STEEL IN 1 M HCL SOLUTION

Michel LAGRENEE[1], **Fouad. BENTISS**[2], **Hervé VEZIN**[3]

[1]Unité de Catalyse et de Chimie du Solide, UMR-CNRS 8181, ENSCL, BP. 90108,
F-59652 Villeneuve d'Ascq Cedex, France, michel.lagrenee@ensc-lille.fr
[2]Laboratoire de Chimie de Coordination et d'Analytique, Faculté des Sciences, Université
Chouaib Doukkali, B.P. 20, M-24000 El Jadida, Morocco, fbentiss@enscl.fr
[3]Laboratoire de Chimie Organique et Macromoléculaire, UMR-CNRS 8009, USTL Bât C4,
F-59655 Villeneuve d'Ascq Cedex, France, herve.vezin@univ-lille1.fr

Some crown ethers were investigated as corrosion inhibitors for C38 carbon steel in 1 M HCl solution by Ac impedance technique. The Nyquist plots of impedance expressed mainly as a depressed capacitive loop with different compounds and concentrations. Data obtained from ac impedance study show a frequency distribution and therefore a modelling element with frequency dispersion behaviour, a constant phase element (CPE) has been used. Adsorption of the crown ether derivatives on the carbon steel surface is in agreement with the Langmuir adsorption isotherm model. The calculated Gibbs free energy values showed that inhibition of C38 steel corrosion in 1 M HCl solution by the crown ethers is due to the formation of a chemisorbed film on the steel surface. The structural and electronic properties of these inhibitors, obtained using DFT method are correlated with their experimental efficiencies.

Quantum chemical study of some amino acids as corrosion inhibitors of copper

Gökhan Gece, Semra Bilgiç
Department of Physical Chemistry, Ankara University, Ankara/Turkey

Research is still underway to find non-toxic corrosion inhibitors in corrosion science and due to their eco-friendly properties amino acids have aroused periodic interest as corrosion inhibitors in the last two decades. Advances in computer hardware and software and in theoretical chemistry have brought high-performance computing and graphic tools within the reach of many academic and industrial laboratories.Hence, quantum chemical calculations are being utilised by a continually increasing range of corrosion scientists. However, to date, no theoretical study of a wide range of amino acids as corrosion inhibitors of copper has been reported in the literature. For this reason, as a continuation of previous experimental works, the inhibition efficiencies of nine amino acids, i.e., aspartic acid, glutamic acid, asparagine, glutamine, tryptophan, glycine, alanine, valine and tyrosine (Fig.1) on corrosion of copper in acidic media have been studied by using density functional theory (DFT) method.

The neutral and protonated forms of amino acids were optimized at the B3LYP/LANL2DZ level, both in gas and aqueous phases, using Gaussian 03 program. Theoretical calculations were also carried out on model systems consisting of an amino acid and a copper atom. The following quantum chemical parameters were considered: the energy of the highest occupied molecular orbital (E_{HOMO}), the energy of the lowest unoccupied molecular orbital (E_{LUMO}), energy band gap, $\Delta E = E_{LUMO} - E_{HOMO}$. The relation between the inhibition efficiency and the calculated quantum chemical parameters has been discussed in order to elucidate the inhibition mechanism of these compounds. It has been found that theoretical data relevant to the protonated forms of the amino acids support the experimental findings.

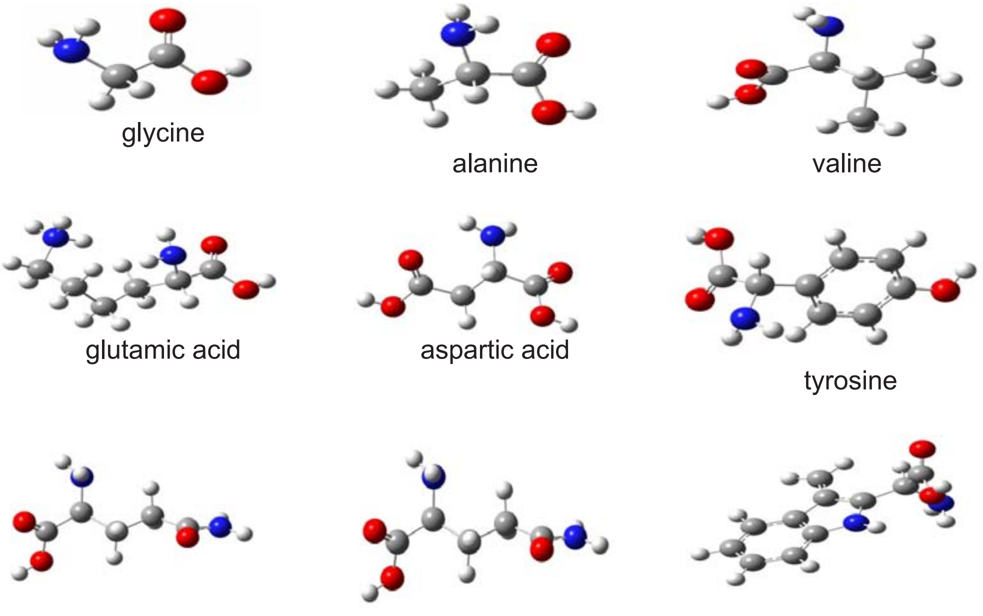


Fig. 1. Optimized structures of the investigated amino acids.

Effect of volatile inhibitors structure and medium properties on hydrogen sulfide corrosion of steel equipment and pipelines

KASHKOVSKIY R.V.[1], **KUZNETSOV Yu.I.**[1], **VAGAPOV R.K.**[2]
[1]*A.N.Frumkin Institute of Physical Chemistry and Electrochemistry of Russian Academy of Science, Moscow, Russia*
[2]*GAZPROM VNIIGAZ, Razvilka, Russia*

The most important tasks in the development of oil and gas fields are reliable operation and long life of equipment and pipeline systems. It’s known that the presence of corrosive components, such as hydrogen sulfide and carbon dioxide, in transported hydrocarbon raw materials causes the steel corrosion and hydrogenation.

Unlike contact inhibitors, volatile ones can spontaneously adsorb on a surface from a vapor-gas phase and easily penetrate into hard-to-reach regions (various slots and gaps).

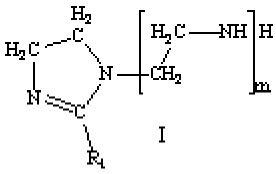
We carried out the broad complex of corrosion experiments in liquid and vapour phases modeling the oil and gas field conditions to investigate the influence of H_2S concentration, initial solutions pH, temperature, exposure time, nature of aggressive environment dynamics and presence of hydrocarbon phase on protective ability of the different heteroatom organic compounds. We studied the chemical structure effect of above mentioned compounds on their inhibitor properties as well. Now we find few substances in terms of received results that could become a basis for creation of the efficient volatile inhibitors against H_2S corrosion.

Inhibitors universality by the hydrosulphuric and carbon dioxide corrosion

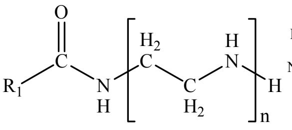
L.E. Tsygankova, A.I. Fedotova, K.O. Strelnikova
Tambov State Technical University, Tambov, Russia

The Inhibitors universality is determined by their sufficient protective effect (Z) valid to the solution corrosion activity by the combined exposure of some process stimulants. By the hydrosulphuric and carbon dioxide corrosion in acidified mineralized solutions it can be $O_{2,\ SOLUTED}$, H_3O^+, also H_2S, H_2CO_3 and their dissociation products.

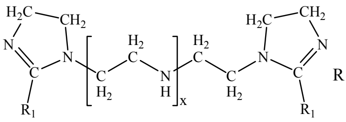
There are analysis results represented in report of the protective effect (Z, %) in such conditions of EM-inhibitors series with the following conditional formulas (mixtures of imidazolines (I) and amides (II) for (EM-12, EM-13, EM-14) and bisimidazolines (III) and diamides (IV):



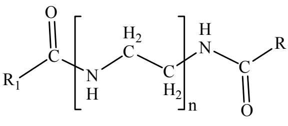
I



II



III



IV

R_1 are carbon acids alkyls , n = 2, 3 and 4; m = 1,2 and 3, x = 0,1.

The inhibitor nature and concentration (10 – 200 mg/L), pH_{INTIAL} = 2 – 6, the CO_2 equilibrium pressure (10^5 Pa) and test duration (0,1 – 24 hours) influence upon the carbonaceous steel corrosion (weight loss tests and polarization resistance) is researched. The compositions bactericidal activity against the sulfate-reducing bacteria (SRB) and inhibitor's and different kind of barrier coatings contribution to Inhibitor / Coating system $Z_{\sum}$ are estimated.

E.g. by the 200 mg/l EM-12, pH = 2, 50 mg/l NaCl

τ from the corrosion start, h.	$C(H_2S)$, mg/l								
	0			50			200		
	Z_{COAT}	Z_{INH}	$Z_{\sum}$	Z_{COAT}	Z_{INH}	$Z_{\sum}$	Z_{COAT}	Z_{INH}	$Z_{\sum}$
~ 0	-	45	45	-	0,1	0,1	-	81	81
2	68	10	78	71	1	72	67	29	96
8	67	18	85	73	6	79	71	26	97
24	64	22	86	74	11	85	73	22	95

By the steady state (after 8 – 10 hours) Z amounts to 95 % in the hydrosulphuric and 85 – 90 % in carbon dioxide solutions. By the combined H_2S and CO_2 content Z amounts to its top limit. The investigated materials reduce strongly the SRB activity by the $C_{Inh} \geq 100$ mg/l, $C_{INH} = 10$ mg/l increases the log-phase duration up to 1, 2, 3 and 3 days (EM-12, EM-13 and EM-14 and EM-20 respectively). After 7 days tests the H_2S-producing by the SRB decreases up to 10 times.

The inhibitors solutions integral toxicity (CCO, BCO_5) is estimated.

Cu(II), Co(II) and Ni(II) complexes of –Br and –OCH_2CH_3 substituted Schiff bases as corrosion inhibitors for aluminium in acidic media

A. Aytaç *

Department of Chemistry, Faculty of Science, Gazi University, 06500, Teknikokullar, Ankara Turkey

Abstract

A new class of corrosion inhibitors for aluminium by group of Cu(II), Ni(II) and Co(II) complexes of –Br and –OCH_2CH_3 substituted Schiff bases has been studied. Investigation of inhibiting properties of the –Br and –OCH_2CH_3 substituted Schiff bases as well as their corresponding complexes with Cu(II), Ni(II) and Co(II) ions, was performed in 0.1 M HCl in concentration of 10 ppm by potentiodynamic polarization, electrochemical impedance spectroscopy, linear polarisation methods and gas evolution tests at 25 ^{o}C. The inhibition efficiencies obtained from all methods employed are in good agreement. Results show Ni(II) complex of -OCH_2CH_3 substituted Schiff bases to be the best inhibitor with a mean efficiency of 69% at 10 ppm additive concentration. The potentiodynamic polarization curves showed both cathodic and anodic processes of aluminium corrosion were suppressed, and the Nyquist plots of impedance expressed mainly as a capacitive loop.

Keywords: Aluminium; Corrosion; Inorganic compounds; Electrochemical techniques

Corrosion inhibition by environmental friendly sodium metavanadate-spirulina system

V. Sribharathy[1] and Susai Rajendran [1,2]

1. Corrosion Research Centre, Post Graduate and Research Department of Chemistry, GTN Arts College, Dindigul-624 005, Tamilnadu, India. Email: bharathy_chem@yahoo.co.in
2. Corrosion Research Centre, Department of Physical Sciences, Servite College of Education for Women, Thogamalai-621 313, India. Email: srmjoany@sify.com

Abstract

The inhibition efficiency (IE) of sodium metavanadate (SMV) in controlling corrosion of carbon steel in an aqueous solution containing 60 ppm of chloride ion has been evaluated by weight loss method. SMV has good IE. 200 ppm of SMV has 98% IE. 50 ppm of SMV has only 48% IE. The IE of this system is improved by addition of various concentrations of spirulina solution (0.5 % aqueous solution). When 2 ml of spirulina solution is added to 50 ppm of SMV, the IE tremendously enhances from 48% to 98%.The 't- test' reveals that this enhancement is statistically significant. The protective film formed on the metal surface has been analyzed by FTIR spectra and fluorescence spectra. The mechanistic aspects of corrosion inhibition have been investigated by electrochemical studies such as polarization study and electrochemical impedance spectra (EIS).

Keywords: corrosion inhibition, carbon steel, spirulina, sodium metavanadate, green inhibitors

Influence of henna extract on the inhibition efficiency of Diethylenetriaminepentamethylene Phosphonic acid – Zn^{2+} System

B. Shyamala Devi[1] **and S. Rajendran**[2,3]

1. *Department of Chemistry, Vivekanandha Institute of Engineering and Technology for Women, Tirchengodu, Tamil Nadu, India, Email : shyapranesh@yahoo.com*
2. *Corrosion Research Centre, Post Graduate and Research Department of Chemistry, GTN Arts College, Dindigul – 624 005, India, Email : srmjoany@sify.com*

3. *Department of Physical Sciences, Servite College of Education for Women, Thaogamalai- 621 313, India*

Abstract

The inhibition efficiency (IE) of various concentrations of diethylenetriaminepentamethylene phosphonic acid (DTPMP) - Zn^{2+}- henna system in controlling corrosion of mild steel immersed in well water was evaluated by weight – loss study. The formulation consisting of 50 ppm of DTPMP and 25 ppm of Zn^{2+} has only 52% inhibition efficiency. Addition of 1ml of henna extract (20%, aqueous), tremendously enhances the efficiency to 90%.. A synergistic effect was noticed between diethylenetriaminepentamethylene phosphonic acid (DTPMP)-Zn^{2+}- henna system. In the presence of henna, DTPMP - Zn^{2+} system has excellent inhibition efficiency. The mechanistic aspects of corrosion inhibition have been investigated by electrochemical studies such as Polarization studyand AC impedance spectra. SEM and AFM studies reveal that a protective film is formed.

Keywords : Corrosion inhibition; carbon steel; diethylenetriaminepentamethylene phosphonic acid ; synergistic effect; henna extract

Corrosion inhibition by an aqueous extract of turmeric powder - (curcuma longa l) - a medicinal plant

V.Saravanakumar[1] and Susai Rajendran[2,3]

1. **Rajasthan Drugs and Pharmaceuticals Ltd, Jaipur-302013, India. Email: saravanan.kumar.vsk@gmail.com**
2. **Corrosion Research Centre, Department of Physical Sciences, Servite College of Education for Women, Thogamalai-621313, India. Email: srmjoany@sify.com**
3. **Corrosion Research Centre,PG & Research Department of Chemistry, GTN Arts College, Dindigul – 624 005, TamiNadu, India,**

Abstract

An aqueous extract of the plant material Rhizome powder has been used as corrosion inhibitor in controlling corrosion of carbon steel immersed in well water by weight loss method, in the absence and presence of Zn^{2+}. The main constituent of this plant extract is curcumin. It has good inhibition efficiency (IE). In the presence of Zn^{2+}, there exists a synergistic effect. Synergism parameters have been calculated. The protective film has been analyzed by FTIR spectroscopy. The film consists of Fe^{2+} - curcumin complex and $Zn(OH)_2$. Electrochemical studies such as potentiostatic polarization and AC impedance have been used to know the mechanistic aspects of corrosion inhibition.

Key words : Corrosion inhibition, carbon steel, plant extract, curcumin, synergistic effect, green inhibitor, synergism parameter

Inhibition corrosion of mild steel by liquorices

M. Koolivand-Salooki, M. Peykari, Petroleum University of Technology, Ahwaz/IR; A.R. Kiani-Rashid, Ferdowsi University of Mashhad/IR

The application of inhibitors controlling the corrosion of metals and alloys which are in contact with aggressive environment is an accepted practice. Large numbers of organic compounds were studied and are being studied to investigate their corrosion inhibition potential. All these studies reveal that organic compounds especially those with N, S and O show significant inhibition efficiency. But, unfortunately most of these compounds are not only expensive but also toxic to living beings. It is needless to point out the importance of cheap and safe corrosion inhibitors. Plant extracts have become important as an environmentally acceptable, readily available and renewable source for a wide range of inhibitors. These are the rich sources of ingredients which have very high inhibition efficiency. In the present study Liquorices (Glycyrrhiza glabra) was synthesized and its inhibiting effect on the corrosion of mild steel in 4% hydrochloric acid solutions was investigated by means of weight loss and electrochemical experiment. Results obtained revealed that Liquorices acted excellently as a corrosion inhibitor for mild steel in 4% hydrochloric acid medium and its efficiency is more than 62.4% at 0.5% of inhibitor in weight loss experiment.

Corrosion by Hot Gases and Combustion Products

Process equipment made of graphite, silicon carbide and carbon steel for production and treatment of process gases, containing gaseous hydrogen chloride (HCl) and hydrogen fluoride (HF) at temperatures in the range of 1200°C to 2200°C.

Authors: Dr. Marcus Franz, Dr. Peter Pöllmann, Thomas Grünberger and Dr. Sören Götz

SGL Group, The Carbon Company, Process Technology

Abstract

In general corrosion appears in industrial applications as a multi-parameter problem. Technical solutions as well as the material selection depend on the task of the process equipment. Especially in the chemical and recycling industry one faces three different cases when processing hot HCl- or HF-containing gases: 1. Inhibition of the formation of dioxins and furans by quenching the flue gases originated in fossil fired thermal combustion units (e.g. refrigerant decomposition), 2. Economical need for heat recovery e.g. from high exothermal operating HCl-synthesis units or other high temperature reactions and 3. Cooling HCl-gas or HF-gas for further down-stream processing.

The three tasks require different types of equipment, namely quenchers, directly or indirectly operating, boilers and coolers, respectively. Materials of construction are steel, impregnated graphite or silicon carbide. It is shown, that each material has specific strengths in terms of corrosion resistance. The material selection is not only constrained by chemo-physical issues, but also by economical factors, in particular life time or, in other words, in corrosion resistance. Moreover pressure vessel codes and restrictions have to be addressed.

Evaluation of the corrosiveness of an environment requires knowledge of all involved chemical compounds and elements of the gasmixture and the related kinetics of reactions, especially of reactions on the surface of the process equipment. A technical approach is possible by applying means of experimental data, such as provided by the Dechema data base, and appropriate temperature design of the process equipment.

Two technical examples of process equipment for high temperature application are provided: A) Heat recovery in HCl-synthesis units by steam production, B) Quenching of HF-flue gases coming form thermal destruction of refrigerants. Design criteria are discussed, including the dependency of corrosion on material temperature and flue-gas composition.

Principles of protection from high-temperature oxidation of niobium and carbon materials

A.V. Kasatkin
A.N. Frumkin Institute of physical chemistry and electrochemistry of Russian Academy of Sciences, Moscow, Russia.

Analysis of literature data and results of our investigations shows that successful protection of niobium and carbon materials (graphite, C-C composites) from high-temperature oxidation can be realized only by means of complex protective coatings. The ultimate part is played, according to our opinion, by special structural composition and by the exact combination of the phase components in the coating.

Niobium. Process of simultaneous diffusion saturation of Ti and Si in powder mixtures has been investigated. The coatings can be divided into two basic types: Nb-Ti solid solutions and Nb and Ti silicides. The coatings of the first type obtained in Ti-Ti_5Si_3 powder mixtures. The complex silicide layers were observed in the packs with higher silicon activity (Ti_5Si_3-TiSi and $TiSi_2$-TiSi mixtures). The activity of Ti and Si have been shown to be principal controlling factories in coating phase in composition. The temperature limit for exploitations of traditional diffusion coatings on niobium and its alloys in oxidation gaseous media does not exceed 1500°C. It is well known that it a possible to increase the limit temperature by combination of deposition methods. This work investigates features of forming for Ti-Si system coatings, their composition and heat resistance in air as well. The utilization time at 2000°C is 1-1,5 hrs. This is significantly more than for known diffusion coatings silicide type specifically.

Carbon materials. The three-zoned structure of protection coatings was grounded. The kinetic of formation and phase composition of diffusion coating C-Me-Si and C-Me-B-Si (Me=Ti, Zr or Hf) systems formed on carbon materials have been studied. The coating received by using sequential metallization, boron- and silicium-deposition from dispersive solid-phased media. The rate of formation coatings by metallization and Si-deposition decreases on the line: Ti-Zr-Hf, and formation carbide layers MeC by diffusion metallization carbon-materials describes liner-parabolic law have been shown. The velocity of boron diffusion of the “carbon materials- MeC layer” compositions is very little and it is increased on the line: Ti-Zr-Hf insignificantly. The formation of MeB_2 layer at the boriding are decreased of the velocity of siliciding. The coating proposed has three-zoned structure formed by compounds of the C-Me-Si or C-Me-B-Si systems and intended for protection carbon materials from high-temperature oxidation (≥ 1400°C). The laws of phase form and destruction at oxidation in air for these coatings are investigated.

Development of pest resistant Nb-Ti-Hf-Cr-Al-Si-Sn composites

S.Knittel, S.Mathieu, M.Vilasi, Institut Jean Lamour - UMR7198, CNRS - Nancy-Université - UPV-Metz, France

Refractory-metal intermetallic in-situ composites have the potential to replace nickel-based superalloys in the hot section of turbine engines. In this class of materials, niobium silicide based composites Nb_5Si_3/Nb offer increased temperature capability (T_m > 1700°C) and reduced density. However these materials suffer from the *pest catastrophic behaviour* between 600 and 900°C which limits to date their application. It consists in the rapid fragmentation of the pieces after a given incubation period.

This behaviour is associated to the in-depth penetration of oxygen in the solid solution of niobium which induces severe stresses to the brittle Nb_5Si_3 silicide. The consequence is a total pulverisation of the alloy in a few hours at moderated temperature (815°C). Two previous studies [1,2] have reported the beneficial effect of tin addition in niobium in-situ composites on the delay before the pest appears.

The aim of this study is to determine the role of tin during the oxidation of niobium silicide based composites and to assess the optimize Sn concentration giving the best oxidation resistance.

For this study, niobium in-situ composites have been prepared by arc melting with tin additions from 1 to 10at.%. The resulting microstructures are studied by metallographic analysis to evaluate the influence of tin content on the distribution of phases and on their compositions. As tin addition increases, the niobium solid solution is progressively substituted by a new tin-rich niobium solid solution.

Oxidation tests are carried out by thermo-gravimetric measurements and cyclic oxidation at 815°C, temperature for which the alloys are very sensitive to the pest. *Post mortem* observations demonstrate the role played by the rich tin niobium solid solution. Oxygen does not solubilise anymore in this phase and a new rich Sn phase is formed at the substrate/oxide interface. The sensibility to the pest is hence reduced.

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Problems of design of heat-resistant coatings for high-temperature materials working in extreme conditions

Terentieva V.S.
Moscow Aviation Institute (MAI), Moscow, Russia.

Problems of forming of new materials need to progress in the aerospace vehicles design are actual during the space investigation period. Main technical problems are functionality securing under high temperatures, non-steady mechanical loads and aggressive gas flows, particularly for space vehicle and engines working in super and hypersonic plasma flows. Prime, new materials must have the surface resistive to high-temperature gas corrosion, erosive mass loss, catalyticity, optical properties etc. Many modern high-temperature materials and its alternatives (refractory alloys, carbonaceous, ceramics and ceramic-like composite materials) are functional in listed above conditions only with special multifunctional protective coatings. All domestic and foreign coatings are designing now for specific material and are not universal. There are no coating meeting all requirements listed above; all coatings lose catastrophically its protective capabilities in extreme conditions (aero capture of space vehicle, engine structures interaction with the ionized high-caloric fuels combustion products etc.). We have no unified theory of high-temperature multifunctional protective coating; it is due principally to problem's multifactoriality and many sub-problems having no solution now. So, the modern coatings are designing using "trial method". In [1, 2, 3] author has proposed a new design conception for universal protective coatings for structural elements unified by surface requirements in specified external condition (velocity, pressure, flow enthalpy, heat and mass transfer etc.). Here are two principal realization directions: science of materials and technology. Based on this problem classification, the new principles of coatings design and forming have been conceptualized and the technological parameters need to realize it in the coating's receipt adopted to specified operation conditions and independent from protecting structure material, dimension, configuration. This design principle is realized by abstracting from the forming technology and supposing that the coating is forming from the protecting material using all possible application methods conserving material phase and structure. In [1, 2, 3] the schema of initial material's structure and it's transform into multilayer coating with n functional layers of micro or sub-micro thickness during high-temperature operation. The theoretical results are realized successfully in some protective coatings.

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Kinetics Principles for Formation of Functional High Temperature Coatings

V. A. Zhabrev, S.V. Chuppina
Grebenshchikov Institute of Silicate Chemistry, Russian Academy of Sciences,
Saint-Petersburg, Russia

Functional coatings are layers or films that differ in chemical composition and structure from a base and fulfill a function not typical of the substrate material.

The coating may play the role of a barrier layer that limits chemical processes of oxidation and corrosion, or retards diffusion processes; change the mechanical properties of substrates and increase its resistance to erosion and abrasion; impart new electrical and magnetic properties to substrates in the development of electrically conducting, electrically insulating, magnetic or antimagnetic layers; regulate the heat transfer due to the increase or decrease in the thermal conductivity and the ability to scatter or absorb radiation, etc. The composition and the method of formation are governed by necessary functions of the material. As the high temperature functional coatings are formed under high temperature treatment we have to know the mechanism and kinetics of those reactions.

In the report we consider reaction-contacted coatings. When we add some amount of inorganic reducer to the oxide melt and introduce the thing made of titanium or ferric steel or their alloys the intermetallic layers (borides, silicides and aluminides) are synthesized in the surface metal layer. These coatings protect metal against high-temperature gas corrosion in the interval up to 900ºC.

At oxidation of composite ZrB_2 – SiC the zirconium-boron-silicate matrix is formed which prevent diffusion of aggressive agent to protected material. These coatings are used for protection of carbon-graphite materials in the interval up to 1500ºC.

Organosilicate coatings formed from suspensions of thin-dispersed layered silicates, inorganic pigments in the solutions of polyorganosiloxanes, possess quite different properties, such as decorative, physicomechanical, and protective properties, the majority of which are manifestation of characteristics of a bulk material. For example, the anticorrosive properties can be considered as a function of adhesive-cohesive interactions, permeability of the coating with respect to different reactants, and the glass transition temperature of the coating, the heat resistance – as the dependence on the bond energy of components, structural regularity. molecular mobility, and intermolecular interaction in the bulk of the material.

ALUMINIDE COATINGS FOR FERRITIC STEELS AGAINST OXIDATION IN STEAM: THERMODYNAMIC AND TG-MASS SPECTROMETRY STUDIES

M.P. Hierro, S.I. Castañeda, J. Marulanda G. Alcalá and F.J. Pérez (*)

Universidad Complutense de Madrid. Surface Engineering Research Group
Facultad de Ciencias Químicas. 28040 Madrid. SPAIN
(*) Phone: +34913944215, Fax: +34913944357e-mail: fjperez@quim.ucm.es

The steels with chromium contents between 9 and 12% wt are used for power plants with advanced steam oxidation conditions. In the last years numerous investigation in development of coatings has been realized with the aim the protected them against the oxidation in order to allow operation of steam turbines at 650^{o}C. In this study, Al-Hf AND Al-Mn protective coatings were deposited by CVD-FBR on ferritic steels followed by a diffusion heat treatment, have shown to be protective at 650^{o}C under steam exposure under atmospheric pressure. Morphology and composition of coatings were characterized by different techniques, such as scanning electron microscopy (SEM), electron probe microanalysis, and X-ray diffraction (XRD). On the other hand, volatile species by mass spectrometry (MS) and thermogravimetric mea surements (TG) during the initial stages oxidation of the P92 ferritic steel without and of Al and Al/Si coating by chemical vapour deposition in fluidized bed reactors (CVD-FBR) at 650ºC in Ar+20%H2O were studied. In order to go forward to coatings design the Thermocalc code as used as base for the MS-data. TG-MS experiments were conducted in a closed steam loop in order to obtain information about the oxyhydroxides formation as reaction between coatings and steam. From those results the role of the different coating element could be established and optimized for the coating durability. An oxidation mechanism based on the TG-MS results is given. The morphology/composition and structure of the oxidized samples were also studied using SEM/EDS and XRD techniques.

Surface Modified Ferritic Steels by Moderate Temperature Si and Cr Enrichment for Steam Oxidation Resistance at 650º C

Alina Agüero, Marcos Gutiérrez and Vanessa González
Instituto Nacional de Técnica Aeroespacial (INTA)
Área de Materiales Metálicos
Ctra. Ajalvir Km. 4
28850 Torrejón de Ardoz (Madrid)
SPAIN

Raúl Muelas
Ingeniería y Servicios Aeroespaciales (INSA)
Dirección de Ingeniería
Paseo de Pintor Rosales, 34
28008 Madrid
SPAIN

The steam oxidation resistance of ferritic steels employed in thermal power plants is presently one of the main important factors limiting the operating efficiency. Under steam, ferritic steels currently in use, oxidize heavily at temperatures higher than 600º C. Thick oxide scales form causing loss of thermal conductivity in heat exchangers, and spall after relatively short exposure times causing tube blockage and bursting as well as erosion of down-stream components. It is known that steels with a Cr content higher than 10 wt. % exhibit appreciably higher steam oxidation resistance and morover, it is also known that Si, in small amounts also significantly improves the behaviour. However, the ferritic steels commonly used in thermal power plants contain only 9-10 wt. % in Cr and very low Si if any, as otherwise, the required creep resistance of these materials would be compromised. Surface modification as well as coatings, allow to increase the oxidation resistance any metallic material without changing the bulk composition. Cr and Si pack cementation processes at 700º C have been developed and employed to enrich the surface of P92 with these two elements. Due to the relatively low temperature, typical diffusion coatings are not formed but the surface is rather enriched down to a depth of a maximum of 5-10 μm. Cr and Si modified P92 have been charaterized by FESEM-EDX and exposed to atmospheric pressure steam for over 20,000 h at 650º C in the laboratory. In both cases, the steam oxidation resistance of P92 was significantly increased.

BEHAVIOUR OF SELECTED COATINGS UNDER TESTING ENVIRONMENT OF BOILERS FOR PLANT BIOMASS BURNING

Josef CIZNER[1], Petr SAJDL[2]

[1] SVUM a.s., Czech Republic, cizner@svum.cz
[2]Institute of Chemical Technology Prague , Czech Republic, sajdlp@vscht.cz

The real environments of plant biomass burning boilers in which the materials are exposed, varies in relatively wide range. This environment depends mainly on the type of burned biomass and the locality.

Evaluation of corrosion behaviour of selected metal and metal – ceramic coatingss exposed in model environment of biomass burning process under synthetic deposits was done by several methods.

Metallographic and gravimetric analyses was used, also microanalysis of exposed layers showed good data for corrosion attack identification.

The best results were achieved with sprayed on layers of nickel alloys.

Phase transformations in Inconel 625 during oxidation at 800-1000°C

A.D. Chyrkin, *P. Huczkowski, L. Singheiser, W.J. Quadakkers*

Research Centre Juelich, Institute of Energy Research (IEF-2), 52425 Juelich, Germany

Abstract

The commercial wrought superalloy Inconel 625 relies for its high temperature oxidation resistance on the formation of a continuous, slow growing, and well adherent chromia layer. The oxidation behavior of Inconel 625 has been studied in air and water containing atmospheres in the temperature range between 800 and 1000°C. The SEM images of the cross-sectioned specimens suggest that high temperature exposure caused distinctive microstructural changes in the alloy underneath the chromia oxide layer, i.e. a continuous layer of intermetallic precipitates was formed followed by a precipitate-free zone turning eventually into bulk alloy. The former result might be of great practical importance because the thick intermetallic layer beneath the oxide scale can eventually cause oxide delamination and thus earlier component failure.

Thermodynamic computer modeling was used along with a diffusion simulation software to predict phase formations and phase changes in Inconel 625 as a function of temperature. The modeled results are compared with the experimental ones involving optical microscopy, scanning electron microscopy (SEM), sputtered neutrals mass spectrometry (SNMS) and glow discharge optical emission spectroscopy (GDOES).

The present study focuses on the influence of the alloying elements (niobium and molybdenum) on the precipitation of the strengthening phases underneath the chromia layer. The effect of compositional changes due to chromium depletion during oxidation on the phase distribution is explained in on the basis of phase equilibria in the system.

FERRITIC STAINLESS STEEL DURABILITY IN GAS CONDENSING BOILERS

Stephanie LASSIAZ[1], José LECLERCQ[2], Alain GAUGAIN[1], Lionel PEGUET[1]

[1]*ArcelorMittal Isbergues Research Center, BP15, 62330 Isbergues, France,*
stephanie.lassiaz@arcelormittal.com; alain.gaugain@arcelormittal.com;
lionel.peguet@arcelormittal.com
[2]*ArcelorMittal Stainless Europe, Place des forges Bat 26, 71130 Gueugnon, France,*
jose.leclercq@arcelormittal.com

Critical species causing corrosion in gas condensing boilers are sulfuric and nitric acids generated by condensation of combustion by-products. Due to significantly better corrosion resistance of stainless steels in comparison to aluminium in such acids, these steels are recommended for heat exchanger material. Moreover, thanks to their easy forming, SS tubes allow very compact condensing modules.

The alternation of condensation/drying phases is suspected to be the worst service conditions because of medium concentration during drying. In order to simulate condensation phenomenon and the on/off phases alternation in the gas condensing boiler, a "dip-dry" apparatus was used. This device allows tests with alternation of sample immersion in condensate and drying at controlled temperature. Samples, fixed on a mobile beam, are alternatively immerged in thermostated beakers and dried in a furnace. Two types of condensates were used: the first one is a mix of sulfuric and nitric acids to investigate generalized corrosion risk. In the second one, chlorides were added to investigate a likely aerial pollution and the related localised corrosion risk. Five stainless steels were studied: four ferritic grades, AISI 409 (EN 1.4512), AISI 441 (EN 1.4509), AISI 444 (EN 1.4521) and AISI 445 (EN 1.4621), and one austenitic grade AISI 304 (EN 1.4301).

For each grades, corrosion was estimated by weight loss measurements, chemical analyses of condensates and attack profiles. The influence of the main alloying elements on corrosion behaviour is discussed. Taking durability and price into consideration, AISI 441 type stainless steel seems to be the most relevant choice for heat exchangers.

HIGH TEMPERATURE BEHAVIOR OF WATER ON METALLIC MATERIALS WITH CORROSIVE ATMOSPHERES WITH CHLORINE

[1]Sánchez-Pastén MIGUEL, [2] Alcántara-Gutiérrez JUAN ALBERTO, [2] Chávez-Alcalá FEDERICO

[1]Instituto Politécnico Nacional, Departamento de Ingeniería Química Industrial, Edificio 8, ESIQIE, 07738 México, D.F., Mexico, msanchezpa@ipn.mx
[2]Instituto Politécnico Nacional, Departamento de Ingeniería Metalúrgica,, Edificio 8, ESIQIE, 07738 México, D.F., Mexico, claudette173@hotmail.com

The presence of chlorine in a corroded atmosphere can show parabolic effects in the mass gain for discontinuous exposures. If this atmosphere is dry, it can show even more effect to the mass gain. There were realized different discontinuous exposures with dry atmosphere and with water in an atmosphere with chlorine. After that, the samples were characterized with MEB and XRD to propose a mechanism of high temperature corrosion with water. The metallic materials were melting to prepare different alloys with iron base. It was too studied different mechanical properties before and after the exposure.

EFFECT OF TEMPERATURE ON THE RELATIVE IMPORTANCE OF SURFACE CONDITION AND FURNACE ATMOSPHERE IN THE OXIDATION OF CARBON STEELS

Henry MARSTON[1], Bridget STEWART[2], Mick BUGDOL[1], Bob RATCLIFFE[1]

[1]Corus Research Development and Technology, Swinden Technology Centre, Moorgate, Rotherham, S60 3AR, United Kingdom
[2]Corus Research Development and Technology, Teesside Technology Centre, Grangetown, Middlesbrough, TS6 6US, United Kingdom Bridget.Stewart@corusgroup.com

The present configuration of almost all steel processing routes is characterised by successive steps of heating and cooling. During most of these operations, a large portion of the product surface is exposed to oxidising conditions at high temperature resulting in the formation of scale. From improved understanding of the mechanisms of scale development, it is envisaged that the scale morphology, growth and intermediate removal (by descaling) can be controlled to prevent scale-related defects created in the early stages of steel processing from persisting to the final product.

Controlled reheating tests have been carried out to determine the relative importance of surface condition and furnace atmosphere on scale growth as a function of temperature. Isothermal and continuous heating thermobalance tests were conducted on three different plate grade steels in five different test atmospheres. A qualitative Taguchi analysis was applied to determine the effect of different test variables on the observed oxidation rate. The steels were a conventional plate grade and low silicon and weathering steel variants.

At the relatively low temperature of 950 °C, the driving force for oxidation was relatively low and therefore factors such as the surface condition and composition of the steel were relatively important. Oxidation proceeded relatively slowly and oxygen supply could be satisfied from the atmosphere containing 0.3% oxygen. At higher temperatures, the high driving force for the reaction was very high and hence scale growth was not affected by the surface condition. The steel type was significant through effects at the scale-metal interface such as nickel entanglement and fayalite formation. At 1250 °C, the atmosphere containing 0.3% oxygen initially provided insufficient oxygen for all of the observed scale formation to be by this species directly; in the early stages of the isothermal test some oxidation occurred by the breakdown of water vapour or carbon dioxide. Accordingly, the rate of scale growth (and hence the value of the oxidation constant) depended on the oxygen level at high temperatures. This interpretation was confirmed by metallographic examination of the samples produced in the tests.

Investigation of Cracking in the Shell of a Reactor of MTBE Plant Catofin Unit

Abdulaziz Al-Meshari, Abdelgader Abdelgalil, Saad Al-Enazi
SABIC Technology Centre, P.O.Box 11669, Jubail Industrial City 31961, Saudi Arabia

Krishnaswamy Jeganathan
Saudi European Petrochemical Company (Ibn Zahr), P.O.Box 10330, Jubail Industrial City 31961, Saudi Arabia

Abstract

This paper reports an investigation of cracking in the shell of a reactor of MTBE plant Catofin unit. Hot air leaks through the reactor shell were observed, resulting in emergency shutdown of the unit. The reactor had been in service for 15 years and is made of ASTM A515 Grade 60 carbon steel and lined with refractory. Several techniques were used in this investigation: XRF, C/S analyzer, optical microscopy, SEM/EDX, tensile testing, and hardness testing. Thorough investigation showed that the cracking of the reactor shell is attributed to corrosion fatigue (oxidation fatigue), due to thermal cycling and graphitisation. Graphitisation led to degradation in the steel mechanical properties and a significant reduction in fracture toughness facilitating crack growth and catastrophic fracture. It is recommended that all reactor shells in the MTBE plant Catofin unit be inspected for graphitisation. The rise in the shell metal temperature might be attributed to inefficient thermal insulation provided by the refractory lining. The metal temperature should be kept below 427°C in order to prevent graphitisation. The condition of the reactor shells must be evaluated using metallographic techniques. Ideally, the extent of graphitisation can be investigated through removal of representative samples for metallographic examination. The shell material can be upgraded to chromium-containing low alloy steel.

Keywords: Corrosion fatigue, Graphitisation, Elevated temperature oxidation

In situ corrosion testing of various high nickel alloys at Måbjerg waste incineration plant

M. Montgomery, DTU Mekanik/Vattenfall/Dong Energy, Lyngby, Denmark
S.A. Jensen, DONG Energy, Copenhagen, Denmark;
T. Vilhelmsen, Vattenfall Heat Nordic, Odense Denmark
N.H. Nielsen, Babcock and Wilcox Vølund, Esbjerg, Denmark.

In Denmark, the majority of waste is disposed via waste to energy (WTE) incineration plants. Such waste incinerators are built from low alloyed carbon steel. However due to the increasing corrosiveness of waste over the years, more corrosion resistant alloys are required. In Denmark, Inconel 625 (UNSN06625) is the weld overlay material currently being used to give improved corrosion resistance. Weld overlay protection is applied either when corrosion in a certain area has been noted to be exceedingly high, or in new plants where high corrosion rates are anticipated. It has also been chosen as a replacement for refractory lining where maintenance cost of the refractory lining has been significant.

In order to assess the use of alternative nickel alloys, test panels have been manufactured by Babcock & Wilcox Vølund and inserted into Måbjerg waste incineration plant. Inconel 625 as a 50% weld overlay, two layered weld overlay and as a spiral weld overlay was exposed. Other nickel materials exposed were alloy 686, alloy 50, and Sumitomo super 625. Exposure has been undertaken from 2003-2009 in the 1st pass and 2005-09 in the 2nd pass and sections have been removed and investigated during this period. It has been previously observed that deposit composition high in heavy metal and chlorides results in high corrosion rates. Thus the composition of the deposits from the exposed waterwall panels was also monitored. This paper will compare the various nickel alloys in the two areas.

Corrosion Education and Computer Applications

INTERDISCIPLINARY RELATIONSHIPS IN CORROSION EDUCATION AT SCHOOL, COLLEGE AND UNIVERSITY

***Alec Groysman* and Olga Groysman**
ORT Braude College of Engineering, Karmiel, Israel
E-mail: galec@orl.co.il

The subject of *corrosion* has entered as a part of a required course of the program in chemical education at many schools, and as a part of voluntary subject of the program in materials science, chemical and mechanical engineering, and chemistry in many colleges and universities. Today we can find such courses in nearly 350 universities around the world.

What are the interdisciplinary connections and relationships in teaching of *corrosion* in the educational system, from school to college to university? How can we present such a nasty phenomenon as *corrosion* in an entertaining form in order to excite the curiosity of pupils and students so that they will choose this subject for acquiring a profession in the future?

Which subjects from chemistry, physics, materials science, physical chemistry, history, literature, and philosophy must be included in *corrosion education* at different levels of curricula? What is interesting in *corrosion* for education? Are there perilous and attractive sides in *corrosion*? *Corrosion* as any subject in our diverse and contradictory world has two sides of a coin, and we have to distinguish between them.

The *aim* of this work is to analyse different aspects of *corrosion* for teaching it in a lucid and attractive manner including humanitarian aspects of *corrosion education* based on the authors' experience of teaching corrosion at school, college and university.

Keywords: *corrosion education.*

About the training of experts in the field of protection against corrosion at Mendeleyev University of Chemical Technology of Russia (MUCTR)

Kapustin Y.I. Vagramyan T.A.
D. Mendeleyev University of Chemical Technology of Russia, Moscow, Russia

The Department of materials technology and protection against corrosion was created in MUCTR in 2007. The Department has been intended to train bachelors and masters in the field of protection against corrosion. The training of holders of Bachelor’s degree has been carried out for four years as part of the program Chemical Technology and Biotechnology, the total amount of classroom hours for the specialization being 700 hour. In training holders of a Bachelor's degree we give an expanded course of materials technology, basis of corrosion theory and basis of anticorrosive protection taking into account the general wide range of jobs for the graduate. The training of holders of Master’s degree in corrosion and metal corrosion protection has been put into effect for two years. The holders of Master’s degree are supposed to have had special courses like theoretical electrochemistry, theory of metal corrosion, anticorrosive protection methods including paint-and-lacquer coating PLC and plasma coating methods, the equipment used for anticorrosive protection, methods of structure research as well as methods of research of surface properties, and some other optional subject. Professors of the Department are giving the materials technology course for all the students majoring in engineering, 8 classroom hours being about corrosion and corrosion protection methods.

For the purpose involved professor Kapustin Y.I. has developed e-Book on the subject Corrosion and Protection of Metals for putting into effect the interactive training of students.

The electronic manual has been created by means of software product HyperMetod 3.5 which makes it possible to have a manual as the combination of diverse information organized in a demonstrative and clear form for the student. As a matter of fact that is a teaching complex learner's guide on the subject Corrosion and Protection of Metals which includes the curriculum, teaching techniques, textbook, workbook, laboratory practical work guide in an electronic form, and self-testing system for the student as well as continuous knowledge assessment system. In the course of the training the student is offered to do a number of tasks and exercises in a limited time and then given information of the wrong or right steps. By means of the section Laboratory works the student can carry out electrochemical, chemical, and technological processes directly as well as observe them that makes for mastering the teaching material. The computer experiment has been realized by means of LabWiew program. For example an installation named Research of cathode and anode processes under conditions of metal corrosion has been created. The installation involved includes a mathematical model setting voltage-current characteristic of processes occurring on electrodes and a set of drivers and representing devices. We believe that using such model will encourage students to improve their creative abilities. It should be noticed that we clearly realize the necessity of harmoniously complementary components of the training such as lectures, seminars, practical work in the laboratory, learner’s guide laser disc, the Internet. Depending on personality of a student and their teaching style the domination of this or that component is possible though we think that the combination of all components is an indispensable condition for training the qualified specialist.

Association of corrosion engineers (VACOR) offers skills upgrading to corrosion practitioners

Vladimir A. Rabinkov
Association of Corrosion Engineers (VACOR), Moscow State University of Civil Engineering, Moscow, Russia;
rabinkov@corrosion.ru

The VACOR Association of Corrosion Engineers was set up in early 2005 as a nonprofit partnership.

VACOR has expanded vigorously; by the end of 2006, it brought together a range of entities and corrosion professionals based in Moscow, St. Petersburg, Veliky Novgorod, Krasnodar, Ufa, Novokuznetsk, Novosibirsk, Samara, Chelyabinsk and many other Russian cities.

VACOR has affiliates in a number of Russia's key industrial sectors, such as natural gas extraction, chemical and petrochemical industries, oil refining, nuclear and space engineering.

VACOR holds annual research-to-practice conferences bringing together delegates from all over Russia. We also sponsor periodical "retreats" aimed at upgrading the skills of corrosion engineers. These workshops are very popular among practitioners in a range of industrial sectors as an opportunity to learn, in a short time, about the latest achievements in such areas of corrosion prevention as are of interest to them.

Upon completion of these courses participants are issued standard certificates of skills development.

VACOR strives to build on the national traditions of corrosion prevention training; this is why leading scientists of the Russian Academy of Sciences (RAS), professors of various Russian universities and experts working for large companies that develop corrosion-preventive products and leading-edge anticorrosion technologies, have all been taking an active part in running these "retreats".

Hands-on training is provided to trainees during the "retreats" by the RAS Physical Chemistry and Electrochemistry Institute, ROCOR® R&D and Production Company, and other entities.

Training periods are usually chosen so as to coincide with a VAKOR-sponsored conference and/or a large-scale international exhibition.

Given the range of the VACOR training programs, we believe that, by and large, they already reflect the EUROCORR 2010 slogan, *From the Earth's Depths to Space Heights*.

The centerpiece of the VACOR web site is a newsfeed featuring current developments in the corrosion prevention field both in Russia and abroad.

VAKOR seeks to carry on the tradition of the All-Union Association of Corrosion Engineers that ceased to exist by force of circumstances. We make ample use of the unique past scientific and technological experience while striving to live up to the challenges of the 21st century.

Updating the content of the course “Corrosion and protection of metals” delivered in Udmurt State University

S.M. RESHETNIKOV, Udmurt State University, Izhevsk, Russia

At the Udmurt state university the course ”Corrosion and protection of metals “is provided for students majoring in chemistry, physics of condensed state of substances, gas and oil production, drilling of gas and oil wells and operating electric power stations. A long –standing experience in training university students proved the necessity of dividing the course into two modules. The first module can be titled as “Theory of corrosion and protection of metals” in which the basic problems of corrosion, the role of thermodynamics in corrosion protection, kinetics and mechanisms of a gas high temperature corrosion alongside with the principles of electrochemical corrosion, passivity and inhibition are to be discussed. The module is followed by a number of lectures over viewing the corrosion electrochemical properties of metals and constructive materials. The second module is tailored in accordance with the needs of students’ specializations. Thus, the students getting the university degrees in chemistry and physics get a profound knowledge in theory of metals, structure of a solid body, properties of inter phase boundaries, gas and other substances adsorption, theoretical electrochemistry, principles of anticorrosion protection. The diploma papers as a rule are done at the corresponding departments of the University or in the laboratories of the research institutes of the Academy of Sciences. For students specializing in applied fields of science the content of the second module is practically oriented. The syllabus design of these courses is focused on corrosion issues of concrete demands of technological schemes, equipment and communications. Course papers often made on a team based work of a group of students are aimed at solving some current concrete problems vital for industrial enterprises. The transition of Russian universities to a two level system of training “bachelors” and “masters” highlights a tendency to change the proportion between the amount of fundamental and applied knowledge in favor of the last one. But the fact that the educational standards of the third generation to be implemented in Russia in 2010, include some variable components gives hope that the course “Corrosion and protection of metals” will manage to reflect the needs both of industry and fundamental science. However, the up-to-date training of University graduates is impossible without updating the existing text-books and resources. The most effective way to do this is to announce an open and transparent competition in creating a new generation of teaching materials.

Problems of corrosion education in oil-and-gas branch

© 2009 г. M.L.Medvedeva
Gubkin Russian State University of Oil and Gas , Moscow, Russia

It is known that oil and gas branch is the most metal-requiring industry. Unfortunately, corrosion remains the main reason of accidents in our branch. The experience in revealing the reasons of corrosion accidents shows that in most cases they are connected with insufficient training of personnel in the field of corrosion.

Operating conditions of the equipment of oil-and-gas industry are rather specific. An expert with general corrosion education cannot always cope with them. Main reason of accidents in oil and gas pipelines is connected with the influence of soil electrolyte on metal which operates under triaxial tension and at additional action of induction currents from the high-voltage electric mains, earth currents and bacterial corrosion. Operating of refinery equipment is subject to all known kinds of corrosion damages: pitting and chloride stress corrosion cracking of heat-exchange tubes made of stainless steel, intergranular corrosion and cracking of reformers equipment, structure-selective corrosion of duplex steels, component-selective corrosion of brass heat-exchanger tubes, fuel ash corrosion of heaters, sulfidic corrosion, hydrogen attack, naphtenic acid corrosion and many others.

Short courses of basic corrosion which students are given in some of the oil-and-gas universities are absolutely insufficient. In our opinion, both education of dedicated corrosion experts for oil and-gas industry, and training of all students of oil-and gas universities in corrosion are absolutely necessary. It is seems to me that such training should be carried out in three following directions

1. Training of the students of engineering degrees. For example, students of departments on oil and gas field development should receive basic knowledge of corrosion and know in general about fretting-corrosion and corrosion cracking of drilling and field equipment, about modern inhibitors. Students of pipeline departments should learn basics of corrosion, to know about corrosivity of soils, bacterial corrosion, earth corrosion, and modern protection methods and so on.

2. Education of corrosioner-oilmen. Training of students of profile departments in corrosion will not solve a problem of the corrosion prevention in general. It can occur only when every enterprise of the field will have a corrosion service with well educated experts. Training of future corrosioners should first of all include such subjects as physical chemistry, physical metallurgy and mechanics of destruction. Students should get knowledge of basic corrosion, on corrosion prevention of equipment in oil and gas fields, pipelining and refineries. Simultaneously they have to cope with corresponding technological disciplines. The demand for experts educated in such way is quite high in the oil and gas industry.

3. Education of the scientific staff of corrosioners. This direction should include continuous work with postgraduate students. Activity of graduate schools should be incorporated with the activity of the academic and branch institutes.

Such all-round education demands much of scientific, as well as methodical work. But it is necessary.

Training of the specialists of corrosion theory and metal protection in the classical University

L.E. Tsygankova, V.I. Vigdorovich
Tambov State University named after G.R. Derzhavin, Tambov, Russia

Two years training in the network of specialization «Chemical resistance of materials and protection against corrosion» is conducted in Tambov State University named after G.R. Derzhavin. The students study :

1. Theory of corrosion and metal protection;
2. Oxygen and hydrogen depolarization;
3. Kinetics and mechanism of the electrode reactions in the metal corrosion process;
4. Inhibitors of metal corrosion.

A year and a half laboratory practical training session is conducted in parallel.

Textbooks have been written for all the subjects and have been published.
The students perform the early project and the degree work. Every year some of the graduating students enter the postgraduate study.

Corrosion in Oil & Gas Production

Materials behavior in extreme conditions: influence of large amounts of H_2S on steel toughness in low temperature environments

P. Fassina, R. Morana**, L. Alleva**, G. Mortali**, L. Vergani***, A. Sciuccati+++*
**ENI, Exploration & Production Division,, San Donato Milanese, Italy*
***Centro Sviluppo Materiali S.p.A., Roma, Italy*
****Politecnico di Milano, Dipartimento di Meccanica, Milano, Italy*

In the presence of H_2S, carbon and low alloy steels may suffer hydrogen damage and hydrogen embrittlement. This is the reason why so-called sour service materials must be used in compliance with international accepted standards, used worldwide in oil & gas field, when fluids are classified as sour.

When the temperature is low, the effect of hydrogen on the reduction of toughness and ductility of the materials could be enhanced. Such event might represent a risk for oil and natural gas transporting pipes in low temperature field: in winter time, during the shut down and the subsequent re-starting operations, they can reach very low temperatures (-40°C) in presence of high H_2S content and high pressure.

The aim of this paper is to study the combined influence of hydrogen and low temperature on mechanical properties of two pipeline materials, X65 and F22.

An extensive experimental test was carried out, without hydrogen, and with different hydrogen charge. For each test condition Charpy, J_{Ic} and crack propagation tests were carried out by varying the temperature.

The fracture surface of the specimens after the experimental tests were examined by a scanning electron microscope, SEM, to evidence the fracture behaviour differences between the specimens without and with hydrogen.

Hydrogen was charged by the methods described in the paper “Hydrogen charging of carbon and low alloy steel by electrochemical methods” by F. Bolzoni, P. Fassina*, G. Fumagalli. L. Lazzari in this conference, and by means of autoclave exposure to an hydrogenating environment containing H_2S. Presence of hydrogen and effective value was measured in the specimens.

Tests carried out so far show that there is an influence of hydrogen on the transition temperature. This influence seems to increase if the hydrogen charging increases. Such phenomena has been related to materials microstructural features, trying to explain the mechanical properties reduction detected due to hydrogen introduction in the steel lattice.

RECOVERY OF INITIAL SSC RESISTANCE IN OCTG PIPE ENDS AFTER END-SIZING AND STRESS-RELIEVING FOR INTEGRAL CONNECTIONS THREADING

Hervé Marchebois[1], Arnaud. Gateaud[2], Florian Thébault[1], Christelle Gomes[1], Eric Cadiou[2], Stéphane Kemtchou[3], Christoph Bosch[4], Stefan Jäger[4]

[1] Vallourec Research Centre, FRANCE, herve.marchebois@vallourec.fr
[2] VMOG R&D, FRANCE, arnaud.gateaud@vmtubes.fr
[3] V&M E&I, GERMANY, stephane.kemtchou@vmtubes.de
[4] SZMF, GERMANY, christoph.bosch@du.szmf.de

End-sizing (swaging, expansion) of OCTG pipe ends prior to the threading of premium integral connections is a processing method routinely used to provide sufficient material for proper machining operations. Though plastic strains impact both mechanical and H_2S embrittlement resistance properties of HSLA (High Strength Low Alloy) sour grades, subsequent stress-relieving under controlled conditions allows recovering initial pipe properties in the deformed areas.

The present work addresses how laboratory heat treatments of as-deformed OCTG pipe end coupons help define pertinent variables for process monitoring.

Robustness of the industrial stress-relieving process is then discussed through the compatibility between material response and heating apparatus consistency. Practical cases of SSC resistance recovery in C110 and C125 sour grades casing pipe ends after end-sizing and stress-relieving operations are documented.

Keywords: OCTG, Sulfide Stress Cracking (SSC), end-sizing, swaging, expansion, stress-relieving, C110, C125, integral connections.

Hydrogen Induced Cracking of sour gas pipeline- Case Study

D.Masouri[1], Mahmoud Zafari[2] , Enayat Mohemmi[3] , M.Askari[4]

1-Pars Oil & Gas Co. (POGC),Tehran/IRAN,dmasouri@yahoo.com
2-National Iranian South Oil Co. (NISOC),Ahwaz/IRAN, zafari.m@nisoc.ir
3- National Iranian South Oil Co. (NISOC),Ahwaz/IRAN, mohemmi.e@nisoc.ir
4- Pars Oil & Gas Co. (POGC),Tehran/IRAN, me.askari@gmail.com

ABSTRACT

The presence of H_2S in hydrocarbon carrying pipelines requires significant precautions regarding designing, manufacturing processes and inspection to be considered.

The purpose of this paper is to focus on carbon steel oil and gas field pipeline associated with its exposure to H_2S –containing production fluids, which led to failure in sour service pipelines. Furthermore it discusses the supplementary requirements which can prohibit the failure and makes more reliable services.

Keywords: Pipeline, Hydrogen Induced Cracking (HIC), Sour Gas, Segregation

Effect of microstructure on hydrogen diffusion in X70 grade pipeline steel and its weldments

Magnus Skjellerudsveen, O.M. Akselsen, Vigdis Olden, Roy Johnsen,
Anna Smirnova,
Norwegian University of Science and Technology, Trondheim/Norway

Hydrogen diffusion was studied in API grade X70 pipeline steel, simulated coarse grained heat affected zone (HAZ) and weld metal of type HBQ Coreweld using the electrochemical permeation technique. Hydrogen diffusion measurements were carried out at 25, 50 and 70ºC. The results were similar for all three metals with the values of effective diffusion coefficient at 25ºC ranging from $1.2 \cdot 10^{-7}$ to $1.4 \cdot 10^{-6}$ cm^2/s. The values decreased in the order: HBQ Coreweld metal > X70 grade steel > simulated HAZ. The metals showed similar response to increased temperature with respect to the diffusion coefficient. The X70 grade steel showed the highest values for the subsurface hydrogen concentration and also the highest increase with increasing temperature. The number of reversible trapping sites was in the order of 10^{18} $sites/cm^3$. The values of their binding energy varied from 34 to 40 kJ/mol.

EFFECTS OF STRAIN AND TRAPPING ON HYDROGEN-INDUCED CRACKING IN HIGH STRENGTH LOW ALLOY STEELS

Cédric BOSCH[1], David DELAFOSSE[1], Xavier LONGAYGUE[2]

[1] *Ecole des Mines de Saint-Etienne, UMR CNRS 5146, Saint-Etienne, France, E-mail: bosch@emse.fr*
[2] *IFP, Rueil-Malmaison, France;*

In pearlitic steels, trapping at interphase boundaries may induce hydrogen-cracking in the absence of applied stress such as in blistering and Hydrogen Induced Cracking. However, in low alloy steels containing a much lower amount of such trapping sites and/or when hydrogen activity is reduced, most instances of hydrogen-induced cracking involve strong interactions between local plasticity and hydrogen effects.

We investigated the effects of these variables on the crack growth rate in two quenched and tempered HSLA steels. Slow strain rate tensile and low-amplitude cyclic tests were conducted on micro-notched specimen in conditions of variable hydrogen activity. The results indicate a strong dependence of crack growth rate with the tempering on the one hand and both the notch-tip plastic zone and hydrogen activity on the other. At low activity, dynamic strain seems to be the major factor affecting hydrogen embrittlement, while trapping effects appear dominant at higher hydrogen activity.

An Empirical Model for Indication of M13Cr-110 NACE Method A Test Acceptability

Caldwell, E. Gibson, G. Jordan, L.
GATE, LLC
Houston, Texas, USA

Martensitic stainless steels have been used extensively in the oil and gas industry for over twenty years, yet only a few application limits exist to provide materials selection guidance in sour service production environments or when reservoir souring has to be considered. Fitness-for-service testing is required to verify sufficient sulfide stress cracking (SSC) resistance exists when these materials are exposed to low H_2S partial pressure environments with variations in pH and chloride concentrations not addressed by current industry guidelines. As the first stage of a project to provide broader materials selection guidelines for the industry, a review of published NACE TM 0177 Method A test data on 110 ksi grade modified 13Cr martensitic stainless steels (referred to as "13-5-2" martensitic stainless steels by ISO 13680) has been undertaken with the aim to support the development of SSC application limits. Open literature data was compiled from several from different mills and third party laboratories and then analyzed using H_2S partial pressure, chloride content and pH as inputs. Acceptable chloride concentrations were determined to be a function of both H_2S and pH, with pH having a significant influence at the test temperature of 25℃ (75℉). Evaluation of these findings allows th ese test results to be separated into three different regions: No SSC Expected, SSC Possible, and SSC Probable. These limits and regions have subsequently been converted into a versatile system that provides an empirical model that indicates if a NACE Method A test is expected to pass for a modified 13Cr stainless steel in multiple different H_2S and chloride containing environments at 25℃ (75℉).

Keywords: Modified 13Cr, SSC, Martensitic stainless steel, Sour service, NACE Method A Test

Effect of mechanical load on hydrogen diffusion in 13% Cr super martensitic stainless steel

Anna Smirnova, Roy Johnsen and Kemal Nisancioglu
Norwegian University of Science and Technology, Trondheim/Norway

New equipment for investigation of hydrogen diffusion at different temperatures, mechanical stresses and hydrostatic pressures has been developed. The hydrogen diffusion measurement is based on the Devanathan-Stachurski permeation method. Hydrogen diffusion was studied in 13% Cr super martensitic stainless steel at 50%, 80% and 100% of the yield stress. Hydrogen diffusion coefficient increased with mechanical stress due to deformation induced martensitic transformation. Subsurface hydrogen concentration increased due to increased number of active sites on the surface. Microstructure investigations before and after loading are presented and discussed.

RELATIONSHIP BETWEEN THE GROWTH OF CORROSION SCALE AND CO_2 CORROSION

Ming-wen Gao, Ke-wei Gao, University of Science and Technology Beijing, Beijing/China

Abstract

Carbon dioxide corrosion of carbon and low-alloy steels is a common problem in oil and gas industry. The characteristic of CO_2 corrosion scale, affected by temperature, flow rate and CO_2 partial pressure, play an important role in CO_2 corrosion. In this work, the structure of CO_2 corrosion product scale formed on X65 pipeline steel under 75^0C or 90^0C was investigated by means of scanning electron microscope (SEM) and X-ray diffraction (XRD), and the porosity of the scale was evaluated by N_2 adsoption approach. Linear polarize resistance and electrochemical impedance spectrum (EIS) measurement were performed to trace the structure evolution of CO_2 corrosion product scale under high temperature and high CO_2 partial pressure. Ultraviolet spectrophotometer was used to survey Fe^{2+} concentration above the sample surface in order to determine the change of supersaturation of $FeCO_3$ near CO_2 corrosion scale.

Surface and cross-section morphologies of CO_2 corrosion scale formed in different corrosion time reveal a multi-layer structure. A dramatical increase in linear polarization resistance indicates that the multi-layer scale started to form, and EIS result proves the existence of the multi-layer scale. Most $FeCO_3$ crystals exhibited rhomboedric form and the main crystal face was [021]. Synthesis experiments reveal that this feature could be observed under high supersaturation. Under low $FeCO_3$ supersaturation the crystal face includes rhomboedric [021] and hexagonalprism [100]. Based on the investigation result of CO_2 corrosion product scale, a mathematical model was established to relate the growth of $FeCO_3$ corrosion scale and CO_2 corrosion.

LEAN DUPLEX STAINLESS STEEL WITHIN THE OIL AND GAS INDUSTRY

Elisabeth JOHANSSON[1], **Rachel PETTERSSON**[2]

[1]*Outokumpu Stainless AB, Sweden, elisabeth.johansson@outokumpu.com*
[2]*Outokumpu Stainless AB, Sweden, rachel.pettersson@outokumpu.com*

Due to the desirable combination of mechanical strength and corrosion properties lean duplex stainless steels are candidates for applications in less demanding oil and gas environments. They can substitute standard duplex (e.g. 2205) or super duplex (e.g. 2507) grades where these grades are over-specified. However, application in H2S-containing environments is currently limited by the fact that many such steels fall outside the category PREN (Cr + 3.3x (Mo + 0.5W) + 16N) ≥ 30 which is specified in NACE MR0175/ISO 15156-3.

In this paper data are presented for lean duplex steels in various types of tests and environments of relevance to the oil and gas industry. They include not only sour service conditions, but also environments which can give rise chloride-induced stress corrosion cracking or pitting. The point is made that stainless steels should be specified on the basis of property limits rather than compositional requirements.

Effect of intermetallic content on the pit stability and propagation kinetics of duplex stainless steel exposed to CO_2 saturated production brine

Raymundo P. Case, Sudhakar P.V. Mahajanam, Hernan E.Rincon, Dale R. McIntyre, Tom McWalter*
ConocoPhillips, Production Assurance Technology, Bartlesville, OK 74004

ABSTRACT

To establish the susceptibility to Environmentally Assisted Cracking the pit stability and growth kinetics were evaluated for 2205 (UNS S32205) and 2507 (UNS S32750) duplex stainless steel (SS) samples that had been heat treated in order to produce volumetric fractions of intermetallic compounds between 0-14% dispersed within the ferrite grain boundaries. The study was performed in conditions simulating oilfield production brine, using saturation at 1 bar CO_2, at 250ºC and 800ºC and the intermetallic content as the main independent variables.

Experimental evaluation of pit growth was done using galvanostatic polarization between $10\mu A/cm^2$ up to $1 mA/cm^2$, coupled with potentiodynamic polarization scans to evaluate the repassivation behavior. Complimentary cyclic polarization was used to assess the behavior of the critical parameters associated with pit nucleation and stability.

The results indicate that the minimum current for stable diffusion controlled pitting increases with temperature. However, it is found to decrease with intermetallic content in the duplex SS. Comparison of the results for both SSs indicates that pit stability is found at lower current densities for the 2205 duplex SS.

Estimation of pitting potentials from the values of the stable diffusion controlled pitting currents shows a difference with values observed from the polarization curves in both duplex SS's; this gap being consistent with the intermetallic phase content. These results suggest that at electrode potentials below those associated with stable pitting, localized dissolution occurs between the ferrite and the intermetallic phase's, leading to crevice corrosion behavior, which was found in the SEM inspection of the electrode surfaces (Figure 1).

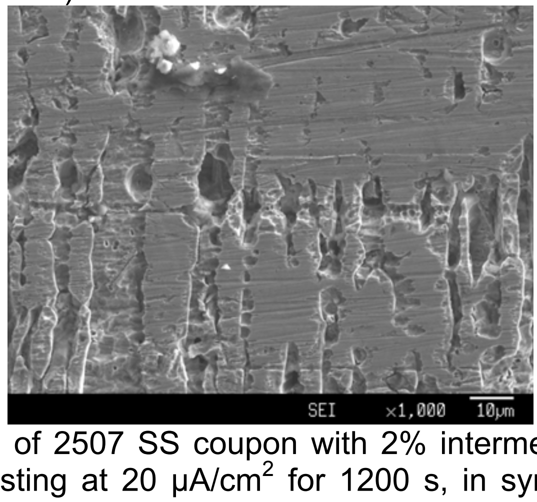

Figure 1 .- SEM image of 2507 SS coupon with 2% intermetallic fraction, following testing galvanostatic testing at 20 $\mu A/cm^2$ for 1200 s, in synthetic production brine saturated with CO_2 at 25ºC.

Environmentally Assisted Cracking Behavior of Super 13Cr Stainless Steel under Cathodic Polarization Condition in Carbon Dioxide Environment

T. Haruna[1], M. Hirose[1], H. Takabe[2], D. Motoya[3], H. Amaya[3], M. Ueda[3]
[1]Department of Chemistry and Materials Engineering, Kansai University, Japan
[2]Corporate R&D Lab., Sumitomo Metal Industries, Ltd., Japan
[3]Pipe & Tube Company, Sumitomo Metal Industries, Ltd., Japan

Super 13Cr stainless steel has been widely used in oil and gas industries as OCTG and line pipe because of its superior corrosion resistance. However, it was reported that the steel was susceptible to environmental-assisted cracking (EAC) with intergranular fracture in sweet environments at elevated temperatures, and the EAC mechanism of the material in the environments has not been well established. We investigated that the EAC behavior of Super 13Cr stainless steel under anodic polarization conditions in concentrated NaCl solutions with CO_2, and reported in the previous conference that the EAC initiation region on the potential – chloride concentration diagram, and intergranular fracture initiated at the pit in the first stage. In the present research, we have investigated the behavior of hydrogen embrittlement for the steel in the same solution.

Specimens were prepared from Super 13Cr stainless steel with the following heat treatment; quench-temper, additional heating (1300 ^{o}Cx1.8 ks), and then quench. The specimen had the structure simulating high-temperature HAZ of quenched martensite with coarse grain. An aqueous solution containing 20 mass% NaCl was used at 333 or 373 K in the EAC test. CO_2 gas was continuously bubbled in the solution during the test. The EAC test was carried out by slow strain rate technique at various strain rates under various cathodic potentials. A potential of the specimen was measured and controlled against Ag/AgCl (3.3 kmol m^{-3} KCl) reference electrode.

The effect of cathodic potential on fracture strain was investigated to the specimen tested in the solution at 373 K. It was found that the fracture strain was decreased with lowering the applied potential, and in particular, the strain was in the elastic deformation region at a potential of -1.4 V. The effect of strain rate on fracture strain was also examined in the solution at 333 K, and it was obtained the specimen tested at relatively rapid strain rate of 35×10^{-7} s^{-1} fractured even in the elastic deformation region, and more rapidly fractured as the strain rate decreased. From the observation of fracture surface, intergranular and transgranular fracture was seen at the edge and the center portion in the fracture surface, respectively. A size of a intergranular facet was similar to that of prior austenite grain boundary. Therefore, it is considered that the specimen exhibits susceptibility to hydrogen embrittlement with intergranular fracture mode. As the fracture strains obtained at the two temperatures were replotted against cathodic charge density, the strain at the lower temperature was more rapidly decreased at the smaller charge density. The fact suggests that the lower temperature enhances the hydrogen embrittlement in this system. The EAC behavior under cathodic polarization condition will be discussed in comparison with that under anodic polarization condition.

The Effect of Environmental Factors on SCC Resistance of 110ksi Strength Grade Super 13Cr steel

Hideki Takabe[1], *Masakatsu Ueda*[2] , *Taro Ohe*[2], *John William Martin*[3]
and Perry Ian Nice[4]
1 Sumitomo Metal Industries, Ltd., Corporate Research & Development Laboratories, Amagasaki City, Japan
2 Sumitomo Metal Industries, Ltd., Pipe and Tube Company, Wakayama city, Japan
3 BP Exploration Operating Company Limited., Sunbury, UK
4 Statoil ASA, 4035 Stavanger, Norway

110ksi strength grade super 13Cr steel has been used all over the world as an OCTG tubing material for oil and gas environments containing CO_2, with and without small amounts of H_2S.

The high temperature chloride-induced stress corrosion cracking (SCC) resistance is important, in addition to the sulphide stress cracking resistance, in deciding whether super 13Cr steel is applicable for specific applications (environmental conditions). However, the SCC resistance is not so clearcut because of the complex manner by which the combination of environmental factors, such as pH, Cl^- concentration and H_2S, can affect the SCC susceptibility.

The SCC resistance of super 13Cr steel (UNS S41426) was evaluated for CO_2 and CO_2 + 0.01bar H_2S environments at 175°C by using the 4 point bent test technique with various pH and Cl^- concentrations (pH=3 to 4.5, Cl^- =1000 to181000mg/l). The SCC domains at 175°C in CO_2 and CO_2 + 0.01bar H_2S environments for 110ksi strength grade super 13Cr are proposed in this Paper as a function of pH and Cl^- concentration. The SCC cracking initiated from the bottom of corrosion pitting and so the SCC susceptibility is considered to be related to the stability of the passive film on super 13Cr steel. Therefore, the depassivation pH was also measured in CO_2 and CO_2 + 0.01bar H_2S environments with various Cl^- concentrations.

From these test results, the effects of pH, Cl^- concentration and H_2S on SCC resistance of super 13Cr and the application limits based on SCC resistance are presented and discussed.

Key words: super 13Cr steel, super martensitic stainless steel, SCC, CO_2, H_2S, Cl^-, pH

Mechanical Properties and Corrosion Resistance of Post-Expanded SM2535

Taro Ohe[1], Hideki Takabe[2], Masakatsu Ueda[1] and Robert P. Badrak[3]
1 Sumitomo Metal industries, Ltd., Pipe & Tube Company, 1850 Minato, Wakayama, 640-8555, Japan
2 Sumitomo Metal Industries, Ltd., Corporate Research & Development Laboratories, 1-8 Fuso, Amagasaki, 660-0891, Japan
3 Weatherford International Ltd., 11909 Spencer Rd, Houston, Texas, 77041, USA

SM2535 is one material used for applications such as expandable sand screens because of its good ductility and corrosion resistance. For these applications it is important to investigate the performances of the post-expanded condition for developing the expandable technology. In this investigation, mechanical properties and corrosion resistances were studied for rotary expanded SM2535 with different expansion ratios and cone expanded SM2535 materials. The effects of expansion ratio and expansion methods on mechanical properties and corrosion resistances for post expanded SM2535 materials are presented.

Keyword: Solid tubular expansion, rotary, cone, cold work, plastic deformation, corrosion resistant alloy, stress corrosion cracking

Investigation of Corrosion Resistance and Mechanical Properties of Aluminum Tubular Products for Oilfield Injection Applications

Robert P. Badrak
Weatherford International Ltd.
Houston, Texas, USA

Mikhail Gelfgat
Weatherford Holdings
Moscow, Russia

Valery Chizhikov
Weatherford, LLC
St. Petersburg, Russia

Sergey Kolesov
Weatherford, LLC
St. Petersburg, Russia

Oilfield injection applications usually require high alloy corrosion resistant alloys or glass lined steel pipe because of potentially high corrosion rates. Aluminum alloys could potentially more economically displace these higher alloyed products. The unknown areas that require investigation for this type of application include corrosion resistance in injection environments and long term mechanical properties at potential application temperatures.

This investigation presents the results of static and flowing corrosion tests in saltwater at various pH levels, galvanic corrosion tests between aluminum and steel in saltwater environments, sulfide stress corrosion cracking tests and mechanical property tests after elevated temperature aging. Corrosion tests to 85°C and mechanical property tests to 165°C are included.

An initial performance envelope is presented for the aluminum alloys tested for water injection applications.

Keywords: Aluminum, tubulars, water injection, elevated temperature tensile properties, corrosion resistance, galvanic corrosion, erosion corrosion, stress corrosion cracking, flow corrosion

Environmentally Assisted Cracking Behavior of Nickel Alloys in Oil and Gas Applications
A review

Raul B. Rebak
GE Global Research, 1 Research Circle, Schenectady, NY 12309, USA
rebak@ge.com

A wide range of materials are used in the oil and gas industry as components for oilfield environments, depending on the aggressiveness of the environment. Two main factors are considered for the alloy selection process: (i) mechanical properties and (ii) corrosion resistance. Stronger alloys are preferred to minimize the section of the materials but at the same time the susceptibility to SCC generally increases with the strength of the alloy. The corrosion resistance of stainless Ni alloys generally increases with increasing the chromium and molybdenum contents. One general index to determine resistance to localized corrosion (and SCC) is the pitting resistance equivalent number (PREN = %Cr+3.3%[Mo+W/2]). The higher is the PREN the more resistant is the alloy to localized attack. The main factors affecting the cracking resistance of materials in an oil and gas well are the chemical composition, heat treatment, microstructure, strength of the material, and the environmental conditions (partial pressure of H_2S, pH, chloride concentration, oxygen, carbon dioxide, elemental sulfur, temperature, etc). Nickel based alloys are commonly used in sour wells where the hydrogen sulfide (H_2S) pressures and chloride concentrations are particularly high combined with temperatures at times exceeding 200°C. The MR0175/ISO15156 recommends environmental and material limits for nickel alloys in two groups, (a) annealed and cold worked solid solution Ni based alloys and (b) precipitation hardened Ni based alloys. For example, a cold worked solid solution Ni based alloy such as C-276 (N10276) is suitable for use up to 218°C (425°F) in an atmosphere containing up to 700 kPa (100 psi) partial pressure of hydrogen sulfide and any chloride concentration and the corresponding in situ pH provided the maximum hardness is lower than 40 HRC and the yield strength is lower than 1034 MPa (150 ksi). However, the presence of elemental sulfur may cause catastrophic cracking in this alloy. Other Ni based alloys that are used in the oil and gas industry to resist SCC for sour wells applications include 825 (N08825), and higher end alloys such as alloys 22 (N06022) and 59 (N06059) and the age hardenable alloys 625 (N06625), 718 (N077178), 925 (N09925) and 945 (N09945). Alloys such as C-276, 825, 22 and 59 can only be strengthened by cold working, so they may not be suitable for thick sections and intricate shapes and generally cold working does not produce a uniform microstructure. However alloys 625, 718 and 925 can be aged hardened without large impact on the corrosion resistance. Strengthening occurs by the precipitation in the austenitic matrix of small particles containing Nb, Ti and/or Al that interfere with the movement of dislocations.

The Value of Data

Ian George Winning; Richard Payne; Wendy Awosika,
Ionik Consulting,
Thames Plaza,
5 Pine Trees,
Chertsey Lane,
Staines,
Middlesex,
TW18 3DT

Abstract

In oil and gas developments the key to maintaining the integrity of assets for their full life is the correct upfront design of the system. In materials selection at the design stage a high reliance is placed on understanding the corrosion mechanisms and determination of corrosion rates based on various mathematical models. There has been a lot of effort placed in refining these models over the last few decades so that true picture of the corrosion risk can be seen, however, one area where the focus has not been so clear is in obtaining the correct data for use in the models. This is key to design and in fact to determining if a project goes to construction at all. In this study different factors will be studied to see how this affects the design of a project in a technical and a financial way. The study has looked at aspects of the data and how they affect the design decision. The areas covered are the effects of various levels of dissolved gases including Oxygen, CO_2 and H_2S as well as flow regimes.

Top of the Line Corrosion (TLC) – A Field Failure

Mike Joosten, Dean Owens, Allan Hobbins,
Dave Lanktree, Hejian Sun, Mohsen Achour
ConocoPhillips Company

Abstract

Top of the line pipeline failures are typically catastrophic due to the difficulty in predicting the conditions under which such failures may occur. This paper describes a field failure by providing an in-depth analysis of the pipeline operating conditions, the corrosion morphology, and active corrosion mechanisms. The information is utilized to evaluate the suitability of top of the line corrosion predictive techniques and to identify gaps and specific needs of TLC modelling efforts.

Key Words: top of the line corrosion, prediction, pipeline, mechanism

Problem of corrosion of oil gathering system pipelines and solutions

Ross Wharfe, Alexander Kichenko, Salym Petroleum Development, Salym, Russia

Presently, Salym Petroleum Development (SPD) develops three oil fields in Tyumen Region of Russia. Water content in produced oil varies from 5 to 40%. Produced liquid contains almost no corrosive components (almost no H_2S and CO_2 concentration is up to 1%) and for this reason no serious corrosion issues in oil gathering system were expected.

Pipelines of oil gathering system are made of X52 API 5L steel with diameters ranging from 219 to 426 mm and different lengths and pipeline routes. Their continued operation period is from 2 to 4 years.

Inhibition is used for prevention of possible corrosion of pipelines. Intensity of corrosion and effectiveness of inhibition in pipelines is controlled by gravimetric method using corrosion coupons, analysis of dissolved iron ion concentration in water and analysis of concentration of corrosion inhibitors in liquid.

Despite expected low aggressiveness of produced liquid and implemented corrosion protection measures serious pit corrosion was found in the lower pipe zone in Spring 2009 during in-line inspection at some sections of oil gathering pipelines. In some cases its depth reaches 50% and more of rated thickness of pipe wall. At the same time applied corrosion control equipment recorded insignificant intensity of corrosion and absence of its propagation.

For this reason the issue of detection of causes of development of pipeline corrosion and its elimination becomes critical.

In this case for resolving corrosion issue the following approaches are selected:

1) analysis of impact on development of pipeline corrosion of velocity of media for forecasting it;
2) analysis of reasons of insufficient efficiency of applied corrosion control for assessment of corrosion and its improvement;
3) analysis of causes of insufficient efficiency of applied inhibition and its improvement.

For implementation of corrosion control program critical oil flow velocity rates needed for removal of water from pipeline, i.e. for prevention of corrosion, were calculated based on available methodologies and input data. These velocity rates were compared with actual records of liquid velocity rate at pipeline section damaged by corrosion detected during in-line inspection. (Calculations and comparisons factored in profiles of pipeline routes and watercut of oil at corroded sections). As a result, the analysis allowed to define satisfactory correlation between presence of corrosion damage and low velocity of liquid which is not sufficient for removal of water from pipelines. It will allow to forecast the level of intensity of corrosion in pipeline and adjust inhibition protection accordingly.

The applied corrosion control system does not detect expanding local corrosion and for this reason it was decided to improve it by installing additional corrosion control units at potentially hazardous sections and installing there control equipment aflush with lower joint generating line. For increasing of the quality of inhibition immediate-action means will be used - polarization resistance probes. Required control equipment is selected. Preparation for installation of corrosion control units is under way.

Necessity of improvement of efficiency of applied inhibition is indicated by development of local corrosion at some sections of oil gathering pipelines. The issue of improvement of inhibition is addressed by analysis of more efficient corrosion inhibitor and calculation of optimum dosage for specific operating conditions in compliance with developed concept about methods for improvement of the quality of inhibition protection of oilfield pipelines.

It is expected that practical implementation of aforementioned measures will reduce local corrosion in oil gathering pipelines of SPD to minimum level. And it will facilitate stable oil production and protection of environment.

EFFECT OF OXYGEN AND TEMPERATURE ON AQUEOUS SOUR CORROSION SYSTEMS

Yuan SONG[1], Attila PALENCSÁR[1], Gaute SVENNINGSEN[1], Tor HEMMINGSEN[2], Jon KVAREKVÅL[1]

[1]Institute for Energy Technology (IFE), Kjeller, Norway, attila.palencsar@ife.no
[2]University of Stavanger, Stavanger, Norway, tor.hemmingsen@uis.no

Localised H_2S corrosion has been a corrosion problem of serious concern in the oil and gas industry for many years. The intricate mechanisms involved in the initiation, propagation and eventually localized attacks in the presence of H_2S environment are still not fully understood. Various compounds containing sulfur in different oxidations states could be formed in the presence of O_2, making the prediction of localized sour corrosion a difficult task. This report is mainly about the study of the effect of O_2 on aqueous sour corrosion system initiated at IFE aimed at generating more data for understanding the mechanisms of localized corrosion relevant to oil and gas pipelines where oxygen and H_2S are present. The effects of temperature and the exposure time with/without presence of O_2 on sour corrosion system are studied. The equilibrium and possible reactions of H_2S and O_2 are also studied to provide clues for assessing reaction paths and kinetics for sour corrosion system.

Local Microelectrochemical Aaproach to CO_2 Corrosion Measurements

Bruce Brown*, Lei Huang*, Brian Kinsella*, Thomas L. Ladwein**, Srdjan Nesic*

*: Insitute for Corrosion and Multiphase Technology, Ohio University, Athens, OH, USA
**: ecKORR- Department for Surface and Material Science, Aalen University of Applied Science, Aalen, Germany

A new approach using localized electrochemical measurement was utilized to measure the corrosion behavior of carbon steels and carbon steel weldments in a CO_2 corrosion system. The microelectrochemical cell was designed to perform the electrochemical tests on a small spot size (300 µm diameter). Conventional experiments in immersion glass cells were performed to compare the results of these two approaches and also to results obtained in large scale flow loops.

Linear polarization resistance, potentiodynamic sweep and electrochemical impedance spectroscopy were made on base metal, heat affected zone and weld metal of a standard weldment without the galvanic effect have been measured by the microelectrochemical technique under room temperature, 1 wt% NaCl and pH 3.9 in equilibrium with a 1 bar CO_2 atmosphere. To make a comparison, the intrinsic corrosion rates of three different segments were recorded in a glass cell using the same electrochemical techniques by uncoupling the segments cut from the weldment. The consistent results between measurements made with the microcell and and immersion type glass with a further good correspondence to results obtained in flow loops demonstrate that the local microelectrochemical technique can be applied to the investigation of carbon steel including weldments in CO_2 systems.

Key parameters influencing erosion corrosion of passive materials in a three phase flow

T.Vogl, G. Mori, J. Haberl, Christian Doppler Laboratory of Localized Corrosion,
University of Leoben, Franz-Josef-Str. 18, A-8700 Leoben, Austria,
W. Havlik, OMV Exploration & Production GmbH, Laboratory Materials & Corrosion,
Protteserstr. 40, A-2230 Gänserndorf, Austria
T. Schöberl, Department Material Physics, University of Leoben, Jahnstraße 12, A-8700 Leoben, Austria

A combined flow loop - jet impingement pilot plant has been built up. The test medium is a mixed gas - saltwater - sand multiphase flow with impact velocities up to 60 m/s. Artificial brine with a salt content of 27 g/l was used as liquid phase. Sand content with grain size below 150 µm was up to five times higher than the field conditions to accelerate the testing. CO_2 at a pressure of 15 bar was used as gas phase.

Tests were performed on passive materials being applied in oil and gas production. Among these are martensitic stainless steel 1.4021, two types of austenitic stainless steels 1.4301 und 1.4563 (solution annealed and cold worked), duplex stainless steel 1.4462 and nickel base alloy 2.4856.

Damaged specimen surfaces, which have been exposed to the high velocity multiphase flow, were investigated by stereo microscopy, scanning electron microscopy (SEM) and an optical device for 3D surface measurements. Metallographic cross sections of the tested samples were prepared to characterize the microstructure under the damaged surface areas by magnetic force microscopy and nanoindentation measurements. Moreover electrochemical investigations according to ASTM G 61 were performed to determine electrochemical behavior of tested materials including critical pitting potentials E_{pit} and protection potentials E_{prot}.

Influence of chemical composition, microstructure and mechanical properties on mass loss rates is presented.

Keywords: erosion, corrosion, erosion-corrosion, multiphase flow, stainless steel,

Study on corrosion process at sand-deposited surfaces in carbon dioxide media

Kateřina Lepková and Rolf Gubner
Western Australian Corrosion Research Group
Curtin University of Technology
Perth, Western Australia

The corrosion of carbon steel under model conditions typical for oil and gas industrial processes has been investigated. The applied test methodology represents a novel approach to the study of the under-deposit corrosion and enables the measurement of previously undetermined reaction parameters.

Potentiodynamic techniques have been employed to describe electrochemical behaviour of the sand-covered surfaces. The experiments were carried out in a specially designed cell that allows simulation of a compact deposit layer. The results were discussed in terms of corrosion mechanism and compared to those obtained for non-deposited surfaces. The corroded surfaces were further examined ex-situ with SEM and GI-XRD. The analysis revealed structural differences at surfaces with and without the sand coverage.

The corrosion inhibition tests were carried out using inhibitors of various generic types. The inhibitor performance was related to their chemical structure as well as the corrosion reaction.

The results provide an enhanced understanding of the corrosion reaction proceeding at deposited surfaces and contribute to the development of more sophisticated corrosion mitigation technologies.

Acid gas removal by amine solvents: bridges between CO_2 capture and natural gas treatment.

Jean KITTEL, Elisabeth FLEURY, Serge GONZALEZ, François ROPITAL, IFP-Lyon, Solaize (France)

Abstract

In the oil and gas industry, acid gas removal is required for the treatment of natural gas. New applications were also recently pushed forward for CO_2 capture from the flue gas of power plants. For both applications, the most widespread industrial processes use absorption – desorption by an alcanolamine solvent. In such amine units for acid gas removal, corrosion represents an important operational concern.

The aim of this paper is to review some of the parameters influencing the corrosivity of amine solvents. In the light of literature data and of new experimental results, the influences of temperature and of acid gas loading are discussed. These two parameters appear to have a strong impact on corrosion rates of carbon steel, with extrapolated corrosion rates of several tens of mm/year for the highest temperature and acid gas loading condition.
It is then proposed to discuss about similarities and differences between natural gas processing and CO_2 capture from flue gas. The most significant gap concerns the lean amine sections. In acid gas treatment, the regeneration of the solvent is often performed down to zero loading. Under these conditions, an extremely low corrosivity of the lean solvent is expected. On the contrary, CO_2 capture from flue gas requires only a partial stripping of the CO_2 in the regeneration section, due to energy efficiency reasons. Then, the lean solvent still contains some acid gas, and subsequently a higher corrosivity.

Finally, the general principles for material selection for the different parts of acid gas removal units are discussed, considering both cases of natural gas processing or CO_2 capture.

The comprehensive program of measures for the guarantee of corrosion resistance of trade pipeline systems and technological equipment

Michael Getmansky, LLC «INTERCOR, Moscow, Russia, Anatoly EMELYANOV, LLC «INTERCOR», Moscow, Russia, Valery MELNIKOV, JSC “Gazprom neft Orenburg”, Orenburg, Russia

Experience of operating the pipeline systems of the large is oil-field it shows that one of the most negative factors, which lead to considerable reduction in reliability and longevity of equipment, is the action of the corrosive environments of different composition on the metal, which, in the majority of the cases, is in the complex stress-strained state. Processes of destroying the metal turned havoc in this case have ambiguous nature and can be avoided only by development and subsequent elimination of all its reasons. In connection with this the conducted in many instances measures, directed toward the liquidation of any established reason, are, as a rule, little effective, they do not decide problem as a whole, and they also require significant material and technical expenditures.

From the point of view of the authors, the application of a comprehensive program of measures, which makes it possible to ensure high corrosion resistance of intra-trade pipeline systems, can serve as a way out situation. This type of program, inculcated and successfully utilized in JSC “Gazprom neft Orenburg”, includes the following basic stages:

1. Analysis of the formation of the structure of pipeline fund in the specific temporary space (by the shops, the designation of conduits, the composition of the transported medium and its water contaminability, on the stamps of the used inhibitors of corrosion, to the diameters of pipes, on the manufacturing plants of pipes and the periods of the introduction of conduits into the operation);
2. Analysis of the accident rate of conduits taking into account the influence on it of factors enumerated above and their possible combinations;
3. On the basis of the operating conditions of conduits the selection of methods and means of corrosive monitoring at each point of control. Composition of the list of the necessary equipment for corrosive monitoring with the indication of model and custom-made parameters taking into account the parameters of conduit (diameter, the wall thickness, material, etc);
4. Development of the regulations of corrosive monitoring and inhibiting protection, and also of schedule chart of the systematic conducting of the measurements of the rate of corrosion;
5. Realization of the control of the rate of corrosion according to regulations and with the periodicity, established by the developed by plan- graph. Systematic evaluation of the speed of corrosion and effectiveness of inhibiting protection according to the results of the conducted measurements, the interpretation of obtained data;
6. Organization of the laboratory system of the control of the rate of corrosion, effectiveness of inhibiting protection and of receiving inspection of the inhibitors of corrosion to the correspondence of their indices to technical specifications;
7. The receiving inspection of the chemical reagents, utilized with the acidic workings of bore holes to the correspondence of their indices to technical specifications, and also the control of the technology of their dosing and the effectiveness of use with the mastery of bore hole after conducting of its acidic working;
8. During exceeding of the rate of corrosion are higher than the regulated limits, and also reduction in the effectiveness of inhibiting protection development of the reasons of this type of changes, and also making decisions and measures, directed toward reduction in the rate of corrosion and/or improvement of the system of inhibiting protection, with the introduction of the necessary changes in the corresponding regulations.

Effectiveness of the Corrosion Inhibitors for the Petroleum Production under Various Flow Conditions.

Alla Y. Furman, Margarita A. Kharshan, Boris M. Miksic,
Cortec Corporation, White Bear Lake MN/ USA

Objective

As large number of oil fields continues to mature, the maintenance and operating costs of oil recover continue to rise. Use of corrosion inhibitors is currently the major way of protecting against corrosion in all petrochemical facilities. Drag reduction is a physical phenomenon in which friction decreases in turbulent flow through pipelines. It results in increased fluid flow and/or reduced pressure loss. Goal of this study was to find the combination of corrosion inhibitor and drag reducing additive which not affect or act synergistically in the water transporting pipe line in the secondary petroleum recovery operation.

Significance of Work

Effective combinations of corrosion inhibitors were found utilizing volatile corrosion inhibiting technology and drag reducing compounds. These products provide a very high level of protection for steel subjected to a broad range of corrosive attack and flow restriction. The investigated systems are an effective way to cope with pressure and/or capacity limitations due to increased water production in existing fields and corrosion caused by electrolytes, carbon dioxide, hydrogen sulfide, and other corrosive contaminants.

Experimental

Two options of using VpCI products in conjunction with two different drag reducers were studied: VpCI-A is corrosion inhibitor, containing drag reducing ingredient (DR1) in its formulation. VpCI-B is corrosion inhibitor, used in combination with a drag reducer (DR2) as a two part system. The main corrosion inhibiting compound in VpCI-A and VpCI-B based on fatty acid imidazoline chemistry; anionic water soluble polymer and quaternary ammonium salts were used as flow enhancers.

Followed corrosion tests were performed to evaluate the inhibiting level of the treatment: static test in sweet/sour conditions in an oven set at 70^{o}C for 48 hours; Rotating Cylinder Electrode test was performed under continuous purging of CO_2 at the temperature of 70°C. The affect of the flow on corrosion inhibition was studied at the rotating rate of 500 - 3000 r/min. Corrosion rate was determined by analyzing the polarization curves obtained in Linear Polarization technique. Vortex test was applied for evaluation of compatibility of the system of VpCI -B and DR-2. The time to close the vortex was determined.

Summary

VpCI A and VpCI B are effective corrosion inhibitors in sweet/sour electrolyte The effectiveness of VpCI A and VpCI B depends on the flow rate; the increase of the concentration is necessary to suppress corrosion when it is high. VpCI B is compatible with DR-2 and this two part system provides both drag reducing and corrosion protection under high flow rate.

CORROSION INHIBITOR COMPATIBILITY WITH OTHERS ADDITIVES USED IN OILFIELD

TONG EAK POU

ARKEMA/CECA centre de recherche rhone alpes, France, tong-eak.pou@arkema.com

In oilfield applications, the selection of corrosion inhibitor (C.I) will faced to several problems such as performance, cost, HSE and particularly it compatibility with others additives present such as scale inhibitors, hydrate inhibitors, demulsifiers etc…

Scale inhibitors (S.I) are generally incompatible with corrosion inhibitor. The presence of S.I in corrosive medium can generally have a negative effect on the corrosion inhibition efficiency. Scale inhibitor molecule, very hydrophilic, can sequester iron molecules from carbon steel surface to the solution. There is a competition reaction on the carbon steel surface with corrosion inhibitor. And the efficiency of C.I will be diminished. Corrosion inhibitor molecule will do the same way versus scale inhibitor. And the effect will be the same. Depending on the molecular structures of C.I and C.I, we can have a corrosion inhibitor compatible with scale inhibitor and vice versa.

Corrosion inhibitor is also incompatible with hydrate inhibitor in particularly kinetic hydrate inhibitors (KHI). A hydrate is an ice like crystal formed by gas, methane, molecule surrounded by waters molecules. Hydrate is called Clarthrate. In gas production under high pressure and low temperature, hydrate can be formed and block the gas flow and hence the lost of gas production. KHI is used to delay the hydrate formation for a shot in period. The mechanism of action of KHI is based on the adsorption of the anti hydrate molecule on the hydrate nucleï that can delay the formation of the hydrate crystal. Corrosion inhibition mechanism is also based on the adsorption reaction. By this way C.I molecule can disturb even destroy the efficiency of the KHI.

Demulsifiers can also decrease the efficiency of corrosion inhibitor especially for oil soluble corrosion inhibitor. However some demulsifiers molecules can increase the performance of corrosion inhibitor.

The present paper describes the work carried out in our laboratory relative to the compatibility of corrosion inhibitors molecules with scale inhibitors, kinetic inhibitors and demulsifiers.

STUDYING THE EFFECT OF TWO CORROSION INHIBITORS IN REDUCING THE CORROSION RATE OF 1018 CARBON STEEL PETROLEUM PIPELINES IN SEA WATER

Rihan Omar Rihan[1], **Nawaf Ibrahim Al-Bakr**[2], **Reyad A. Shawabkeh**[3]

[1] *Center of Engineering Research - Research Institute*
[2,3] *Department of Chemical Engineering*
King Fahd University of Petroleum & Minerals (KFUPM)
Dhahran, Saudi Arabia
[1]*rihan@kfupm.edu.sa*
[2]*bakrni@aramco.com.sa*
[3]*rshawabk@kfupm.edu.sa*

A study was carried out to experimentally investigate the effect of amine-base inhibitors AR-505 and N-211 on the corrosion of 1018 carbon steel in sea water solution at pH 8.2 and 55°C. The experimental apparatus was a circulating flow loop system inside an autoclave. The speed of the impeller was 1000 rpm. The corrosion rate was determined using weight loss method and electrochemical methods such potentiodynamic sweep and linear polarization resistance methods. The experimental results indicate that the N-211 inhibitor has significantly reduced the corrosion rate of 1018 steel more than that of AR-505 inhibitor.

Surface Chemical Characterization of Environmentally Acceptable Polymeric Corrosion Inhibitors for Oilfield use

Per-Erik Hellberg, AkzoNobel Surface Chemistry AB,
R&D Lab. Hamnvägen, Stenungsund/Sweden
per-erik.hellberg@akzonobel.com

This paper will introduce newly developed polymeric corrosion inhibitors intended primarily for use within the oil- and gas production application area. Some of the products fulfill British and Norwegian environmental criteria for off-shore use, which are considered to be the most stringent in the world. The intention is to characterize the products with respect to e.g. static and dynamic surface tension as well as critical micelle/aggregation concentration. Additionally, more advanced surface- and interfacial chemistry analyses may possibly also be applied. Further, surface adsorption characteristics on different relevant surfaces using QCM-D (Quartz Chrystal Microbalance with Dissipation) will be presented and correlated with the results of standard oilfield corrosion inhibition tests such as static bubble tests and RCE tests. There are also plans to carry out unique flow-sequence tests with different oilfield-relevant liquids using the QCM-D equipment to assess the adsorbed layer persistance under various conditions.

Further, the intention is to compare the polymeric structures in all aspects detailed above with standard monomeric oilfield corrosion inhibitors having related chemistry.

Finally, environmental test data of the new products according to North Sea regulations will be discussed.

AUTOMATED SYSTEMS OF COMPLEX CORROSIVE MONITORING AND PROSPECTS OF APPLICATION OF ACOUSTIC EMISSION METHOD IN THEIR STRUCTURE

Kharebov Vladimir
«INTERUNIS» ltd, 101000, Moscow, Russia.

Today, there are several methods to assess the intensity and determine the corrosive damage nature. In practice, the most common are a weight method, an electrical resistivity method, and a linear polarization method [3]. Until now, the application of these methods is carried out mainly in manual mode, the key failing of which is the periodicity of taking monitoring data and measurement errors, caused by the human factor. Automation of corrosive prevention activities allow to do away with these shortfalls.

The purpose of applying of the automated systems of the Complex Corrosive Monitoring (CCM) is a trouble-free maintenance of the process equipment and raise of economic efficiency of enterprises. Whereby, it addresses the following problems: an optimization of supply of chemical reagents and the protection of equipment from internal corrosion, timely response to corrosive variation, gathering and storage of the corrosive monitoring data and prediction of variation of a corrosive state of constructions in a productive time, automation of provisions on security of the equipment against internal corrosion and decrease of a role of the human factor in an appraisal of results of corrosive monitoring.

Research of corrosion activity and efficiency of protection of the Oil & Gas producing equipment of JV Vietsovpetro.

A.L.Bushkovskiy,Nguen Thuc Khang, *Le Cong Thuy, T.N.Galljamov.*
/ JV Vietsovpetro /Vungtau City/ SR Vietnam.

The Oil &Gas producing of Vietsovpetro is made from offshore installations 120 km of the coast. Growth of water part in well production (up to 25,4 % in 2009г.) and reduction of producing volumes lead to water separation and necessity of corrosion monitoring of producing systems. Separated producing water is dumped to the sea after cleaning. A mineralization and pH of water are up to 29g/l and 7,85 in comparison with 34,9 g/l and 8 units for seawater. Content of H_2S-1.12 -1,6mg/l, solid phase- up to 20-25mg/l. Corrosion rate of carbon steel in produced water is 3 times less than in sea water due to absence of oxygen: 0,268 and 0,77mm/year at 55oC accordingly. Results of the monitoring performed by the common techniques have shown corrosion rate on a well- heads in a three-phase mix isn't more than 0,001mm/year at water part in production up to 62 % (MSP-8) and 58 % (MSP-3) at 67и 33°C after 10 years of exposition.

Corrosion rate of pipelines does not exceed 0,1mm/year (0,028 and 0,075mm/year for different objects), there is marked ulcer corrosion (up to 3,9мм differences in wall thickness on top and bottom line). But corrosion damage of steel is insignificant (less than 3 %), inhibitor protection is not required yet.

Corrosion of tanks, separators of oil and water is insignificant, that is provided with double internal protection (protective coating with thickness 250mcm and cathodic protection).The biggest corrosion rate was marked for modules of produced water preparation (0,13-0,16mm/year on CPP-2 and up to a 0,29mmyear on CPP-3). The reason - presence of oxygen through open dump caissons from the sea. The main corrosion catalyst is oxygen. With equal other conditions removal of oxygen reduces corrosion rate from 0,505 up to 0,0335mm/year, and the addition of inhibitor - from 0,0335 up to 0,002mm/year. So, corrosion rate has exceeded 3,8mm/year at additional water purification by flotation with the technical nitrogen containing up to 1,6 % O_2,.

As a result the scheme of produced water utilisation in reservoir pressure stabilisation system is developed for reduction of ecological damage and the reduction of charge of reagents (corrosion inhibitor, oxygen scavenger etc.)

Fighting against corrosion in oil and gas complex of Russia: problems and the ways of their solving

Anatoly Laptev, [1]OJSC “Company Nalko”, Moscow, Russia,
Dmitry Bugay, Ufa state petroleum technological university, Ufa, Russia

Gradual integration of the Russian and the world economy reveals an urgent necessity in creating a reasonable balance between the legislations and the human life norms in Russia and the developed countries. Thus, nowadays the problem of the human life cost is being actively discussed. There’s no precise juridical definition of this index, that’s why a number of problems arise concerning, in the conference context, the arrangements on oil and gas equipment and pipelines protection against corrosive destruction. In some large corporations the work on the so-called risks’ determination is under way. The main purpose of this work is determining cost and economic effectiveness of anti-corrosion protection arrangements and also enterprises’ corrosion services contribution into risks’ prevention. At oil and gas branch enterprises there’s no precisely formulated norms on determining the corrosion speed, the methods of protection as well as unified regulations and instructions on corrosion control, the aggressive media composition and properties.

Unfortunately, from the beginning of the 90-s of the past century in the period of economic destruction in Russia there was a durable stagnation in the field of oil and gas equipment anti-corrosion protection related to the absence of interest of the state and large branch enterprises in introducing innovative elaborations of Russian science. As a result, the major part of methods applied and protection means manufactured in Russia appeared to be incompetent. At present the niche of fighting against corrosion in Russia is more and more being occupied by the foreign companies.

The policy of conducting tenders and solving technological problems by the enterprises’ financial services leads to the reduction of the reagents’ number being used, cutting accompanying and control programmes. In the long run, the foreign companies, performing the anti-corrosion arrangements with high quality, begin to lose their positions due to the absence of branch norms and standardized ranging methods of equipment failure risks caused by corrosion.

The state also doesn’t care at all about increasing the public prestige of “anti-corrosion protection engineer” speciality in the country of extraordinarily ramified net of metallic communications located in different climatic zones.

Let’s note that the increase of the number of technogenic accidents is caused exactly by the negligent attitude towards the anti-corrosion protection.

For increasing the working effectiveness of anti-corrosion services of the branch enterprises it’s necessary to solve the following main problems:

1. Creating service companies attracted to holding anti-corrosion arrangements which constantly follow the latest achievements in the field of anti-corrosion protection in Russia and abroad and their work in conformity with them.
2. Determining oil and gas equipment failure risks caused by corrosion and their economic evaluation.
3. Elaboration of precise branch norms on diagnostics of equipment and pipelines’ corrosion condition as well as determination and control general and local metal corrosion speed.
4. A more detailed working out of practical skills of fighting against corrosion in training of corrosion engineers and their further branch studying for the work in conditions of concrete industrial enterprises.

Corrosivity of the produced fluids with regard to equipment and pipelines in oil and gas industries

<u>VAGAPOV R.K.</u>
GAZPROM VNIIGAZ, Razvilka, Russia

In the oil and gas production industries, economic losses and ecological damage caused by corrosion stem from the very large amounts of metal equipment structures that come into contact with aggressive media. It is well known that hydrogen sulfide and/or carbon dioxide containing media obtain high corrosive activity. It was determined that produced water itself in the absence of hydrogen sulfide or in the presence of small quantities of hydrogen sulfide is able to causes corrosion damages. The corrosion rate can reach the values of 1-1.5 mm/year, especially by elevated temperatures. Received results show that corrosion processes in the stratal water intensively proceed even in the absence sour gases (H_2S и CO_2). Under such conditions, the corrosion rate increases to 0.5 - 1 mm/year.

Drilling fluids have high levels of mineralization and can contain corrosively active oxygen. The corrosion rate of steel in the solution used for the preparation of drilling fluids is more than 2.5 mm/year. Acidic treatment is often used to intensify oil or gas recovery and increase the efficiency of the deposits. Acidic fluids are very corrosive reagents to steel equipment. Motor oil used at the compressor stations that press the hydrocarbons transmitted by pipelines can be saturated by hydrogen sulfide. Such motor oil is corrosively aggressive to metal.

Analysis of field pipeline failures in the West Siberian oil producing organizations

A.G. Gumerov, L.P. Hudyakova, A.T. Faritov
State Company Institute for Power Resources Transportation (IPTER), Russian Federation, Republic of Bashkortostan, Ufa city, 450075, Prospect Octyabry, 144/3

Institute "IPTER" worked at one of the West Siberian oil producing enterprises analyzing main causes of internal corrosion in oil gathering lines. Here, the analysis of actual failures (626 during three years) was correlated to the working media composition.

Basing on the publications and results of chemical analyses of the pumped water and gas it was supposed that the main factor which influenced corrosion, could be the CO_2 concentration in the associated petroleum gas. To prove this supposition, retrospective data were gathered about CO_2 content at the oil and gas gathering station, and specific rate of failures was calculated for the period of 2005 – 2007. The information obtained during the study is given in Table 1.

Table 1 Specific rate of failures of the pipelines transporting well production to the pumping stations.

Pipeline	Mean CO_2 content in the gas separated at UPSV of DNS, % vol	Specific failure rate, 1/km		
		2005	2006	2007
CDNG-2, DNS-1	0,43	0,25	0,30	0,42
CDNG-2, DNS-3	1,03	0,45	0,61	1,34
CDNG-4, DNS-4	0,30	0,27	0,22	0,24
CDNG-4, DNS-5	0,16	0,10	0,12	0,12
CDNG-3, DNS-1A	1,31	0,50	0,70	0,49

The analysis showed that the dependence of the specific pipeline failure rate on the CO_2 content has good correlation. Correlation factors in the pairs of "specific failure rate – CO2 content" values appeared as follows: 0,96, 0,99 and 0,64 for the years 2005, 2006 and 2007 accordingly.

Analysis of corrosion rate till the first failure, in connection with CO2 concentration, performed for all sampled failures which occurred during three years, also gave high correlation – 0,93.

Basing on the analytical data, the following dependence of the corrosion rate (mm/year) till the first failure on the CO2 concentration (% vol.) in the petroleum gas was offered for the given enterprise:

$$\text{Corrosion rate} = 1{,}15 + 1{,}19 * C_{CO2}$$

High coefficients of correlation of the actual failure data with CO2 content in gas, obtained as the result of the performed analysis, confirm the supposition that carbon dioxide is the main factor of accelerated destruction of steels in this and other West Siberian enterprises.

So, the supposed mechanism of corrosion was confirmed by analysis of sufficiently numerous statistical samples relating to retrospective of failures and the working media compositions. To perform the study, functional capabilities of "Extra, version 6.0" – the program for account and analysis of the field pipelines – were used.

Modern trunk pipeline in-line diagnostics technologies to detect corrosion-related defects

V.A. Kanaykin, O.I. Steklov, ZAO "NPO "Spetsneftegaz", Moscow, Russia

ABSTRACT

The total length of the unique system of trunk gas pipelines, built and successfully run in Russia, exceeds 156 thousand kilometers.

The system's core are pipelines with diameters between 1020 mm and 1420 mm (accounting for 60 percent of the total pipelines length) that operate under highly complicated natural and climatic conditions.

Above 90% of the gas pipelines have been in service for 15 or more years. By that time, the number of pipeline failures starts increasing. Their main causes are general, pitting, and stress-corrosion. Stress-corrosion pipeline defects are the most dangerous ones.

The provision of a reliable and safe gas pipeline operation has been ensured by a complex of measures the most important part of which is in-line inspection applying high-resolution defectoscopes.

The Paper presents modern technologies and means for comprehensive in-line inspection developed by ZAO "NPO "Spetsneftegaz".

It contains generalization of the experience and results obtained while diagnosing above 120 thousand kilometers of trunk gas pipelines. The effectiveness of in-line diagnostics is shown as a factor ensuring the pipeline reliability.

Also presented in the Paper are newly developed means to widen the application of in-line diagnostics.

Forecasting of the lifecycle of gas pipeline section with the corrosion defects

V.V. Kharionovsky, Gazprom VNIIGAZ, Razvilka, Russia

The most widespread defects of the trunk gas pipeline are corrosion, that it why the analysis of its danger and the assessment of pipelines lifecycle with such defects is the point of practically important purpose of ensure reliability.

The agenda of reports:

- analysis of corrosion defects statistics;
- methods of discovery of corrosion defects be the use of in-line inspection;
- definition of danger rank of single and multi corrosion defects;
- estimation of strength of pipeline’s section with the corrosion defects;
- methods of lifecycle estimation including the express method of lifecycle forecasting;
- methods of repair of pipeline sections with corrosion defects.

The materials including research and practical works concerning the increase of the gas pipeline sections reliability with corrosion defects which are accomplished by JSC “Gazprom” are presented in the report.

Corrosion in the Refinery Industry

© PECULIARITIES OF THE CORROSION IN CAT CRACKER AND DELAYED COKER GASOLINE DISTILLATES

V.P. Tomin[1], JSC Angarsk Petrochemical Company, Angarsk, Russia,
Ya.N. Silinskaya[2], JSC Angarsk Petrochemical Company, Angarsk, Russia,
N.A. Korchevin[3], Irkutsk State University of Railroad Communications, Irkutsk, Russia

Severe local corrosion is observed in cat cracker and delayed coker gasoline cuts stabilization units. Corrosion rate of carbon steel in unstabilized gasoline is 0.005 mm/year, in stabilized gasoline – 0.026 mm/year. Mass fraction of mercaptans in gasoline cuts comes up to 0,018-0.160 %, hydrogen sulfide – up to 0.017-0.026 %. Furthermore, unstabilized gasoline can contain up to 0.1 wt.% of emulsified water condensate.

Among physical and chemical properties of water condensate are pH = 8.1-9.5 and presence of phenols, sulfides, ammonium, cyanides and chlorides. Such composition allows forecasting high corrosiveness. However, examination of water condensate corrosiveness using neutralization with hydrochloric acid and dilution with sodium chloride solution uncovered inhibiting properties of water condensate constituents, meanwhile inhibition coefficient reached 19-27. After extractive treatment of water condensates with butyl acetate the corrosion rate became an order of magnitude higher. NMR, X-ray and UV fluorescence, IR spectroscopy, chromatography mass-spectroscopy and potentiometry methods recorded nitrogen and sulfur heterocyclic compounds in resulted extracts. Nitrogen heterocycles were represented by distinct five- and six-membered fragments of porphyrin complexes. Sulfur organic compounds were represented by cyclic trithiole homologues.

Electrochemical tests revealed that the phase barrier films of electrochemical reaction products were formed on the surface at the conditions of carbon steel corrosion in test solutions, active-passive transitions on polarization curve and strong hysteresis on volt-ampere curve recoil were noted. Half-wave potentials found in the extracts are located in steel corrosion potential range.

Imidazoline inhibitor injection into water condensates assists to suppress peaks on polarization curve related to adsorption of water condensate constituents. Practical results of monitoring showed that the imidazoline inhibitor added to stabilized gasoline was able to promote corrosion rate increase by five times while amide inhibitor ensured inhibition coefficient higher than 4 at the same conditions.

The above studies have demonstrated that constituents of cat cracker and delayed coker water condensate exhibit good inhibiting properties. It is necessary to use non-antagonistic corrosion inhibitors for the chemical-engineering protection systems in cat cracker and delayed coker gasoline distillate pipelines.

ELECTROCHEMICAL TREATMENT OF SOUR WATER

In this work laboratory results obtained using an electrochemical method, based upon pulsing electrolysis, suitable to sour water sulphur conversion are presented. Sour water is produced during oil refining operations and is commonly treated by conventional striping process. Electrochemical methods have been investigated as an interesting alternative treatment due to the possibility of extraction of some by products such as hydrogen and sulphur compounds besides a better compliance with future environment requirements. The experiments were performed in order to verify the use of nickel as electrode material suitable for use in sour water containing ammonium. Results obtained led to polysulfide production and reduction of hydrogen sulfide in the water without electrode blocking the nickel interface. Hydrogen sulphide concentration was reduced from 4000 ppm to 500ppm after a 50h treatment cycle. Results obtained may be used in sour water treatment and the products may also be used as catalytic crackers units corrosion inhibitor. Treated water rich in ammonia can be recycled to be used in other units in refineries as well in overhead acid corrosion control technologies.

MATERIALS SELECTION FOR ELECTRODES USED IN ELECTRO-OXIDATION OF AMMONIA

Laisa C. Candido[1], **José Antônio C. Ponciano Gomes**[2]

[1]*Federal University of Rio de Janeiro,Brazil, laisacris@metalmat.ufrj.br*
[21]*Federal University of Rio de Janeiro,Brazil, poncian o@metalmat.ufrj.br*

Electrochemical treatment of effluents is an important alternative to the conventional methods due advantages as environmental compatibility, versatility, high efficiency and low cost. It is known that its efficiency is directly related to the materials selection for the electrodes. These materials should present electro-activity for the oxidation of the desired ions, good corrosion resistance and high activation energy for the undesired reactions. Platinum and DSA® electrodes are known to be effective for the electro-oxidation of pollutants such as ammonia. On the other side, Ni is a cheaper and still effective material in terms of oxidation of small organic and other compounds.

This work presents results of the study of some materials that can be used as anodes in the electro-oxidation of ammonia/ammonium ion. The previous selected materials were Pt, Ni, DSA®, anodized Al and graphite. Cyclic voltammograms pointed the electro-activity of the Ni electrodes and confirmed the electro-activity of Pt and DSA® electrodes in the electro-oxidation of ammonia/ammonium ion. The other electrodes (graphite and anodized Al), apparently, showed no activity for the electro-oxidation of the analyzed ions. The possible influences of the potential sweep rate and number of cycles were evaluated.

AC polarizations were also carried out and the variations of the anodic current amplitude x time and ion concentration were accompanied. Through the AC polarization imposition was possible to filter the reaction of interest – decomposition of ammonia/ammonium ion – and not the NH_x adsorption on the surface of the electrode, which could compromise the efficiency of the electro-oxidation. Ni electrode has shown promising results.

© IMPACT OF THE PRIMARY OXIDATION PRODUCTS OF GASOLINE CUTS AND OXYGEN-CONTAINING COMPOUNDS ON CORROSION BEHAVIOR OF CARBON STEEL

V.P. Tomin, JSC Angarsk Petrochemical Company, Angarsk, Russia,
Ya.N. Silinskaya, JSC Angarsk Petrochemical Company, Angarsk,, Russia,
E.V. Belyaeva, JSC Angarsk Petrochemical Company, Angarsk,, Russia,

According to conventional concepts of corrosion theory a hydrocarbon phase is considered to be an oxygen accumulating, indifferent, diffusion medium. Oxidation of hydrocarbons exposed to atmospheric oxygen in storage is common for petroleum distillate cuts. Peroxides and hydroperoxides are the primary products of hydrocarbon oxidation.

Kinetics of oxidation of gasoline cuts depend on their production process, group hydrocarbon and chemical composition. Catalytic reformer gasoline is characterized by linear increase of oxidation product contents in time, while catalytic cracker gasoline shows an extreme dependence with peak oxidation product content about 30 ppm. Moreover the corrosion rate of carbon steel decreases with an increase of oxidation product concentrations in gasoline. Electrochemical studies revealed that injection of gasoline oxidation products into NaCl solution allows increasing carbon steel polarization in anode and cathode space. Voltammetric measurements on glass carbon electrode showed that half-wave potential of these products equals to (–) 0.2 ÷ (-) 0.3 V.

Addition of dibenzoyl peroxide and 2-ethylhexyl nitrate to test gasolines contributes to corrosion rate reduction, the inhibition coefficient equals to 11 and 14 respectively. These compounds promote polarization of carbon steel in NaCl solution.

Thus it was established that simultaneous and interrelated processes of chemical conversion and corrosion take place in hydrocarbon systems. Compounds with active hydrogen group impact the mechanism and kinetics of corrosion process in hydrocarbons. While fuel oxidation products have an inhibiting effect in hydrocarbon media since they take part in partial electrochemical reactions: in cathodic reaction as a depolarizer, in anodic reaction – in formation of transition complexes and stable surfactants.

Analysis of the obtained results makes it possible to consider oxidative oxygen-containing compounds of the similar structure as the corrosion inhibitors for hydrocarbon systems.

The analysis of oils, fuel and operating fluids spectrometric methods.

***LATYSHEV A.A.,* SURANOV G.I.**
Ukhta State Technical University, Ukhta, Russia

The Contents of elements in sample of oils, fuel and operating fluids estimated methods X-ray-spectral fluorescence analysis on absolute integrated total intensities radiations Kα and Kβ each element without a phone. Precision of definition of the contents of elements in hallmarks in many respects depends on accuracy of definition of counting rate of a background in the field of controllable elements which find usually on size of a background on the right and to the left of a defined element. Thus there are difficulties of definition of a background in case of close located elements which spectrums are partially overlapped, related with obviously expressed nonlinearity of spectrums of these materials and significant change of intensity of a background. (quantity of a phone in the beginning of a spectrum of hallmarks of liquids on sequence above, than in spectrums of samples of metals).

For elimination of such difficulties it is offered to define mathematical model of spectral dependence of a background from wave length (SDP, СЗФ) in the form of a polynom of the sixth degree on which it is possible to count the quantity of a background corresponding wave length of radiation of the defined element in hallmark. SDP find by means of the computer program across the X-ray fluorescence-spectrum hallmarks of oil from which exclude the sites containing analytical lines of elements.

Intensity of a background and nonlinearity of spectrums of hallmarks of these materials are caused by the various contents of hydrogen in researched materials (increase with increase of hydrogen). The greatest background is observed in spectrums of the liquid petrolatum consisting in basic from the saturated hydrocarbons of wax fractions, the least - in hallmarks of aromatic hydrocarbons (benzol, petroleum ether).

The quantity of a phone in spectrums of worked engine oils drops with increase in run of the car and deterioration of oils that is related with change of their fractional composition and with increase, first of all, of quantity of aromatic hydrocarbons. Correlation between change of intensity of a phone and the contents of aromatic hydrocarbons in worked engine oil with increase the car run proves to be true results of the (infra-red) IR-spectral analysis of the same hallmarks of fresh and worked engine oil. Especially intensive changes of fractional composition of engine oils occur {happen} in an initial stage of work (up to 1,0 thousand km. run of the car).

Change of quantity of a background in the beginning of a spectrum of hallmarks of worked engine oils can be used as a diagnostic index of a tentative estimation of operability of oil for the further work.

SCC Resistance of X70 SAW Helical Seam Welded Pipes in Fuel Grade Ethanol

M. Hörstemeier, M. Scheepers, C. Bosch
Salzgitter Mannesmann Forschung GmbH, Duisburg, Germany

C. Kalwa, T. Köppe
EUROPIPE GmbH, Mülheim, Germany

H. Dellaretti Junior
Tubos Soldados Atlantico, Carapina, Serra - ES, Brazil

The resistance of SAW helical seam welded (SAWH) pipes of grade X70M to stress corrosion cracking (SCC) in anhydrous fuel ethanol was investigated using the slow strain rate test method and four-point-bend tests. Corrosion tests were carried out in fuel ethanol under aerated and unaerated environmental conditions within the Brazilian specification of anhydrous ethanol. The SAWH pipe with an outer diameter of 711 mm and a wall thickness of 11.9 mm has been tested in different conditions including a cold bent pipe and a heat treated pipe section to simulate the material condition after coating. Material from the base metal, weld seam and heat affected zone has been investigated.

Slow strain rate tests have been evaluated with regard to ductility parameters such as plastic elongation ratio E_PR and reduction in area ratio RAR and by means of fractographic analysis of fractured specimens. Test results of notched and unnochted specimens are presented. All specimens presented high ductility parameters E_PR and RAR indicating high resistance to SCC in the tested environments. No indication for SCC was found in fractographic analyses of the specimens after testing. Results of 4-point-bend tests revealed no SCC cracks in the base material or in the weld seam for both oxygen free and oxygen rich ethanol environments.

A New Ni-Mo-Cr Alloy for the Most Aggressive Media

Nacéra Sabrina Meck and P. E. Manning
Haynes International, Inc., 1020 West Park Avenue
Kokomo, IN 46902-9013, USA
nsmeck@haynesintl.com, pmanning@haynesintl.com

Abstract

The Ni-Cr-Mo (C-type alloys) are vital to chemical process industries. This family of alloys is particularly known for its corrosion resistance in hydrochloric and sulfuric acids, at moderate concentrations and temperatures, where some standard stainless steels might not perform well, especially when some chlorides are present. Also, the Ni-Cr-Mo alloys possess an excellent resistance to chloride salt solutions which can induce pitting, crevice and stress corrosion cracking. Despite the versatility of Ni-Cr-Mo alloys, there has always been a need for materials with even higher corrosion resistance to hydrochloric and sulfuric acids. Nevertheless, with increasing HCl and H_2SO_4 concentration and temperature these alloys are prone to some corrosion problems. The Ni-Mo (B-type) and Zirconium alloys are often considered in these cases; however, both systems have significant drawbacks with these two mineral acids and small quantities of oxidizing species can lead to very severe corrosion on these alloys. Therefore, an alloy with improved resistance to hydrochloric and sulfuric acids, relative to the Ni-Cr-Mo alloys and without the drawbacks associated with the Ni-Mo and zirconium alloys was developed. The new material, named HASTELLOY® HYBRID-BC1® alloy, falls within the Ni-Mo-Cr system and it fills the gap between the C-type and B-type alloys.

This paper will provide detailed comparative corrosion data between the HYBRID-BC1® alloy and several other Ni-Cr-Mo and Ni-Mo materials in a variety of chemicals, mainly in hydrochloric and sulfuric acids. It was found that the corrosion behavior of the new alloy in hydrochloric and sulfuric acids approaches the performance of the B-type alloys, and exceeds that of the C-type alloys. Also, the HYBRID-BC1® alloy exhibited much better tolerance to dissolved oxygen in hot dilute HCl, and also to ferric and cupric ions contained in hydrochloric and sulfuric acids.

Key words: HYBRID-BC1 alloy, Ni-Cr-Mo alloys, Ni-Mo alloys, sulfuric acid, hydrochloric acid, iso-corrosion-diagram, dissolved oxygen, ferric ions, cupric ions

Reliable solutions for corrosion monitoring in high temperature plant

iicorr's Monitoring Services specialist field team have been installing the Field Signature Method (FSM-IT) corrosion monitoring systems in oil refineries since 1999. The early systems proved that the technology could accurately measure metal loss at high temperatures (greater than 200°C). However the early installations suffered from reliability issues within the ancillary components of the system, due to the elevated temperatures.

The high temperatures were causing the insulation to break down on the wiring, leading to brittle failure of cables. Associated plant vibration affecting the weakened cabling, ultimately caused the system to fail. Other reliability problems with temperature sensors supplied as part of the system also led to system failures.

In its role as a specialist installation company for the FSM-IT system, iicorr has been heavily involved in the re-design of the hardware since 2002, aimed at eliminating these reliability problems.

This paper presents details on the background of FSM-IT as a corrosion monitoring technique and explains how it can achieve a wall loss measurement sensitivity of one part per thousand in high temperature plant.

The paper goes on to demonstrate through two separate case studies, one in an oil refinery and one in a large European chemical plant, how the system installation has been improved over the last six years. This has led to reduced plant shutdown for inspection intervention, improved corrosion inhibition effectiveness and greater confidence in on-going integrity of high criticality equipment.

These improvements have delivered a reliable corrosion monitoring tool for industries operating equipment with high temperatures (up to 450°C) and corrosive product, with around half of the installations being safely carried out on live equipment.

Finally the paper will explore the potential for installation of FSM-IT and similar high temperature corrosion monitoring systems to be applied to energy conversion systems to provide lifetime integrity assurance in an aggressive corrosion environment.

The role of welded joint vulnerability and various damage mechanisms active in process & petrochemical plants: reliability analysis with Risk Based Inspection (RBI) approach.

Marco De Marco – Istituto Italiano della Saldatura – ITALY - marco.demarco@iis.it
Stefano Pinca – Istituto Italiano della Saldatura - ITALY - stefano.pinca@iis.it
Giancarlo Canale – Istituto Italiano della Saldatura - ITALY - giancarlo.canale@iis.it

In this article we've presented an overview on the possible influence that damage mechanisms active in welded joints may have on reliability during the entire life cycle of process plant equipment and in Integrity Management methodology.

The most Damage Mechanisms oriented methodology in Asset Integrity Management and Risk Management is probably the Risk Based Inspections (RBI) analysis which is focused on prioritizing and optimizing inspection strategies on the basis of risk ranking and future projections of risk value.

Risk Based Inspection assessment is considered to be an innovative risk analysis mainly because of the introduction of two new concepts in the evaluation:

- the role of inspection
- the global, analytical and structured approach to the evaluation of all the various damage mechanisms active in process and power generation plants

Any reliability evaluation for pressure vessels and piping systems that takes into account all the possible damage mechanisms active in process plants must deal with welded joints vulnerability and take into account likely mechanical, corrosion and stress-corrosion related influences.

By identifying credible damage mechanisms, determining the damage rate and susceptibility, and selecting an inspection effectiveness category based on defined level of inspection, a probability of failure and associated risk may be determined using equations that in the calculation of probability take into account the role of the condition, or of the damaged state, observed by an inspection program with variable effectiveness.

It is worth noting that in a well developed RBI analysis it is important to identify the damage mechanism. Here, the role of the different personalities involved in the analysis is of primary importance: only a qualified and experienced materials engineer has the ability to identify and properly characterize the damage mechanisms and modes of failure, and only a qualified and experienced NDT engineer can evaluate the best traditional and advanced inspection methods employed in the past and those to be suggested for future plan.

RBI is not for a single *old style-all knowing* expert or consultant but is for structured, skilled and able to communicate TEAMS!

Critical Factors in Rich Amine Solvent Corrosivity

Dr. Brian Chambers[1], Mr. Vishal Lagad[2], Dr. Russell Kane[3]

[1]Honeywell Corrosion Solutions, Texas, USA, brian.chambers@honeywell.com
[2]Honeywell Corrosion Solutions, Texas, USA, vishal.lagad@honeywell.com
[3]iCorrosion, Texas, USA, russ.kane@icorr.net

Amine solvents are commonly used in refinery operations for treatment of gas streams containing acid gases, H_2S and CO_2. Solutions containing amine solvents and dissolved acid gases can result in accelerated corrosion of materials of construction, especially when refinery operations demand higher acid gas loadings than that specified for a particular amine unit design. Unanticipated corrosion can result in reliability problems and unscheduled shutdowns, affecting overall refinery operations and profitability.

The difficulty in anticipating corrosion in amine units stems from the multitude of different conditions present in a given unit and the variety of amine chemistries in use in the refining industry today. The purpose of this paper will be to identify the critical variables controlling corrosion rates in amine solvents under rich conditions, including: (1) amine chemistry, (2) H_2S loading, (3) CO_2 loading, (4) temperature, (5) flow rate, and (6) impurities. Qualitative findings and quantitative trends from a comprehensive laboratory study that simulated refinery conditions will be presented.

HYDROGEN DAMAGE, MONITORING, AND PREVENTION IN THE OIL REFINERY

Alec Groysman and Rami Simon

Oil Refineries Ltd., Haifa, Israel
ORT Braude College of Engineering, Karmiel, Israel
E-mail: galec@orl.co.il

The aim of this work is to analyse *hydrogen damage*, monitoring, and possible prevention at the oil refineries' units.
Hydrogen gas occupies an essential place in the processes in the oil refining industry: *hydro*desulfurizers, *hydro*crackers, and catalytic reformers. In addition to these processes, there are some sources of *hydrogen* gas arising from corrosion of carbon steel equipment in contact with aqueous solutions of acids, such as H_2S (sour water), HCl, HCN, H_2SO_4, and HF. Historically many names of *hydrogen damages* appeared: hydrogen degradation, hydrogen embrittlement, hydrogen blistering, decarburization, hydrogen stress cracking (HSC), hydrogen attack, high temperature hydrogen attack (HTHA), hydrogen-induced cracking (HIC), also known as stepwise cracking (SWC), stress-oriented hydrogen-induced cracking (SOHIC), sulfide stress cracking (SSC), hydrogen flaking, and hydride formation. This profusion of names does not always correctly elucidate and explain them, and can even confuse and complicate their detection, understanding, monitoring, and control.
From analyzing the literature on this subject and based on our own experience, we differentiate all *hydrogen damage* failures into two main groups based on two mechanisms: electrochemical processes (mainly at low temperature, up to ~100^{o}C) arising from acid corrosion and cathodic protection, and high temperature (between 200 and 500^{o}C) arising from the presence of hydrogen gas at high pressures.
Examples of *hydrogen damage* are given for the various units of oil refineries. Different *monitoring methods* were developed for detection of possible *hydrogen damage*. Hydrogen can be detected either in intrusive or non-intrusive devices called *hydrogen probes*. Hydrogen that penetrates through a metallic wall can be detected with manometric (hydrogen pressure,) or vacuum method, electrolytically (hydrogen ionization from H atoms into H^+ ions), heat conduction (gas chromatography), vacuum extraction at 400^{o}C, or hydrogen effusion. Monitoring methods are critically reviewed. *Preventive measures* of hydrogen failures are differentiated into two groups according to low (electrochemical) and high temperature (dissociation of hydrogen molecules) mechanisms. The first group includes protective measures from hydrogen blistering and sulfide stress cracking: metallurgical measures, change of environmental conditions (removing aggressive species such as sulfides, cyanides, and arsenic compounds, neutralization, injection of inhibitors of hydrogen penetration), use of organic, inorganic, and metallic coatings, heat treatment and proper welding. The second group includes metallurgical measures (use of steels containing chromium and molybdenum, and decrease of carbon content in steel), heat treatment, and proper welding. Analysis of *preventive measures* of hydrogen failures was carried out and recommendations were given. **Keywords**: *hydrogen damage, oil refining industry, monitoring, prevention.*

Influence of higher mercaptan levels in crudes on processing units in refineries

Volker Bonitz – Inspection and Integrity Manager
Nicole René de Cotret - Integrity Team Leader
Alexandra Stuke- Materials Corrosion Engineer

Shell Deutschland Oil GmbH
Godorfer Hauptstraße 150, D-50997 Köln, Deutschland

Due to an increase in mercaptan concentration into crude distillation unit – a review of potential increase in corrosion was performed. A review of the available industry information resulted in very limited detailed information about the influence of mercaptans on the theoretical predicted corrosion rates due to high temperature corrosion. Moreover, the material selection (mostly carbon steel with select areas of low alloy steels operating in the HTSC range)) and layout of the distillation units is sensitive to changes in crude sulphur composition.

This paper presents:

- a brief overview of the reviewed industry information,
- historical inspection and processing information for distillation units operating at increased mercaptan levels.
- examples from current online corrosion monitoring and high temperature inspection
- results of laboratory corrosion loop testing
- brief discussion to date of the correlation of crude intake mercaptan level, equipment inspection data and corrosion loop testing

Key words: mercaptan, corrosion, inspection, high temperature sulphur corrosion, sulfidation

A STUDY OF THE ELECTROCHEMICAL BEHAVIOR OF TANTALUM IN RELATION TO HYDROGEN CHARGING

A.G.S.G da Silva, H.A. Ponte, L. M. Moya, C. E. B Marino, G. Arruda
Laboratório de Eletroquímica de Superfície e Corrosão (LESC),
Universidade Federal do Paraná Curitiba PR CEP- 81531-990
aleksantos@hotmail.com

The damage caused by the permeation of hydrogen in metal structures like machines, equipment, pipelines has been one of the major problems encountered in the petroleum industry. The structural damages are caused, in many cases, by hydrogen inclusion into the metallic structures. This hydrogen is generated by acid means that contain free protons (H^+), by chemical processes that lead to the protons formation, by formation of atomic hydrogen (H^0), or even by absorbed gas hydrogen (H_2). The structural damages caused by hydrogen may be: hydrogen induced cracking (HIC), blistering, sulfur stress cracking (SSC) and stress oriented hydrogen induced cracking (SOHIC). In practical terms the challenge is to detect, in a safe, fast and economically viable way, the formation of hydrogen close to a surface subjected to corrosion. This is necessary in order to use preventive control to avoid severe damages that can be caused. The research presented here has the mainly objective to study the electrochemical behavior of tantalum metallic under cyclic charging of hydrogen, through the variation of potential chemical and/or electrochemical for application as a hydrogen probe. Open circuit potential (OCP) and chronopotentiometry were used. This electrochemical probe will be installed on the outer surface of equipment or pipes that operate in contact with corrosive substances which can generate hydrogen. The results indicate the feasibility of the use of tantalum as electrochemical probe for detection of hydrogen, since it presents changes related to electrochemical permeation of hydrogen.

Corrosion Protection of Oil Storage Tank Double Bottoms

Prof. Efim Lyublinski, Eng. Yefim Vaks,
Northern Technologies International Corporation
23205 Mercantile Rd., Beachwood, OH 44122, USA
Eng. Marcelo Schultz, Petrobras,
República do Chile Av., Nr. 65, Rio de Janeiro - RJ,
CEP: 21.949-900, Brazil

Abstract

The proper combination of different corrosion protection methods leads to a more efficient preservation of oil storage tank double bottoms. The protection methods currently in use include cathodic protection systems (CPS) or CPS in combination with soluble corrosion inhibitors (SCI). Considering the unpredictable corrosion environment and application conditions, in most cases, these methods are not efficient enough and do not significantly reduce the frequency of tank double bottom replacement. The new combined methods described in this paper, however, do increase the efficiency of protection. Their use leads to an increase in storage tank service life. The relationships between CPS current densities, SCI and volatile corrosion inhibitors (VCI) concentrations, as well as system efficiencies are discussed.

Keywords: corrosion, inhibitor, cathodic protection, storage tanks, double bottom, efficiency, service life.

Corrosion of sulfided steels by naphthenic acids

Meriem El Kamel[1,2], *Anouk Galtayries*[1], *Grégory Foulonneau*[2], *Xavier Roumeau*[2],
Georges Morel[2], *Philippe Marcus*[1]
[1]*Laboratoire de Physico-Chimie des Surfaces, CNRS-ENSCP (UMR 7045), Chimie ParisTech (Ecole Nationale Supérieure de Chimie de Paris), Paris (F), meriem-elkamel@enscp.fr*
[2]*Centre Européen de Recherches et de Techniques, Groupe Total, Le Havre (F)*

Sulfidation and naphthenic acid corrosion have been the main causes of damage in oil refinery units for decades, with serious safety and reliability issues. Improving the understanding of the involved reactions and the mechanisms is a key factor to better control the corrosion in refinery processes. We present here an investigation based on the surface reaction of model sulfide layers, in laboratory conditions, with mixtures of white oil and naphthenic acid, at 260°C.

Model iron sulfide layers were formed in pure gaseous H_2S at 300°C on carbon steel, Fe-5Cr-0.5Mo (P5 steel) and Fe-18Cr-8Ni (304L stainless steel). The sulfide layers were characterized by grazing X-Ray Diffraction (XRD), by X-ray Photoelectron Spectroscopy (XPS) and Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS). The diffraction patterns showed that the pyrrhotite ($Fe_{1-x}S$) phase was formed, as when sulfidation occurs in a refinery sulfur crude oil at 300°C, in industrial conditions [1]. The ToF-SIMS profiles allowed us to evidence a duplex layer, for all sulfided steels: an external pyrrhotite layer where acid interacts, an internal oxide layer, the composition of which is changing with the type of steels. The thicknesses of the pyrrhotite layers are in the range of 100-200 nanometers, depending on the samples.

The effect of the chemical attack of the iron sulfide layer was investigated by exposing the sulfide layers to a mixture of white oil and naphthenic acid at 260°C. The experiments were performed in a dedicated laboratory set up, designed for controlled exposures : from a few minutes to several tens of minutes. The surface was analyzed by ToF-SIMS. The evolution of the Total Acid Number of the naphthenic acid oil was followed by Fourier Transformed Infrared Spectroscopy (FTIR). The ToF-SIMS data (spectra and profiles) confirm the surface modifications after interaction with the naphthenic acids. The kinetics of the attack is followed by the evolution of the thickness of the model iron sulfide layers (as determined from ToF-SIMS depth profiles). The corrosion mechanisms and kinetics will be described and discussed as a function of the type of steels.

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PROGRESS IN PETROLEUM REFINERY HIGH TEMPERATURE SULPHIDIC CORROSION INHIBITION

Chris CLAESEN[1], **Miomir KULIC**[2]

[1]Nalco Energy Services, Belgium, cclaesen@nalco.com
[2]Nalco Energy Services, Austria, mkulic@nalco.com

The chemical inhibition of petroleum refinery high temperature sulphidic corrosion has been practiced successfully since several years.
The specific type of inhibitor used, the application technology, the corrosion monitoring, the unit metallurgy, operational conditions and the quality of the processed crude oil all play an important role.
This paper discusses the impact of specific crude contaminants and different high temperature sulphidic corrosion inhibitors on sulphidic corrosion in lab autoclaves. It also discusses new refinery applications in the high temperature high shear conditions of a crude destillation unit furnace and the monitoring of the inhibitor performance with FSM technology.

Corrosion Mechanisms & Methods

ATR-FTIR spectroscopy at the metal-water and metal-polymer interfaces - theoretical and experimental studies

Dan Persson and Maria Öhman
Swerea KIMAB, Drottning Kristinas Väg 48, Stockholm, Sweden

As a part of a research program with the aim to understand the stability of metal / polymer interfaces in corrosive environments were theoretical and experimental studies of internal reflection spectra at metal / water and metal / polymer interfaces performed. Theoretical calculations of ATR-FTIR and were performed using classical physical optics and the optical index of the media (metal, water, polymer etc.). The calculated spectra of simple model systems were correlated and compared with the experimental results to increase understanding of the processes that were detected and to support the interpretation of experimental spectra. The calculated spectra can be used for determination of film thicknesses, the amount of water at the interface, delamination processes at the metal / polymer and for general understanding of method and studied phenomena.

SELECTIVE DISSOLUTION OF MODIFIED SINGLE-CRYSTALLINE MODEL SYSTEMS
STUDIED BY IN-SITU X-RAY DIFFRACTION

Frank Uwe RENNER, Aparna PAREEK, Genesis ANKAH

Max-Planck-Institut f. Eisenforschung, Germany, renner@mpie.de

The selective dissolution (dealloying) of model systems in acids has been widely investigated in the past but detailed understanding of crucial effects, e.g. the breakdown of passivity at the so-called critical potential, is still missing. The widespread emergence of synchrotron light sources in recent years enabled in-situ surface X-ray diffraction to become one of the most productive methods next to scanning probe techniques to access structural parameters of (buried) interfaces at the atomic and nanometer scale [1]. Most previous dealloying studies have focused on the critical potential and only few studies have addressed the surface structures in the potential region of passivity. Although traditional methods like Scanning Tunneling Microscope (STM), Atomic Force Microscope (AFM) and other microscopic techniques are widely used, they are limited to address the topmost surface. A better understanding of the formation of passive films and the development of porosity can come from techniques that penetrate deeper in the material, e.g. in-situ x-ray diffraction using synchrotron radiation. We have used ex-situ AFM and in-situ X-ray diffraction to follow the initial steps of selective dissolution with a focus on the influence of additives and applied thin plasma polymer and thiol films on the process and the initial surface structure changes.

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Application of high resolution techniques to characterize sensitization of highly alloyed materials

M. Prohaska[1], T. Wernig[1], G. Mori[1], G. Tischler[2], R. Grill[2]

[1] Christian Doppler Laboratory of Localized Corrosion, University of Leoben,

Franz-Josef-Str. 18, 8700 Leoben, Austria, manuel.prohaska@unileoben.ac.at

[2] voestalpine Grobblech GmbH, Voest-Alpine-Straße 3, 4031 Linz, Austria

Differently sensitized materials (Alloy 625L and 926L) have been investigated with respect to their microstructure. The size and morphology of (mainly) chromium and molybdenum depleted zones was determined by measuring quantitative concentration profiles parallel and rectangular to grain boundaries and by performing element mappings to reveal the distribution of certain elements adjacent the grain boundaries. Additionally, the chemical composition of grain boundary precipitations was determined. These investigations were performed by means of energy dispersive x-ray transmission electron microscopy (EDX-TEM), auger electron spectroscopy (AES) and high-resolution scanning electron microscopy (HR-SEM). In conclusion, the results of high-resolution investigations were related to the type of corrosive attack along grain boundaries after DL-EPR-testing and critically discussed. Results and comparison of different methods lead to recommendations with respect to their cost / effect structure.

Detection of Hydrogen Permeation Through Iron Foil Using a Scanning Kelvin Probe

Geraint Williams [a], *H. Neil McMurray* [a] *and Roger C. Newman* [b]
[a] *Materials Research Centre, School of Engineering, Swansea University*
Singleton Park, Swansea, SA2 8PP, United Kingdom.
[b] *Department of Chemical Engineering & Applied Chemistry, University of Toronto,*
200 College Street, Toronto, Ontario, M5S 3E5, Canada.

In this work we employ a conventional scanning Kelvin probe (SKP), operating on a macroscopic scale, to demonstrate that the egress of hydrogen at the surface of a pure iron substrate produces a marked Volta potential depression (of several hundred millivolts). The approach used here involves the initial evolution of hydrogen on an iron foil by cathodic polarisation of a circular working electrode area in sodium sulphate electrolyte to allow ingress of H_2 into the bulk metal. After halting cathodic H_2 charging, the *reverse* face is subjected to Volta potential mapping using SKP. The interaction of atomic hydrogen with the air-formed surface oxide film of the iron foil substrate, is shown to produce significant Volta potential changes. A similarly sized circular region of depressed Volta potential to the 5 mm diameter working electrode area is produced on the exit side (see Figure), which is shown to spread laterally with time at a rate of 1.8×10^{-8} m s^{-1}. The magnitude of the Volta potential depression decreases with post-cathodisation holding time and exhibits a dependence upon the oxygen partial pressure of the holding environment. It is proposed that the Volta potential depression observed in the area of hydrogen egress results from a change in the Fe(II)/Fe(III) ratio within the surface oxide. This in turn arises from the reduction of Fe(III) by atomic hydrogen at the metal-oxide interface and subsequent re-oxidation of Fe(II) by atmospheric oxygen at the oxide-gas interface. The subject of hydrogen permeation in steel has received significant attention for many decades, since hydrogen evolved cathodically under conditions of low pH or low oxygen partial pressure, can be absorbed into the bulk metal and cause embrittlement. Consequently, it has been proposed by many authors that atomic hydrogen plays a major role in the crack propagation mechanism associated with stress corrosion cracking and corrosion fatigue in stainless steels. The findings presented in this paper suggest that SKP and the (higher spatial resolution) SKPFM are useful techniques for determining the physical distribution of hydrogen emerging through the surfa

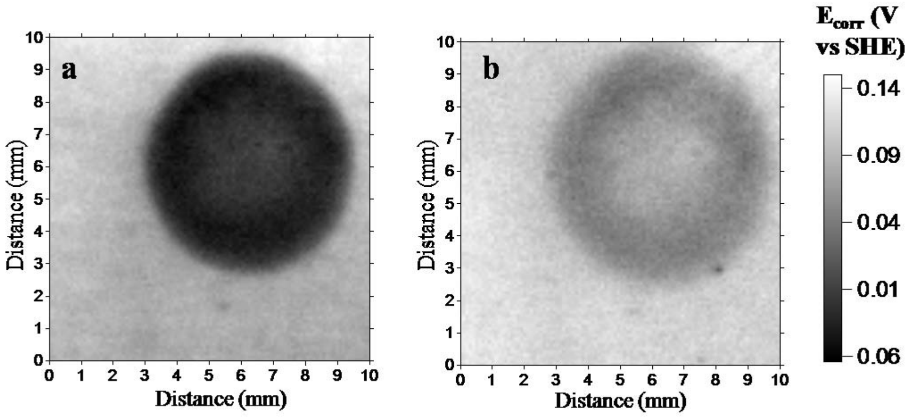

Figure: Greyscale interpolated E_{corr} maps of the *reverse* face of a previously cathodised Fe foil recorded in humidified synthetic air at 95% rh (a) 60 and (b) 480 min after galvanostatic polarisation at -20 mA cm^{-2} was halted.

SCANNING ELECTROCHEMICAL PROBE CHARACTERISATION OF GALVANIC ACTIVITY ACROSS INCLUSION BOUNDARIES IN IRON/NICKEL METEORITES

David GREENFIELD[1], David E. BRYANT,[2] Terence P. KEE[2] Howell G.M. Edwards[3], Tasnim Munshi[3], Ian J. Scowen[3]

[1]Materials and Engineering Research Institute, Sheffield Hallam University, United Kingdom, d.greenfield@shu.ac.uk
[2]School of Chemistry, University of Leeds, Woodhouse Lane, Leeds, LS2 9JT, t.p.kee@leeds.ac.uk
[3]Chemical & Forensic Sciences and University Analytical Centre, University of Bradford, Bradford, BD7 1DP, i.scowen@bradford.ac.uk

Meteoritic material consisting mainly of Fe and Ni contain inclusions of Shreibersite $(Fe, Ni)_3P$ which have been suggested as a possible source of reactive, available phosphorus on the early earth. This phosphorus may have been liberated as a result of redox couples forming between the Shreibersite inclusions and the main Fe-Ni matrix of the meteorite. This work reports the use of novel scanning electrochemical methods to characterise samples from two different meteorites, the *Seymchan pallasite* and the *Sikhote-Alin* meteorite, in terms of galvanic couples formed between the inclusions and the matrix material.

Specimens have been analysed using the Scanning Kelvin Probe (SKP) and the Scanning Droplet Cell (SDC) techniques; both of which are able to characterise samples on a localised level, producing maps of electrochemical activity across the sample surface. SKP maps identify regions of anodic and cathodic activity; these are reinforced by complimentary scans carried out with the SDC which produces maps of both electrochemical potential along with data of the kinetics of the corrosion reactions occurring at discrete localised points.

Electrochemical data is reinforced with analysis carried out using both XPS and micro-Raman spectroscopic analysis of the composition of the surfaces.

On reproducibility of measurements obtained by means of electrochemical micro-cell technique

F. Andreatta[1]*, L. Paussa*[1]*, A.H. Akita*[2]*, C.S. Fugivara*[2]*, A.V. Benedetti*[2]*, L. Fedrizzi*[1]

[1] *Department of Chemical Science and Technology, University of Udine, Italy;*
[2] *UNESP, Instituto de Química, Araraquara, SP, Brazil;*

The electrochemical micro-cell is recognized as a well established local electrochemical technique for the characterization of corroding surfaces. The electrochemical micro-cell enables the investigation of small areas with resolution in the micrometer range by the use of glass capillaries to define the area of the working electrode. This technique is employed for carrying out electrochemical measurements like potentiodynamic polarization with a 3-electrode configuration (working, reference and counter electrode). As compared to other local techniques, the electrochemical micro-cell presents some advantages like possibility to employ aggressive electrolytes for the measurements and high spatial resolution, which is defined by the size of the glass capillary (in the range 10 – 800 μm). In addition, only the area investigated is wetted by the electrolyte. The electrochemical micro-cell technique presents some limitations related to resolution of potentiostat, ohmic drop in the capillary, effect of scan rate and size of the glass capillaries.

This paper targets the reproducibility of results obtained with the electrochemical micro-cell. In particular, a set of measurements on low carbon steel was performed employing two different instruments. The first one is the micro-cell developed by T. Suter, which is available at the University of Udine. The second is a micro-cell constructed at the UNESP - Instituto de Química. Potentiodynamic polarization measurements obtained with the two instruments under the same experimental conditions are discussed in the paper. Moreover, the paper focuses on the effect of capillary size on reproducibility.

Formation of the galvanic cells during atmospheric corrosion of a metal

A. Nazarov, D. Thierry,
French Corrosion Institute, 220 rue Pierre Rivoalon, F-29200 BREST, France

This study investigates the mechanism of atmospheric corrosion of carbon steel, galvanized steel (Zn) and aluminum (alloy AA6016) beneath polymeric coatings. 'In situ' Scanning Kelvin Probe was applied in order to measure the potential around an artificial defect in the coating. The gradient in the potential at the defect and under the intact organic coating determines the mechanism of underfilm corrosion. Measurements of galvanic currents in a model cell (bare – coated metal) and current polarity provides information on the polarization of a metal-paint interface by the defect and on the mode of delamination. In addition, the redistribution of chemical species between the defect and coated areas was evaluated by surface analytical techniques such as EDS and FT-IR.

It was shown that the mechanisms of delamination largely depend on the electrochemical conditions inside the defect. Deposition of thick water electrolyte film containing NaCl leads to cathodic delamination of the coating. In more "dry" conditions, during corrosion in humid air, polymeric coating around the defect is subject to anodic undermining or filiform corrosion.

Signs of the potential gradient across the defect and intact coating are different and defined by the potential of the corroding metal in the defect. The potential in the defect is the function of efficiencies of the anodic and cathodic reactions and the reaction controlling the corrosion process.

Switching one mode of the delamination to another can be governed by the nature of salt deposition. The ability of the cation to support the cathodic oxygen reduction on the metal surface surrounding the defect determines the efficiency of the cathodic delamination. Thus replacing sodium to ammonium cation inhibits the cathodic process and the cathodic delamination mechanism switches to anodic undermining.

Similar experiments were carried out for metal surfaces without polymeric coatings but with local deposition of the corrosion activator. The similarities and the differences in the potential distribution and in the spreading of the corrosion will be discussed.

Development of electrochemical methods for determining of corrosion protection properties of metals, alloys and coatings in laboratory and industrial conditions

***N. Anufriev* , S. Oleynik, A. Akolzin**
A.N. Frumkin Institute of Physical Chemistry and Electrochemistry of Russian Academy of Sciences, Moscow, Russia

Abstract:

For the successful application of corrosion protection technologies are required reliable, fast methods to control the corrosion rate and other parameters of corrosion of metals, alloys, coatings, construction materials. Electrochemical methods of linear polarization resistance, amperometry, potentiometry allow to provide the estimation of corrosion processes in real time, create portable equipment, provide the ability to automate the measurements.

Using well-known foreign and domestic portable devices limited by the lack of a number of important functions, low sensitivity, high cost. As the result of our work it was shown the efficiency of complex electrochemical techniques in the study of corrosion kinetic, metal surface treatment processes, obtaining conversion coatings, determination of protection rate of corrosion inhibitors, the effectiveness of metal and other coatings, construction materials in a variety of water and water-organic media, and in conditions of accelerated climatic corrosion tests. Developed and tested a prototype of an automatic eight-channel portable corrosion meter «Expert-004», which is the variety of measurement parameters and the sensitivity is unique among domestic and imported equipment of the same class. Its distinctive features are the possibilities of practically simultaneous determination of main corrosion parameters - uniform and pitting corrosion rates, corrosion potentials values, contact corrosion processes, implementation techniques of chronopotentiometry and chronoamperometry. The developed techniques and equipment of corrosion-electrochemical control can be used in laboratory, industrial and natural conditions for a wide range of tasks in the areas of corrosion protection, electroplating, metal surface treatment, corrosion monitoring, engineering, nanotechnology.

Keywords:
electrochemical corrosion tests, linear polarization resistance method, techniques and equipment

A local electrochemical approach to study corrosion in plastic encapsulated semiconductor devices

O.V. Elisseeva[1,2], A. Mavinkurve[3], R.T.H. Rongen[3], M.H.M. van der Straaten[3], R. Ambat[4], J.M.C. Mol[2], H. Terryn[1,5], J.H.W. de Wit[2]

[1] Materials Innovation Institute, M2i, Mekelweg 2, 2628 CD Delft, the Netherlands, o.elisseeva@m2i.nl; [2] Delft University of Technology, Department of Material Science and Engineering, Mekelweg 2, 2628 CD Delft, the Netherlands, [3] NXP Semiconductors, Gerstweg 2, Nijmegen, the Netherlands, [4] Technical University of Denmark, Department of Mechanical Engineering, DK-2800 Kgs. Lyngby, Denmark, [5] Vrije Universiteit Brussels, Research Group Electrochemical and Surface Engineering, Pleinlaan 2, B-1050, Brussels, Belgium

Key words: semiconductor devices, bond pads, wires, corrosion, electrochemical local probe techniques

Plastic encapsulated semiconductor devices are present in our daily life inside of our cars, computers, telephones and other electronic devices. The structure of the device is complex and its assembly is a multiple task. Encapsulation is a final step of assembly and is used for environmental protection of the device. An example of encapsulated devices is shown in fig. 1, left. Heart of the device is an integrated circuit (1) which is connected to the lead frame (2) via gold or copper wires (3) and is encapsulated in plastic (4).

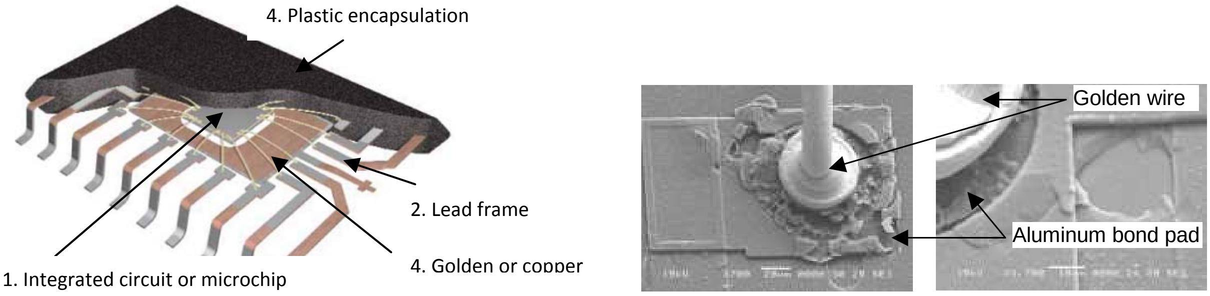

Figure 1 Schematic picture of plastic encapsulated device (left) and an example of aluminum bond pad corrosion (right)

Reliability of the devices depends on many factors, e.g. materials, assembly, usage, environmental conditions and many others [1, 2]. Corrosion of the device is a major reliability risk. Even small amounts of corrosion can cause a problem or a failure of the devices. Particularly, corrosion of metallization pads can be a significant issue (fig.1, right). The most common metallization is aluminum alloyed with small quantities of copper and/or silicon. Both positively and negatively biased aluminum metallization are susceptible to corrosion due to the amphoteric nature of aluminum. In the corrosive process reported, water permeates into the encapsulating plastics and diffuses to the bond-pads. While the ions arrive and accumulate at sites liable to corrosion, the electrochemical reaction occurs between the ionic aqueous solution and the metallization of the bond-pad [3]. In order to avoid corrosion and to increase reliability, it is crucial to study and control the moisture transporting path and the corrosive mechanisms.

Our initial aim is to understand corrosion mechanisms of aluminum bond pads. Taking into account the complex structure of the device and the small dimensions of the aluminum pads

(~50-100 μm) a special experimental approach is developed. Aluminum metallization lines together with gold are fabricated on a silicon wafer using the semiconductor technology in a clean room. Three dimensional electrodes are mimicked by two dimensional model specimens allowing the use of micro-electrochemical local probe techniques.

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Effects of lead free soldering on corrosion of electronics

Morten S. Jellesen, Daniel Minzari, Umadevi Rathinavelu, Per Møller, Rajan Ambat
Dep. of Mechanical Engineering, Technical University of Denmark,
Building 204, Kgs. Lyngby, Denmark, msj@mek.dtu.dk

The recognition of lead as a threat to health and environment has caused the European Union to pass a law which strictly limits the use of lead in electronic devices. This is a result of the Waste Electrical and Electronic Equipment (WEEE) and the Restriction of Hazardous Substances (RoHS) directives. As a replacement, high tin alloys are preferred including Sn/Ag, Sn/Ag/Cu, Sn/Cu, Sn/Ag/Bi, and various versions of these alloys. The use of any of these alloys requires a higher solder temperature during production of Printed Circuit Board Assemblies (PCBAs). For lead containing solder systems, the process temperature reaches approximately 235°C. For soldering with lead free alloys, a higher processing temperature of approximately 255°C is needed due to the higher melting point of such alloys. The actual temperatures at local areas of the PCBA can reach more than 270°C due to the difference in heat capacity of the materials used in a PCBA. This higher soldering temperature will result in degassing of chemicals from the printed circuit board laminate and components. Commonly used PCB laminates contains a flame retardant, e.g. TetraBromoBisphenol A (TBBA) which is known to decompose at 250°C, where it forms HBr as the major decomposition product. Also other aggressive chemicals apart from Hbr can degas from conventional laminate types and influence ElectroChemical Migration (ECM) behaviour and related corrosion aspects.

This work investigates the effects of higher soldering temperature for lead free soldering on corrosion of PCBA´s, specifically the effect of ECM. Clean chip capacitors and capacitors placed on a laminate and heated to various temperatures are investigated for ECM under condensing conditions. Electrochemical migration testing of the chip capacitors were carried out using an in-house built Single Component Electrochemical Migration (SCECM) under a potential bias of 6V. The SCECM equipment is has an in-situ videoing capability to record the dendrite growth sequence. Subsequent analysis of the components have been made using Scanning Electron Microscopy/Energy Dispersive Spectroscopy (SEM/EDS) to understand the chemical composition and morphology of the dendrites. Gas Chromatography Mass Spectrometry (GC-MS), Ion Chromatography (IC) and X-ray Photoelectron Spectroscopy (XPS) was used for analysing degassing chemicals from the laminate. Control ECM experiments were carried out using chip capacitors heated on clean glass plate. Results showed increased migration susceptibility for chip capacitors when heated on laminate within a temperature range of 250 – 300°C, and it was found that apart from bromine there are also other aggressive chemicals degassing from the laminate that could cause corrosion.

MECHANISMS OF ELECTROCHEMICAL MIGRATION OF TIN BY IN-SITU OPTICAL AND ELECTRON MICROSCOPY

Daniel MINZARI[1], **Morten JELLESEN**[1], **Per MØLLER**[1], **Krisitian MØLHAVE**[2], **Eric JENSEN**[2] **and Rajan AMBAT**[1]

[1] *Dep. of Mechanical Engineering, Technical University of Denmark, Kemitorvet Building 204, 2800 Lyngby, Denmark, dm@mek.dtu.dk*

[2] *Dep. of Micro- and Nanotechnology, Technical University of Denmark, Ørsteds Plads Building 345Ø, 2800 Lyngby, Denmark*

The times when electronic devices where expensive, high-end items, that were being taken well care off, are far gone, and today electronic devices are to be regarded as consumables that can be expected to be brought practically anywhere on the planet's surface. This has created challenges to electronic manufacturers, as device reliability is extremely hard to predict before a product is launched, and even the slightest change from a sub-supplier could potentially lead to catastrophic changes in the corrosion behavior of the device. Electrochemical migration in electronics is a process that occurs when two metallic conductors under a potential bias are connected by an aqueous electrolyte, which commonly originates from condensation of humidity from the external environment. Prone metals, such as i.e. Sn, Cu, Ag, Au, Ni, Pb, Pd [1] can be dissolved at the anode and migrate under the electric field to the cathode where they can be deposited in their reduced metallic state. The result can be the growth of a dendrite acting as a metallic bridge from cathode to anode, which short-circuits the two conductors with potential failure of the electronic circuit as a consequence. The main metals that are directly exposed to the environment on a common Printed Circuit Board Assembly (PCBA) are tin and tin solders, making the corrosion mechanisms of these in electronics a very important subject. Electrochemical migration of tin is an extremely delicate process, where even the slightest impurities on the surface can have a profound impact on the migration behavior. For this reason, an extensive research has been conducted over the past years, in order to understand the migration mechanisms of tin and how it is affected by various parameters. A novel chip has been developed, where a nanoscale silicon nitride window allows making in-situ electron microscopy observations of electrochemical phenomena, such as electrochemical migration [2]. This presentation will give an overview of the chemical, electrochemical and thermodynamic mechanisms of the electrochemical migration of tin with examples from in-situ observation from optical and electron microscopy. It is shown that the formation of a pH gradient inside the condensed nucleus is of crucial importance for dendrite formation, and the electrochemical reactions and growth mechanisms are presented, using examples from TEM observations of dendritic structures.

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Tempering effect on corrosion performance of magnesium alloys for biomedical applications

X. Zhang[a], G.M. Ferrari[a], M. Erinc[b], W.H. Sillekens[b]
TNO Science and Industry, Materials Technology, [a] Bevesierweg Gebouw MML,
1780 AM Den Helder, Netherlands
[b] De Rondom 1, 5612 AP Eindhoven, Netherlands

Abstract

As implant materials, magnesium alloys have a low density, specific strength that is near to the strength of bones (lower than of steel but higher than of polymer), and biodegradability advantages. This enables the implant to maintain strength and integrity for the time of recovery, and afterwards without necessity for removing the implant. However, clinical studies showed that the rate of biocorrosion of some magnesium alloys is still too high and there is a desire to slow it down[1].

In this study, the corrosion performance of magnesium alloys thermally treated at different conditions was investigated. AZ80, AE82 and ZM21 alloys were obtained by casting followed by extrusion. This results in a fine-grained, meta-stable microstructure with dissolved alloying elements, which is susceptible to tempering. The alloys were treated at 200 and 330°C for 2 hours, and at 415°C for 8 hours. Their corrosion behavior was studied using potentiodynamic polarization measurements in simulated body fluid (SBF) solution at 37°C. The results show that heat treatments had little effect on the corrosion of ZM21 alloy, but it significantly improved the corrosion resistance of AE82 alloy. The corrosion rate of AE82 decreased by about 10% after being treated at 200°C for 2 hours and decreased by 20% after being treated at 415°C for 8 hours. For the AZ80 alloy, although heat treatment did not significantly decrease the corrosion rate, it increased the breakdown potential about 40 mV, improving pitting resistance.

The morphology and the Volta potential of intermetallic precipitates in AE82 have been analyzed by SEM-EDS combined with SKPFM[2, 3]. This shows that Al-Nd(Y), Al-Mn(Nd,Y), Mg-Al precipitates exist in the AE82 alloy. Most of Mn and Nd were distributed at aluminium enriched areas. Zn was scattered in the matrix. The potential of intermetallic precipitates Al-Nd(Y) is higher than that of the precipitates Al-Mn, which means that the former has more cathodic influence than the latter on the corrosion of Mg alloys. Heat treatment until 415°C cannot melt intermetallic particles, but the β phase building up at grain boundaries provides a barrier against corrosion propagation into the adjacent grains [4].

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Initiation and Propagation of Localized Corrosion in AA 2024-T3 Aluminium Alloy

C. Luo[1], X. Zhou[1], A.E. Hughes[2], G.E. Thompson[1]
[1]Corrosion and Protection Centre, School of Materials, The University of Manchester, Manchester M13 9PL, U.K.
[2]CSIRO Materials Science and Technology, Private Bag 33, Clayton South MDC, Victoria 3169, Australia

A heterogeneous microstructure is intentionally developed in AA 2024 aluminium alloy during solidification and thermomechanical processes. As a consequence, the alloy is susceptible to localized corrosion since the galvanic coupling between the heterogeneous microstructure that provides driving force [1-3]. From previous work of the authors [4], it was found that localized corrosion is generally initiated at intermetallic particles. S-phase particles are considered to be anodic with respect to the aluminium matrix and undergo dealloying of magnesium and aluminium element. In contrast, Al-Cu-Mn-Fe-(Si) phase particles are relatively cathodic and induce trenching in the surrounding matrix. The aim of present study is to advancing the understanding of the relationship between the microstructure and the development of pitting and intergranular corrosion (IGC).

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) equipped with EDX facilities were employed to examine the corrosion sites. Electron backscattering diffraction (EBSD) and X-ray tomography were performed to investigate the development of IGC.

It was found that continuous localized corrosion sites are featured by a relatively large volume of S-phase cluster that is buried beneath the alloy surface with only a small area of connection to the testing environment. This special geometry is thought to restrict diffusion between the local region and the bulk solution, therefore, maintaining the necessary acidity of the solution at the corrosion front for continuous propagation. After initiation, corrosion propagation tends to follow grain boundaries. EBSD mapping shows little evidence correlating grain boundary misorientation to the IGC development. Further, X-ray tomography revealed the connection of IGC to the continuous localized corrosion.

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CORRELATION BETWEEN MICROSTRUCTURE, MICROHARDNESS, AND CORROSION SENSITIVITY OF AA 2024-T3 FSW WELDED JOINTS

Emilie Bousquet*, Angéline Poulon-Quintin, Monique Puiggali*,
Marie Touzet*, Olivier Devos***

* Université Bordeaux, Laboratoire de Mécanique Physique-CNRS-UMR 5469, 351 cours de la Libération, 33405 Talence Cedex, France
**CNRS, Université de Bordeaux1, Institut de Chimie de la Matière Condensée de Bordeaux, 87 avenue du Docteur Schweitzer, 33608 Pessac Cedex, France

An experimental investigation has been carried out in order to find a relationship between microstructure, microhardness and corrosion resistance of AA 2024-T3 FSW welded joints.

Microhardness tests performed showed significant differences across the welded joint corresponding to the four main zones: nugget, thermomechanically affected zone (TMAZ), heat affected zone (HAZ) and an unaffected zone (which corresponds to the base metal).

The nugget zone experiences the higher temperature (around 500°C) as well as the most important plastic deformation. The grains are refined and equiaxed. The size and the arrangement of submicron hardening precipitates and constituent particles are also affected compared to the base metal.

The TMAZ, adjacent to the nugget, is the zone through which the material is plastically deformed and heated. The grains and constituent particles are disoriented and elongated. The combination of deformation and temperature peak results in the growth and the coarsening of the strengthening precipitates.

The HAZ experiences only an heating effect. The grain structure and the constituent particles are the same as the base material. However, the hardening precipitates can dissolve or coarse.

A small electrochemical cell was used to estimate the corrosion sensitivity. Measurements of the local free potential were performed all along the weld.

In addition, microscopic observations were realized after electrochemical tests.

The results show a direct correlation between mechanical, chemical and metallurgical parameters involved in galvanic coupling and local corrosion processes.

Studying, modeling and predicting of pitting corrosion of stainless steels in moving liquids

***Klara TARANTSEVA**, Vladimir PAKHOMOV*
Penza State Technological Academy, Penza, Russia, kr@pgta.ac.ru
Moscow State University of Engineering Ecology, Russia, pakhomov@rambler.ru

Pitting resistance of stainless steels depends on many internal (the alloy nature, composition, structure, and its surface state) and external (solution composition, temperature, motion, etc.) factors of corrosion. The quantitative analysis of combined effect of these factors is hindered by both a lack and a low informativeness of reference data on the corrosion resistance of stainless steels in various media. That is due to the fact that the studies are conducted under conditions of uncontrolled hydrodynamics and mass transfer, on models that do not reflect the main regularities of pit development.

At the same time, the scientific value and feasibility of any study is determined, on the one hand, by completeness and concreteness of information obtained and, on the other hand, by the area of its feasibility. Therefore, a degree of universality of solution is one of the most important criteria of the quality of a study.

The completeness and specificity of information are considered to be achieved, if the methods of determining the effects of all factors (which, according to present views, are of importance for test process) are presented, and the quantitative relations between the values are determined.

The necessity to take into account many factors affecting the process does not pose considerable difficulties, if the problem can be completely solved analytically. However, in the experimental and numerical methods, the study becomes much more complicated with an increase in the number of variables, because neither numerical solutions nor experimental results determine the internal relations characterizing the problem. Thus obtained separate dependences, which correlate some variables and are not combined into a common equation, are not universal, and the results of investigations cannot be adequately carried over to real conditions.

In these cases, the quality of solution and its universality can be enhanced by using the method of generalized variables, that is, the theory of similarity and dimensional analysis. The latter enables one to determine the model conditions, under which the results of the study performed on the model can be carried over to the industrial equipment.

Therefore, to elaborate the structure and the procedure of study of pitting corrosion in moving media, it is necessary to simulate the event, which is similar to the object, and conduct the tests in such a way that the results can be carried over to the industrial conditions.

To do this, it is necessary that the model system has known solutions of hydro- and mass-transfer problem and adequately reflects the processes taking place in a pit. In this case, provided that the similarity criteria are equal, the results which are obtained for the model system can be carried over to and used in the industrial conditions, which are described by the same system of differential equations and identical initial, boundary, geometrical, and physical unambiguity conditions.

In our presentation, we consider the requirements imposed on the corrosion study and propose the procedures of studying, modeling and predicting of pitting corrosion of stainless steels in moving liquids, based on the method of generalized variables.

Corrosion protection of ultra thin aluminium oxide coatings grown with Atomic Layer Deposition on steel substrates

Belen Diaz[1], *Jolanta Świątowska*[1], *Antoine Seyeux*[1], *Vincent Maurice*[1], *Philippe Marcus*[1],
Emma Härkönen[2], *Mikko Ritala*[2]

[1]Laboratoire de Physico-Chimie des Surfaces, CNRS (UMR 7045), Ecole Nationale Supérieure de Chimie de Paris (Chimie ParisTech), Paris, France
[2]Laboratory of Inorganic Chemistry, University of Helsinki, Helsinki, Finland

Ultra thin (10 and 50 nm) protective aluminium oxide films were grown with Atomic Layer Deposition (ALD) on steel (100Cr6) substrates. ALD is a thin film deposition method derived from Chemical Vapor Deposition (CVD). It is based on alternating pulses of precursors (trimethyl aluminium, $Al(CH_3)_3$, and H_2O in the present study) separated from each other with inert gas purging and characteristically enables depositing highly uniform thin films with low defect density and precise thickness control. The deposition temperature was 160°C. The corrosion resistance was measured in deaerated chloride-containing aqueous solutions (0.2 M NaCl, pH7-7.2) at ambient temperature, by means of electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization (CV), and surface analysis was performed before and after corrosive attack by Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) depth profiling and chemical imaging.

The uncovered substrate surface fraction was extracted from the CV and EIS data obtained on the bare and coated samples. Both techniques shows that increasing the coating thickness from 10 to 50 nm improves the sealing performance of the coating by about two orders of magnitude, the uncovered surface fraction reaching the 10^{-4} range for 50 nm thick coatings.

Depth profiling of the pristine coatings shows that some fragments of the organic precursors used for deposition are trapped inside the coating matrix and accumulate in the region close to the interface. Increasing the thickness does not influence this contamination by precursors. A significant reduction of OH contamination has been observed inside the coating but not at the interface when thickening the layer. Iron oxide is observed in the interfacial region due to the presence of native oxide on the substrate surface and/or growth of a spurious oxide in the initial stage of deposition.

The data obtained by chemical mapping after corrosive attack at open circuit potential for 60 min of the 10 nm thick coatings show that pits covering a substantial surface fraction (~14%) are formed. Smaller pits (< 1 μm in average) coexist with the presence of iron in the substrate matrix. They dominate the pit surface fraction due to their high density and likely release the iron corrosion products deposited all over the extreme surface. Larger pits (~5 μm in average) coexist with the presence of chromium in the substrate matrix. They form a crown of hydroxylated iron corrosion products at their periphery indicating a higher iron release. Elemental depth profiling shows a marked decrease of the coating/substrate interface concentration in AlC-containing species.

The data obtained after corrosive attack of the 50 nm thick coatings show no breakdown of the thicker coatings and no deposition of iron corrosion products.

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Composite structures on the base of nanotubular anodic oxide coatings on aluminium and titanium and their possible applications

Yakovleva N.M.[1], Yakovlev A.N.[2], Chupakhina E.A.[1], Kokatev A.N.[3]

[1]Karelian State Pedagogical Academy, [2] Petrozavodsk State University,
[3]Nelan-oksid LTD, Petrozavodsk, Russian Federation

Anodic oxidation is a commonly used method for surface treatment especially in forming self-organized porous alumina structures. Nanoporous alumina (NPA) has become a key template material for fabrication of nanostructured materials. Similar to anodic alumina self-ordered titania nanotubes can be fabricated by anodization of titanium in water and waterless solutions of acids and the salts containing fluoride ions. Nanotubular anodic titania is a very promising material for applications in many scientific and technological areas.

It seems tempting to expand nanostructured aluminas and titanias functional properties by doping of metal ions. In the present paper we summarize our data on (i) nanostructured anodic titania and alumina films concerning their structure and mechanism of growth; (ii) development of the composite materials by modification of oxide matrix with Ag. In this case Ag-nanoparticles are immobilized in oxide pores or tubes. It prevents from their aggregation and protects from external influences. Also the paper deals with the investigation of antibacterial activity of developed nanocomposite structures.

The investigation of highly ordered porous anodic alumina (PAA) films formed in different acid solutions and titania nanotubes (TNT) obtained via constant voltage anodization in water-free electrolytes on the base of ethylene glycol and glycerol added NH_4F were carried out. In the present work we studied growing behavior of amorphous nanostructured anodic oxide films on titanium and aluminium with focusing on their structural analysis on two scales, atomic (mutual atom arrangement), and mesoscopic (mutual pore/tube arrangement). X-ray diffraction (XRD), transmission and scanning electron microscopy (TEM &SEM) as well as Fourier transform infrared spectroscopy (FTIR) were used to analyze the structure of these films. To obtain the qualitative data concerning the size, form and mutual arrangement of the pores/tubes observed on the oxide surfaces the computer procession of TEM and SEM-images was developed.

It has been shown that the morphology of tubular TiO_2 is affected strongly by the anodizing conditions such as solution pH and anodization voltage. The nanotube diameters that can be obtained range from 20 nm to 200nm, the wall thickness – from 10 to 20 nm. As follows from TEM images of the surface of TNT the mutual arrangement of the tubes strongly differs from perfect hexagonal pore arrangement which is typical for highly ordered PAA. The results of SEM investigation clearly indicate presence of Ag nanoparticles on the pore/tube walls. The 24-hours test of cultures Staphylococcus epidermidis and Escherichia coli was used for the definition of antibacterial activity of oxide coatings. It was shown that the presence of composite coatings makes Staphylococcus reproduction rate ten times smaller than without them. Finally the possible applications of the developed nanocomposite coatings for water and air decontamination are considered.

Triggered release of intercalated organic inhibitors from Layered Double Hydroxide nanocontainers: a systematic study

M.G.S. Ferreira[1,2], A.C. Bastos[1], O.V. Karavai[1], S.V. Lamaka[2], M.L. Zheludkevich[1]
[1] DECV/CICECO, Universidade de Aveiro, 3810-193 Aveiro, Portugal
[2] ICEMS, Instituto Superior Técnico, UTL, Av. Rovisco Pais, 1049-001, Portugal
Portugal

The low density and mechanical properties of magnesium alloys make them attractive materials for the aeronautic and automotive industries. The reduction of vehicles' weight lowers fuel consumption and decreases CO2 emissions. The main limitation of magnesium alloys is their weak corrosion resistance. A method currently under development is the use of protective coatings produced by sol-gel that contain Layered Double Hydroxyde nanocontainers with inhibitors. Still difficult to achieve is the inhibition of corrosion at defects that may appear on the coating.

In this communication the corrosion of AZ31 is studied using microelectrode techniques (SVET, pH, O_2, Mg^{2+}) and electrochemical measurements made on the bare alloy and on the coated substrate containing artificial defects. The inert metallic microelectrode was employed here to study the distribution of local oxygen concentration near cathodic and anodic defects. The microcapillary-based potentiometric sensors were used to acquire distribution of OH^- and Mg^{2+} ions during the corrosion processes in micro-defects of coatings and on the bare alloy. The important role of the one-electron electrochemical oxidation process is demonstrated, explaining the intensive hydrogen evolution in anodic zones. Moreover the interdependence of kinetics and mechanisms of corrosion processes in micro-defects and protective properties of the coatings is demonstrated. The sequence of events, determined at the micro-scale, gives new insights on the mechanisms of corrosion process that allow the improvement of the existing protective coatings.

EXPOSURE OF SILVER TO ATOMIC OXYGEN

Antonius de Rooij
European Space Agency
European Space Research and Technology Centre
Noordwijk, The Netherlands

Materials for use in space applications in low earth orbit and exposed to the hostile combination of atomic oxygen and thermal cycling have to be screened for their susceptibility to withstand this environment over very long periods. Since real-life testing on board spacecraft for long duration is not practical accelerated testing on the ground in a controlled environment is of the utmost importance to be able to predict the behaviour of materials under atomic oxygen conditions. One of the difficulties of laboratory simulation is translation of the test results to the real space conditions. To obtain reasonable test durations, acceleration times of a factor 1000 are necessary. The testing is performed in the ESTEC ATOX system, which used the laser breakdown principle to obtain neutral atomic oxygen with an energy of ca 5eV, comparable to the impact energy of the oxygen atoms on spacecraft surfaces in the ram direction. Test environmental factors like specimen temperature, atomic-oxygen flux etc. are held constant during the test. Silver can also be oxidized in a plasma asher using an oxygen leak. For the purpose of this investigation both systems are used. Slow oxidation using a low oxygen pressure and high temperature in the plasma asher produces the brownish coloured Ag_2O. High oxygen pressures and a low operating temperature produce the black AgO.

An important property in a space environment is the work function. The work function WF is measured using a Kelvin probe. The ΔWF(AgO-Ag) is measured as 1.1V while the ΔWF(Ag_2O -Ag) is measured as 0.2V. The Ag_2O shows semi-conductor properties. Heating the AgO to ca 130C to transform it to Ag_2O lowers the workfunction but the resulting layer does not show semi-conductor properties.

The silver-oxide is characterized using scanning electron microscopy. The black AgO is a powdery layer easily removable having numerous pores. The size of these pores is estimated from SEM as 100-250 nm. Under this layer the brown Ag_2O is visible having a different morphology and pore size and it adheres very well to the silver substrate.

In the space environment the silver oxide layer shows heavy flaking due to thermal and mechanical stresses with a flaking thickness of 0.5 µm. Laboratory experiments in the past showed that the silver oxidation follows a linear process up to 50 nm after which the growth rate is parabolic and a volume oxide/metal ratio of 2. An oxide growth model is proposed which takes into account free-molecular flow in micropores.where the conductance of the pores is calculated using the Clasusing factor. The tortuosity and non-circular shape of the micropores are taken into account. Classical diffusion through the non-porous areas is assumed. This model predict linear-parabolic growth for the oxide layer. The constants in the model are used for calibration with the oxide thickness obtained in the space environment. In this way the growth model can be used for prediction of the oxide growth under other circumstances.

Oxide nanofilms on silver, copper and their alloys with gold: the kinetics of anodic formation and semiconductor properties

S. Grushevskaya, S. Ganzha, A. Vvedenskii, D. Kudryashov

Voronezh State University, Universittskaya pl. 1, Voronezh, 394006, Russia

alvved@chem.vsu.ru, tel. +7(4732) 208546, fax +7(4732) 208755

Oxide nanofilms were formed during the anodic potentiostatic polarization in deaerated 0.1 M KOH solution on polycrystalline copper, silver, Ag-Au and Cu-Au alloys (X_{Au} = 1; 4 and 15 at.%) as well as on single crystals (001), (011) and (111) of silver. The state of the electrode surface was monitored with use of SEM and XPS.

Photoelectrical *in situ* measurements of semiconductor properties were performed by means of photocurrent i_{ph} and photopotential E_{ph} spectroscopy with the set of light-emitting diodes. The original equipment allowed us to measure the photocurrent and the polarization current synchronously. Photopotential was measured in the open circuit after the polarization switching off. The intensity of light flux was constant and equal to $2 \cdot 10^{15}$ photon s^{-1} cm^{-2}.

The kinetics of oxide formation on all electrodes is solid phase diffusion. At the initial stages the role of nucleation processes is important.

It was found that in Ag(I) oxide formed on silver and Ag-Au alloys $E_{ph} < 0$ and $i_{ph} > 0$ independent of the potential of Ag_2O formation and the film thickness. It proves the n-type conductivity connected with the excess of metal in oxide structure. The band gap is 2.1 - 2.3 eV depending on the substrate. The amplitude of photocurrent and photopotential increases with the growth of the film thickness L form 2 to 100 nm. At the initial stage of Ag(I) oxide formation the equations $i_{ph} \sim L$ and $E_{ph} \sim L^2$ are valid [1]. The concentration of donor defects decreases in the row $Ag_{poly} > Ag_{hkl} >$ Ag-Au.

Cu(I) and Cu(II) anodic oxides formed on copper and Cu-Au alloys are p-type semiconductors that is proved by $E_{ph} > 0$ and $i_{ph} < 0$. The amplitude of photocurrent and photopotential increases with the growth of the film thickness as was the case with Ag(I) oxide. However, the process of copper corrosion by the trace of dissolved oxygen in deaerated alkaline solution is thermodynamically possible.

An effect of changing of the photocurrent polarity was revealed in Cu(I) oxide at certain thickness and potential. Such an effect was not revealed in Ag(I) oxide. The change of the photocurrent polarity could be caused by the change of the product of copper oxidation - from n-type Cu(I) hydroxide to p-type Cu(I) oxide as well as the change of the donor-acceptor balance in the crystal lattice of Cu_2O.

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1. A. Vvedenskii, S. Grushevskaya, D. Kudryashov, S. Ganzha, J. Solid State Electrochemistry, in press (available on-line; DOI 10.1007/s10008-009-0952-9)

Atmospheric corrosion of silver coated phosphorous bronze: morphological evolution

D. Mombello, S. Grassini, B. De Benedetti, E. Angelini
Dip. Scienza dei Materiali ed Ingegneria Chimica, Politecnico di Torino, Torino, Italy
Corresponding Author: sabrina.grassini@polito.it

As well known P is added in percentage of approximately 0,50 wt% to bronze alloys, not only to deoxidize the alloy, but also to increase the mechanical properties. The combination of good mechanical and electrical properties and a low cost makes P-bronze suitable for the manufacturing of electric contacts in electronic devices.

In the present work the effects of the P on the corrosion behavior of P-bronze switches are described. The P-bronze was silver coated only on the working surfaces of the contact areas.

The samples have been submitted to controlled atmospheric corrosion tests lasting 1 year. The corrosion process has been studied at different steps.

After each step the evolution of the corrosion products was studied by means of a Field Emission Scanning Electron Microscope equipped with a Energy Dispersive X-Ray Spectrometer for elemental analysis. The comparison between the images deriving from different samples has been done at different magnitudes.

After the first step the surface of the samples showed a dispersion of little spots of corrosion products (in the order of 1 nm diameter) mainly localized at the silver grain boundaries. The EDS analysis pointed out the presence of phosphates right on the areas occupied by the products. Furthermore the EDS images underlined a low content of Ag in the areas interested by the corrosion products.

Subsequently, with the progress of the atmospheric attack, the corrosion products covered completely the silver grain boundaries. At the same time, a new phenomenon occurred, consisting in the formation of bigger corrosion products with the appearance of rollers with rough surface.

The investigation has underlined not only the growth of the products (the diameter reaches 10- 20 nm), but also their dispersion on the silver grains. The bigger products, previously observed, have been converted to a not well defined shape. The EDS analysis pointed out the presence of a spread corrosion on the sample, with big corrosion areas in correspondence to the above-mentioned products.

At the end of testing, the products on all the surface have reached the dimension of 50- 100 nm.

FESEM analysis conducted to a satisfactory morphological investigation, which allowed the evaluation of the corrosion process. Moreover, the EDS analysis has confirmed the data obtained by the FESEM.

This work has identified a not previously described mechanism. Specifically the diffusion of P from the bronze matrix has been detected. Fluorescence analysis underlined that the P content on the silver surface reached a value which is more than 5 times the original content in the alloy. The corrosion is clearly affected by the defects of the silver layer and produces, in some cases, the undesired effect of insulating the surface of the electrical contact. It is demonstrated that the break of the electrical contact depends from the quantity and the consistence of the corrosion products.

Corrosion mechanisms of silver thin films in alkaline Na_2S solutions

N. Li [1,2,3], *A. Galtayries*[1], *I. Frateur*[1], *V. Maurice*[1], *P. Marcus*[1], *S. Grachev*[2],
E. Søndergård[2], *L. J. Singh*[3], *D. Nicolas*[3]
[1] *Laboratoire de Physico-Chimie des Surfaces, UMR 7045 CNRS/Chimie ParisTech, 11 rue Pierre et Marie Curie, F-75005 Paris, France*
[2] *Surfaces du Verre et Interfaces, UMR 125 CNRS/Saint-Gobain, 39 quai Lucien Lefranc, F-93303 Aubervilliers, France*
[3] *Couches Minces, Saint-Gobain Recherche, 39 quai Lucien Lefranc, F-93303 Aubervilliers, France*

Silver thin films are increasingly used in the glass industry as thermal control layers. Ultra-thin Ag layers are transparent in the visible range and reflect infra-red radiations. However, Ag is prone to deteriorate due to corrosion in humid environment. Corrosive species (*e.g.* S^{2-}, HS^-, Cl^-) dissolve in moisture and attack Ag films by electrochemical processes. The aim of our work is to understand the corrosion mechanisms of the Ag thin films in order to improve their performance.

Ag films (10 nm to 1 µm thick) were prepared by DC magnetron sputter-deposition. For such layers, the influence of the Ag film thickness and annealing conditions on the Ag grain size and roughness was studied by atomic force microscopy (AFM). The electrochemical behaviour, kinetic, and structural aspects of Ag were investigated in 1mM Na_2S solutions (pH 13). On the one hand, ~360 nm thick Ag were used for the cyclic voltammetry and the electrochemical quartz crystal microbalance (EQCM) measurements. On the other hand, *in situ* electrochemical scanning tunnelling microscopy (EC-STM) was performed on 1 µm Ag layers. Surface chemical characterisations by XPS and ToF-SIMS were also performed.

The polarization curves recorded with a sweep rate of $5\ mV.s^{-1}$ showed that for $-0.53 \leq E \leq 0.24$ V/ENH, 3D layers of Ag_2S were formed with a thickness of several tens of nanometres. From curves plotted at different Na_2S concentrations (1 and 10 mM), it was concluded that Ag_2S growth was limited by the diffusion of HS^- from the bulk solution to the electrode surface (for $-0.10 \leq E \leq 0.24$ V/ENH). These 3D sulphide layers were cathodically reduced for $E < -0.53$ V/ENH. A similar reversible electrochemical behaviour of Ag was observed for 10 nm and 360 nm thick films. The growth rate of Ag_2S at open circuit potential was determined *in situ* by EQCM to be $0.1\ nm.min^{-1}$.

EC-STM was used to investigate the structural evolution of the Ag films at the nanometre scale. Facetted crystalline 3D silver grains were observed at $E= -1.10$ V/ENH. Terraces at the surface of the grains separated by single atomic steps could be resolved. In the potential range of $-1.07 \leq E \leq -0.87$ V/ENH, no specific 2D adsorbed structure could be resolved because of the multiatomic surface roughness of the grains. For $E > -0.57$ V/ENH, the formation of 3D grains of sulphide could be observed at the surface of the silver grains and their growth was observed with increasing polarization time. After electrochemical cathodic reduction, the surface roughness increase of the silver grains was observed to persist, showing the irreversible modification of the electrode topography once the 3D growth of sulphide has been initiated. These irreversible modifications were not observed if anodic polarization was limited to the range of 2D sulphur adsorption (*i.e.* for $-1.07 \leq E \leq -0.87$V/ENH).

INFLUENCE OF PLASTIC STRAIN AND TEMPERATURE ON THE HYDROGEN EVOLUTION REACTION ON NICKEL (100) SINGLE CRYSTAL SURFACES IN SULPHURIC ACID

Choukri LEKBIR[1], Hafida EL ALAMI[1], Corinne HUVIER[1], Juan CREUS[1], René SABOT[1], Egle CONFORTO[2],
Xavier FEAUGAS [1]

[1]LEMMA, EA3167, Université de La Rochelle, Av. Michel Crépeau, 17042 La Rochelle, France, choukri.lekbir@univ-lr.fr
[2]FREDD, CNRS 3097, France, egle.conforto@univ-lr.fr

The HER reaction pathway on nickel (100) single crystal surfaces in sulfuric acid medium can be presented by a Volmer-Heyrovsky mechanism. The corresponding elementary kinetic parameters as symmetry coefficients, activation enthalpies, number of active sites, have been simulated via a thermokinetic model using experimental data. These parameters can be affected by plastic strain. Plastic strain modifies the density and the distribution of storage dislocations affecting the surface roughness at atomic scale and generating additional active adsorption sites. Furthermore, surface emergence of mobile dislocations induces the formation of slip bands which modify the surface roughness and the electronic state of the surface. The consequence of plastic strain on HER is explored. Single crystal specimens are plastically prestrained by uniaxial tensile test at different levels of plastic strain. We found a maximum of surface excess due to the emergence of slip bands at the surface for $\varepsilon_p = 50\%$. The height of steps and distances between consecutive steps caused by the emergence of dislocation bands have been evaluated using atomic force microscopy (AFM). A statistical approach has then been performed on all specimens and it is shown that the strain bands are homogeneously distributed over the whole surface of specimens with an average total height of 100 nm. Moreover, a study by transmission electronic microscopy (TEM) allows to approach the dimensional characteristics of heterogeneous dislocation distributions. The effect of plastic strain and temperature on HER on unstrained (US), strained with suppression of strain bands (SWB) and strained (S) Ni (100) single crystal surfaces is electrochemically studied in 1M H_2SO_4 solution over the temperature range of 283-313K using cathodic polarization tests. The polarisation curves of Ni (100) specimens show that plastic strain and temperature significantly influence the cathodic current densities. The cathodic current densities on US samples increase as temperature increases, which mean that the HER is a thermally activated process. For S specimens, independently of temperature and potential, the cathodic current densities increase when plastic strain level increases from 0 to 2%. Over 2%, the current densities decrease and seem to stabilise at values higher than the values of the US specimens. The increase of current density is due to the development of homogeneous dislocation structures and the decrease is due to the development of heterogeneous dislocation structures. The comparison of electrochemical behaviour of SWB and S states shows a deactivation process associated with the appearance of the Ni (111) surfaces in relation with slip band emergence.

Study of the Hydrogen diffusion and trapping mechanisms into quenched and tempered HSLA steels using electrochemical permeation technique

Simon Frappart[1-2], **X. Feaugas**[2], **J. Creus**[2], **Florian Thébault**[1], **Laurent Delattre**[1], **Hervé Marchebois**[1], **M. Hörstemeier**[3]

[1] *Vallourec Research Aulnoye (VRA), SCC Department, 59620 Aulnoye-Aymeries, FRANCE*
[2] *Laboratoire d'Etudes des Matériaux en Milieux Agressifs (LEMMA), Université de la Rochelle, FRANCE*
[3] *Salzgitter Mannesmann Forschung (SZMF), Duisburg, GERMANY*

Hydrogen embrittlement may be responsible for premature failure of steels when exposed to sour service environment. Different mechanisms (HIC, SSC, SOHIC…) have been described in the literature.

The purpose of this article is to contribute to the understanding of the hydrogen diffusion and trapping mechanisms in High Strength Low Alloy (HSLA) steels, expecting to discriminate critical parameters for the susceptibility to hydrogen embrittlement. Investigations were carried out on Fe-C-Mo steels with a quenched and tempered martensitic microstructure. Hydrogen diffusion has been modelled by using an electrochemical permeation setup under a cathodic charging within an acid media (H_2SO_4). The influence of charging conditions at ambient temperature shows a relation between the apparent diffusion coefficient D_{app} and the apparent subsurface concentration of hydrogen C_{0app}. It leads to the definition of two charging domains, associated either to hydrogen diffusion or to hydrogen trapping into the material. This distinction is directly correlated to the amount of irreversible traps occupied in the steel. Experiments at different temperatures have also been performed to determine the activation energies of the diffusion and trapping processes.

Effect of SMAT on corrosion properties of biomaterials

Jelliti Sami[1], Richard Caroline[1], Retraint Delphine [2]
[1]Roberval laboratory, UMR 6066 CNRS, University of Technology of Compiegne,
60200 Compiegne, France
[2]LASMIS, FRE 2848 CNRS, University of Technology of Troyes, 10100 Troyes,
France

Abstract:

By means of Surface Mechanical Attrition Treatment (SMAT), a nanostructured surface layer was formed on a 316L and TA6V. Microstructure features of various sections in the surface layer, from the strain-free matrix to the treated top surface, were systematically characterized by using Optical microscope (OM), Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) observations.

In this study, potentiodynamic polarization tests were performed to evaluate the corrosion resistance of various biomaterials in a Ringer's solution.

The surface oxide film formed on biomaterials and its stability in biological environments play a decisive role for the biocompatibility of implants. In this study, passive oxide films formed on biomaterials surfaces and their natural growth in a Ringer's solution have been investigated by Scanning Electron Microscopy (SEM), Atomic Force Microscope (AFM) and X-ray Photoelectron Spectroscopy (XPS).

Keywords : corrosion, biomaterials, microstructure, oxide films, Ringer's solution.

Influence of deformation on the corrosion behavior of biomedical alloys

J.C.S. Fernandes[a,]*, T.M. Silva[a,b] and M.J. Carmezim[a,c]

[a] ICEMS/DEQB, Instituto Superior Técnico, TULisbon, 1049-001 Lisboa, Portugal
[b] Mech. Eng. Dept., Instituto Superior de Eng. de Lisboa, 1959-007 Lisboa, Portugal
[c] Mech. Eng. Dept., Inst. Politécnico de Setúbal, ESTSetúbal, 2914 Setúbal, Portugal

Abstract

In recent years, nearly equiatomic NiTi or Nitinol has been attracting considerable interest for biomedical applications due to its unique combination of shape memory effect and superelasticity with a biocompatibility comparable to that of Ti. The shape memory effect has been successfully used for many clinical applications in orthopaedics, orthodontic archwires, dental implants, scoliosis correction, vena cava filters and cardiovascular endoprostheses [1].

The wide spectrum of application in implantology imposes special requirements on the biocompability of Nitinol. The two main factors that determine the biocompatibility are the host reaction induced by the material and its degradation in the body environment. Because Ni is capable of eliciting toxic and allergic responses, corrosion, with release of Ni ions, is the greatest problem that can be faced after NiTi implantation.

The characterization of Nitinol corrosion resistance in static conditions has been studied by this group, among others, and the results have already been published [2]. However, implants in the body are working under loading/unloading conditions, being deformed in the plastic regime [3], but there is still little information on the behaviour of the alloy under mechanical stresses. As it is known, the corrosion resistance of Nitinol is due to the TiO2 rich surface oxide that naturally forms on its surface. Although the bulk alloy is expected to withstand large deformations, due to its superelasticity, there is a concern relative to the response to mechanical stresses of the surface oxide layer that may crack, exposing the underlying alloy and allowing for the release of nickel.

The aim of the present work is to assess the Nitinol corrosion performance after elastic and plastic deformation. The results obtained from d.c. polarization, electrochemical impedance spectroscopy, photoelectrochemical measurements and XPS surface analysis will be presented. Moreover, the knowledge acquired will be the keystone for the development of a surface treatment that guarantees a low Ni content in the passive film.

Keywords:

NiTi Alloys, corrosion,deformation, biomedical materials,

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Problem of phase transformations in the surface layer of homogeneous alloys at selective dissolution: thermodynamic, kinetic and corrosion aspects

Alexander VVEDENSKII, **Igor MARSHAKOV, Oleg KOZADEROV**
Voronezh State University, Russian Federation, alvved@chem.vsu.ru

During selective dissolution (SD) or corrosion of homogeneous A,B-alloy under certain conditions there are sharp changes in morphology of an initial surface. Such changes showing as system of micro- and macropores, fractures, ulcers and canals, routinely influence corrosion and mechanical durability of alloys in extreme negative way. Mechanism of morphological instability origin is extremely combined. Now it was established that surface development is caused by assemblage of interdependent chemical, nano-structural and phase changes in a state of surface layer of an alloy, in turn stimulating by anodic process. In the given work various aspects of the problem of phase transformations (PT) with participation of an electropositive component B at SD of a binary alloy are discussed.

By methods of thermodynamics of nonequilibrium processes it is shown, that nonequilibrium vacancy subsystem of A,B-alloy (originating as a result of vacancies injection in its surface layer during A ionization) changes electrochemical potential of both components and forms a thermodynamic basis for anodic disintegration of the solid metal solution. Low efficacy of vacancies sinks not only favours to PT realization, but also provides an opportunity for enough intensive diffusive transfer of A component from alloy volume to its surface.

Role of PT in originating of concentration borders of corrosion resistance of binary alloys is discussed. It is shown that excess in an alloy potential of critical potential E_c serves as necessary condition of PT, but a sufficient condition of process $B_{(alloy)} \rightarrow B^0$ (and also of corrosion resistance fallout) is achievement of a critical supersaturation of surface layer on vacancies; this parameter is convenient to characterize with the critical anodic charge q_c. Within the framework of the model taking into account the lateral diffusion of ad-atoms B and evolution of electrode surface, calculation of E_c is carried out. It was established that analysis of dependences E_c on $c_{A^{z+}}$ and X_A allows us to reveal the nature of controlling stage of alloy SD in the overcritical regimen of polarization. Volume diffusion at comparable rates of mass-transfer in an alloy and solution is such stage for systems Ag-Au | Ag^+ and Cu-Au | Cu^{2+}.

The special attention is given to determination of PT process kinetics actually at $E > E_c$. It is based on the original graphical method of nucleation mass-transfer determination from the data of A,B-alloy chronoamperometry. For Cu,Au- and Ag,Au-alloys it was established that process $Au_{(alloy)} \rightarrow Au^0$ proceeds in the surface-diffusion regimen of growth of gold 3D-nuclei in conditions of instantaneous nucleation. Presence of different surfactants in the corrosion medium, as well as doping of an alloy (Ti, Ni, Si) does not change kinetics of recrystallization, but results in arise of E_c and reduces the rate of PT.

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On the role of electron structure in corrosion-electrochemical behaviour of iron-based alloys

Olga Kasparova[1]***, Yuri Baldokhin***[2]
[1] Karpov Institute of Physical Chemistry, Moscow, Russia, [2] Semenov Institute of Chemical Physics, Russian Academy of Sciences, Moscow, Russia

By means of gamma-resonance (Mössbauer) spectroscopy the hyperfine magnetic and electron structure of the iron-based alloys containing different corrosion-resistant alloying elements (Cr, Ni, Si) is studied. With the Normos program package Mössbauer spectra are processed and their parameters are estimated. The Mössbauer spectroscopy data are considered in relation to the corrosion-electrochemical behavior of the alloys studied.

It is shown that with an increase in chromium content from 5.8 to 30.7 wt. % in Fe–Cr alloys the effective magnetic intensity decreases and isomer shift becomes more negative. This evidences the chromium-caused increase in the *s*-electron density at iron nuclei. It is important to emphasize that noticeable changes in the electron structure of the Fe–Cr alloys take place on reaching the first chromium critical concentration (~11–12% Cr) that provokes drastic improvement in the passivability in dilute sulfuric acid solutions

The hyperfine structure and stability of the passive state of Fe–23% Cr alloy in 1 n sulfuric acid solution are studied as a function of the impurity-elements content and the heat treatment conditions. The passive state of the alloy is most easily destroyed after the ageing at 475°C, which is caused (according to Mössbauer spectroscopy data) by the solid solution separation, with the formation of zones with lower chromium concentration. In such zones isomer shift is more positive. The zones depleted in chromium play the part of active sites of dissolution, which leads to the disturbance of the passive state.

Alloying of Fe– (15, 20, 25)% Cr alloys with ~5% Si is found to substantially affect the shape and parameters of the Mössbauer spectra. The effect is most pronounced in Fe–25% Cr–5% Si alloy. Silicon changes the atomic structure of the alloys studied making it more heterogeneous and promoting the formation of chromium-based clusters with different number of chromium atoms in the nearest neighborhood of iron atoms. The presence of alloying silicon additions in annealed Fe–Cr alloys increases isomer shift, which indicates the decrease in the charge density on iron nuclei. Based on combined data of Mössbauer spectroscopy and electrochemical investigation, we suppose that the improvement of passivability of the alloys containing silicon in the active-passive transition range and the acceleration of the dissolution in the active range are caused by silicon, which changes the charge density on iron nuclei and, hence, the hemisorptive interaction between surface iron atoms and solution components.

It is shown that with an increase in chromium content from 10 to 20% in quenched Si-containing or Si-free austenite stainless steels the isomer shift becomes more negative. Additional alloying of the steels with silicon (*sp*-element) leads to the opposite effect. The results obtained make us conclude that the electron structure of the grain-boundary chromium-depleted zones and the grain body must differ. There are good grounds to believe that this may be the reason of selective dissolution of such zones in numerous corrosion media (especially in weakly and moderately oxidizing ones). This conclusion is of fundamental importance because in discussions concerning the intergranular corrosion mechanism in earlier literature no allowance for the electron structure of grain boundaries was taken into account.

Mechanism of the protective PEO-layers formation and the corrosion process at the heterooxide structure/electrolyte interface

S. Gnedenkov, S. Sinebryukhov/ Institute of Chemistry Far Eastern Branch of the Russian Academy of Sciences, Vladivostok/ Russia

Composite protective layers formation and corrosion process taken place at their surface in the corrosion active media have being considered in the relationship with charge transfer mechanism realized at the heterooxide /electrolyte interface.

The multifunctional composite coatings possessed by practically important properties (anticorrosive, antiscale, bioinert/bioactive and etc.) on titanium, aluminium, magnesium alloys as well on the steel and nitinol surfaces were obtained by means of the unipolar or bipolar modes of the plasma electrolytic oxidation (PEO) in different water electrolytes. The application of the nanosizable polymer and inorganic compounds in the coatings composition allows increasing their stability in corrosion active media. The chemical composition of the heterooxide coatings, their morphology, electrochemical properties and protection against scale formation in the sea water were investigated by different modern physical-chemical methods. The investigation of the PEO-coatings and composite layers with using the impedance spectroscopy method allowed determining their morphology structure, homogeneity and to research the charge transfer mechanism which is realized at the oxide heterostructure/electrolyte interface. The composite coatings obtained may be used in shipbuilding, aircraft industry, machinery construction, and implant surgery as well.

Application of the local electrochemical impedance spectroscopy method enable one to research the kinetics of the development of the defect zones in the PEO-coating obtaining on the surface of the magnesium alloy during the sample exposure in the corrosion-active solution. The developmental stages of the corrosion-active process have been established. The Randles equivalent electrical circuit which adequately interpret the mechanism of the corrosion process in the defect of the protective PEO-coatings has been suggested. The Randles circuit simulates the charge transfer process in the investigated heterostructure and takes into account the rate of the electrochemical reaction and the diffusion limitation. Using the method of local electrochemical impedance spectroscopy enable one to ascertain the presence of the amorphous sublayer under the PEO-coating, which electrical resistivity is considerable more than the resistivity of bulk crystalline layers of the metallic substrate.

The possibilities of plasma electrolytic oxidation for development of the composite coatings containing hydroxyapatite and calcium phosphates on the titanium and nitinol (NiTi) surface were demonstrated. Such layers include pores in the outer part of the coating which can be used as carriers for medicine (antibiotics, hydroxyapatite, etc.).

The availability of PEO method for composite coatings formation with better anticorrosion properties and morphology at the low carbon steel surface was shown. The combination of polarization and plasma influences on the samples surface realized under PEO process allows obtaining the protective coatings with good adhesion and continuity to metal. The application of superdispersed polytetrafluoroethylene in the steel composite coating allows increasing its stability in the corrosion media. The putting of the polymer compounds at the surface of the galvanic couple titanium/steel enable one to decrease the of galvanic corrosion currents by one order of magnitude.

Rust Morphology of Low Carbon Steel in Long Term Atmospheric Exposures

<u>M.Morcillo</u>, I. Díaz, J. Simancas and D. de la Fuente.
Dept. Materials engineering, Degradation and Durability/National Center for
Metallurgical Research (CENIM-CSIC),
Avda. Gregorio del Amo Nº 8
28040 Madrid/Spain.
Tel. 34915538900, E-mail. morcillo@cenim.csic.es

Atmospheric corrosion is an electrochemical process in nature, sum of the corrosion that takes place each time a film of electrolyte (rain, dew, etc.) forms on the metal. The factors that determine the rate of the corrosion process are as follows: (a) the time of wetness (TOW) of metallic surface, (b) atmospheric contaminants (SO_2, NO_x, aerosols of sea water, etc.), and (c) the conditions of exposure (open air, sheltered exposures, etc.)

It is widely accepted that a long term atmospheric corrosion of steel conforms to an equation of the form

$$C = C_1 t^n \quad (1)$$

where C is the metal loss after t years, C_1 is that in the first year, and n is an exponent usually less than unity. The exponent n is in turn a function of the type of atmosphere where the metal is exposed.

It is well known that the corrosion of metals in the atmosphere follows a mechanism controlled by the diffusion of the reactants across the rust layer. The exponential law, equation (1), with n close to 0.5 can result from and ideal diffusion controlled mechanism when all corrosion products remain on the metal surface. This situation seems to occur in slightly polluted inland atmospheres. On the other hand, n values greater than 0.5 arise from an acceleration of the diffusion process (e.g. as a result of rust detachment by erosion, dissolution, flaking, cracking, etc.). This situation is typical of marine atmospheres even for those of low chloride contents. Conversely, n values smaller than 0.5 result from a decrease in the diffusion coefficient with time through recrystallisation, agglomeration, compaction of the rust layer, etc.

The present study places emphasis on the morphology of the corrosion product films formed after long-term atmospheric exposure (13-16 years) in five Spanish atmospheres of different types: rural (El Escorial), urban (Madrid), industrial (Bilbao), mild marine (Barcelona) and severe marine (Alicante). The characterisation was performed by scanning electron microscopy (SEM)/energy dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD).

Goethite and lepidocrocite are found in the rural, urban and industrial atmospheres. However, in the marine atmospheres together with goethite, the presence of akaganeite and magnetite is detected.

The behaviour in the Spanish atmospheres of El Escorial and Madrid deviates from that predicted by equation (1). The log-log plot of steel corrosion vs. time for these two atmospheres is a broken line consisting of two linear segments: an initial segment of slope 0.73 (El Escorial) or 0.48 (Madrid) followed by a second segment with a very small slope (0.08 and 0.09, respectively). Looking for the main cause of this anomalous behaviour the authors consider the possibility of the formation of extremely compact rust layers, in which the diffusion of reactants is hindered.

Corrosion Products Formed on Prepainted Zn55Al and hot-dip galvanised steel upon long term atmospheric weathering conditions

Dominique Thierry[1], **Dan Persson**[2], **Nathalie Le Bozec**[3]

[1]*French Corrosion Institute, France, dominique.thierry@institut-corrosion.fr*
[2]*Swerea Kimab, Sweden, dan.persson@swerea.se*
[3] *French Corrosion Institute, nathalie.lebozec@institut-corrosion.fr*

Prepainted Zn55Al and hot-dip galvanised steel have been exposed for several years at different sites representing climatic conditions such as rural, marine, severe marine and marine industrial atmospheres. The corrosion products formed at the unprotected edge have been analysed using different analytical techniques such as FTIR spectroscopy, X-ray diffraction and Scanning Electron Microscopy. From the results it is shown that the corrosion products formed on Zn55Al have the general composition of hydrotalcites $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2][A^{n-}_{x/n}\cdot zH_2O]$. The type of anion in the structure is dependent upon the type atmosphere. For instance, Zn-Al-(OH)-$SO_4 \circ xH_2O$ was found in combination with Zn-Al-(OH)-$CO_3 \circ xH_2O$ in marine/industrial atmospheres whereas only Zn-Al-(OH)-$CO_3 \circ xH_2O$ was found in pure marine atmospheres. The results are also compared to that obtained after exposure to different accelerated corrosion tests. Finally the results are compared to that of unpainted materials obtained under the same exposure conditions.

PASSIVE LAYER STABILITY OF ALLO 904L IN HIGH-PURITY WATER BY MEANS OF ELECTROCHEMICAL NOISE MEASUREMENTS

Helmuth Sarmiento KLAPPER[1], **Andreas HEYN**[2], **Andreas BURKERT**[1], **Joachim GOELLNER**[2]

[1]*Federal Institute for Materials Research and Testing (BAM), Germany, helmuth.sarmiento-klapper@bam.de*
[2]*University of Magdeburg, Germany, andreas.heyn@mb.uni-magdeburg.de*

Rouging had been observed as a common phenomenon in pharmaceutical facilities, where stainless steel surfaces are in contact with high-purity water at temperatures above 60 °C. This corrosive phenomenon consists in the formation of a colored surface film containing mainly iron and represents a potential risk of contamination of the pharmaceutical products. Numerous hypotheses about the origin of rouging had been proposed. However, a clear explanation for the mechanism leading to a well passivated surface corrodes almost uniformly is currently still lacking.

The acquisition and analysis of the electrochemical noise (EN) allows a sensitive examination of the electrochemical reactions taking place at the passive layer of stainless steels. Therefore, EN measurements concerning passive layer stability of alloy 904L in high-purity water (0.5 µS/cm) with different oxygen concentrations at 70 °C were carried out in order to improve the current understanding about the origin of rouging. The experimental results showed that the cathodic process plays a relevant role in the stability of the passive layer of Alloy 904L. Thus, the origin of rouging could be directly related with a weakness of the electron-consumption process avoiding the repassivation of the surface.

CORROSION BEHAVIOR OF HIGH-ALLOYED MATERIALS IN AN ARTIFICIAL GEOTHERMAL FLUID AT SERVICE CONDITIONS

Ralph BÄßLER[1], **Helmuth Sarmiento KLAPPER**[1], **Andreas BURKERT**[1]

[1] *Institute for Materials Research and Testing (BAM), Germany, ralph.baessler@bam.de*

Since geothermal wells are a feasible energy source to replace fossil fuel supply, many technologies have been developed to take advantage of geothermal energy. Nevertheless, service conditions in geothermal facilities are due to the chemical composition of hydrothermal fluids and temperatures, in many cases, extreme in terms of corrosion. Therefore, materials selection based on preliminary material qualification is essential to guarantee a secure and reliable operation of the facilities. This paper is hence devoted to the evaluation of the corrosion behavior of different high-alloyed metals including two high-alloyed stainless steels and a nickel-based-alloy in an artificial geothermal fluid having the chemical composition of the North German Basin. The limitations of suitability of alloy 24, alloy 31 and alloy 59 in this high-saline geothermal fluid obtained by means of electrochemical measurements and exposure tests are presented. While alloy 59 shows an excellent corrosion resistance against pitting corrosion and represents, excluding their high cost, a very good alternative to be used in the construction of geothermal facilities, stainless steels exhibit a limited corrosion resistance concerning pitting and crevice corrosion.

Corrosion protection of Zn-Al-Mg coated steel with and without plastic deformation in chloride containing environment

Susanne Schuerz, Christian Doppler Laboratory of Localized Corrosion, University of Leoben, Austria
Gerald H. Luckeneder, voestalpine Stahl GmbH, Austria
Martin Fleischanderl, voestalpine Stahl GmbH, Austria
Anna Elisabeth Raab, voestalpine Stahl GmbH, Austria
Gregor Mori, Christian Doppler Laboratory of Localized Corrosion, University of Leoben, Austria

Recent studies already showed the excellent corrosion resistance of zinc alloy coatings for steel sheets with additional aluminium and magnesium. The influence of the alloying elements on the corrosion mechanism is an important topic for many research groups world wide.

This work focuses on the corrosion resistance of a specific Zn-Al-Mg alloy coating (ZM) in comparison to a conventional zinc (HDG) coating for steel sheet, both produced via hot-dip galvanising and comprising a coating thickness of 7 µm, in standardised salt spray test. Analysis of the sample cross-sections by SEM and EDS showed that on HDG material the corrosion progress is determined by the formation of loose corrosion products, and after 100 h decisive attack of the steel substrate is detectable. In contrary ZM with the same coating thickness forms a well adherent aluminium-rich protecting layer next to the steel substrate in a short period of time, which protects the steel substrate against corrosive attack. By the means of X-ray diffraction (XRD) this aluminium-rich protecting layer could be identified as zinc aluminium carbonate hydroxide, $Zn_6Al_2(CO_3)(OH)_{16} \cdot 4\ H_2O$.

Thereupon corrosion tests on plastically deformed ZM coated samples were carried out. For this purpose the ZM samples were strained to 5 %, 10 % and 15 % of plastic deformation, respectively and after that exposed to standardised salt spray test. Analysis of the sample surface and cross-sections before exposure showed that the plastic deformation causes decisive cracks in the ZM coating, even through to the steel substrate. Analysis of the sample surface and cross-sections after exposure showed that these cracks do not significantly influence the corrosion progress. No attack of the steel substrate takes place due to the cracks. The already known aluminium-rich protecting layer can form upon the steel substrate on plastically strained samples as well. However, the transformation of the metallic ZM coating into the aluminium-rich protecting layer proceeds faster on the plastically strained samples than on samples without any deformation. But on both sample types, those with and those without plastic deformation, the time of first red rust appearance is in the same range.

The found aluminium-rich protecting layer is responsible for the enhanced corrosion resistance of ZM coated steel with and without a further plastic deformation (up to 15%) in comparison to HDG.

CORROSION CEMISTRY OF GALVANIZED STEEL IN BORIC ACID MEDIA

Wolfgang Hoffmann, Holger Kryk, Frank-Peter Weiß

Forschungszentrum Dresden-Rossendorf e.V., Institute of Safety Research,
P.O. Box 51 01 19, D-01314, Dresden, Germany

Loss-of-coolant accidents (LOCAs) pose some of the most severe design-basis challenges to the safe operation of pressurized water reactors (PWR). To prevent the release of radioactive material and to remove residual heat from the radioactive decay after a LOCA, boric acid containing (borated) cooling water (max. boron concentration 2500 ppm) from the primary cooling circuit leak is collected in the reactor sump and recirculated to the reactor core. Strainers at the inlet of sump pumps keep any debris formed from the emergency core cooling system (ECCS). Several forms of debris may influence the sump strainer clogging behavior as well as the cooling water chemistry. Especially hot-dip galvanized steel grids, installed near the reactor vessel, maybe the major source of corrosion products. The composition of the coolant and the temperature are the main influences on the corrosion mechanisms and rate. Therefore, different experimental methods are used to study the complex nature of the electrochemical corrosion mechanisms of zinc at LOCA process conditions.

Batch experiments were carried out for a week per run in a double jacket 1.5 liter stirred glass reactor at 45, 70 and 90 °C. Hot-dip galvanized steel coupons were used as corrosion material samples. Based on the results, the test conditions for the long-term experiments were specified, which are carried out in a corrosion test facility, based on a scale-down of an assumed LOCA with a typical PWR sump geometry. The leakage is represented by a sprinkling section including samples of hot-dip galvanized steel gratings. A bath of about 50 liters is used as sump to collect the solution. At its bottom, a separately prepared insulation material fiber bed acts as clogged sump strainer. Temperature and flow rate of the solution are controlled by a supply unit, consisting of a heat exchanger with a thermostat, a circulating pump and an additional solvent filter.

Additionally, electrochemical measurements are performed at elevated temperatures with embedded samples of zinc and steel in the boric acid media with additional pH adjustment with LiOH.

A significant increase of the concentration of zinc ions up to 90 mg/l was observed within the first day in boric acid solutions. Subsequently, the concentration remained nearly constant during the corrosion experiments. This can be explained by saturation with soluble corrosion products. Experiments with deionized water lead to a much lower zinc concentration.

White spherical particles of about 10 µm diameter were only observed on samples treated in batch experiments at 90 °C in the presence of borated solutions. These particles were identified by laser Raman microscopy as zinc borate. An anomalous decrease of its solubility with increasing temperature was noticed. This explains the observed decrease of zinc ion concentration at elevated temperatures.

It is remarkable that there were no observations of Fe-ion concentrations above the detection limit of 10 ppb in the liquid phase in all the experiments performed. Thus, the Zn coating prevents the corrosion of steel in the investigated media and at elevated temperatures.

Furthermore, the results of electrochemical measurements at elevated temperatures will be discussed.

The anodic dissolution of zinc, aluminum, and 5% zinc –aluminum alloys in alkaline solution

K. Ogle, V. T. Nam, M. Mokaddem, P. Volovitch*

Surface Engineering Team (LPCS, UMR 7045), Ecole Nationale Supérieure de Chimie de Paris, ParisTech, 11 rue Pierre et Marie Curie, 75005 Paris

The behavior of galvanized steel coatings in alkaline solution is of considerable importance as these materials are routinely exposed to alkaline conditions during degreasing and during corrosion in confined zones (for example under paint) when a pH increase may be induced by oxygen reduction. A large body of literature exists concerning the mechanism of Zn and Al dissolution and yet it is clear that basics questions concerning the mechanisms have yet to be clarified. Further, very little is known about the Zn-Al alloy system.

In this work we will review recent progress from our group in understanding the dissolution of pure zinc and pure aluminum in dilute NaOH solution and we will present an in depth study of the dissolution of the 5% Al-Zn alloy coatings. The objective will be to clarify the extent to which the behavior of the alloy system may be predicted from the behaviour of the component elements. To this end, we have used a novel technique *Atomic Emission SpectroElectrochemistry (AESEC)* to measure directly and simultaneously the rate of Zn and Al dissolution either at open circuit or under conditions of polarization. A typical AESEC polarization curve for 5%Al-Zn is shown in Figure 1. In summary, zinc dissolution was found to be almost completely independent of Al, while the Al dissolution was inhibited in the potential range of active zinc dissolution. The Al dissolution began again as soon as the active to passive transition for zinc had been achieved. Kinetic studies as a function of hydroxide concentration and applied potential will be presented and compared with the evolution of surface composition and morphology so as to shed light into the mechanism of these effects. The results will be interpreted in terms of the coupling between the Al rich and Al poor phases in the alloy, the formation of surface oxides, and the availability of hydroxide for the dissolution mechanisms.

In addition, initial studies on the effect of adding 1,2-diaminoethane to the electrolyte will be presented. This molecule complexes with zinc ions enhancing the solubility of zinc oxide/hydroxide and thereby increasing the rate of zinc dissolution. The effect on aluminum is much smaller. This allows us to directly probe the kinetic effect of insoluble zinc based oxides and hydroxides on the overall reaction rate.

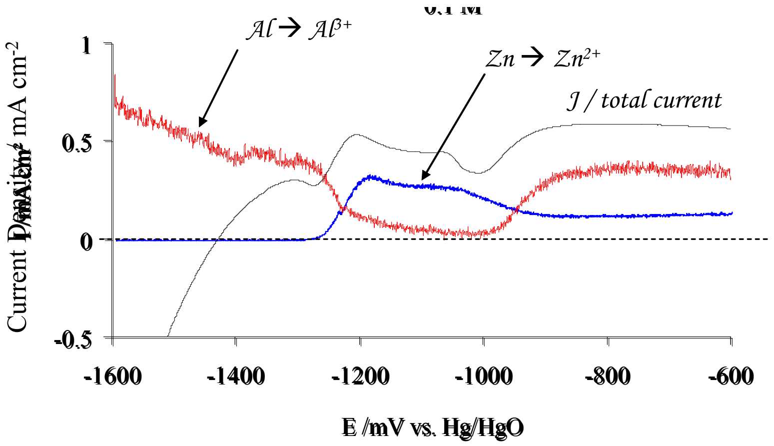

Figure 1
AESEC polarization curve of 5% Al-Zn in 0.1 M NaOH showing total current (J) and the partial elementary currents for Al and Zn dissolution.

Influence of chromium grain-growth inhibitors on the corrosion behavior of WC-Co hardmetals

Florian Kellner, University of Erlangen-Nuremberg, Erlangen/Germany
Erdmann Spiecker, University of Erlangen-Nuremberg, Erlangen/Germany
Sannakaisa Virtanen, University of Erlangen-Nuremberg, Erlangen/Germany

Hardmetals are composite materials, with a wide range of applications in industry such as drills or cutting tools. The special feature of these composites is the combination of a hard material phase, mostly WC, with a tough Co or Ni binder matrix. This arrangement of phases leads to a high strength connected with a relatively good toughness, resulting in an excellent wear resistance. Cr_3C_2 is known as one of the most effective grain-growth inhibitors for hardmetals, reducing the grain size of the hard material phase. A smaller grain size increases the wear resistance and thus the material performance of hardmetals. A second advantage of using chromium is that alloyed Cr increases the corrosion resistance of hardmetals. By adding chromium in the production process, alloyed hardmetals show higher polarization resistances and lower corrosion current densities than unalloyed ones. The corrosion performance of chromium alloyed WC-Co hardmetals was investigated with standard electrochemical techniques. In addition, high-resolution TEM investigations (EDXS and STEM) with a Titan 80/300 instrument were carried out. The distribution of Cr in the hardmetal (grain boundaries, binder matrix) and in the corrosion layer was determined. Indications on Cr passivation effects protecting the surface were obtained.

Influence of metallurgical parameters on electrochemical behaviour of electrodeposited nickel coatings

Aurélie Godon, Juan Creus, Xavier Feaugas*, Catherine Savall

Laboratoire d’Etudes des Matériaux en Milieux Agressifs, EA3167, Université de La Rochelle, Avenue Michel Crépeau, 17042 LA ROCHELLE Cedex 1 - France
*Corresponding author.Tel.: +33 546458211. Fax: +33 546457272. E-mail: csavall@univ-lr.fr

Protection of metallic surfaces against aqueous aggressive environments is a matter of great concern due to economical reasons and environmental issues. Several studies have reported that despite their high fraction of grain boundaries, nanocrystalline metallic coatings show improved corrosion resistance compared to their microcrystalline bulk counterparts. The mechanisms have not been explained yet and some limitations of the published studies can arise from a lack of control of the microstructure and the purity of the coatings. The aim of this work is to acquire a better knowledge of the interplay between microstructure, composition, and corrosion resistance. To carry through these objectives, nanocrystalline nickel was chosen as a model material.

Nickel coatings with grain sizes ranging between 50 nm and several micrometers were obtained by DC and pulse electrodeposition in a sulphamate bath without additive, in order to minimize sulphur incorporation. Several studies shown that sulphur contamination can strongly influence both mechanical properties and corrosion behaviour. The composition of the coatings was analyzed by GDOES and SIMS to be able to quantify metallic contaminants and light elements. Different tools (SEM, XRD, TEM, EBSD, AFM) were used to carefully characterize the structure at different scales. Polarization curves (in H_2SO_4 1M) were used to study the anodic behaviour and the kinetics of the Hydrogen Evolution Reaction. Our experimental approach aims to separate the influence of different parameters which can influence electrochemical reactivity (for example, grain size, grain boundaries character, crystallographic texture, roughness, contamination ...). Thus, the behaviour of the coatings was compared with different forms of nickel (coarse-grained bulk samples and single-crystals with several crystallographic orientations) and a special attention was given to the surface preparation.

The causes of electrochemical corrosion of phase homogeneous and heterogeneous iron-chromium alloys

Reformatskaya I.I., Podobaev A.N.
Karpov Institute of Physical Chemistry, Moscow, Russia

Is shown, that not only additional phases and segregations of impurities, but also the nonmetallic inclusions are capable to strongly affect on corrosion-electrochemical behavior of steels. Under formation of nonmetallic inclusions of manganese sulphide (MnS) in structure of stainless steels and alloys the ability to passivation and pitting corrosion resistance of metal is reduced on orders of magnitude.

The set of critical structures of iron - chromium alloys (6,5; 12; 17; 25 and 27 % Cr), corresponding to their corrosion-electrochemical characteristics of the ability to passivation and stability against local kinds of corrosion discontinuous changes, is explained by discontinuous changes of an alloy structure, and conforming discontinuous changes of electronic gas density.

This explanation is affirmed by straight tunnel micro- and spectroscopy methods. For the first time by this methods is demonstrated an energetic heterogeneity of a surface of homogeneous solid electrodes under conditions of equipotentiality.

Silicon Dissolution under Negative and Positive Polarizations in HF Free Media

D. Starosvetsky, T. Zaid, and Y. Ein-Eli
Department of Materials Engineering, Technion-Israel Institute of Technology, Haifa 32000, Israel
davstar@tx.technion.ac.il

Electrochemical etching is one of the most effective and inexpensive techniques for fabrication of three-dimensional structures, which offers several advantages over other etching techniques, such as, wide variations in etch rate, accurate control and monitoring of the etching processing.

Traditional electrochemical etching is usually associated with anodic polarization within the potential range of active dissolution. The wider this potential range is, the higher the etching rate. Considering silicon, a wide potential range of active anodic dissolution occurs only in solutions containing hydrofluoric acid (HF) [1]. It is thought that in HF-free aqueous solutions, silicon is either totally passive, or active only in a narrow potential range, as in the case of alkaline solutions [1], with inability to regulate the etching rate.

However, it was established that silicon can be dissolved in alkaline solutions under application of negative (cathodic) potentials. Especially strong increase in corrosion rate was observed at potentials below –5 V (SCE). Etch-rates values higher than 6 μm/min were achieved for both p and n- Si under cathodic bias in alkaline solutions. In the case of p-Si the increase in the etch rate at cathodic bias was obtained only under silicon illumination.

We also demonstrate the possibility of p-Si etching in alkaline solutions by applying positive (anodic) potentials. The attempt to accelerate silicon etching using anodic polarization doomed to fail at first glance, since in HF-free solutions silicon undergoes anodization in a wide potential range. In many acidic and neutral aqueous solutions silicon anodization occurs up to voltages above 100 V [1]. However, in alkaline solutions, the range of silicon anodization is much lower (less than 20 V) [1].

In order to clarify anodic behavior of p-Si in alkaline solutions, potentiostatic measurements in a wide potential range between OCP and +60 V were performed. We show that the etch-rate of p- silicon strongly increases with potential in potential range above 20 V. The most significant acceleration in etch rate was obtained between 30 and 40 V. A maximum etch rate of 32 m/min was achieved in 50 wt% KOH solution.

The effect of applied potential, solution concentration, and other parameters on electrochemical behavior of n- and p-Si, dissolution rate and topography of etched Si surface will be discussed. Features of silicon dissolution under negative and positive applied voltages will be compared.

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Thermodynamic calculation of the Flade potential of metals Fe, Ni and Cr taking account of their surface Gibbs energy

Yu. Ya. Andreev, *Moscow Institute of Steel and Alloys (MISIS), Moscow,Russia*
yuandr@rambler.ru

In the calculation we proceeded from an equilibrium reaction

$$mMe + nH_2O = Me_mO_n + 2nH^+ + 2ne^- \qquad (1)$$

Using (1) the formula for the calculation of the Flade potential (SHE, in V) of metal is proposed

$$E^0_{F(s)} = E^0_F + \frac{m(\Delta G^0_{s,Me})}{2nF} + 1.229 \qquad (2)$$

where the potential $E^0_{F(s)}$ is distinguished from the one “normal” E^0_F (pH=0) by the value of emf that is equivalent to the surface Gibbs energy of metal $\Delta G^0_{s,Me} > 0$. The definition of $\Delta G^0_{s,Me}$ employed here is based on the concept of self-adsorption of Me atoms (A) in the surface layer that is expressed by the Gibbs equation $\sigma = -\Gamma_A \Delta\mu_A$ [1]. When a metal is passived, its excess of surface energy is equilibrated with the excess energy of chemical bonds Me-O. The data on $\Delta G^0_{s,Me}$ at T=0 were used [2] with correction for temperature. The calculation of $E^0_{F(s)}$ by equation (2) was compared with the known experimental data (in the brackets): for Ni 0.463 (0.48) and Cr -0.192 (-0.25). The passive film on Fe involves the inner layer of $(FeO)_{ads}$ with $E^0_{F(s)}$=0.432V and layers of Fe_3O_4 and Fe_2O_3 (their contribution to the experimental potential 0.58V of Fe is ~0.15V). The inference has been done: passivation of metals is accompanied by the formation of bonds Me-O the strength of which is weakened at the expense of surface energy. This can bring about the formation of non-stoichiometric or chemosorptions oxide film [3].

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Mutual influence of simultaneously proceeding electrode reactions: from competitive adsorption to thermodynamic coupling

I. D. ZARTSYN
Voronezh State University, Voronezh, Russian Federation, zamet@comch.ru

Theoretical fundamentals of electrochemical kinetics have been formulated as a result of generalization of the experimental data obtained in the course of one reaction on an electrode, as a rule of hydrogen release. At the same time during the solution of both the applied and fundamental problems the researchers are faced with the fact that on an electrode several simultaneous reactions take place. Therefore the study of a mutual influence of simultaneously proceeding reactions is referred to fundamental problems of electrochemical kinetics. This problem has become especially urgent with respect to the corrosion theory.

For theoretical modeling of simultaneously proceeding reactions it is necessary to involve multiroute kinetic schemes. By means of the method of kinetic graphs the kinetic equations of metal dissolution under the conditions of competitive adsorption of electrolyte components are obtained. The kinetic adsorption isotherms are also obtained. The dependences of the reaction order by separate solution components on the composition of the electrolyte and the electrode potential are analyzed. The conditions necessary for changing the kinetic route under the change in the composition of the electrolyte and the electrode potential have been analyzed and simulated. The models quantitatively describing the experimental data obtained in the course of the study of metal dissolution in the electrolytes containing several components capable of participating in the metal ionization reaction are obtained.

The method of kinetic graphs has also been applied to the description of the influence of organic inhibitors on the regulations of metal dissolution and corrosion. The conditions of competitive adsorption of organic compounds and inorganic anions on a metal surface have been simulated. The equations explaining the change in sign of the reaction with respect to the organic compound under the change of electrolyte composition are obtained.

It is shown how to use the method of kinetic graphs under non-stationary conditions, in particular, at simulation of the phenomenon of «non-oxide passivation» of metals in the presence of some organic compounds.

The metal surface is always a common intermediary participant for simultaneously proceeding electrode reactions. It is shown that under certain conditions this results in the change of not only kinetic, but also thermodynamic regularities of simultaneously proceeding reactions in comparison with their separate course. The method of kinetic graphs can be applied to the analysis of thermodynamic coupling of electrode reactions, in particular, to the explanation of metal dissolution under cathodic polarization and the influence of oxidizers on the regularities of metal dissolution.

Kinetics and mechanism of nanoobjects formation on single crystal electrodes

A.I.Danilov, E.B.Molodkina, A.A.Rybin, R.G.Fedorov, M.R.Ehrenburg,
Yu.M.Polukarov
A.N.Frumkin Institute of Physical Chemistry and Electrochemistry,
Russian Academy of Sciences
Moscow, Russia

Kinetics and mechanism of formation of an adatomic layer and nanocrystallites of copper on platinum, gold and silver single crystals have been studied using electrochemical methods (cyclic voltammetry and potentiostatic current transients) and scanning probe microscopy. It was found that copper nucleation on Pt(111) and Au(111) follows the Stranski-Krastanov mechanism (the nuclei are formed on top of the adatom monolayer), but the Volmer-Weber mechanism is valid for the nucleation on a silver substrate: the new phase is formed immediately on the Ag(111) surface.

The factors affecting the kinetics of the process have been studied. It has been shown that specific adsorption of sulfate anions accelerates the charge transfer due to local electrostatic effects in the dense part of the double electric layer. In the case of copper nucleation on silver in the solution of 0.1 M $HClO_4$ + 10 mM $Cu(ClO_4)_2$ + H_2SO_4 (the concentration of sulfuric acid was varied from zero to 0.5 M), the nucleation rate increased considerably even at 1 mM of the additive.

Adsorbed copper oxides exercise a similar influence. Electronegative particles of copper oxides are the active centers (in addition to structural defects, steps and kinks) of adlayer formation and growth of three-dimensional nanocrystallites of copper on platinum. It has been shown that the number of active sites can be controlled by means of electrochemical pretreatment. For instance, long-term polarization of Pt(111) at 0.6-0.8 V or slow potential cycling leads to an increase in the number of active centers (formation of copper oxides from coadsorbed copper and oxygen atoms). Reduction of copper oxides at low potentials decreases the rate of Cu electrodeposition.

Catalytic properties of copper nanoobjects have been studied for reactions of nitrate and nitrite electroreduction. It was shown for instance, that nitrate reduction on copper-modified Pt(111) electrodes in perchloric acid solutions occurs much faster as compared to pure platinum. The steady-state currents are higher by 4 and 2 orders of magnitude at 0.12 and 0.3 V, respectively. The catalytic effect of copper adatoms is largely caused by the facilitation of nitrate adsorption on the platinum surface near Cu_{ad} and/or on the islands of Cu(1x1) monolayer (induced nitrate adsorption).

Corrosion of Acheaological and Heritage Artefacts

Alternative coatings for stabilization of iron archaeological artefacts

Stoulil J., Krecanova E., Jamborova T., Mundil R.

Tannates and phosphates are usually used for the stabilization of iron artefacts. Tannates show very low stability under humid conditions, while phosphates have more complex application. Alternative coatings based on hydrophillic polymers (polyvinylpyrrolidone, acrylophosphonate), organosilane and carboxylate were studied in present work. They were subjected to exposure in water as well as humid atmosphere and analyzed by means of scanning electron microscopy, infrared spectroscopy, spectrophotometry, image analysis, contact angle and impedance measurements. Tests showed organosilane and carboxylate as a good alternatives to the classical coatings.

Contribution of VIAM to restoration of V.I. Mukhina’s sculpture “Worker and collective farmer “

Karimova S.A., Belous V.Ya., Zhirnov A.D.
All-Russian Institute of Aviation Materials (VIAM)

In December 2009 the 28meters sculpture of V.I.Mukhina ” Worker and collective farmer”, that has been restored, was placed again on 35meters pedestal near the North entrance of All-Russian Exibition Centre in Moscow.

Starting from 2006, by the request of a sculptor V.M.Tserkovnikov, VIAM has been taking an active part in the process of restoration. A regular team of scientists and engineers was organized, among them a considerable part included young specialists.

In the first turn, a technical condition of the sculpture was estimated and a conclusion was issued about a possibility to carry out the restoration.

A spectral-optical non-destructive control method for inner skin was developed, the electronic technique, allowed to create a database with more, than 5000 colour photographs of the technical condition of all 40 pieces, into which the sculpture was cut in 2003.

Testing for mechanical properties of the skin material and welded joints, metallographic investigation was carried out selectively.

On the base of the performed investigation the conclusion was issued about a possibility of restoration and a replacement of 10% of skin fragments only.

By recommendation of VIAM a washing and cleaning of the outer and inner surface of the sculpture from impurities was performed.

Products of corrosion were removed using anticorrosive VPT-1 paste (1500kg), developed and manufactured at a pilot bay of the institute specially.

In connection with a full replacement of a power frame because of intensive corrosion, VIAM has developed engineering methods on manufacture of upper section of the sculpture frame from a stainless steel, a technology of manufacture of the power structure profiles, a welding technology for components and a complex anticorrosive protection of the whole sculpture for the service life of more, than 100 years.

Special power fasteners from high-strength stainless steel 14X17H2 were developed to fix the frame components. More, than 2500 bolts and nuts were manufactured at “Salut” plant.

To perform the restoration, manufacture of parts, assemblies and mounting of the sculpture a set of necessary technical documentation was developed.

VIAM performed an author accompaniment over the recommended technologies on all the steps of works.

ENRICHMENT OF SILVER AT THE GOLD LAYER OF GILT SILVER EMBROIDERY WIRES OF QAABA CURTAINS

Gulsu SIMSEK[1], Ali Fuat CAKIR[2]

[1]*Istanbul Technical University, Turkey, simsekg@itu.edu.tr*
[2]*Istanbul Technical University, Turkey, afcakir@itu.edu.tr*

The deterioration of metal threads occurs because of the environmental conditions and also because of the contact with textile fibers. The main corrosion products of gold gilt silver threads (e.g. wires, strips) are silver sulphide (Ag_2S) crystals grown on the gold surface in flower-like shape. The formation of Ag_2S on silver based by the corrosion of historical objects is previously documented. In electronic products, diffusion of silver and its enrichment at the gold coating layer produced silver sulfide at the surface when the gilt layer was contaminated with sulfur and heated by the passage of current. It is reported that sulfuric atmosphere accelerates the silver diffusion process. The present work is the first communication about silver enrichment towards the outer layer of gold coating in gilt wires, at room temperature without heat treatment, throughout centuries. The formation of Ag_2S corrosion products are visualized by field emission scanning electron microscope (FE-SEM). In addition to these techniques, Raman spectroscopy is used to identify the corrosion products on the gilt layer surface. The enrichment of silver towards the gold surface layer is investigated by using electron probe micro analysis (EPMA) and concentration profiles of silver and gold were obtained. The results show that there is a local silver enrichment on the gold surface where sulfur which lead to the enrichment of silver at the surface leading to the formation of Ag_2S crystals at the gold coating layer, was also detected.

Non-invasive assessment of the corrosion behaviour of precious artefacts displayed in museum showcases

*E. Angelini**, *S. Corbellini°, S. Grassini*, Y. Mao*, M. Parvis°, M. Piantanida**

**Dip. Scienza dei Materiali ed Ingegneria Chimica, Politecnico di Torino, Torino, Italy*
°Dip. di Elettronica, Politecnico di Torino, Torino, Italy
Corresponding author: emma.angelini@polito.it

One of the main problems of archaeological metallic artefacts stored in museum showcases is their long-term conservation.

Corrosion in soil leads to the degradation of metallic artefacts mainly due to the long-time interaction with aggressive ions (i.e. chlorides) and to the soil water and oxygen content. After the excavation the high relative humidity and the presence of aggressive agents in the atmosphere may accelerate these phenomena.

Many kinds of patinas could be present onto the surface of silver and copper-based archaeological artefacts: in the case of bronze the patina is usually preserved for its protective properties and interesting aesthetical appearance. On the contrary, silver's tarnishing is rarely regarded as a valuable patina and detracts from its qualities; tarnishing film has, therefore, to be removed and its formation needs to be hindered.

Museum curators and restorers may, consequently, face the problem not only to clean the artefacts in order to recover the original surface and decorations, but also to protect and get them in a stabilised condition. For these reasons a satisfactory conservation approach requires a constant monitoring of the stability of the materials employed during restoration and of the corrosion processes, which occurs onto the artefact’s surface.

This study deals with the development and validation of a non-invasive and easy-to-use diagnostic tool that can be employed for the in situ monitoring of the conservation state of metallic works of art. The proposed approach, based on a 2D-FFT (*Fast Fourier Transform*) imaging processing of the artefact digital photographs, allows one to detect the failure of a protective coating and permits a rough estimation of the corrosion process, simply by looking at the surface uniformity changes. In this way it is possible to avoid artefacts manipulation that can increase the damage, as well as to overcome the problem of maintaining standard photographic lighting that is one of the main limitations of the digital image solutions based on colour change measurement. A high resolution digital camera is employed to acquire the artefacts photographs. The images are converted to black and white using the brightness parameter of HSV (hue, saturation, and brightness) colour space; then, the FFT algorithm is computed and interpreted to extract a compact index, which can be able to estimate the corrosion presence and its importance. Although this technique could not allow a quantitative measurement of the corrosion rate, it has proved to be an effective approach to ensure a long and stable life to cultural property, to identify conservation problems, as well as an easy and fast method for the estimation of the aggressiveness of the environment in which the artefacts are exposed.

The 2D-FFT imaging approach has been used to assess the tarnishing susceptibility of a set of silver and copper-based samples in laboratory. The samples coated with SiO_x thin films via plasma, have been submitted to a tarnishing test in the presence of H_2S vapours (10 ppm per hour) for 30 days.

Some corrosion issues in ancient Chinese Cu-based coins - Influence of minor elements in corrosion susceptibility

M.J. Furtado, CENIMAT/I3N and ITN, Lisbon/Portugal; R.J.C. Silva, CENIMAT/I3N, Monte de Caparica/Portugal; M.F. Araújo, ITN, Sacavém/Portugal; F.M. Braz Fernandes, CENIMAT/I3N, Monte de Caparica/Portugal

Ancient Chinese cash coins are an important part of the Chinese metallurgical cultural heritage. Having used almost the same casting method for about 2000 years, the study of these coins alloys allows an insight into the Chinese history. Understanding the corrosion processes they endure is essential for the future preservation of these everyday artefacts.

A group of thirty brass coins was selected from a broader collection belonging to the Macau Scientific and Cultural Centre Museum (Lisbon, Portugal) to assess the microstructures through optical and scanning electron microscopy observation. The coins rims were freshly polished and analysed by micro-energy dispersive X-ray fluorescence spectrometry to obtain alloy compositions. Energy dispersive spectroscopy was also used in SEM observation to obtain phase composition, and micro X-ray diffractometry was occasionally used to confirm the presence of some phases.

In these complex composition brasses the main elements are Cu and Zn, but significant amounts of minor elements as Pb, Sn, Sb, Fe and As are frequently present. The microstructures in these coins are typical as-cast, and the identified phases were α-Cu, β-brass, γ-brass, as well as (Pb), α-Fe and Fe_2As, the latter four not common in binary brasses. These results are discussed in previously published papers [1, 2].

Concerning the corrosion, the most common occurrence, due to dezincification, is copper redeposition. Some phases are preferentially corroded although the corrosion sequence is not always proportional to the amount of Zn content in those phases: the presence of some elements as Sn or Sb can modify corrosion susceptibilities in some phases. The Pb-rich phase has its boundaries oxidized but does not seem to be significantly leached in the analysed coins. The Fe-rich phase seems to be more susceptible to corrosion and consequent leaching. The presence of As seems to promote the corrosion resistance of Fe-rich phases. Overall, the presence of some elements, even in small amounts, can alter the susceptibility to corrosion.

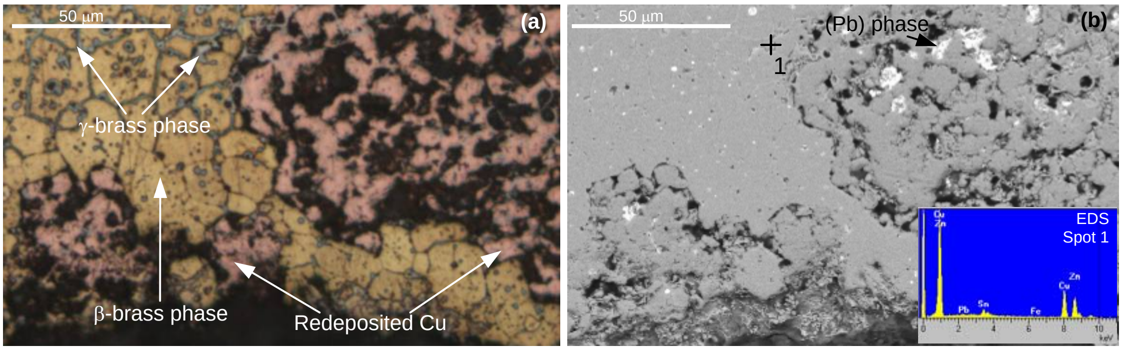

Fig.1 – Corrosion in a brass coin (no.2767) in (a) OM-BF (etched) and (b) SEM-BSE (non-etched)

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ANALYTICAL APPROACHES FOR CORROSION INVESTIGATION AND CONSERVATION OF COPPER-BASED ARTeFACTS IN EGYPT

Nabil A. ABDEL GHANY[P*] **and Venice K. GOUDA**

Electrochemistry and Corrosion Dept., National Research Centre, Dokki, Cairo, Egypt.
****Email: na_manakhly@yahoo.co.uk***

Corrosion is a phenomena that occur spontaneously for metals and alloys, which can compete using several ways and materials. However, if we are talking about corrosion in metallic artifacts, we are talking about degradation of valuable treasures of human beings. These treasures have crossed centuries and should be transmitted in good shape to future generations. Many corrosive factors can influence the reactivity of these metallic objects, which lead eventually to deterioration. These corrosive parameters affect metals in different ways depending on the environments (atmosphere, soil or marine). Thousands of ancient Egyptian copper-based artifacts have been excavated and much of them are displayed in showcases, not only in Egyptian museums but also in several other countries in the world. The rest are put in storage without good care. For the purpose of better understanding of the corrosion and conservation processes, analytical strategies, namely, portable X-Ray Fluorescence (XRF), X-Ray Diffraction (XRD), Optical microscope (OM) and Scanning Electron Microscope (SEM) were employed to investigate artifact compositions, structures, and corrosion products. Air of museum and storage rooms as well as excavation soil sites of selected copper artifacts in Egypt were also of concern. Accelerated corrosion testing procedure based on electrochemical technique was also found to simulate the degradation processes occurring on Cu -base artifacts.

Key words: Copper-based artifacts, corrosion, portable XRF, XRD, SEM

Corresponding Author: Email na_manakhly@yahoo.co.uk *

Studying the mechanisms of long-term atmospheric corrosion of steel: new strategies for protection of cultural heritage artefacts

H. Faiz [1,2], E. Rocca [2], P. Dillmann [1,5], F.Mirambet [4], E. Burger [1,3], D. Neff [1]

[1] Laboratoire, Archéomatériaux et prévision de l'altération, SIS2M/LAPA CEA-CNRS UMR 3299 91191 Gif/Yvette cedex, France
[2] Institut Jean Lamour UMR CNRS 7198 – Dept CP2S – Université Henri Poincaré - Vandoeuvre Les Nancy, France
[3] laboratoire, LECA, CEA, DEN, DPC, SCCME, F-91191 Gif Sur Yvette, France
[4] C2RMF, Ministère de la Culture-CNRS, Paris, France
[5] LMC IRAMAT UMR5060 CNRS, France

The prediction of very long term corrosion behaviour of ferrous alloys is crucial for the field of heritage artefacts conservation and restoration [1]. Presently, significant quantities of ferrous archaeological artefacts are stored in museum storerooms, often without particular control of the environmental conditions. Moreover, on heritage buildings numerous ferrous reinforcements were massively used since the Middle Age and an important part of them are subjected to indoor atmospheric corrosion. In order to predict the evolution of corrosion for very long period, as well as to set-up a diagnosis methodology, the corrosion mechanisms have to be understood.

In atmospheric conditions, the corrosion mechanisms are induced by successions of wet and dry periods [2]. After several ten to hundred years, this leads to rust layers of several hundred micrometer thickness, constituted of a goethite matrix sometimes crossed by reactive phases: maghemite (γ-Fe_2O_3), ferrihydrite ($Fe_5HO_8{\bullet}4H_2O$), feroxyhyte ($\delta FeOOH$).etc [3]. Previous studies have shown that the corrosion mechanisms are drastically influenced by the nature and reactivity of theses latter phases [4]. This point is of primary importance as it may consequently influence the global corrosion rate.

The aim of the experiments presented here is to study the influence of reducing/oxidising cycles of several iron oxides and oxyhydroxydes on reference powders. For that purpose, two complementary axes are used.

The first concerns the evaluation of the electrochemical behaviour of reference powders with the help of a carbon paste electrode. They are studied in voltammetric cyclic mode as a function of pH (pH=11, 7 and 5). The reduction curves of the different reactive phases (goethite, lepidocrocite, feroxyhyte, maghemite, etc.) will be presented and discussed.
In a second stage, the electrochemical measurements are coupled with in-situ techniques (XRD, XANES and µRaman spectroscopy), in order to characterize the nature of the reduced compounds. These experiments have been performed using different kinds of electrode cells (carbon paste, amorphous carbon, or gold electrode). These cells have been specifically designed to study the reaction under a thin film of electrolytes, both on transmission and reflexion mode. In particular, we will show how in situ analyses by XAS and µRaman spectroscopy coupled to the reduction of maghemite (γ-Fe_2O_3) in slightly alkaline medium (pH= 9) clearly testifies to a reduction into a non-stable magnetite, which regenerates into maghemite in aerated water.

Finally, these experimentations bring new insight both on the kinetics and the mechanisms of reduction of the reactive phases. This enables us to propose a hypothesis of long-term corrosion mechanisms in atmospheric conditions.

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Keywords: indoor atmospheric corrosion, iron, rust layer, reduction electrochemical.

In-situ monitoring by µXRD and µXAS of the corrosion products' evolution on ferrous archaeological artefacts during a dechlorination treatment

Florian Kergourlay, UMR 3299 CEA/CNRS SIS2M/LAPA et DiffAbs Synchrotron SOLEIL , 91191 Gif/Yvette, France
Solenn Reguer, DiffAbs Synchrotron SOLEIL, 91191 Gif/Yvette, France
Delphine Neff, UMR 3299 CEA/CNRS SIS2M/LAPA, 91191 Gif/Yvette, France
Eddy Foy, UMR 3299 CEA/CNRS SIS2M/LAPA, 91191 Gif/Yvette, France
François Mirambet, C2RMF, France
Elodie Guilminot, laboratoire Arc'Antique, 44000 Nantes, France
Céline Rémazeilles, LEMMA, 17042 La Rochelle, France
Philippe Refait, LEMMA, 17042 La Rochelle, France
Philippe Dillmann, UMR 3299 CEA/CNRS SIS2M/LAPA et IRAMAT LMC CNRS UMR5060, 91191 Gif/Yvette, France

After excavation, iron archaelogical artefacts need to be stabilized by removing chloride ions trapped inside the corrosion products. For that, conservation-restoration laboratories have developed dechlorination treatments. To better understand the underlying mechanisms occuring during a treatment, an original approach is proposed. It consists to study by *in situ* analyses during the first times of chemical (NaOH) dechlorination treatments the evolution of both β-$Fe_2(OH)_3Cl$ (main Cl-containing phase) and β-FeOOH, identified on iron archaeological artefacts immersed during 2000 years in a marine environment [1]. Specific cells have been designed so that *in situ* analyses can be performed on the corrosion layer of archaeological samples by using a rotating anode and synchrotron beamlines.
The µXRD data obtained on rotating anode highlighted several interesting results. It has been showed that β-$Fe_2(OH)_3Cl$ and β-FeOOH behave differently during a dechlorination treatment [2]. In a same time, while the phase β-$Fe_2(OH)_3Cl$ evolves towards magnetite (Fe_30_4), the phase β-FeOOH doesn't undergo any structural transformation. Moreover, the pathway from β-$Fe_2(OH)_3Cl$ to magnetite seems to occur firstly by the transformation of β-$Fe_2(OH)_3Cl$ into $Fe(OH)_2$, detected on hundreds of micrometers.
To refine these results, specific experiments using the combination of XAS at Fe K edge and XRD were performed under synchrotron radiation. It allows us to detect the appearance of poorly crystallised phases thanks to XAS measurements. In addition, XRD aquisitions, performed on a 2D detector in a short time allow studying the kinetics of the phase transformation more precisely.
These data contribute to a better understanding of the first transformations occuring inside the corrosion products of archaeological artefacts, what is fundamental to improve the dechlorination treatments.

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Modelling the corrosion of chloride infested archaeological iron: What can it tell us about corrosion rate of real objects?

The corrosion of chloride infested archaeological iron occurs at very low humidity values.[1,2] In very short time periods it can produce catastrophic outcomes that destroy the value of an object as an information resource. The post-excavation corrosion process has been examined by laboratory modelling that examined how ferrous chloride and Akaganeite (βFeOOH) corrosion products interacted with iron powder as a function of relative humidity.[1-3] By identifying relative humidity no-corrosion values these studies offered information to aid the safe storage of chloride infested iron using desiccation. Experimental method involved recording oxidation by dynamic weight change to offer data on corrosion rate as a function of relative humidity. As expected, corrosion rate increases as relative humidity rises, with significant rate rises on reaching 30% relative humidity. Best practice for preventing corrosion of archaeological iron by desiccation has been developed using this data. However, the dependency of control methods on mechanical techniques and/or human input mean that high values of relative humidity may often occur where management is lax. In some instances exceptionally high relative humidity can be generated, such as inside polyethylene bags wrongly used on excavation or exhausted silica gel desiccant in a closed container housing iron. Consequently it is necessary to examine the effect of these corrosion products on iron at higher relative humidity values.

This study examines the influence of selected humidity values above 30% on the iron/βFeOOH and iron/$FeCl_2 4H_2O$ reactions. Dynamic weight gain methodology is employed to monitor oxidation of samples in a climatic chamber operating to ±1% rh and ±0.5 C. The resulting corrosion rates are linked to existing data on reaction rates below 30% relative humidity to build comparative corrosion rate data. This is extrapolated against time to facilitate a discussion on the usefulness of such extrapolation for considering 'lifespan' of objects. This discussion takes into account the limitations of experimental design in relation to the chemistry and morphology of archaeological objects, as well as the constraints imposed by the needs of the object as an archive. The goal is to consider how useful such modelling can be for predicting how rapidly differing relative humidities influence the survival of archaeological iron objects as a heritage resource. Focus is on what the experimental work can usefully reveal about corrosion rates for archaeological iron, which involves an examination of the variables that dictate post-excavation corrosion. Discussion is completed by considering which other options for determining post-excavation corrosion rates for chloride infested iron can potentially offer meaningful insight into predicting longevity of objects as a function of environment. This could then be used to calculate risk when storing archaeological iron.

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An electrochemical impedance spectroscopy system for the in-situ assessment of the conservation state of archaeological bronzes

E. Angelini, S. Corbellini°, S. Grassini*, M. Parvis°, M. Piantanida**
**Dip. Scienza dei Materiali ed Ingegneria Chimica, Politecnico di Torino, Torino, Italy*
°Dip. di Elettronica, Politecnico di Torino, Torino, Italy

The corrosion process occurring onto a copper-based alloy during burial leads firstly to the formation of a cuprite layer; then, various corrosion products of copper II can grow, forming a brown-black color or a green *patina*. The composition, the thickness and the porosity and consequently the barrier properties of this corrosion layer depend both on the chemical composition of the bulk material and on different environmental parameters, such as the moisture content, the temperature, the pH and the salts present in the soil. A low pH value is required to keep corrosion products stable; chlorides and phosphates affect the corrosion rate in an opposite way: the first increasing it and the second acting as a corrosion inhibitor. After the excavation if the *patina* is unstable, the conservation state of the artifacts gets worse and worse with time; consequently, a protective coating should be employed to prevent them getting damage.

The purpose of the present study is to develop an in situ, non-destructive approach for the assessment of barrier properties of the *patina* and of the protective effectiveness of the coating applied during restoration on bronze artifacts. Among the available techniques that can be employed to carry out these kinds of investigations, the Electrochemical Impedance Spectroscopy (EIS) is one of the most promising since it could be potentially implemented in situ by means of compact and portable instrumentation, despite the fact that at present the majority of available instruments are intended to be used in the laboratories only. In addition, the EIS could be satisfactory applied in the field of cultural heritage thanks to the small alternating voltage that can be applied as a stimulus to perform the measurements. The only strong limitation arises from the necessity to employ a chemical cell filled with an electrolyte, whose action can be detrimental for the artifact. Moreover, these cells, which are based on a three electrode structure, require a rather large and flat surface on the object to be analyzed, but in most of the practical cases such areas are not available, making the available probes practically unsuitable. For these reasons, a new EIS portable instrument is proposed to work in conjunction with new kinds of probes in order to permit the in-situ analysis of small artifact.

The new proposed EIS system is based on a low-cost and very compact measurement instrument that is designed to synergistically work in connection with a common laptop computer so that advanced processing algorithms can be easily implemented, allowing the system to match the performance of classical laboratory instruments at a very low cost and directly in the field. An auto-calibration method is adopted in order to reduce the measurement uncertainty and to extend the measurement range still avoiding the use of costly components; the stimulus can be in the range from 1 mHz to 100 kHz while the measurement range can span from about 100 Ω to more than 10 GΩ. This very wide measurement range allows the proposed system to be employed not only for the analysis of *patinas*, but potentially for every kind of coating characterized by high protective properties.

The system has been tested on several patinas and the results have been compared with the ones obtained by employing a classical EIS probe.

REAL TIME CORROSION MONITORING SYSTEM FOR PROTECTION OF CULTURAL HERITAGE

Milan KOUŘIL[1], Tomáš PROŠEK[2], Bert SCHEFFEL[3], Jan STOULIL[1], Yves DEGRES[4]

[1]*Institute of Chemical Technology, Prague, Czech Republic, kourilm@vscht.cz*
[2] *Institut de la Corrosion, France, tomas.prosek@institut-corrosion.fr*
[3]*Fraunhofer Institute for Electron Beam and Plasma Technology, Germany, bert.scheffel@fep.fraunhofer.de*
[4] *nke SA, France, ydegres@nke.fr*

A monitoring system aimed at enabling continuous measurement of the metal corrosion rate was developed within the European Commission's FP6 project. A new project Musecorr supported by 7th Framework Programme leads to development of wider spectrum of modifications of the monitoring system as well as full material scale of corrosion sensors that allow corrosion monitoring in both indoor and outdoor conditions. Development of the sensors is especially focused on satisfying the needs of conservators active in preventive conservation. The materials selection for the sensors covers a wide variability of materials in museums and depositories – iron, copper, silver, zinc, lead, tin, bronze and brass. The measuring system in small and watertight optimized for working at indoor and outdoor conditions. Optionally, the system is able to measure corrosion rate of two different sensors at the same time and to store the data autonomously in inner memory or to transfer the data by using a built-in GPRS unit. The system records ambient temperature and relative humidity, simultaneously. The software is able to evaluate corrosion depth of the metal in time, corrosion rate and to classify the actual corrosion rate to aggressivity classes according to the standards. The system and the sensors sensitivity have been tested during many corrosion tests. The sensitivity to different air pollutants is very variable with the material selection and thickness of the metallic track on the sensors which affects the service life as well. For the outdoor sensors the resolution of the corrosion depth goes to nanometres. New sensors for indoor conditions having the track thickness 50 or 500 nm were developed ant tested as well.

The concept of the measuring device is simple and yet highly effective. The electronic unit measures and registers the change over time in the electrical resistance of a thin metal track applied on an insulating substrate. If the metal corrodes, the cross-sectional area of the track decreases and the electrical resistance increases. A part of the metal track is protected by an organic coating and, thus, serves as a reference to compensate for resistivity changes due to varying temperature.

Beside the cultural heritage care, the logger can be applied in various fields where monitoring of corrosion is vital: pollution detection (SO_2, NO_x or organic acids by using proper materials sensitive to given pollutant), transportation and storage (design of better measures for corrosion protection of vehicles and transported goods), civil engineering (monitoring of the corrosivity of structures and materials used in the civil engineering in order to select proper materials and designs) or electronics (protection of electronic equipment in e.g. GSM stations, cars and ships).

Environmental degradation studies on some ancient metallic artifacts of Jiroft civilization (3 millennium BC)

M. Saremi[1] ; M.Bakhshandehfar[2],A. Soltaninejad[3]

1- Faculty of Metallurgy and materials Engineering, University of Tehran, saremi@ut.ac.irTehran, Iran. E-mail:

2,3 - University of Art. Tehran, Iran.
E-mail :
anis_soltaninejad@yahoo.com ; hr.bakhshan@yahoo.co.uk

Abstract

Jiroft civilization belongs to jiroft districts in south of Iran which has records of being the center of civilization 2-3 millennium BC. The extend and variety of the found artifacts from recent and old systematically diggings indicates the presence of specific metallurgical techniques in the area. The found artifacts can be categorized in tools, coins, pots, decorative and worshiping items which are mainly made of impure copper having arsenic, chloride and sulfur as the main impurities ties coming from copper minerals.

The corrosion and protection of these item as well as the understanding of the metallurgical techniques have been used in that civilization are the main concern of the cultural heritage organization.

The aim of this work is to study the micro structural degradation of the artifacts and find the role of each elemental imparity in its corrosion process.

Microstructual studies revealed that in most of the articles the metallic copper is gradually converted to the minerals depending to the environments they have been remained in for the years. Two type of corrosion was taking place, one from outside due to the presence of chloride, sulfur and phosphates in the vicinity soil and water and the second process was developed from inside because of the presence of chlorides in the metallic inclusions and in the main phase. X-Ray analysis by XRF and PIXE revealed that chloride and sulfur coming from the minerals were not fully separated during casing of some articles but in pots made of copper sheets no chloride were present and these items remained un-attacked. Presence of internal chlorides is harmful to the ancient artifacts preservation and consequently must kept dry.

Corrosion of Polymer Materials

Influence of Residual Stresses on Lifetime Prediction for Plastic Pipes

Dipl.-Wirtsch.-Ing. Jürgen Heinemann, Dipl.-Ing. Hansgeorg Haupt, Dipl.-Ing. Alexander Bockenheimer, Prof. Dr.-Ing. Christina Berger, Technische Universität Darmstadt, Zentrum für Konstruktionswerkstoffe, Staatliche Materialprüfungsanstalt Darmstadt / Fachgebiet und Institut für Werkstoffkunde, Darmstadt, Germany, M.Sc. Raquel Maria, Dr. Robert Brüll, Deutsches Kunststoff-Institut, Darmstadt, Germany

The strong significance of plastic pipes in comparison to competitive materials amongst other advantages is due to their long lifetime verified on the basis of international standards. However, the effects of residual stresses caused by manufacturing and their later relaxation have not been yet subject to a systematic investigation.

The principal suitability of the procedure for the lifetime analysis of plastic pipes described in ISO 9080 is substantiated by long-lasting test and practical experience for almost 60 years now. In addition, no cases are known of systematic damage due to the failure of plastic pipes because of an insufficient lifetime analysis. Finally, tests conducted on pipes in operation for over 40 years do not provide any contrary evidence.

The production of plastic pipes is usually done via extrusion through a form-giving profile tool, after which a dip or spray cooling of the external pipe wall takes place. The form-giving profile tool induces a different orientation of the polymer chains. Additionally, the developing temperature gradient in the pipe wall during the cooling process leads to the formation of a distinct morphology profile across the pipe wall. Furthermore, the solidification process which progresses from the outside inwards causes an uneven volumetric contraction.

The effects of residual stresses resulting from the aforementioned processes and their later relaxation are examined through a collaborative research project, which will enable an even more accurate lifetime analysis for plastic pipes compared to the standard lifetime extrapolation.

Within the scope of the project, internal pressure creep rupture tests at four different temperatures are conducted. Plastic pipes made of three different materials (PE 100, α-nucleated PP-H and β-nucleated PP-H), with two different dimensions (63 mm and 110 mm) and three different residual stress levels (normal, high, tempered), are examined. The results form the basis of a lifetime analysis using the standard extrapolation method.

Subsequently, an evaluation of the results as a function of the occurring residual stresses is carried out with respect to an accompanying material characterisation and chemical analysis. This includes the determination of the distribution of the residual stresses, the degree of crystallinity and the orientation of the polymer chains over the pipe wall as well as the analysis of the thermal behaviour and different mechanical characteristics.

Test results of the progressing research project will be shown.

Comparison of the stress crack resistance of polyethylene grades with the test performance behaviour of packagings for the transport of dangerous goods

Margit Weltschev and Ute Niebergall, Federal Institute for Materials Research and Testing (BAM),
Unter den Eichen 87, 12205 Berlin, Germany

Resistance to stress cracking by wetting solution is one of the selected properties together with the corresponding test method FNCT and tolerances for a comparison of polyethylene grades of one design type in the procedural rule on suitability proof for alternative plastic resins used for packagings and intermediate bulk containers (IBCs) for the transport of dangerous goods.

The environmental stress crack resistance determined by Full Notch Creep Test (FNCT) represents the impacts from the stacking tests at 40 °C performed with standard liquid wetting solution (without pre-storage) and with normal butyl acetate saturated wetting solution (pre-storage with normal butyl acetate).

Environmental stress crack resistance determined with FNCT for the polyethylene grades was related to the times to failure of different jerrican samples made of these grades in stacking tests with 5 % wetting solution and a n-butyl acetate saturated wetting solution (pre-storage with n-butyl acetate) at 40 °C. The FNCT is suitable for comparison of polyethylene grades in relation to environmental stress crack resistance independent of their use as drum, IBC or jerrican material. The stiffness of polyethylene grades should be taken into account to the comparison as jerricans are not only chemically but also mechanically stressed.

Influence of processing conditions and inner properties on the environmental stress cracking resistance of polycarbonate

Prof. Dr.-Ing. Dr.-Ing. E.h. Walter Michaeli, Dipl.-Ing. André Potthoff, Institute of Plastics Processing (IKV), Aachen, Germany

Environmental stress cracking (ESC) is the most common failure reasons of plastic parts during their use. There are many factors that influence the resistance of plastic products that are affected by a combination of a mechanical load and a liquid medium which may lead to environmental stress cracking. The most obvious factor is the interaction between plastic and medium which could be described by using the Hansen solubility parameters. Other parameters are the type and extent of the mechanical load, the time of applying this load and the surrounding temperature. The influence of the processing conditions e.g. of the injection molding process has not been investigated yet. For this reason there are several tests carried out at the IKV. Test specimens are injection molded with different parameters for melt temperature, mold temperature and injection rate. These parameter-variations are causing variable inner properties of the molded parts, for example residual stresses and molecular orientations. Investigations show that the resistance against environmental stress cracking of specimens with different inner properties differs in a wide range. As it can be seen in the figure lower values for melt temperature and mold temperature lead to a higher durability. The higher value is about as twice as high as the lower value. Lower temperatures correlate with higher molecular orientations in the surface layer of the parts and higher residual stresses. So there is an interrelationship between inner properties and the environmental stress cracking resistance of injection molded parts made of polycarbonate. The results of the investigations are discussed in-depth.

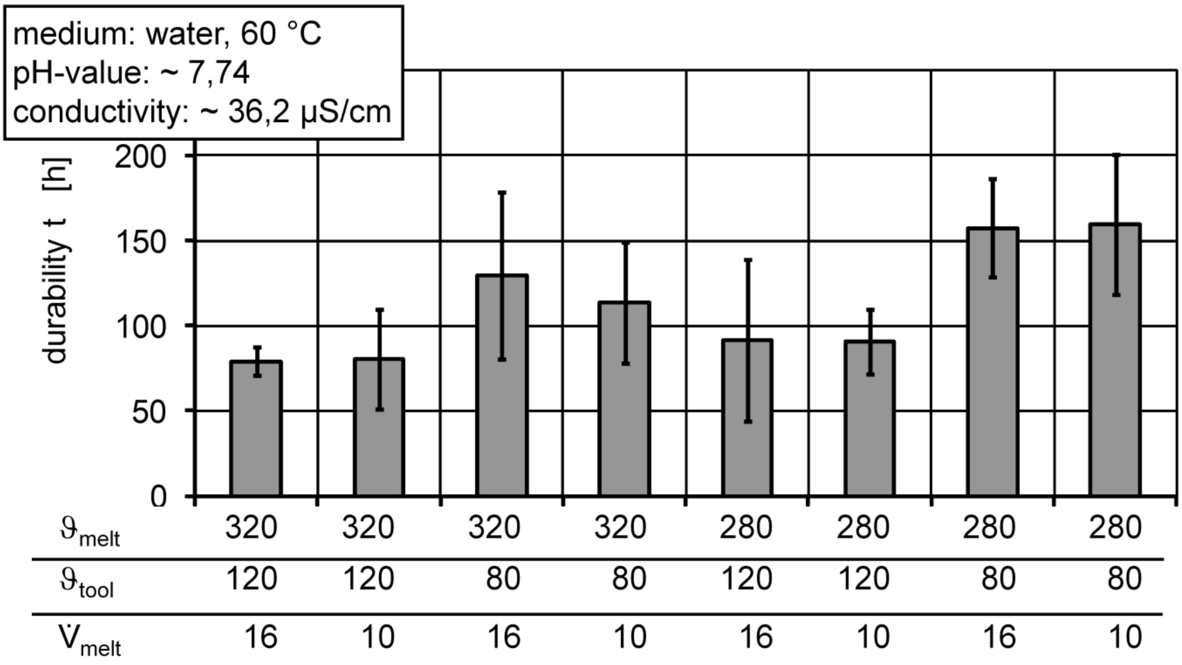

Figure: Comparison of the durability (PC, Makrolon 2858, σ = 20 MPa)

FRP Solutions for Sodium Hypochlorite Service

Authored by:
Michael Jaeger, Arie van Buren and Georges Kappenstein
Ashland Performance Materials

ABSTRACT

Sodium hypochlorite is used and occurs in many processes, such as water treatment / disinfection, odor control, chemical synthesis, and flue gas scrubbers. Liquids containing sodium hypochlorite are corrosive to many materials. Fiber Reinforced Polymers (FRP) has been (and is) the preferred material of construction for many years, as confirmed in a recent industry survey (1), and as demonstrated in numerous published case histories.

This paper reviews main hypochlorite applications, historical and new chemical resistance studies, and proposes solutions for best service life.

Internal Pressure Testing as a Tool for Life Cycle Management of Piping Systems

R. Morach, G. Schlecht
INTERTEK Expert Serives, CH-4002 Basel, Switzerland

Beside its use for quality control, hoop stress testing proved to be a valuable method to assess the condition of plastic piping systems. The presented applications show the benefit of the methodology but also the pitfalls.

More than 30 years experience showed that internal pressure testing is a useful tool to monitor the degradation of thermoplastic piping systems. It can be used for quality control as well as for the decision making on investments by estimating the remaining lifetime. Substantial savings were achieved by delaying investments for several years.

However, the field data clearly demonstrate that the information about changes in the conveyed chemicals is key to a successful lifetime extrapolation. More severe conditions will result in unexpected failure.

The experience from field applications shows that 5% remaining life time in the lab test is a lower limit. Below this limit in lab test the pipe may fail at any time, hence the pipe should be replaced immediately.

Keywords: Thermoplastic piping, degradation, lifetime prediction, field data, internal pressure testing, hoop stress

Corrosion of Steel in Concrete

CORROSION OF STEEL REINFORCEMENT IN CONCRETE OF DIFFERENT COMPRESSIVE STRENGTHS

L. Abosrra, A. F. Ashour and M. Youseffi
School of Engineering, Design and Technology, University of Bradford, Bradford, BD7 1DP

A. Elhoud

University of Aberdeen, School of Engineering, Aberdeen, AB24 3UE, UK

ABSTRACT

Corrosion of steel bars embedded in concrete having compressive strengths of 20, 30 and 46MPa was investigated. Reinforced concrete specimens were immersed in a 3% NaCl solution by weight for 1, 7 and 15 days. In order to accelerate the chemical reactions, an external current of 0.4A was applied using portable power supply. Corrosion rate was measured by retrieving electrochemical information of polarization technique. Pull-out tests of reinforced concrete specimens were then conducted to assess the corroded steel/concrete bond characteristics.

Experimental results showed that corrosion rate of steel bars and bond strength between corroded steel/concrete were dependent on concrete strength and acceleration corrosion period. As concrete strength increased from 20 to 46MPa, corrosion rate of embedded steel decreased. First day of corrosion acceleration caused a slight increase in steel/concrete bond strength, whereas sever corrosion after 7 and 15 days of corrosion acceleration significantly reduced steel/concrete bond strength. Visual and metallographic observation of steel bars removed from concrete samples after testing revealed that the severity of corrosion reactions and reduction of steel bar diameter increased as the corrosion acceleration period increased. Presence of localized corrosion pits as well as sever corrosion grooves of steel bars was confirmed after 7 and 15 days of corrosion acceleration, respectively.

Keywords: concrete, steel reinforcement corrosion, bond strength, polarization technique

Steel corrosion resistance in model solutions, containing wastes

D. A. Koleva[1], J. Hu[1], K. van Breugel[1], J. H. W. de Wit[2], J. M. C. Mol[2]

[1,2]Delft University of Technology, The Netherlands
[1]Faculty of Civil Engineering & Geosciences, Dep. Materials & Environment; Stevinweg 1, 2628 CN, Delft; [2]Faculty 3mE, Dep. Surfaces & Interfaces, Mekelweg 2, 2628 CD Delft.

The study reports on the corrosion performance of low-carbon steel in extracts of Ordinary Portland Cement (OPC) and Blast Furnace Slag cement (BFS), containing waste products i.e. "Red Mud" (RM). The motivation is related to several aspects, mainly: increased corrosion resistance in chloride containing environment in the presence of RM; superior properties of the passive layer in BFS concrete (BFS has a good tolerance to chloride, however the steel passive layer has a worse performance, compared to OPC concrete); corrosion control in an ecologically friendly manner (since RM and BFS are widely generated wastes).

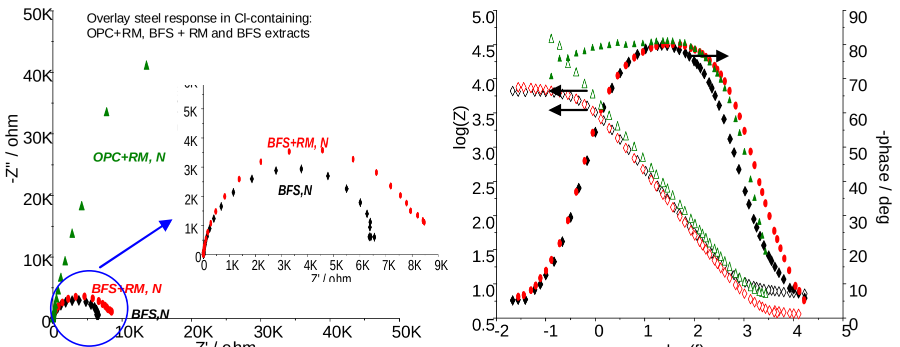

Fig.1 EIS response

sample	Rp[1] kΩ.cm^2	Rp[2] kΩ.cm^2
OPC	543	
OPC,N	293	136
OPC+RM+N	346	207
BFS	515	
BFS,N	6.72	5.21
BFS+RM,N	8.65	8.64

[1]Rp from EIS; [2]Rp from PDP

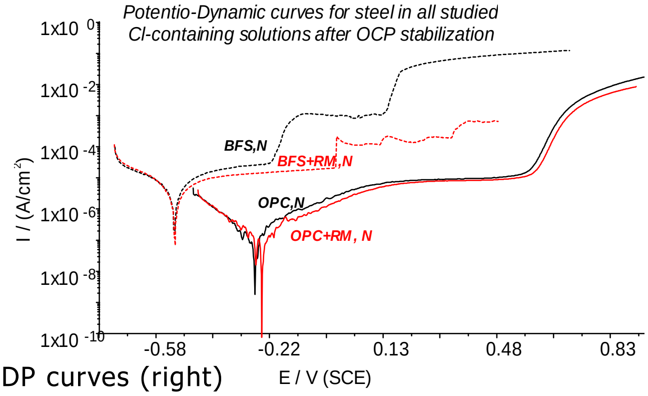

Fig.2 Rp values (left) and PDP curves (right)

The paper presents electrochemical tests of St37 (C~12%) steel electrodes in model solutions: control solutions are designated OPC, BFS, OPC+RM and BFS+RM; Cl^--containing solutions (2% NaCl) are OPC,N; BFS,N; OPC+RM,N and BFS+RM,N (RM denotes for 20% RM cement replacement). The investigation is on-going. At this point it can be stated that the addition of RM stabilizes the passive layer on the steel surface in BFS solutions, especially in the presence of chloride. Fig.1 presents the EIS response, Fig.2 the potentio-dynamic curves after OCP stabilization only. Significantly higher corrosion resistance (higher |Z|, Fig.1) is relevant for the OPC+RM,N (as expected), compared to BFS+RM,N solutions. The addition of RM to the BFS (BFS+RM,N) leads to increased corrosion resistance, compared to BFS,N only, evident by the higher magnitude of |Z| and lower anodic currents (Fig.2). Table 1 summarizes the derived *Rp* values, proving the positive effect of RM in both OPC and BFS extracts. Further the paper will discuss longer immersion intervals, microstructural and morphological aspects of the passive layers.

COMPARATIVE STUDY OF TECHNIQUES TO EVALUATE THE CORROSION STATE OF REBARS EMBEDDED IN CONCRETE

Elisabeth MARIE-VICTOIRE[1], Florence VALLOT[2], Alain PROUST[3]

[1] Laboratoire de Recherche des Monuments Historiques, 29 rue de Paris, 77420 Champs-sur-Marne, France, elisabeth.marie-victoire@culture.gouv.fr
[2]Laboratoire Régional de l'Est Parisien, 319 avenue Georges Clemenceau, Vaux-le-Pénil, B.P.505, 77015 Melun Cedex, France, Florence.Vallot@developpement-durable.gouv.fr
[3]Euro Physical Acoustics, 27 rue Magellan, 94373 Sucy-en-Brie Cedex, France, Aproust@epandt.com

Carbonation induced corrosion of the rebars is the main decay mechanism encountered on historical buildings made of reinforced concrete. This type of corrosion can generate heavy spalling, and therefore important loss of concrete, which is of major concern in the field of cultural heritage.

Consequently, to be able to evaluate the corrosion state of rebars embedded in concrete is essential, either for diagnosis purpose, or to evaluate conservation treatments.

Potential mapping or LPR measurement are commonly used for such purpose, but they are clearly climatic condition dependant and they are disturbed by conservation treatments such as migrating corrosion inhibitors or realkalisation, which generate a perturbation of the electrochemical equilibrium of the concrete.

On another hand, acoustic emission techniques are among the most used for corrosion diagnosis (in pipelines…) and could represent an interesting alternative monitoring technique for concrete.

So the purpose of this study was to determine if acoustic emission detection could be applied to reinforced concrete. Therefore a set of small concrete slabs, reinforced with 3 rebars were cast, artificially carbonated and submitted to natural aging for several years. Then they were placed in a controlled environment, favorable to corrosion (20°C, 90%HR), and LPR measurement and acoustic emission monitoring were performed. In order to validate the results of these comparative tests, a final autopsy was realized.

Corrosion behavior of reinforcing steel in concrete in high chloride and low pH environment

T. Nishimura,
National Institute for Materials Science (NIMS), Japan

It is important to estimate the corrosion of reinforcing steel in concrete facilities, because the concrete structures are frequently located near the sea side. Moreover, recently in the east Asia, the acidic rain is a severe problem for the deterioration of concrete. In the case of environmental factors in mortar, the Cl ion concentration and pH were monitored by inserting microelectrodes into artificial pores in the mortar which was exposed in 0.5 Mol/L chloride solution (pH 4.0). At the same time, the electrochemical behavior of the reinforcing steel was investigated by EIS. In the EIS measurements of the reinforcing steel, as compared with a 10mm cover thickness, a 20mm cover thickness showed a higher impedance behavior. The Cl ion concentration in the mortar was obtained using Ag/AgCl microelectrodes, showing that this behavior is generally controlled by diffusion. When the diffusion equation was used in this work, the diffusion coefficient (Dc) showed a high value of $Dc=9.5\times10^{-5}$ mm^2/s. Similarly, the pH in the mortar was obtained using W/WOx microelectrodes. With a 20mm cover thickness, pH was limited to approximately pH8.4, but with a 10mm cover thickness, pH continued to decrease to pH8.0. The latter phenomenon was considered to be the result by penetration of H^+ ions from the surface. Based on the results of monitoring with the microelectrodes, solutions simulating those in the pores in mortar were prepared and used in EIS measurements. The charge transfer resistance Rct in the simulated solutions showed good correspondence with the impedance (Z_{1mHz}) in the low frequency region (1mHz) in the actual mortar. This is attributed to the fact that the corrosion of reinforcing steel was controlled by the solution conditions (mainly Cl concentration and pH) in the pores in mortar. If these solution conditions (Cl concentration, pH) exceed threshold values, it was found that the passivation film is destroyed, resulting in high corrosion.

Early Corrosion Testing on Concrete and the Importance of the Interpretation to Provide long term Preventive Measures

Paul A. Noyce Electro Tech CP LLC, Florida, USA
Gina L Crevello, EChem Consultants LLC, New York City USA

Corrosion failures account for the degradation of infrastructure causing billions of dollars in repairs annually. These failures, more importantly, cause health and safety issues which have led to the loss of human life. This has recently been brought to the attention of the broader public and congress in the Corrosion Prevention Act, March 2007 and the Bridge Life extension act March 2009. As corrosion engineers have often stressed stricter procedures on when, what and who should be assessing corrosion behaviour can curb these significant losses and monetary costs. The following paper addressed preventative maintenance and testing, proper specification of the required tests based on a multitude of factors, and the importance of accurate interpretation of this data by qualified professionals.

Engineers are called in to test for corrosion behaviour once a structure has exhibited corrosion related damages. At this stage of the structure's life, the costs of repairs have increased exponentially over taking a preventative approach. This leads to significant costs to the owners for the repair alone, without dealing with the root cause.

By testing and analyzing corrosion in the early stages of a structure's life preventative corrosion mitigation can be implemented to avoid the unnecessary cost of repairs and failures. Unfortunately, due to budgets and the preconceived notion that "if corrosion is not visible then there is not problem" corrosion testing is generally not incorporated into maintenance budgets. It is imperative that this preconceived notion of visibility be changed and that testing be carried out in the earlier stages of a structure's life.

When a structure is being evaluated for corrosion, there are many methods to test various conditions that can determine corrosion behaviour as well as conditions that accelerate the corrosion activity. Test procedures are also dependent on various materials, microclimates, and external temperatures and environmental factors. The team specifying the testing must understand all the relevant factors that are at play on a structure prior to determining what to test.

It is commonly known that standard test procedures such as ASTM C876 can provide some information regarding corrosion risk, but not a true evaluation of the structures behaviour. Accurate information can be gained through testing, but it is the interpretation and integration of this data that needs to be formulated by an experienced engineer or professional. Recent graduates, technicians, and inexperienced personnel may not have the true understanding and knowledge of corrosion behaviour to determine the actual conditions and factors at play. It has often been found that what one test company may assess and interpret is far different than what the experienced corrosion engineer would interpret from the same data.

The key to avoiding the loss of materials and more importantly the loss of human life, is to approach corrosion in a preventative manner and ensure that testing for corrosion is carried out and interpreted correctly.

Non contacting corrosion method, NCCm, applied to the steel corrosion rate determination in different solutions and reinforced concrete specimens

C. Andrade, I. Martínez, Institute of Construction Science, CSIC, Madrid, Spain.

All the current techniques used to measure the metallic corrosion require contact with the metal. Particularly, in the case of reinforcement corrosion, this signifies the need to reach the bar that is embedded in the concrete, which may consequently result in the disruption of the integrity of the structures.

In a recent paper it has been published the feasibility of using a new method for polarizing the reinforcement or any metal in an electrolyte, without the need of direct contact with it (NCCm). The polarization was obtained through the induction of current from an external electrical field. The current runs through the electrolyte and the metal in parallel, depending on the electrode arrangement. The resulting Polarization Resistance calculated is termed as Inductive, $R_p = R_{pi}$. The Inductive Polarization is calculated by the model of resistances in parallel, which requires a separate measurement of the electrolyte ohmic resistance.

In the present paper, an extension to different electrolytes of the feasibility of the method is presented. Solutions with several different resistivities and concrete specimens with and without chlorides have been used. The main aim of this study is to explore the limits of application of the non-contacting equations proposed for the R_{pi} calculation. The method has been calibrated by means of verifying the agreement between the electrochemical and the gravimetric losses.

The results also indicate that electrolytes of low resistivity mask the measurement, and consequently, R_{pi} could not be calculated in the manner tried. In electrolytes with high resistivity, such as concrete, the feasibility is found to depend on the relative values of R_e and R_{pi}. The incorrect results obtained in this condition could be due to the particular equivalent circuit selected to represent the system. Other different circuits are under study for a better understanding of the phenomenon.

KEYWORDS: corrosion, rate measurement, non-metallic contact.

Determination of self - corrosion in the case of element corrosion of steel in concrete

M. Beck, A. Faulhaber, B. Isecke, BAM Federal Institute for Materials Research and Testing, Berlin/ Germany

Safety and durability of reinforced concrete structures is one of the most important requirements for projecting buildings. The standards and guidelines only contain common requirements about concrete quality and concrete cover. In very critical cases, for example the ingress of chlorides, the application of different coatings is presently the only possibility to protect the reinforced concrete structures, before corrosion is initiated. In case of depassivation of reinforcement the modelling of corrosion would be more practical. One subproject of a DFG-research project (FOR 537) is currently performed at BAM, the Federal Institute for Materials Research and Testing.

In practice the reinforcement is depassivated locally by the ingress of chloride and parts of the steel become anodic and other cathodic areas. At the anode a significant mass loss can be determined after a period of time, caused by an electric current between the local anodic and cathodic areas. Thereby the relation between both areas can be in a range of decades, the effect is called element corrosion. In civil engineering practice higher mass losses can be observed, caused by an additional part of mass from the hydrolysis at the anode. This part is called self-corrosion and must be considered for the life time prognosis.

Therefore the aim of the work presented is to identify the part of self-corrosion by the determination of electrochemical parameters and mass losses. The electrochemical parameters were detected by suitable electrochemical measurements, depending on different concrete parameters and different climates.

In this paper the development and the scale of self–corrosion are presented. Furthermore the results of the electrochemical measurements, like potential and polarization resistance are shown. The results are compared and discussed, considering the different concrete parameters and storing conditions.

Mathematical models of carbonation process (corrosion) in concrete subjected to aggressive carbon dioxide attack

B.V. Gousev, V.F. Stepanova,
Scientific R&D Institute for Concrete and Reinforced Concrete, NIIZhB, Moscow, Russia

Main task of this work is development of universal corrosion model for the concrete subjected to aggressive environs of natural and industrial origin. Complicated process of corrosion is presented in the form of elementary constituents, for each of these constituents the mathematical equation of the process is correlated. Corrosion model comprise of the system of differential equations in partial derivatives, initial and boundary conditions of which define the character of corrosion attack. Equations for the liquid, air and salt corrosion are made. The models are constructed the way that complicated cases of corrosion contain simpler ones in which they are transformed under certain simplifications. Some attention is paid to the problems of systematization and unification of experimental data.

For the particular case the analytical relations between corrosion front's movement and the time (liquid and air carbon dioxide corrosion) are obtained. Received formulas contain as a partial case well-known "relation of square root out of time", but sufficiently improve it, that is verified as by numerical computation, so by the experimental data.

Application of mathematical model for the corrosion process circumscription represents great advantage, enabling to circumscribe corrosion processes (carbonation) with sufficiently high degree of accuracy without experiments. In this case one can arrange numerical experiment (modifying parameters in equations, in initial and boundary conditions it is possible to check any amount of variants in a very short time) and from the other side - money saving on real experiments conduction is achieved.

Electrochemical behaviour of AISI 304 stainless steel in alkaline media simulating concrete. The effect of pH and chlorides.

M.F. Montemor[1], L. Freire[1], M.G.S. Ferreira,[1,2], A.M.P. Simões[1], A. Catarino[3], I. Godinho[3], M.J. Ferreira[3], M.J. Carmezim[1,4], A.S. Castela[1,5]
1.ICEMS, Instituto Superior Técnico, Universidade Técnica de Lisboa, Lisboa, Portugal.
2. CICECO, Universidade de Aveiro , Aveiro, Portugal
3. Instituto Superior de Engenharia de Lisboa, Lisboa, Portugal
4. EST Setúbal, DEM, Instituto Politécnico de Setúbal, Setúbal, Portugal
5. EST Barreiro, Instituto Politécnico de Setúbal, Setúbal, Portugal

Abstract

Nowadays, stainless steel reinforcements appear as one of the most effective solutions to prolong the lifetime and to decrease the maintenance costs of reinforced concrete structures exposed to very aggressive environments.

In the present work, different electrochemical techniques, including electrochemical Impedance spectroscopy (EIS) were used to study the pitting corrosion behaviour of austenitic stainless steel (AISI 304) and mild steel (AISI 1040) in alkaline solutions, simulating the interstitial concrete electrolyte contaminated with chloride ions. The electrochemical behaviour was studied in solutions of different pH, in the alkaline range (13 - 9).

The morphology of the steel surface was evaluated by Scanning Electron Microscopy (SEM) and chemical analysis (EDS).

The results reveal that both pH and chlorides have a marked effect in the corrosion resistance of stainless steel rebars. The work highlights the benefits of SS rebars comparatively to ordinary mild steel.

Keywords: Stainless steel, concrete, corrosion, passivity

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Investigations on the Impact of Decreasing Chloride Concentration on the Corrosion State of Reinforcing Steel in Alkaline Environment in Consequence of Cathodic Polarisation

Thorsten Eichler[1], **Bernd Isecke**[1]

[1]*Federal Institute for Materials Research and Testing (BAM Berlin), Germany,*
thorsten.eichler@bam.de
[1]*Federal Institute for Materials Research and Testing (BAM Berlin), Germany,*
bernd.isecke@bam.de

Since more than 30 years the cathodic protection (CP) of steel in concrete is well acknowledged to be an efficient and in many cases cost effective rehabilitation measure for reinforced concrete structures which suffer from chloride induced depassivation of the reinforcement. In the recent literature the efficiency of cathodic protection is frequently discussed. The comparatively small protection currents as well as the often observable potential ennoblement of open circuit potentials (EOC) are explained by repassivation effects occurring during polarisation or during depolarisation after sufficient polarisation times. Considering the fundamentals of electrochemistry it becomes obvious that cathodic polarisation induces chemical alterations at the steel concrete interface, which are beneficial concerning the corrosiveness of the environment. As consequence of forcing the cathodic reaction, the hydroxide ion concentration adjacent to the steel surface increases and therefore the pH value increases. The applied electric field additionally causes the migration of chlorides to the external anode. Thus, the chloride concentration decreases, when the applied field is strong enough to overcompensate the back diffusion of chloride ions. The investigations discussed in this paper aim to clarify to which extent the migration of chlorides has impact on the remaining corrosion rate of the reinforcing steel in open circuit conditions. For this purpose different techniques are applied to laboratory test specimens. The changes in corrosion state are investigated by electrochemical test methods like impedance spectroscopy and current-potential curves, which provide the basic data on the corrosion state as well as on the prevalent mechanisms. It can be shown, that the remaining corrosion rate decreases when the chloride concentration of the medium decreases below a critical threshold, even when more or less significant corrosion loss could be observed before starting to decrease the chloride concentration.

ELECTROCHEMICAL BEHAVIOUR OF GALVANIZED STEEL FOR PRESTRESSED CONCRETE STRUCTURES IN ALKALINE ELECTROLYTES

Ioan PEPENAR[1]

[1]*The Research Centre-CERTINCON, Romania, ioan.pepenar@e-altfel.ro*

The paper presents the results of the researches on the electrochemical behaviour of galvanized steel for prestressed concrete structures in saturated calcium hydroxide solutions, in the absence and in the presence of chloride ions.

The galvanized steel passivates in Portland cement concrete pore solution, phenomenon emphasized by the electrode potential shifting towards less electronegative values. The hydrogen, released during the first stage of the reaction between zinc and saturated calcium hydroxide solution has not induced hydrogen embrittlement of the tensioned galvanized steel.

In order to establish the critical value of the chloride ions concentration in the electrolyte solution, beneath which the passive state of the galvanized steel is preserved, there have been drawn up the anodic potentiodynamic curves in alkaline electrolytes with various amounts of chloride ions. At the same time, the influence of the exposure time to the atmospheric corrosion, of the immersion time of zinc coated steel in electrolyte solution and of the local faults of the zinc layer on the anodic corrosion process have been studied.

There has been pointed out that the presence of a passive layer of calcium hydroxizincate on the zinc surface provides a decrease of the corrodibility of the zinc coated steel in alkaline solution containing chloride ions, i.e. the growth of the limit of chloride ions concentration at which the passive state of the zinc is no more affected, from 0,05M to values over 0,1M. For comparison, this limit value for ungalvanized steel is of 0,01M.

The conclusions of this study show that in some corrosive environments, the use of zinc coating represents an effective protection of steel for reinforced and prestressed concrete structures.

INVESTIGATIONS INTO THE CRITICAL CORROSION INDUCING CHLORIDE CONTENT OF STEEL IN CONCRETE

Jörg Harnisch[1], Amit Kenny[2], Michael Raupach[3]

[1] *Institute of Building Materials Research (ibac), RWTH Aachen University, Germany, harnisch@ibac.rwth-aachen.de*

[2] *Technion, Israel Institute of Technology, Haifa, Israel; amitk@tx.technion.ac.il*

[3] *Institute of Building Materials Research (ibac), RWTH Aachen University, Germany, raupach@ibac.rwth-aachen.de*

The chloride induced corrosion of steel in concrete is one of the most critical issues in the durability of modern reinforced concrete structures. One main parameter in the service life modelling of reinforced concrete structures subjected to chloride attack is the so called critical (corrosion inducing) chloride content. Recent studies of modern cementitious systems have indicated that the threshold value can vary over a wide range, from 0.15 to 3.0 % by cement weight, a range which is much higher than the 0.2 to 0.6 % by cement weight which are currently in use in life time calculations.

The aim of the presented joint research project between the Technion in Haifa, Israel and the Institute for Building Materials Science in Aachen, Germany consisted of the investigation into the impact of defined boundary conditions (mix properties, production process) on the critical chloride threshold level by means of an extended electrochemical test series as well as SEM analyses of the interfacial transition zone.

The corrosion tests revealed that the chosen variations of mix properties (w/c – ratio; content of an inert filler) do not seriously affect the critical chloride content. But both, the SEM analysis and the corrosion tests showed that there is a clear impact of the rebar position with regard to the cast direction of the concrete. In all cases the critical chloride content turns out to be significantly lower in case of horizontally arranged rebars. This phenomenon could be explained by the poor quality of the interfacial transition zone between steel and concrete (sagging) which could be shown by means of optical and SEM analysis in Haifa. Additionally first results of a promising technique to detect the distribution of the chloride content in concrete with a high spatial resolution are presented.

Detectability of active corroding areas in reinforced concrete structures with potential mapping

Sylvia Kessler, Christoph Gehlen, Technische Universitaet Muenchen, Germany
Klaus Menzel, Material Testing Institute, University of Stuttgart, Germany;

Potential mapping is a widely used inspection method for detection of ongoing corrosion in reinforced concrete structures. Herein, potential differences of macro-cell corrosion elements are obtained by applying a reference electrode on the concrete surface. Based upon these results further economical repair actions are planned. Hence, the accuracy of the method is a crucial factor. Nowadays, a lot of discussions on the appropriate interpretation of the potential mapping results can be found.

The expansion of the potential field in the concrete is affected by different factors, which have to be taken into account during interpretation of potential differences. Some of these factors are cover depths, rebar spacing, chloride content, electrical concrete resistivity and anodic area. The intention of the presented paper is to quantify the influence of the controlling factors using numerical models, e. g. a model of a reinforced concrete slab is used for the numerical simulations realized with the boundary element method. The influences of cover depths, resistivity, anodic area and anode to cathode area ratio are investigated. The results of the numerical models are compared with the results from field test from existing structures.

Other types of errors are electrokinetical effects like diffusion potentials and streaming potentials. Diffusion potential results from local differences of ion concentrations caused by non-uniform impact of chlorides and streaming potential from local differences of moisture in the concrete. Experimental studies determine the range of the electrokinetical effects and their influence on the potential mapping.

The studies will show which evaluation method of potential mapping measurement is appropriate to distinguish between passively and actively corroding reinforcement and which additional information are needed for a reliable statement. Finally the reliability of the potential mapping technique will be analyzed.

Efficiency of concrete coatings to control chloride induced corrosion of rebars

F. Bolzoni, A. Brenna, M. Ormellese
Politecnico di Milano, Dipartimento di Chimica, Materiali e Ingegneria Chimica “G. Natta”, Milano, Italy

Concrete coatings are widely used to improve durability of new structures, as well as in rehabilitation. Nowadays, various coatings systems are available, suitable for maintaining their protectiveness for long times and for a good service life, providing that a proper application and an adequate maintenance of the coating are assured.

The paper deals with the study of coatings based on organic and polymer modified cementitious mortars applied on concrete surface in order to protect reinforcement against corrosion in chloride containing environment. Different commercial products have been tested on concrete with two water/cement ratio.

In the paper the effect of the coatings on time-to-corrosion has been studied by the monitoring of the corrosion behaviour of reinforced concrete specimens subjected to chloride ponding: corrosion potential, corrosion rate and chloride profile have been carried out.

The main results of the study are the following:

- polymer modified cementitious mortars shows the best efficiency in term of delaying corrosion initiation, due to their higher thickness (2-3 mm compared to 500 μm), although organic coatings have shown lower permeability;
- concrete permeability also has a great effect on corrosion initiation.

The results have been elaborated to estimate the chloride diffusion coefficient of the tested coatings. Data have been used to predict the effect of the coatings on the service life of reinforced concrete structures subjected to chloride corrosion by using analytical solution of the 2nd Fick’s law of non-stationary diffusion derived from an analogy with heat transfer (Fourier’s law).

The Influence of Admixed Nano-Aggregates on Corrosion Performance of Reinforced Mortar

J. Hu[1], D.A.Koleva[1], K.van Breugel[1], J. M. C. Mol[2], J. H. W. de Wit[2]

1,2Delft University of Technology, The Netherlands
1Faculty of Civil Engineering & Geosciences, Dep. Materials & Environment; Stevinweg 1, 2628 CN, Delft; 2Faculty 3mE, Dep. Surfaces & Interfaces, Mekelweg 2, 2628 CD Delft.

This study reports on the corrosion behavior of reinforced mortar in the presence of very low concentration (0.006 wt % per mortar weight) polymeric nano-aggregates (PEO_{113}-b-PS_{70} micelles). After curing in fog room conditions (98% RH and 20°C) for 28 days, the specimens were immersed in tap water (controls) and 5% NaCl solution (corroding cells) for 20 days (test is ongoing). Electrochemical Impedance Spectroscopy (EIS) and Potentio-dynamic polarization (PDP) were employed for evaluating the corrosion performance of embedded steel at different time intervals.

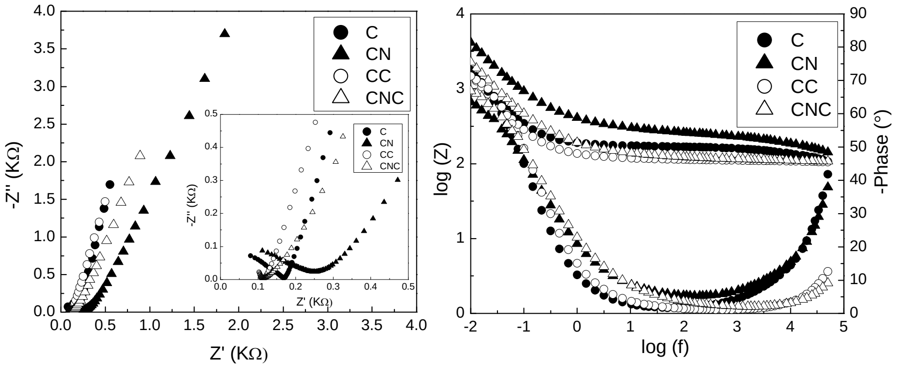

Fig. 1 EIS response in Nyquist and Bode format for reinforced mortar

Sample	Icorr (uA/cm^2)
C	0.154
CN	0.101
CC	0.145
CNC	0.120

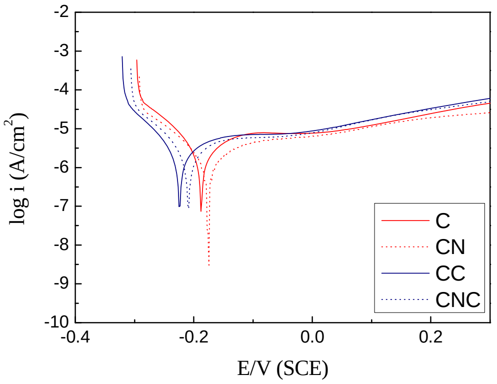

Fig. 2 corrosion current densities (left) and PDP curves (right) of reinforced mortar

The specimens' designation is as follows: C and CC represent the mortar without nano aggregate and immersed in tap water (C) and 5% NaCl (CC) respectively; CN and CNC represent the micelles-containing mortar, immersed in tap water (CN) and 5% NaCl respectively. At this point of investigation (20 days of immersion), it can be stated that the micelles-containing specimens (both control CN and corroding CNC cells) exhibit higher corrosion resistance, evidenced by the EIS response (Fig.1), behavior with external polarization (Fig.2 right) and the derived corrosion current densities (Fig.2 left). Further the paper will discuss the electrochemical behaviors of the reinforced mortar at longer immersion intervals and microstructural analysis of both bulk matrix and the interface between steel and concrete.

An experimental and numerical analysis of the cracking processes due to corrosion in a reinforced concrete beam

French Public Works Laboratory (LCPC)
58 boulevard Lefèbvre, 75732 PARIS CEDEX FRANCE

Any building located in the natural environment may be subjected to several pathologies such as the alkali-reaction, the internal swelling reaction, the corrosion phenomenon, etc. Stakeholders reported that corrosion could be considered as one of the main contributing factor of the performance decrease of existing buildings. Dioxide carbonyl or chlorides are the main aggressive chemical agents susceptible to lead to corrosion initiation at the steel concrete interface. Once a critical amount of aggressive agents has penetrated the cover concrete thickness, corrosion process can start progressing. Corrosion leads to two main effects: the swelling of the rusts products and the reduction of the steel cross section. As the consequences of the first effect, tensile stresses in the concrete appear and bond strength is modifying. The scope of this paper is to present both an experimental and numerical study of the concrete cracking when subject to corrosion without any mechanical loading. The crack pattern is analyzed and discussed. A numerical modelling has also been realized.

PARTIE EXP: description

PARTIE EXP: résultats essais

PARTIE EXP: résultats électrochimie

A steel/concrete interface model based on damage mechanics has been recently developed by the authors. It allows taking into account refine mechanisms such as the specific behaviour related to rust products. It has been used in order predict the mean crack width due to the swelling of corrosion products. The numerical results are very close to the experimental measurements. These results were very promising because they seem to show that this model could turned as a practical tool for civil engineers dealing with in-site repair and maintenance issues.

PHYSICOCHEMICAL PRINCIPLES FOR THE CREATION OF MIGRATING CORROSION INHIBITORS

N.N.Andreev*, *E.V.Starovoytova, I.A.Gedvillo and A.S.Zhmakina
A.N.Frumkin Institute of Physical Chemistry and Electrochemistry
Russian Academy of Sciences, Moscow, Russia

The strength and durability of reinforced concrete structures often depends on reinforcement corrosion state. Due to the alkalinity of the pore fluid, steel in concrete is passive provided that no chlorides are present. However, penetration of chlorides to the metal from outside, chloride additions during concrete preparation, and decreasing the pore fluid pH due to concrete carbonation create a hazard of reinforcement corrosion.

The problem of corrosion prevention can be solved using corrosion inhibitors. Such inhibitors are generally added during concrete preparation. However, an approach that is intensely developing in recent years is to protect steel reinforcement by migrating corrosion inhibitors (MCIs) that can penetrate the concrete stone and reach the steel reinforcement to slow down its deterioration. MCIs are applied onto the surface of a reinforced concrete article or added to concrete that is used in repair operations. The use of such inhibitors to ensure protection of structures that are already in use and are subject to corrosion shows high prospects. However, products available on the market show low efficiency. As we believe, this is due to weakly-developed scientific bases underlying the creation of migrating inhibitors.

It has been shown in our study that the ability of liquids to penetrate concrete stone is determined by the wetting of capillary pores. By selecting a surfactant one can vary broadly the permeability of solvents. It has been shown that the methodology of directed creation of MCIs can be reduced to (i) development of inhibitors efficient in the concrete pore fluid, and (ii) selection of surfactants that ensure inhibitor penetration into concrete stone.

A systematic study of the effect of structures of amines and substituted benzoates on the efficiency of steel protection in electrolytes simulating the pore fluid of concrete stone has been carried out. It has been shown that the protective effect of amines under these conditions depends on pK_a and is mainly determined by electrolyte alkalization. The contribution of adsorption to the protective effect is more significant for ethanolamines whose interaction with the metal is enhanced by the alcohol groups present in the molecule. It has been found that the protective effect of substituted benzoates and nitrite – benzoate formulations under the same conditions can be described by Hansch substituent constants in terms of the “linear free energy relationship” approach. The efficiency of steel protection by inhibitors decreases as hydrophilic or hydrophobic substituents are introduced in the aromatic ring.

Consideration of the above “structure – protection efficiency” regularities combined with rational selection of surfactants allow one to create highly efficient MCIs. Examples are provided to demonstrate the capabilities of this approach to the creation of MCIs.

INHIBITION OF REBAR CORROSION IN CHLORIDE POLLUTED CARBONATED CONCRETE BY TWO SPECIFIC INHIBITORS

Alessandro Frignani, Cecilia Monticelli, Andrea Balbo, Daniele Gelli, Fabrizio Zucchi
Corrosion Study Centre "A. Daccò", University of Ferrara, via G. Saragat 4a, 44121 Ferrara, Italy

Introduction

The use of corrosion inhibitors can be an efficient way to reduce rebar corrosion in a carbonated and chloride polluted concrete, where the formation of a protective passive layer on steel is prevented. It is a common practice studying corrosion inhibition in synthetic solutions first and then verifying the results in concrete. The efficiency of a mix of two inhibitors (one efficient towards the attack of chlorides, the other towards the carbonation effects) in a synthetic solution simulating the electrolyte in a carbonated chloride-polluted concrete has already been documented [1]. The present research aims at confirming these results in concrete.

Experimental

Two steel rods (diameter 1 cm, sand-blasted and degreased, exposed surface with an area of 73 cm^2 delimited by thermosetting tape), obtained from a FeB44k type steel rebar, were embedded in a concrete mould (dimensions 25x25x3 cm), prepared with CEM II A/L 42.5R (water/cement ratio 0.6). Two inhibitors, one (A) efficient towards the attack of chlorides, and the other (B) towards the carbonation effects) and sodium chloride were admixed to water (Cl- % : 1 % vs. cement; [Cl-]:[A]:[B] = 1 : 0.5 : 0.5).

Density and compressive strength measurements of inhibited concrete have also been measured. The limited thickness of the concrete specimens facilitated the complete specimen carbonation, which was carried out in about 4 months, following 28 day curing. Carbonation rate was monitored, both on blank and inhibited specimens

Three symmetrical auxiliary electrodes (stainless steel rods) and two activated titanium quasi-reference electrodes were also embedded to perform electrochemical tests.

The evolution of the corrosion process was monitored by electrochemical impedance measurements (FRA1260-EI1287 Solartron-Schlumberger apparatus, +/- 5 mV rms alternative perturbating signal, 10^4-10^{-4} Hz frequency range scanned, 5 points per decade).

Results

The positive results obtained in synthetic solution have been confirmed in concrete. In fact, during 1 year period EIS spectra showed that the inhibiting mix succeeded in reducing the corrosion attack on the rebar, with inhibiting efficiencies over 80%.

The impedance spectra have been interpreted by best fitting procedures.

The inhibiting mix does not reduce significantly the compressive strength.

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Environment Sensitive Fracture

Scientific-technical aspects of stress-corrosion in trunk gas pipeline

V.V. Kharionovsky, Russia, V_Kharionovsky@vniigaz.gazprom.ru
Gazprom VNIIGAZ, Razvilka, Leninsky District, Moscow region, Russia

Stress-corrosion is a factor that shapes the operational status of the trunk pipelines. Being a complex and ambiguous phenomenon underlain by various environmental conditions, stress state, structure and metal-specific properties, stress-corrosion is known as one of the most dangerous types of damages affecting pipes.

These days, OAO Gazprom is implementing a plan package to mitigate risks of failures due to stress-corrosion. The root causes of stress-corrosion have been detected; a pipeline maintenance methods have been adopted (including methods of inspection, evaluation of strength properties and scope of repair); a pipeline re-insulation program has been launched (under this program a large variety of coatings have been developed to ensure reliable corrosion-proof operation of pipelines).

Pipeline protection projects may focus on the following areas:

- regular inspections of trunk pipelines by running "Spetsneftegaz" magnetic flaw detectors that are capable of detecting the longitudinal cracks;
- development of production models of scanners to detect flaws during re-insulation;
- development of regulations for inspecting and evaluating severity of stress-corrosion defects;
- research projects focusing on analysis of stress-corrosion in compressor stations flowlines;
- development of repair methods involving welding, application of pipe couplings, or removal of damaged sections.

The scope of stress-corrosion field research is required to include the following:

- the study of impact of pipe structure and factory defects on physical properties of the pipes, stress cracking resistance, and operational reliability.
- development of methodical framework and tools enabling control of physical and chemical environment metrics that stimulate stress-corrosion, general, and sub-coating corrosion during pipeline construction and operation.

Modeling the Effects of Local Anodic Acidification on Stress Corrosion Cracking of Nickel

Hans Hoffmeister
Institute for Failure Analysis and Failure Prevention ISSV e.V.
c/o Helmut Schmidt university of the Federal Armed Forces
D-22043 Hamburg
Germany

Abstract

In recent work of the author the effects of pH, chlorides and sulfides on local anodic acidification has been modeled by coupling polarization and phase precipitation inside occluded cells of nickel and iron. In the present work, the experimentally verified model is extended to demonstrate the capability of accumulated and reduced hydrogen ions to provide critical conditions for local hydrogen assisted crack propagation. Based on experimentally determined crack critical hydrogen reduction charges and fracture strains from tensile SSR testing the model explains quantitatively the effects of chlorides , hydrogen sulfide , pH and mechanical loading on cracking by hydrogen locally produced by hydrogen ion reduction at the tip of an advancing anodic corrosion path. In particular, the known effects of pH, chlorides and hydrogen sulphide on cracking of metallic materials applied in the oil and gas industry are reflected by the results of the calculations as well as the effects of impurities on SCC in nuclear pressure vessels at shutdown conditions.

System of monitoring of gas pipelines on stress corrosion cracking

A.S.Kuzbozhev, Open Company branch «Gazprom VNIIGAZ – Severnipigaz»,
Ukhta, Russia, a.kuzbozhev@sng.vniigaz.gazprom.ru
V.O. Solovej, Open Company «Gazprom transgas Ukhta», Ukhta, Russia

The system of monitoring of processes stress corrosion cracking (SCC) on the main gas pipelines which realise in four stages is developed.

At the first stage spend carry out gathering and ordering of the initial materials characterising probability of course of processes SCC on separate sites of the main gas pipelines (lines of several gas pipelines) within a site in the extent of 40-50 km (site between cranes). Result are lists of potentially-dangerous sites (PDS) SCC.

At the second stage carry out an estimation of technical condition PDS of the main gas pipelines by carrying out of unitary field land inspection PDS by methods electric measurements:

- revealing of the sites having discrepancies to standard potentials electrochemical protection;
- revealing of sites with defects of insulating covers.

Result is the list of deviations from a design condition of the main gas pipelines.

At the third stage carry ground investigation on PDS of the main gas pipelines electrochemical methods. Result is the list places of digging out of the pipeline and offers on additional diagnostics.

At the fourth stage carry out diagnostics PDS of the main gas pipelines in excavation places. Spend search of defects SCC with application diagnostics the control. At absence defects SCC carry out the control of dynamics of change of parametres of the is intense-deformed condition of the pipeline physical methods. At revealing of defects SCC spend their elimination.

ON MECHANISM OF INITIATION OF CORROSION-MECHANICAL CRACKS IN GAS PIPELINE METAL

T.S. Yessiev

Gazprom VNIIGAZ LLC, Razvilka, Moscow region, Russia

According to modern views, stress corrosion cracking at underground pipelines is a result of aggregate exposure to stress state, metallurgical and electrochemical factors. All known models and hypotheses that explain stress-corrosion cracking nature of gas pipeline vulnerability are based on classical theory of stress corrosion cracking and can be roughly divided into two groups. The first group of models considers local anodic dissolution (LAD) to be the reason of crack initiation and propagation, while the second group stays for hydrogen embrittlement (HE). However, none of the existing hypotheses can explain the mechanism of crack initiation in pipe metal. This is because diluted electrolytes, which the majority of ground waters belongs to, do not provide conditions for LAD and HE.

It is assumed that the most probable mechanism that initiates cracks in metal is a local plastic yield at some overstressed sections of pipe surface. Such sections appear in pipes due to discontinuity of the deformation of the rolling sheet during pipe processing. Continuous plastic strain (microcreeping) causes maximum strain energy density in some micro or submicroscopic metal sections and this leads to local destruction, i.e. crack initiation. Local plastic strain that stimulates crack initiation and propagation at gas pipeline surface is driven by decrease (relaxation) of existing overstrains. In this case corrosion environment disturbs unstable balance of dislocation metal structure by adsorption processes, anodic dissolution and hydrogenation. Actually, such an approach combines two alternative mechanisms of stress-corrosion crack growth within the single model, as it implies the possibility of simultaneous running or interchange of LAD and HE. It is important that both processes are induced and accompanied by active plastic strain. Thus for example, adsorptive reduction of strength and electrochemical corrosion activate subsurface dislocation sources, promote atomic mass transfer by vacancy complexes (divacancy), while hydrogen diffusion and accumulation in metal increase lattice distortion and stimulate motion of dislocations. Thus, according to the proposed model not the environment determines the probability of crack initiation, but it is plastic strain that provides conditions for adsorption and electrochemical processes at the surface of the pipe metal. It means that cracking becomes possible even when there are no hydrogenation drivers and components, which cause local metal dissolution, in the corrosive environment.

NONLOCAL EFFECTS IN LIQUID ENVIRONMENT-INDUCED CRACKING

***Alexander MALKIN* and Dmitry POPOV**
A.N. Frumkin Institute of Physical Chemistry and Electrochemistry RAS,
Moscow, Russia.

Liquid environment-induced cracking is observed for a broad spectrum of solid-environment combinations examplified by stress corrosion and liquid metal embrittlement of metals, cracking of silicates in water solutions and polymers in organic fluids. Although atomic mechanisms of cracking for such diversified systems are clearly distinct, the crack evolution has a number of common features. It is widely believed that qualitative similarity of kinetic diagrams is dictated by the rate-determining role of transport of active environment to a crack tip. The specific mechanisms of transport effects are not however understood.

Here the object is to elucidate the rate-determining transport processes in crack kinetics. We discuss size effects and strain rate dependence of crack starting stress, typical shape of kinetic diagrams, temperature and stress dependence of growth rate. The rewiev of experimental data suggests that nonlocal solid-environment interaction (i.e. the interaction out of the crack tip) can have a profound impact on the evolution of a crack.

Basing on theoretical analysis of hydrodynamic, diffusion, thermo- end electrokinetic processes we suggest a number of self-consistent semiempirical models of crack evolution. Within the models a phenomenological description of the processes in a pre-cracking zone is combined with the proper account of nonlocal interactions of different nature.

Analytical and computational investigation of crack evolution is performed. Hydrodynamic and diffusion rate-determining mechanisms are considered. For the both mechanisms the strain rate dependence of crack starting stress and the dependence of crack growth rate on the stress intensity factor are calculated.

The results are found to be in agreement with the available experimental data on liquid metal embrittlement, stress corrosion cracking and cracking of rocks under the influence of salt melts. One can conclude that taking account of nonlocal interaction offers reasonable quantitative explanation of the common regularities of environment-induced evolution of a crack, specifically, the existence of near steady rate stage of the growth, the relatively small or negative activation energy of the growth rate at that stage, and the dependence of the steady rate on the external load.

The Influence of Surface Film Modification on the Mechanical and Electrochemical Properties of Austenitic Stainless Steel

Salah Gnefid, Robert Akid
Materials & Engineering Research Institute, Sheffield Hallam University, Sheffield/UK

Abstract

The influence of material surface condition, notably passive film condition and surface residual stress and the effect of applied surface stress on the development of corrosion pits has been assessed in relation to their role on the fatigue behaviour of stainless steel materials, in particular the early stages of corrosion fatigue. Several experimental techniques have been used to quantify changes in material response during stress and corrosion interactions.

A special system has been assembled and designed for this study. This system consists of a miniature fatigue rig, and electrochemical droplet cell, both being contained in a Faraday cage.

The original surface film was modified electrochemically using an alternative voltage passivation process (AVPP) to study the effects of this modification on the mechanical and corrosion properties.

The composition, structure and residual stress state of the original and modified oxide films were analysed applying X-Ray photoelectron spectroscopy (XPS) and X-Ray Diffraction (XRD) techniques. Chromium enrichment in the modified passive film surface was observed for the modified surface. XRD measurements show reduction in the surface compressive residual stress as a result of the introduction of the modified film.

Potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) tests were performed in artificial seawater, on the original and the modified passive film, in order to evaluate the differences in corrosion behaviour of the material. Results show improvement in the corrosion resistance in material surface with the modified film.

Nanoindentation tests for measurement of load–depth curves have been conducted to assess the changes in the mechanical properties of the material passive surface because of the electrochemical treatment AVPP. It was found that the hardness of the material surface slightly increases after the native film modification. However, the elastic modules of the material surface decreases with new film.

Fracture mechanic investigations of a CrNiMo austenitic stainless steel in different cold worked states

C. Vichytil[1], G. Mori[1], M. Panzenböck[2], R. Pippan[3], R. Fluch[4]

[1] *Christian Doppler Laboratory of Localized Corrosion, Department of General, Analytical and Physical Chemistry, University of Leoben, Franz-Josef-Straße 18, A-8700 Leoben, Austria*

[2] *Department of Physical Metallurgy and Materials Testing, University of Leoben, Franz-Josef-Straße 18, A-8700 Leoben, Austria*

[3] *Christian Doppler Laboratory for Local Analysis of Fracture and Deformation, Department Material Physics, University of Leoben, Franz-Josef-Straße 18, A-8700 Leoben, Austria*

[4] *Böhler Edelstahl GmbH & Co KG, Research and Development Special Materials, Mariazeller Straße 25, A-8605 Kapfenberg, Austria*

For applications in highly corrosive media and dynamic loads highly alloyed austenitic stainless steels are often used. A CrNiMo stabilized austenitic stainless steel in solution annealed condition and different cold worked states has been investigated in this paper.

Crack growth rate versus stress intensity factor curves have been recorded at 120°C in glycerine as an inert medium, as well as in 43Wt% calcium chloride solution as corrosive environment. The crack growth was measured with the direct current potential drop method. The experiments were carried out with a lower to upper stress ratio of 0.05 to maintain a continuous crack growth without destroying the fracture surface. The threshold value for long crack growth as well as the influence of cold working on crack growth was the main focus of this research. For evaluation the principles of linear elastic fracture mechanics were applied. Additionally electrochemical and exposure tests were performed to determine damage mechanisms. The investigated CrNiMo steel shows hardly any corrosive attack due to its well established passive layer in hot chloride solution. In this environment it usually fails due to corrosion fatigue and shows no susceptibility to stress corrosion cracking.

Fracture surfaces of specimens tested in inert and aggressive environment were investigated with a scanning electron microscope and evaluated as a function of the medium and degree of cold working. Effects of the environment and cold deformation on the crack propagation and crack growth velocity are thoroughly discussed. The results of the accompanied investigations were critically compared and interpreted.

Keywords: austenitic stainless steels, crack growth, direct current drop potential method, corrosion fatigue

Cohesive zone FE modeling of hydrogen induced fracture in grade X70 pipeline steel

Initiation of hydrogen induced fracture in X70 subsea pipeline steel is simulated using cohesive zone modeling. Hydrogen from welding and from cathodic protection reduces the threshold stress intensity factor (K_{HE}) of structural steel to an extent that residual stresses from reeling and welding and external stress from operation in sum may cause crack initiation. It is thus important to be able to assess the critical stress level at different levels of hydrogen concentration. Cohesive elements are used to represent the critical energy necessary to initiate fracture. This critical cohesive energy decreases as the hydrogen concentration increase, see Fig1. The cohesive zone elements are calibrated using fracture toughness constant load SENT testing with and without hydrogen influence.

The analyses combine simulations of elastic plastic stress, hydrogen diffusion and cohesive zone stress. In the transient diffusion simulation both stress and plastic strain are taken into account. Information from the hydrogen diffusion simulation is given as input to the cohesive simulation in which K_{HE} and the critical applied stress for hydrogen induced crack initiation is calculated.

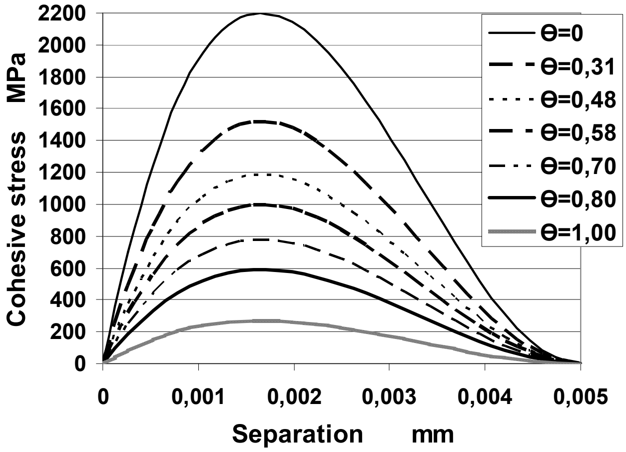

Figure 1 Reduction in cohesive stress (and energy) due to hydrogen coverage.

Corrosion creep of metals and its role in stress corrosion cracking

Yakov B. Unigovski, Emmanuel M. Gutman,
Dept. of Materials Engineering, Ben-Gurion University of the Negev, Beer-Sheva, Israel.
Zamir Koren
Israel Institute of Metals, Technion, Haifa, Israel

Experimental observations show that mechanical creep at a crack tip plays an important role in failure processes, especially in stress corrosion cracking and corrosion fatigue. In active environment, mechanical creep can be significantly accelerated by anodic surface reactions (chemomechanical effect). An additional creep rate $\Delta\dot{\varepsilon}$ can be expressed in a simple form within the limits of linear polarization as

$$\Delta\dot{\varepsilon} \approx \frac{JV_m\overline{\alpha}\overline{b}\Lambda\upsilon^2}{\dot{\varepsilon}_0 t + \varepsilon_0},$$

Where J is the anodic reaction rate, t is the time since the moment of pulse-wise immersion of deformed metal into the electrolyte, $\dot{\varepsilon}_0$ and ε_0 are the creep rate and strain for this initial moment, $\overline{b}$ is the Burgers vector, V_m is the molar volume of metal, parameters $\overline{\alpha}$, Λ, υ are properties characterising dislocation kinetics.

Consequently, the investigation of environment-assisted creep, which greatly influences the mechanical stability of alloys in real service conditions, is a very important tool for discovering mechanisms of processes occurring in the tip of a corrosion crack.

Environment-enhanced creep which we call “corrosion creep” (CC) has been investigated in such metals as commercially pure magnesium, die-cast magnesium and aluminum alloys and austenitic stainless steel. Pure metals and alloys with relatively small amounts of second phases, e.g., Mg-5%Al (AM50) and austenitic steel 304, show significant plasticization in corrosive solutions with final fracture at ambient temperatures. Meanwhile, common low-temperature transient creep with small elongation without fracture is observed in air at temperatures less than a half of the melting point T_m (in Kelvin scale).

A greater amount of intermetallics in an alloy leads to a shorter creep life of the sample due to a higher sensitivity of the material to various corrosive solutions (borate buffer solution, 3.5% NaCl, etc.) during creep. For example, creep life of Mg-9Al-1Zn and Mg-5%Al alloys containing 28% and 16% of $Mg_{17}Al_{12}$ in the surface layer was 250 h and 350 h, respectively, (borate buffer solution, 25^oC, 120 MPa). The effect of processing and coating on the corrosion creep behavior of die-cast rheoformed and conventional Mg-9Al-1Zn alloys was studied. Rheoformed alloy with much larger globular grains as compared with a dendritic microstructure of a conventional alloy has a better corrosion resistance and creep resistance in corrosive media. Corrosion creep life of anodized alloys is much longer than that of uncoated alloys.

The influence of active environment on the creep is mainly caused by plasticization of metal assisted by surface electrochemical reactions and, in the first place, anodic dissolution of metal. It is concluded that the main reason for the change in viscoelastic properties of metals in active media is the chemomechanical effect causing additional dislocation flux on the alloy surface.

Joint Session: Local Microprobes to Study Surface Treatments and Coatings

Electrochemical deposition of copolymers in titania nanotube layers

T. Djenizian, N. A. Kyeremateng, I. Hanzu, F. Vacandio, and P. Knauth
University of Aix-Marseille I, II et III-CNRS, UMR 6264: Laboratoire Chimie Provence, Electrochemistry of Materials Research Group, Centre Saint Jérôme 13397 Marseille Cedex 20,
*thierry.djenizian@univ-provence.fr

Due to the wide range of applications, polymer coating technology has attracted attention of scientists. Among all techniques, the electrochemical synthesis of polymers is an interesting approach to fabricate thin films for protection against corrosion, micro and optoelectronics, sensors, energy harvesting,… Particularly, electrodeposition of polymers in porous matrices is a convenient way to produce new nanocomposite materials (See e.g. Ref. [1,2]).

In this paper we report the electrochemical deposition of copolymer thin films on self-organized titania nanotubes (ntTiO_2). First the influence of the anodization parameters on the nanostructuring phenomena is studied in order to control accurately the morphological, physical, and chemical properties of ntTiO_2 layers.

Then, ntTiO_2 layers are used as host matrices for the electrochemical synthesis of copolymer electrolytes such as poly(methyl methacrylate) (PMMA) and polystyrene (PS) polymers carrying POE-block as side chain substituents. Beside its simplicity, the electrosynthesis procedure allows to i) produce highly pure and adhesive polymers ii) control the thickness of the polymer layer in the sub 10 μm scale iii) increase the interface due to the total filling of the nanotubes. Titania nanotubes, electrodeposited copolymer thin films as well the COP/ntTiO_2 interface are characterized by SEM, EDX, AFM, FTIR, XPS, etc… The use of these complementary analysis techniques allow to control the electrochemical deposition parameters of polymers, achieve the complete and homogenous filling of the nanotubes, establish a stable COP/ntTiO2 interface and understand the nucleation and growth mechanisms involved during the electrodeposition of copolymers on and into ntTiO_2 layers.

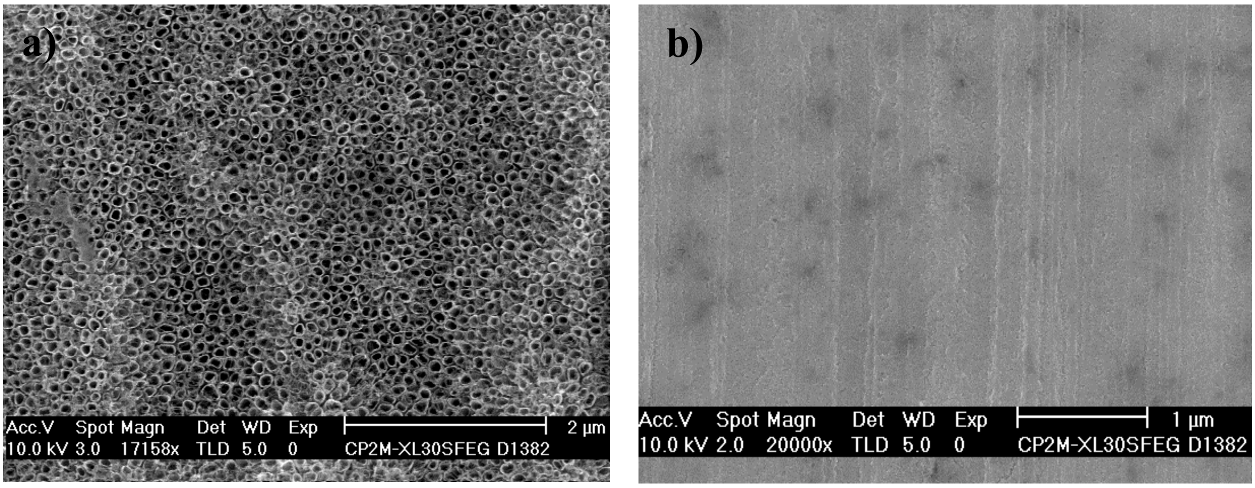

Figure 3. SEM images of bare ntTiO_2 layer a) and ntTiO_2 layer after electropolymerization of methyl methacrylate substituted with PEO b).

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Influence of metallic coated steel pre-treatment on the cut-edge corrosion studied by local electrochemical techniques

Ana Alvarez Pampliega, Vrije Universiteit Brussel, Pleinlaan 2 , 1050-Brussels / Belgium
Myriam Madani, OCAS, ArcelorMittal R&D Industry Gent; J.F.Kennedylaan 3, 9060 Zelzate/ Belgium
Jan Wielant, OCAS, ArcelorMittal R&D Industry Gent; J.F.Kennedylaan 3, 9060 Zelzate/ Belgium
Javier Gonzalez, OCAS, ArcelorMittal R&D Industry Gent; J.F.Kennedylaan 3, 9060 Zelzate/ Belgium
Franz Hörzenberger, OCAS, ArcelorMittal R&D Industry Gent; J.F.Kennedylaan 3, 9060 Zelzate/ Belgium
Els Tourwé, Vrije Universiteit Brussel, Pleinlaan 2 , 1050-Brussels / Belgium
Herman Terryn, Vrije Universiteit Brussel, Pleinlaan 2 , 1050-Brussels / Belgium

The surface treatment of metallic coated steel surfaces is an area which has a big influence on the corrosion protection offered by organic coatings applied afterwards [3]. The nature of the interfacial chemical interactions and the adhesion strength of metal-coating interfaces are crucial factors to characterize the surface properties studies of the interfacial oxide films [1] and can allow a better understanding on the delamination processes.

In this work, the influence of the surface pretreatment of metallic coated steel in the cut edge corrosion mechanism is studied. The system under study is metallic coated steel of ArcelorMittal, which composition is: 55% aluminum, 43.4% zinc and 1.6% silicon.

Different thermal [2] and acid/base pretreatments have been chosen and corrosion performance has been checked by wet-dry cycles. In order to follow the delamination and to have a first clue about the corrosion mechanism two local electrochemical techniques have been used: Scanning Kelvin Probe (SKP) and Scanning Vibrating Electrode technique (SVET).

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The use of spatially resolved electrochemical tools to assess self-healing ability in small defects formed on coated galvanised steel

D. Snihirova, M. Taryba, S. Lamaka, M.F. Montemor, ICEMS, Instituto Superior Técnico, Technical University of Lisbon, Portugal,
W.K. Wijting, G. Grundmeier, Technical and Macromolecular Chemistry, University Paderborn, Germany

Abstract

Spatially resolved electrochemical techniques are the most powerful tools to assess self-healing ability of coatings modified with active species filled with corrosion inhibitors.

In this work different electrochemical localised techniques like the scanning vibrating electrode technique (SVET), the scanning ion-selective electrode technique (SIET). electrode technique (SIET) and the scanning capillary cell (for localised impedance measurements) were combined with microscopic and analytical tools (SEM/EDS and Fluorescence microscopy) in order to study the corrosion activity over model defects prepared in coatings applied on galvanised steel samples. The coatings investigated contain smart nanoreservoirs modified with different corrosion inhibitors, which will be identified by different codes, due to restricted information.

The work aims at highlighting the most recent advances on the use of localised electrochemistry to quantify the corrosion/passivation processes and to assess the most relevant aspects of the corrosion mechanisms involved on the self-healing processes.

Keywords: self-healing, localised electrochemistry, corrosion, nanocontainers

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In situ SKP probing of zinc-epoxy interphase

A. Nazarov, D. Thierry,
French Corrosion Institute, 220 rue Pierre Rivoalon, 29200 Brest, France
P. Volovitch, K. Ogle
Université Pierre et Marie Curie, 11 rue Pierre et Marie Curie, 75005 Paris, France

Adhesion is generally determined by adsorption forces including van der Waals, ionic and donor-acceptor bonding. In addition, the "interphase" can be formed at the metal-polymer junction which is responsible for the adhesion stability and the strength of the joint in different environments. The interphase is generally described as a complex region with a mixed organic-inorganic nature and an heterogeneous morphological-chemical structure, which links two phases with very different properties (i.e. surfaces energy, density, elasticity, etc.).

In this work, the interaction of simple amine molecules that with Zn/ZnO and Au/ZnO electrodes dc voltammetry and Electrochemical Impedance Spectroscopy. FT-IR microscopy was also applied for identification of the adsorbed species. The amine molecules were chosen to model the epoxy hardeners used in technical systems. It was shown that bi-dentate ligand (ethylendiamine) led to stable chelate complexes able to dissolve zinc oxide with re-deposition of the Zn-EDA interphase. This ligand shifts the potential of Zn/ZnO in the air or in the water electrolyte to the value of oxide free Zn electrode. The mono- and bi –dentate ligands with low chelating effect has less influence on the potential.of Zn/ZnO.

The potential distribution across Zn/ZnO/air interfaces as a function of the ZnO thickness was studied by SKP. It was observed that the Volta potential is a sensitive measure of ZnO thickness. On the other hand, it was found that the potential distribution across the Zn/ZnO/epoxy resin joint is a function of the resin composition. During curing, the components of the epoxy resin can dissolve the ZnO layer leading to the formation of a mixed organic-inorganic interphase. Hence, SKP provides information on the ability of the resin to dissolve the oxide. From the results, it is thus possible to rank different epoxies according to their abilities to form the interphase. The contribution of the interface charging due to donor-acceptor or ionic bonding to the potential drop is also discussed.

Study of the effect of cerium nitrate on AA 2024-T3 by means of electrochemical micro-cell technique

L. Paussa[1], *F. Andreatta*[1], *C.N. Rosero Navarro*[2], *M. Aparicio*[2], *A. Duran*[2], *L. Fedrizzi*[1]

[1] *Department of Chemical Science and Technology, University of Udine, Italy*
[2] *Instituto de Cerámica y Vidrio (CSIC), Campus de Cantoblanco, Madrid, Spain*

Aluminium alloys like AA2024 are susceptible to severe corrosion attack in aggressive solutions (e.g. chlorides). Conversion coatings like chromate or rare earth conversion coatings are usually applied in order to improve corrosion behaviour of aluminium alloys. Sol-gel films deposited with sol-gel technique might be an alternative to conversion coatings. Barrier properties, paint adhesion and possibly self-healing ability are important aspects for replacement of chromate-based pre-treatments. This work evaluates the behaviour of cerium nitrate as corrosion inhibitor in aggressive solutions for AA2024-T3 in the view of its introduction in sol-gel coatings in order to promote self-healing ability.

The electrochemical behaviour of AA2024-T3 was initially characterized by means of open circuit potential and potentiodynamic polarization measurements in NaCl solutions containing cerium nitrate. Since it is well established that deposition of Ce species is activated by cathodic sites like intermetallics on the aluminium substrate, the objective of this paper is to investigate the behaviour of AA2024-T3 in presence of Ce species in aggressive solutions by means of a local technique, the electrochemical micro-cell. This technique enables the investigation of small areas with resolution in the micrometer range by the use of glass capillaries to define the area of the working electrode. This technique was employed for carrying out potentiodynamic polarization measurements on areas containing intermetallics in order to clarify their effect on corrosion inhibition due to cerium species. The approach by means of electrochemical micro-cell technique is part of a research optimizing sol-gel coatings doped with cerium for corrosion protection of AA2024-T3.

Development of a Zn^{2+}-Ion Selective Microelectrode and its Application to Corrosion Studies

A. C. Bastos[1], *M.G. Taryba*[2], *O.V. Karavai*[1], *M.L. Zheludkevich*[1], *S.V. Lamaka*[2], *M. G. S. Ferreira*[1,2]

[1] *DECV/CICECO, Universidade de Aveiro, 3810-193 Aveiro, Portugal*
[2] *ICEMS, Instituto Superior Técnico, UTL, Av. Rovisco Pais, 1049-001, Portugal*

Abstract

Zinc has a huge technological importance, being extensively used in galvanising of steel, batteries, brass metallurgy, die casting and metal sheet. As a consequence, the detection and quantification of Zn^{2+} is of interest to many different areas. Potentiometry is a common and simple technique suited for many practical situations and ion selective electrodes (ISE) for Zn^{2+} have been proposed by several authors (see [1,2] and references cited therein). Miniaturized ISE can be of great value when small volumes are to be probed or when the spatial distribution of the Zn^{2+} is to be mapped at the microscale. A microelectrode for potentiometric Zn^{2+} detection was described in reference [3]. Alternatively, an amperometric mini-sensor has been used to investigate the spatial distribution of Zn^{2+} during galvanic corrosion of a Zn/steel couple [4]. In spite of these advances, it's difficult to find published work using microelectrodes for Zn^{2+} detection, either potentiometric or amperometric.

In this communication we describe the development of a Zn^{2+}-selective microelectrode based on a new cocktail containing tetra-n-butyl thiuram disulfide ionophore [5]. Details of construction are given, together with a characterization of the electrode's properties. Successful application to cases of zinc dissolution, zinc electroplating and corrosion in defects of coated galvanised steel shows the suitability of this microelectrode for materials science and corrosion research.

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Joint Workshop EFC-CEOCORR: Materials and Disinfection

Effect of material and water quality on disinfection and risks of corrosion

L.R. Hilbert[1], H.J. Albrechtsen[2], A. Andersen[1]
1) FORCE Technology, 2605 Brøndby, Denmark, LTH@force.dk
2) DTU Environment, Technical University of Denmark, Denmark

Disinfection of drinking water is generally avoided in Denmark and the original ground water is treated as little as possible. Correct design, material quality and process control are therefore important to avoid problems for the consumers – corrosion, increased metal release, microbiological influenced corrosion (MIC) of stainless steel, pathogenic microorganisms like *Legionella*, and growth of unwanted species introduced by ingress of polluted water. In the future more shut-downs of groundwater wells can be expected due to increased levels of contaminants and as a consequence the drinking water sources will be reduced. Introduction of alternative water sources is therefore considered, whereby water treatments and potentially disinfection may be necessary either at waterworks or locally at the consumer.

Very hard water is common in Denmark and softening or partially desalination of the hard water types is considered, as well as merging water from different waterworks thereby mixing hard and softer water types. Introducing different water types in the distribution network and mixing different water types can cause threats in terms of microbial growth and more corrosive water. If disinfection is applied the necessary disinfection mode must be adapted to these conditions.

During the last 30 years the use of stainless steel and polymer materials has been steadily increased in drinking water installations and today almost all installations in Denmark are built with pipes of these materials. In other European countries copper pipes are still widely used while the use of hot dip galvanised steel pipes is decreasing. The number of failures reported on stainless steel pipes of EN 1.4401 is fairly low and metal release insignificant. Stainless steel installations are commonly chosen for critical water distribution systems as in hospitals and public swimming baths, where the development of biofilm and pathogens in the system must be limited, and welded connections may be preferred to press fittings. Plastic pipes may facilitate the microbial growth and if installed upstream e.g. stainless steel installations, this may increase the risk of MIC. For stagnant systems like fire protection systems the corrosion resistance becomes crucial to avoid development of MIC. For industrial process water installations stainless steel ensures improved cleanability and corrosion resistance, but a number of corrosion failures can be directly linked to very aggressive disinfection. Thus, it is not trivial to balance the positive and negative effects of disinfection vs. the use of natural water with a low level of treatment.

This paper focuses on the research and test programme necessary for evaluating the consequences on installation integrity of 1) changing water quality to less ground water and more treated water types and 2) disinfection by central or local disinfection methods. Before changing the water system, interaction between materials, corrosion and disinfection must be elucidated to ensure a reasonable lifetime for existing installations.

Electrochemical Measurements of the corrosion behaviour of X5CrNi-18-10 in different disinfectants

J.W. Erning, U. Klein, U.-M. Steinhoff Federal Institute of Material Research and Testing, Berlin, Germany

Chlorine is broadly used as a disinfectant for tubes and surfaces. The influence of such disinfectants on the corrosion behaviour of stainless steels is known in general, but the potential for corrosion failures depends on the composition of the specific disinfectant as well as on application time and concentrations. Thus a method to evaluate the corrosivity of such disinfectant solutions is described and the usability is shown.

Potentiodynamic and ECN Measurements of the corrosion behaviour of X5CrNi-18-10 were used to show the corrosive properties of different disinfectants. The disinfectants were produced in electrochemical processes, mainly described as electrolysis of chlorides to chlorine species in aequeous solutions. For the potentiodynamic measurements a setup as described in prEN 16056 using a flushed port cell according to ASTM G150. ECN Measurements were made using small embedded working electrodes.

The results show the influence of the concentration of free chlorine and chloride on the pitting potential of the stainless steel.

Principles of Lifetime Analysis for Plastic Pipes

Dipl.-Wirtsch.-Ing. Jürgen Heinemann, Dipl.-Ing. Hansgeorg Haupt, Dipl.-Ing. Alexander Bockenheimer, Prof. Dr.-Ing. Christina Berger, Technische Universität Darmstadt, Zentrum für Konstruktionswerkstoffe, Staatliche Materialprüfungsanstalt Darmstadt / Fachgebiet und Institut für Werkstoffkunde, 64283 Darmstadt, Germany

Almost six decades ago, plastic pipes were for the first time introduced on a large industrial scale. Since that time they have gained strong significance and are used today especially in the areas of drinking water and gas supply, sewage engineering, sanitary and heating installations as well as industrial pipe systems. Causative for this development are not least their low manufacturing costs, the low placement and installation effort required and the long lifetime verified on the basis of international standards.

Depending on the area of application and the connected operating conditions, pipes are exposed to a multitude of different loads. These are reflected in a complex stress collective with predominantly static and/or quasi-static, but also cyclic portions in addition. Internal pressure and internal pressure surges as well as outer loads cause mechanical stress, which find expression in a tri-axial state of stress in the pipe wall. Both the ambient temperature and the temperature of the flow medium lead to thermal stress. Chemical stress is caused for example by the flow medium. The aforementioned stresses influence the usability of the pipe over the intended lifetime to different degrees, whereas the stress resulting from internal pressure and temperature are of prominent importance.

The long lifetime of plastic pipes presuppose the necessity of a lifetime analysis on the basis of an accelerated test with a subsequent extrapolation of the material behaviour, which is standardized in ISO 9080 describing the determination of the long-term hydrostatic strength of thermoplastic materials by statistical extrapolation. The required datasets are experimentally gained using the internal pressure creep rupture test according to ISO 1167 concerning the determination of the resistance of pipes made of thermoplastics against internal hydrostatic pressure.

The ascertained datasets can be illustrated in a so-called internal pressure creep rupture diagram, in which the different curve branches portray the different effective failure modes subject to internal pressure and temperature. Whereas the first area is characterised by high internal pressure and only short failure times leading to ductile failures due to creep of the polymer chains, the quasi-brittle multi-fractures occurring in the second area are due to stress crack formations at medial internal pressure values and failure times. In comparison, the third area is characterised by low internal pressure and high failure times as well as a brittle fracture. Regardless of their differences, all aforementioned failure modes can be ascribed to the mathematical approach of the Arrhenius function.

The principal suitability of the procedure for the lifetime analysis of plastic pipes described in ISO 9080 is substantiated by long-time test and practical experience for almost 60 years now. Also, no cases are known of systematic damage due to the failure of plastic pipes because of an insufficient lifetime analysis and tests conducted on pipes in operation for over 40 years do not provide any contrary evidence.

Impacts of Disinfection Treatments in Hot Water Distribution Systems on Pipe Material Durability

J. Castillo Montes[a,b], O. Correc[a], J. Creus[b], S. Touzain[b], F. Derrien[c], N. Berthelot[d]

[a] Centre Scientifique et Technique du Bâtiment Nantes, 11 rue Henri Picherit, BP 82341, 44323 Nantes Cedex 03, France.

[b] Laboratoire d'Etude des Matériaux en Milieux Agressifs, EA3167 Université de La Rochelle, Avenue Michel Crépeau, 17042 La Rochelle Cedex 1, France.

[c] Centre Scientifique et Technique du Bâtiment Marne La Vallée, 84 avenue Jean Jaurès Champs sur Marne 77447 Marne la Vallée Cedex 2.

[d] Anjou Recherche, Chemin de la Digue-B. P. 76, 78603 Maisons-Laffitte Cedex, France.

The hot water quality control inside buildings is commonly achieved by disinfectant treatments, the most common in France being sodium hypochlorite. The aim of this work is to study and compare the long-term performance in chlorinated hot water of four different hot water pipe materials: galvanized steel, copper, CPVC (Chlorinated PolyVinyl Chloride) and a multi-layer material PERT/Al/PERT (PolyEthylene Raised Temperature/Aluminium).

This multi-physical subject was analyzed through a factorial approach, leading to a rationalization of experiments in order to evaluate the ageing of the different materials in usual or accelerated conditions. Using the most severe condition of ageing (100ppm sodium hypochlorite solution at 70°C), the degradation criteria were defined for the four materials.

For metallic materials, the corrosion kinetics were monitored and the corrosion products were analyzed by XRD and Raman spectrometry. The presence of chloride in copper corrosion products led us to think that residual chlorine plays a role in corrosion.

For polymeric-based materials, the degradation was evaluated using DSC and Total Reflection Fourier Transform Infrared Spectroscopy (ATR). The measurement of the Oxidation Induction Time (OIT) showed that the antioxidant concentration reduction in PERT was independent of the chosen chlorine concentration.

These preliminary results, in stagnation conditions, will help us to set up the experimental conditions of ageing in a hot water pilot scale system.

Marine Corrosion

Environmental Behavior and Corrosion Costs of Naval Aluminum Alloys and ST52 in Sea Water Ports

Amir ELIEZER[1], Addis GARCIA [2], Benjamin VALDEZ [2], Michael SCHORR[2] , Jehuda HADDAD[1]

[1]*Corrosion Research Center,Nano-Bio & Advanced Materials*
Sami Shamoon College of Engineering, Israel, amir@sce.ac.il
[2]Institute of Engineering, Dep. of Materials, Minerals, Corrosion.
Universidad Autonoma de Baja California, Mexico*, mschorr2000@yahoo.com*

The corrosion behavior of naval aluminum alloy UNS A 95052 was investigated by exposure of specimens in two ports seawater: Ensenada, on the Pacific Ocean, Mexico and Ashdod, the Mediterranean Sea, Israel. This is a naval Al-Mg alloy; its corrosion resistance is due to the formation of a natural alumina (Al_2O_3) layer on its surface, imparting a passive behavior. The stability of this oxide film and the relationship between corrosion, electrode potential and pH of an aqueous solution is depicted in the Pourbaix diagram for aluminum. Marine corrosion is an electrochemical process that occurs on the metal surface by its interaction with the constituents of saline water. ST52 was exposed to the Mediterranean sea environment and was examined in both lab and sea conditions. The dominant factors are salinity, chlorinity and the concentration of dissolved oxygen. When Cl^- penetrates the passive film it initiates pitting and crevice corrosion at localized sites. Port seawater immersion and laboratory corrosion test in seawater were conducted on carefully measured specimens, recording their changes in surface appearance. The following standards were applied: NACE standard TMO 69-2000 and ASTM standard G 31 for laboratory testing; ASTM standard G 4 for plant equipment tests and ASTM G 3, G 5 and G 106 for electrochemical measurements. At the end of the exposure period, corrosion rates were calculated and electrochemical corrosion parameters: potential and corrosion current were measured and plots of electrochemical impedance spectroscopy were displayed. The results of this investigation show that UNS A 95052 is corrosion resistance to stagnant and moving sea water of Ensenada and Ashdod seaports. The corrosion resistance derives from the formation of a passive layer of hydrated alumina. Results of these gravimetric and electrochemical measurements are presented, interpreted and evaluated. The obtained electrochemical results were interpreted to corrosion costs preliminary modeling corrosion costs predictions up to 80 years.

Study of stress corrosion cracking of austenitic steels in seawater

A.S. Oryshchenko, S.Y. Mushnikova, A.A. Kharkov, G.Y. Kalinin
Central Research Institute of Structural Materials “Prometey”, St.Petersburg / Russia

Stress corrosion cracking (SCC) behavior of several grades of austenitic steels was studied. The first group of steels chosen for investigation of SCC - Fe-Mn steels contained from 17 to 26 per cent of manganese by weight. High nitrogen stainless steels (20Cr-14Ni-6Mn and 20Cr-6Ni-11Mn) were a second group of materials studied. The steels were in the hot-rolled, annealed, aged condition. Influence of the different phases namely δ-ferrite, ε-martensite, nitrides and carbonitrides on sensitivity to SCC was investigated.

Steel resistance to SCC was determined by slow strain rate tests (SSRT) and by cantilever bending of precracked specimens. SSRT is designed to detect the initiation of stress corrosion cracks. Already existing crack propagation possibility was investigated by using the method of cantilever bending, based on the application of techniques of linear fracture mechanics.

SSRT were carried out under the following conditions:

- the rate of deformation was $2 \cdot 10^{-7}$ c^{-1};
- tested in air to characterize the material and to use it as reference;
- tested in 3.5 % NaCl at a free corrosion potential;
- tested in 3.5 % NaCl and the different controlled electrochemical potentials (cathodic and anodic polarization);
- tested in 3.5 % NaCl and the different pH values;
- tested in $FeCl_3$ solutions (including conditions of crevice corrosion);
- tested in 20 % NaCl at temperatures from 20 to 95°C.

The cantilever bending of precracked specimens was carried out at room temperature in the same corrosive media.

When the specimens were fractured, elongation and reduction of area were measured. The fracture surfaces were examined using light and scanning electron microscopy. The maximum rupture stress was determined in the stress-strain curves. The deformation, at which the difference of curves observed in air and in corrosive environment, was considered the critical deformation. The results showed that the most representative characteristic of sensitivity to SCC was the critical deformation.

It has been found that high manganese Fe-Mn steels were susceptible to SCC in aqueous chloride solutions at a free corrosion potential. Moreover, the anodic polarization and the presence of $FeCl_3$ increased susceptibility to SCC significantly. Such behaviour is typical of anodic dissolution mechanism of SCC.

Specimens of Fe-Mn steel with the fully austenitic structure at the applied cathodic potentials showed good resistance to SCC, whereas the specimens of γ + ε-martensite steel underwent SCC. Fracture mode of the specimens and the kind of the stress-strain curves indicated of the hydrogen embrittlement mechanism.

High nitrogen stainless steels showed excellent resistance to SCC in all environments tested at room temperature. SCC of these steels was observed only in 20 % NaCl at the temperature 95°C. The steels in aged condition with precipitation of nitride and carbonitride phases at grain boundaries exhibited strong SCC in 3.5 % NaCl even at room temperature.

The SSRT and the cantilever bending tests with controlled potential, temperature, pH and concentration of chlorides create specific conditions that reveal different SCC behaviours for different types of steels.

An optional material selection for plate heat exchangers

Plate heat exchangers are frequently used for cooling of process media where large heat transfer surfaces are needed. The traditional material selections for sea water duties have been Titanium due to its good corrosion resistance in this environment. A few years ago a market situation existed where Titanium was hardly available or only available at high costs and long lead time. This introduced an idea to study other material options to lower costs and lead times. It is well known that stainless steel can be cathodically protected with very low current demand as compared to carbon steel. Further tube heat exchangers have been successfully cathodically protected with e.g. Resistor controlled Cathodic Protection (RCP^{TM}) for many years. A test was carried out to determine whether the same approach could be utilised to protect a 254 SMO stainless steel plate heat exchanger operating in high temperature chlorinated seawater. The paper will review the test, results and conclusions.

Keywords: Stainless steel plate heat exchangers, Chlorinated seawater, Resistor controlled cathodic Protection,

SEAWATER PIPING SYSTEMS: EVALUATION OF GALVANIC COUPLINGS BY USE OF COMPUTER MODELLING AND COMPARISONS TO EXPERIMENTAL RESULTS

Anne-Marie GROLLEAU (1), Hervé LE GUYADER (1), Valérie DEBOUT (1) , Nicolas DOLIGNON (1), Jean-Pierre PAUTASSO (2), Jérôme BLANC (2)

(1) *DCNS Cherbourg/NA, France*

(2) *DGA/DT BAGNEUX, France*

A full scale seawater loop has been implemented to evaluate the corrosion rate of steel components galvanically coupled to alloy 625 in natural seawater. The particular design of the corrosion loop has allowed precise corrosion current measurements and potentials. The corrosion profile of the steel part as a function of the distance from the alloy 625 interface has been determined throughout the experiment using NDT techniques and by final metallographic examination.

In addition to full scale corrosion measurements, computer modelling has been carried out using the Boundary Element Method software PROCOR and based on relevant polarization input data.

The results show that experimental, modelling and ultrasonic testing accord well.

STUDY OF Al ALLOY CORROSION IN NEUTRAL NaCl BY THE PITTING SCAN TECHNIQUE

Monica Trueba, Stefano P. Trasatti

Dept. of Physical Chemistry and Electrochemistry, Università degli Studi di Milano,
Via Golgi 19, 20133 Milan,Italy
Email addresses: monica.trueba@unimi.it, stefano.trasatti@unimi.it

Pitting corrosion of Al in chloride-containing medium has been intensively investigated [1]. Many electrochemical methods were used in the last 30 years, among which single-cycle polarization (or pitting scans) has been much less reported. The method allows qualitative interpretation of pitting corrosion of Al alloys as well as determination of electrochemical characteristic parameters of the pitting process, such as pitting (E_{pit}) and repassivation or protection (E_{prot}) potentials [2,3].

The corrosion behavior of as-received commercial Al alloys was studied in neutral 0.6 mol/L NaCl by using pitting scans. Results in both de-aerated and naturally aerated NaCl solution, with the aid of corrosion morphology characterization, allowed to infer the features of localized corrosion as a function of Al substrate nature. Besides electrochemical characteristic parameters such as E_{pit} and E_{prot}, the pit transition potential, E_{ptp} was repeatedly identified in the reverse scans as pitting was highly promoted [4]. The significance of E_{ptp} as an insight into highly constricted forms of localized corrosion is demonstrated as a function of the corrosive environment. The difference $\Delta E = |E_{pit} - E_{prot}|$, is proposed as a useful parameter for predicting the susceptibility towards pitting corrosion of Al alloys in a specific corrosive environment.

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Corrosion Issues with Duplex Stainless Steels for Marine Chemical Tankers and Storage Tanks

E. Johansson, Carolina Canderyd, Rachel Pettersson, Outokumpu, Avesta/Sweden

Duplex stainless steels are excellent materials for chemical tanker ships and storage tanks due to their combination of good mechanical properties and corrosion resistance. The range of duplex steels from the lean duplex 1.4162, via the widely-used 1.4462 to the super duplex 1.4410 means that an appropriate grade can be selected depending on the application. The resistance to various corrosion types can therefore effectively be utilized for the storage and transportation of chemicals in marine environments.

Both storage tanks and ships are exposed to air-borne chlorides, structural components on ships can also be subjected to seawater splashing, so there is a risk of pitting and crevice corrosion. Seawater is often used to clean the tanks and this procedure also gives a potential risk for initiation of localised corrosion. If the proper steel grade is not used the presence of chlorides in combination with a hot cargo can cause to stress corrosion cracking. Results from electrochemical measurements, carried out with the purpose of mapping the pitting and crevice corrosion susceptibility of the duplex stainless steels frequently used in chloride containing waters, are presented. Stress corrosion cracking data which illustrates the superior resistance of duplex stainless steels compared to their austenitic counterparts is included.

There are also high demands on the uniform corrosion resistance of construction materials which are in contact with the chemical load, since different inorganic acids (e.g. sulphuric acid, phosphoric acid and nitric acid), organic acids (e.g. acetic acid and formic acid) and caustic solutions need to be handled. In such environments duplex stainless steels can often remain passive and thus be suitable materials. However, there are limitations and some examples, including the effect of impurities such as chlorides and the dilution of concentrated sulphuric acid, are discussed in detail in the paper.

Susceptibility of epoxy coatings to microbial influenced degradation.

A. Heyer[1], G. Ferrari[2], F. D'Souza[2], H. Bakuwel[3], J.M.C. Mol[4] and J.H.W. de Wit[4]

[1]*M2i Materials Innovation Institute, Mekelweg 2 2628 CD Delft, The Netherlands, a.heyer@m2i.nl*
[2]*TNO Science and Industry, Bevesierweg 1781 CA Den Helder, The Netherlands,*
gabriele.ferrari@tno.nl, fraddry.dsouza@tno.nl,
[3]*Defence Materiel Organisation, Royal Netherland Navy, H.Bakuwel@mindef.nl*
[4]*Delft University of Technology, Department of Materials Science and Engineering*
Mekelweg 2 2628 CD Delft, The Netherlands,
j.m.c.mol@tudelft.nl, j.h.w.dewit@tudelft.nl

Ballast water tanks on board of ships are usually protected by epoxy coatings. Microbial influenced corrosion (MIC) is known to occur at the location of coating defects. This type of corrosion, in particular caused by sulfate reducing bacteria (SRB), leads to very fast local attack and can jeopardize the structural integrity of the ship. Biofilms are known to have a significant impact on their local environment forming microbial niches and concentration gradients which can have a strong impact on the coating integrity. Studies have indicated that certain micro-organisms and fungi are able to degrade the intact coating creating defects and giving the opportunity to SRB to attack the steel. A specific study has been set up to investigate the susceptibility of epoxy coating to this kind of attack. An epoxy coating used in practice in ballast tanks has been applied on steel and exposed to a culture of micro-organisms grown in laboratory as well as cultures obtained from a practical ballast tank. The same has been done for free films of epoxy coating. On the steel panels the coating degradation has been studied by electrochemical impedance measurements (EIS), free films were evaluated visually and by surface analysis techniques such as fluorescent microscopy.

Bacteria culture isolated from the practical ballast tank showed utilization of free film epoxy coatings as a sole carbon source. This reveals the degradation of epoxy coating, which was also clear from the EIS measurements. EIS measurements also showed increase in water or ion uptake of epoxy coating in the presence of laboratory grown acid-producing bacteria.

The study proved also that EIS in combination with surface analysis techniques is a powerful tool to elucidate the coating-bacteria interaction and finally to increase coating integrity and performance.

Key words: epoxy coatings, microbial influenced corrosion, MIC, electrochemical impedance measurements, EIS, fluorescent microscopy,

Using adhesive film as corrosion protection in maritime industry

Stefan MARION[1], Florin Turcu[2], Astrid Bjørgum[3],
[1] DNV Research&Innovation, Veritasveien, N-1322 Høvik
[2] DNV, Johan Berentsens Vei 109-111, N-5020 Bergen
[3] SINTEF Materials and Chemistry,7465 Trondheim, Norway

Corrosion and corrosion protection is a major concern for shipbuilding and shipping. The industry is constantly looking for new solutions that are cheaper and more reliable in production and offer lower in-service costs. Adhesive polymer films have been identified as a possible solution to replace conventional corrosion protecting coatings. DNV initiated the MarFilm project together with partners to evaluate the possibilities and limitations of adhesive film for corrosion protection purposes. The paper summarizes the results of laboratory tests of adhesive film on aluminium surfaces as well as coated steel surfaces.

Characterization of different anticorrosive protection systems on AA 5083 applied to marine construction

I. N. Alves[1], C. Brites[1], M. J. Marques[1], A. Soares Vieira[1], R. P. Gonçalves[1],
M. R. Costa[1], M.T. Santos[1], T. C. Diamantino [1]
[1] LNEG – Laboratório Nacional de Energia e Geologia, LMR – Laboratório de Materiais e Revestimentos, Estrada do Paço do Lumiar, 1649-038 Lisboa, Portugal.
(Tel.: 351-210924652 Fax: 351 – 217163796, isabel.nascimento@lneg.pt)

The strong increase of aluminum alloys applications registered some decades ago, for marine constructions, e.g. shipbuilding has led to a considerable number of cases of structure damages. Those are in great part due to corrosion problems. As well known, aluminum alloys have a thermodynamic instability to sea water and so a week corrosion resistance, which implies a suitable anticorrosive protection of marine structures.

Ship hulls for example, present different areas with highly specific operating conditions: ship bottom, splash area and top sides. Therefore and specifically for the permanently immersed surface, there is the need to keep them free from marine organisms in order to minimize drag resistance and reduce fuel consumption. Antifouling (AF) paints are applied on ship hulls to avoid this type of colonisation of surfaces. A great development of AF paints has been registered aiming for a better efficiency in compliance with emerging environmental regulation and legislation.

Therefore, it is necessary to consider several issues in order to define a suitable anticorrosive protection either for a new shipbuilding or a maintenance procedure.

In this context 7 commercial anticorrosive protection system environmentally friendly selected by paint manufacturers specializing in marine paints, applied on the 5083 – H111 aluminum alloy panels were studied. From those, 4 of the anticorrosive protection systems pretend to simulate the protection of the ship top side and splash areas and 3 systems intend to simulate the protection of the ship bottom area.

All panels were submitted to a previous surface preparation. For the top side and the splash areas the 4 systems were applied on the panels with and without conversion treatment.

With the purpose of evaluate the anticorrosive behaviour of the systems, tests were carried out including artificial ageing (salt spray, cycles of salt spray/humidity, cathodic disbonding) and natural exposure (immersed zone, splash zone and emerged zone). In addition, morphological characterization of surfaces by scanning electron microscopy (SEM/EDS) and visual assessment was carried out. Physical characterization of the coatings was done by measurement of thickness, adhesion, colour, gloss, hardness and falling weight test. Furthermore the assessment of the properties of the paints used is this work and chemical characterization by Fourier transform infrared absorption spectroscopy (FTIR) were also carried out.

Key-Words: 5083 aluminum alloy, anticorrosive protection, antifouling paints, shipbuilding.

Microbial Corrosion

Tubercles and Localized Corrosion on Carbon Steel

R.I. Ray, J.S. Lee and B.J. Little, Naval Research Laboratory, Stennis Space Center, MS 39529-5004, USA

Abstract

Experiments were designed to compare the structure, chemistry, and mineralogy of tubercles that formed in a decades-old drinking water distribution system (DWDS) with the same properties of tubercles that formed within months on carbon steel pilings in Duluth Superior Harbor (DSH), MN and WI, a freshwater estuary. Coupons of 0.9525 cm thick A328 (0.035% max P, 0.04% max S and 0.20 % min Cu) cold rolled sheet pile were cut to an average size of 19.3 x 11.6 cm and placed in holders at locations throughout DSH. Divers have collected coupons annually (prior to ice formation) for three consecutive years. Tubercles were recently identified in association with pitting on carbon steel pilings in DSH (Ray et al., 2009). Ray et al. (2009) identified microorganisms and amorphous iron, in addition to other heavy metals, within the tubercles. Copper, isolated in a distinct stratum at the base of the tubercles, was the most abundant heavy metal (other than iron). They concluded that the aggressive corrosion in DSH was due to the galvanic couple between the deposited copper and the carbon steel pilings. DSH is icebound from mid-December to mid-April and during that time has a durable, well-defined ice cover. Freeze ice thicknesses in DSH range from 0.5 to 1.4 m in addition to snow ice, stack ice, and ice from wave and splash action along harbor walls. Ice scour breaks and removes tubercles each year and tubercles reform within a few months. Gerke et al (2008) examined the morphology, mineralogy and chemistry of five tubercles from 90 year-old cast iron piping in a single DWDS. Tubercles in the DWDS were not associated with deep localized corrosion. Five tubercles have been removed from a 3-year DSH coupon and are being examined in detail and compared to tubercles from the DWDS. Tubercles from DWDS were larger (4-6 cm wide and 2-3 cm high) compared to those from the year 3 DSH coupons (2.4 cm wide and 0.5 cm high). Pit depths in the 3-year coupon ranged between 0.65 mm to 0.85 mm, 7-9% of the total thickness of the coupons. The structure of the tubercles from DWDS and DSH were strikingly similar, despite the differing water chemistry, formation conditions and age. Experiments are underway to determine the chemistry and mineralogy of the strata within the DSH tubercles and to test the hypothesis that tubercles on pilings in DSH reform in approximately the same location year after year.

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Menace of Micro Biological Corrosion in Hydrostatic Testing

Deepak Mankar
Materials Engineering Technology
Bechtel Corporation
Houston Texas USA

Abstract

Hydrostatic testing is commonly performed to determine the integrity of pressure retaining components or system of components such as valves, compressors, piping, and vessels. The primary function of hydrotest is to detect leaks; it is also applied as a strength proof test. The quality of water mandated by specification is intended to alleviate the menace of microbiological induced corrosion (MIC) is often compromised either due to availability or due to ignorance. The retained water after hydro testing over a period of time causes MIC attack. Case studies for MIC attack are visited, and some mitigation tools discussed.

Electrochemical Studies on Corrosion of Pure Copper Influenced by *Desulfovibrio* sp

Mert Onan [a], Esra Ilhan-Sungur [b], Nurhan Cansever [a], Nihal Doğruöz [b], Ayşın Çotuk[b]

[a]Yildiz Technical University, Faculty of Chemistry-Metallurgy, Department of Metallurgical and Materials Engineering, 34210, Esenler, Istanbul/Turkey
[b]Istanbul University, Faculty of Science, Department of Biology, 34134, Vezneciler, Istanbul/Turkey

ABSTRACT

Copper is commonly used in heating and cooling systems due to its excellent thermal conductivity and mechanical workability. Copper belongs to the group of materials that are resistant to corrosion thanks to a protective film that grows naturally in certain environments. One of the most frequent problems that appear on copper is microbiologically influenced corrosion (MIC), which can be attributed to the presence of bacteria that changes the condition in the metal/electrolyte interface and promote localized corrosion. Copper and its alloys, although toxic to fouling organisms, such as seaweed and shellfish, are subject to microbiologically influenced corrosion, undergoing severe attack by sulfide if conditions allow the growth of sulfate reducing bacteria (SRB).

Microorganisms cause biofilm layer on the material, resulting in development of corrosion mechanisms and/or quickening of the process. Anaerobic sulfate reducing bacteria is the most important type of bacteria causing microbiologically induced corrosion.

In this study, the effect of *Desulfovibrio* sp, the most common type of sulfate reducing bacteria, on the corrosion of pure copper at aqueous environments was investigated. Experiments were performed in sterile Postgate C medium, Postgate C medium contains *Desulfovibrio* sp., and Postgate C medium contains *Desulfovibrio* sp. and biocide, corrosion rates which were obtained by the electrochemical techniques were used in determining the corrosive effect. At the end of the experiment, surface of copper specimens were investigated with Field emission scaning electron microscopy (FESEM). In addition, Energy dispersive X-Ray spectrometry (EDS) analyses were performed to estimate corrosion products formed on the copper coupons.

As a result of FESEM analyses, biofilm formation was detected and spiral-rod shaped *Desulfovibrio* sp. bacteria were observed on the surface of pure copper. In the experiments with potentiodynamic method, change in corrosion potential (E_{corr}) of pure copper metal under different conditions was observed. E_{corr} was found to be at more active values in Postgate C medium contains *Desulfovibrio* sp. when compared to the values in sterile Postgate C medium. Contrast to previous potentiodynamic method measurements, change in E_{corr} was observed in experiments done with biocide.

Keywords: Copper, Microbiologically Influenced Corrosion, Sulfate Reducing Bacteria, *Desulfovibrio* sp., Potentiodynamic Method.

A study of electron transfer processes through biofilms in marine environments

A. Heyer[1], F. D'Souza[2], G. Ferrari[2], J.M.C. Mol[3] and J.H.W. de Wit[3]

[1]*M2i Materials innovation institute, Mekelweg 2 2628 CD Delft, The Netherlands,*
a.heyer@m2i.nl
[2]*TNO Science and Industry, Bevesierweg 1781 CA Den Helder, The Netherlands,*
fraddry.dsouza@tno.nl, gabriele.ferrari@tno.nl
[3]*Delft University of Technology, Department of Materials Science and Engineering,*
Mekelweg 2 2628 CD Delft, The Netherlands,
j.m.c.mol@tudelft.nl, j.h.w.dewit@tudelft.nl

Conductivity of biofilms can be considered to be beneficial for technical applications such as microbial fuel cells. On the other hand conductive properties of living biofilms may have a strong impact on microbiologically influenced corrosion (MIC) mechanisms. To investigate the conductive properties of biofilms in marine environments electrochemical impedance measurements (EIS) were performed under laboratory culture conditions. Experiments were conducted in modified artificial seawater with single or mixed bacterial strains: *Pseudomonas fluorescence* DSM 4358 and *Desulfovibrio indonesiensis* DSM 15121 over a period of 14 days.

From step by step investigation of living and dead biofilms as well as purified exopolymeric substances (EPS) of the chosen bacterial strains detailed information can be obtained about the possible electron transfer process within the biofilm.

This study indicates that pure EPS compounds have a strong impact on conductive properties of biofilms. Parallel microscopy work by fluorescent staining and AFM imaging gave additional information on the topography of the biofilm.

Furthermore the conductivity of some species of marine bacterial biofilms could be proven. Further studies on the biological and physical properties of marine biofilms are necessary to fully understand this electron transfer process and its underlying mechanism.

Keywords: biofilm, EPS, electron transfer process, MIC, EFM, AFM

Mitigation of biofouling and microbial induced corrosion using non-biocidal sol-gel coatings

R.Akid[1], J. Gittens[1,2], H. Wang[1], T. J. Smith[2], D. Greenfield[1]
[1] Centre for Corrosion Technology, Materials and Engineering Research Centre and
[2] Biomedical Research Centre, Sheffield Hallam University, Howard Street,
Sheffield, S1 1WB.
(corresponding author - r.akid@shu.ac.uk)

Introduction

Traditional methods of counteracting the development of surface biofilms within aqueous environments have involved implementing chemical biocides. These chemicals are either added directly to the electrolyte or they are contained within a surface coating applied to the material being protected. The exact composition of the biocide is dependent upon the prevalent forms of microorganisms that exist, being governed by the nature of the environment. Unfortunately microorganisms can often be resistant to inactivation by biocides since the bacteria within the biofilm are protected by a matrix of exopolymeric substances (EPS) [1]. Studies involving the use of ‘protective’ bacteria such as *Pseudomonas fragi* and *Paenibacillus polymyxa,* have shown that the biofilms formed can actually inhibit corrosion [2,3].

Sol gel coating technology offers a convenient route for immobilizing functional additives, e.g. inhibitors [4] or in the case of this study, immobilisation of biologically active microorganisms [5,6]. This combination of sol-gel and microorganism offers a unique coating that reduces biofouling and inhibits corrosion on metal substrates [4, 5], being low-cost, effective and environmentally friendly.

The paper presented here highlights the results of a study on the anti-fouling and corrosion resistance of the coating system in a selection of laboratory and natural environments. Further, the study shows that the viability of colony growth is not markedly affected by the sol-gel formulation chemistry. The corrosion resistance and anti-fouling behaviour of the active coating is compared with that of an abiotic coating of identical sol-gel formulation but without added bacteria.

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Physicochemical aspects of microorganisms interaction with passive films on the alloys

<u>Beleneva I.</u>[1], Kharchenko U.[2],Karpov V.[3]
[1]A.V. Zhirmunsky Institute of Marine Biology FEB RAS, Vladivostoc, Russia
[2]Institute of ChemistryFEB RAS, Vladivostoc, Russia
[3]A.N. Severtzov Institute of Ecology and Evolution RAS, Moscow, Russia

Now the research results and long-term observation of metal corrosion in water environments prove not only participation, but an important role of microorganisms in corrosion of metals. Influence of bacteria covers a great number of metal materials, including corrosion resistant steels and alloys characterised by presence passive film on a surface. It is experimentally established that the aerobic biofilms formed on a surface of some alloys in seawater catalyze the cathodic reaction of oxygen reduction increasing the rate of corrosion process. However not all materials are subject to bacterial influence.

It is known that the electrochemical behaviour of corrosion resistant materials is defined by properties of surface passive films. Therefore the research of a chemical composition, electrochemical and electrophysical properties of passive films is an essential part of studying materials corrosion behaviour in different environments. The aim of our work is to study the influence of biochemical activity of microorganisms on change of composition, structure, physical and chemical properties of passive films on the metal surface. Strain Pseudomonas sp. has been chosen as test object. Strain was isolated with corroding metal surfaces in tropical seawater. Research was spent on samples of stainless steel, titanium alloy, nickel, chrome, brass with natural and modified passive films.

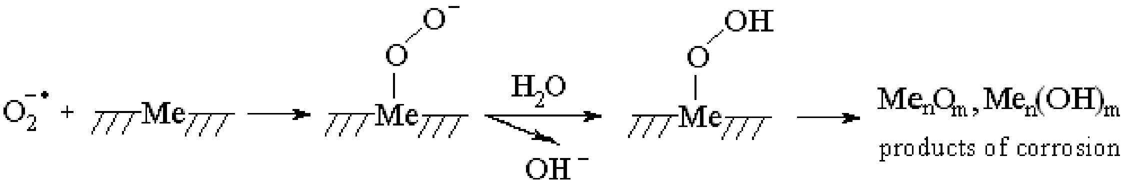
In this study the combined approach in apply of surface science methods (atomic force microscopy, scanning electronic microscopy, X-ray analyses) and electrochemical methods (measurement of semi-conductor properties of passive films and kinetics of electrode processes) was used. Thanks to a combination of the data received by different methods, connection between physical and chemical properties of passive films and stability of materials to microbiological influence has been established.

Reactive oxygen species in corrosion of metals

M. V. Chelnokova, D. V. Belov, T. N. Sokolova, V. P. Smirnov, V. R. Kartashov
Nizhni Novgorod state University of N.I.Lobachevsky, Nizhni Novgorod, Russia

Microscopic fungi’s influence on a surface of aluminium and its alloys, and also Mg, Zn, Cd, Bi, Sn, Pb was investigated. Microscopic fungi’s culture were chosen from the most widespread sorts in a nature (*Aspergillus, Penicillium, Alternaria*), the most activity microscopic fungus to investigated metal were detected (*A. niger, A. orizae* and *Alt. alternata*). Characteristic features were discovered in initiation of biocorrosion as follows: formation easily mobile transparent drops (exudation) on a surface of investigated metals with pH>7 in a local form, which through a number of stages (gel formation, solidification) and transform into a corrosion products oxide nature.

For the explanation of the receiving data the assumption about initiating influence of reactive oxygen species (ROS), in particular, superoxide anion-radical ($O_2^{-\bullet}$) which is produced and secreted in the process of vital activity of a microscopic fungi was advanced. The scheme of biocorrosion process was offered. This scheme shows that formation of the hydroxide ion (counterion can be cation from a culture medium – Na^+, K^+) is connected with initial adsorption $O_2^{-\bullet}$ on a surface and interaction with a metal:



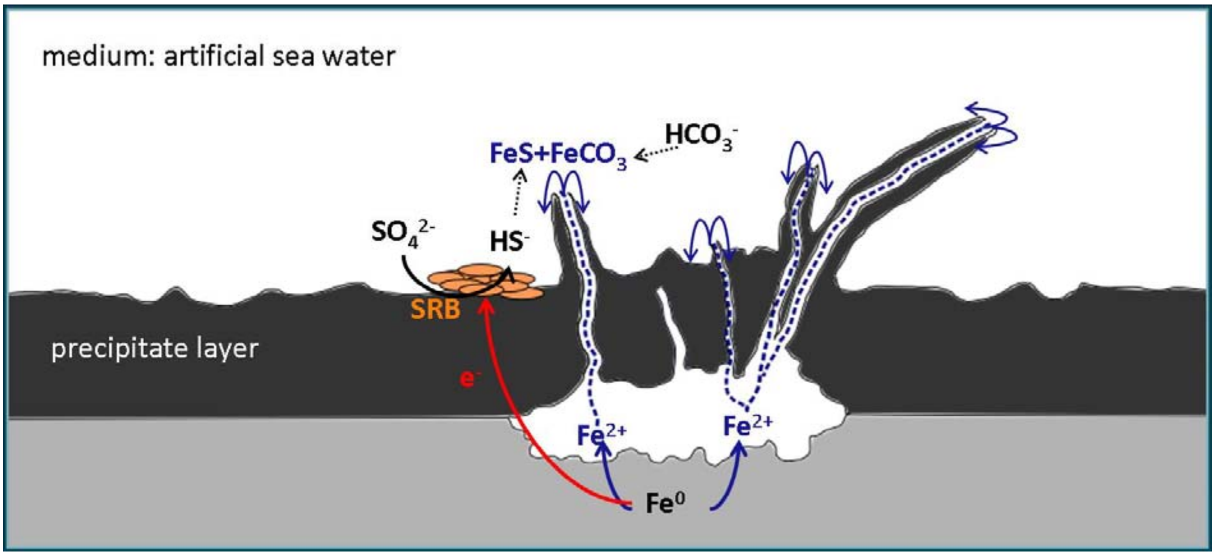
It was established that in the place of contact of the surface of metal with microscopic fungi there is renewal of Nitro Blue Tetrazolium Chloride monohydrate, used as a "trap" for $O_2^{-\bullet}$, to formazan. As an additional argument of participation of ROS in initiation of biocorrosion, in our view, there are results on influencing adsorbed ionol (2,6-di-*tert*-buthyl-4-methylphenol) on the surface of metals. It was shown that destruction of surface of the treated sample of metals takes place more intensively, at the expense of the additional generation of exogenous forms of ROS.

A new model for microbiologically influenced corrosion

H. Venzlaff [1,3], *D. Enning* [2], *F. Widdel* [2], *M. Stratmann* [1], *A.W. Hassel* [3]
[1]*Max-Planck-Institut für Eisenforschung, Düsseldorf/Germany*
[2]*Max-Planck-Institut für Marine Mikrobiologie, Bremen/Germany*
[3]*Johannes Kepler University, Linz/Austria*

Studies on corrosion processes of industrial steel influenced by anaerobic sulfate-reducing bacteria (SRB) is a highly interdisciplinary field between electrochemistry and microbiology with great impact for several important branches like the gas and oil industry.

The severe damages microbiologically influenced corrosion (MIC) causes are well described, but the mechanisms behind are not fully understood yet. There are obvious differences in the amount and structure of corrosion products, investigated by SEM[1], between highly corrosive SRB strains like *Desulfopila corrodens* IS4 and less corrosive strains like *Desulfovibrio ferrophilus* IS5. Additional SEM investigations of corroded surfaces show further differences in the distribution of cells and unique chimney-like structures of precipitates which had never been described before.



In a long-term incubation experiment over several months the growth rate of the bacteria has been measured and correlated to the chemical composition and crystallographic data of the produced precipitates. Based on this experiment a new working model for the mechanism of corrosion by SRB has been set up which includes a direct electron transfer from the metal to the bacterial cells.

Ongoing electrochemical measurements using iron, noble metals as model electrodes as well as oxidic surfaces which can block the direct electron uptake, support this corrosion mechanism. Furthermore microscopic investigations may give new insights into the first step of the MIC process: the attachment of cells to the metal surface.

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A predictive model for microbiologically influenced corrosion in oilfield pipelines

P. Smith, S. Roy, D. Swailes, Newcastle University/UK; J. Lawsom, D. Page, Chevron Upstream Europe, Aberdeen/UK; S. Maxwell, Intertek Commercial Microbiology, Aberdeen/UK

A physical model is presented for the prediction of Microbiologically Influenced Corrosion (MIC) rates in subsea pipelines. Polarisation techniques were used to assess the corrosion influence of biofilms. Sulphidogenic biofilms were grown on corrosion coupons in a bioreactor and transferred to a three electrode corrosion cell where potential sweep measurements were performed. The observed biofilm growth combined with the accumulation of iron sulphide film measured at the surface and the collected corrosion data were used to build a model for MIC. The model developed is based on a material balance describing the processes contributing to biofilm growth and the yield of sulphide within the biofilm. A balance is assumed to exist between the production rate of iron sulphide in the biofilm and the consumption of iron from the steel surface. The effect of biofilm contact area has also been explored yielding a model for MIC based on the generation rate of sulphide in the biofilm and the resultant biofilm contact area with the substratum surface.

Characterization of biofilm/deposit complexes associated with Microbiologically Influenced Corrosion (MIC) in European harbours

F. Marty[1], J.M. Sánchez-Amaya[2], E. Ilhan-Sungur[3] H. Gueuné[4], F.J. Botana[5], M. van Loosdrecht[1], G. Muyzer[1]
[1] Delft Technical University, Environmental Biotechnology Section, Delft, the Netherlands
[2] Titania, Ensayos y Proyectos Industriales, Puerto de Santa María, Spain
[3] Istanbul University, Faculty of Science, Department of Biology, Vezneciler, Istanbul, Turkey
[4] CORRODYS, Cherbourg, France
[5] Universidad de Cádiz, Laboratorio de Corrosión, Puerto Real, Spain

A study performed in 1990-1993 estimated a minimum of 12-13% of European harbours affected by a particularly aggressive localized MIC phenomenon, called Accelerated Low Water Corrosion (ALWC) occurring at or below the low water zone of steel waterfront structures. ALWC is well recognized to affect harbours worldwide, causing drastic reductions of the service life of steel structures due to unusual high corrosion rates. Prevention and mitigation solutions exist, but are costly, while ALWC prediction has so far not been possible due to the lack of understanding of abiotic and biotic factors and of the mechanisms involved. Presence and potential implication of sulfate-reducing and other sulfur bacteria in ALWC has been reported in previous studies. However, the mechanisms and the characteristics of the biofilm-deposit complex involved in ALWC remain unclear.

The objective of this study is to obtain a detailed characterization of ALWC biofilm-deposit complexes taken from one European harbour in order to propose interaction and corrosion mechanisms.

Several samples of corroded and non-corroded zones were recently taken from a European harbour affected by ALWC since 20 years. These samples were studied using different analytical methods: (1) cultivation targeting for the first time almost all MIC associated-bacterial metabolic groups (sulfate-reducing bacteria (SRB), thiosulfate-reducing bacteria (TRB), thiosulfate-oxidizing bacteria (TOB), iron-oxidizing bacteria (IOB), iron-reducing bacteria (IRB), manganese-reducing bacteria (MnRB) and marine aerobic heterotrophic bacteria); (2) 16S rDNA PCR-DGGE fingerprinting methods, (3) microscopic methods (e.g. SEM) and (4) analytical methods to determine chemical composition (i.e. XRD, XRFS, and Raman spectrometry).

All targeted bacterial groups could be enriched from samples originating from ALWC and from the reference sites confirming that the presence of specific metabolic groups is not an exclusive criterion for characterizing ALWC biofilm. However, IOB activities appeared to be higher in ALWC than in reference samples indicating a potential implication of this metabolic group, which was not yet considered in ALWC. Analysis of SRB and TRB enrichments indicated specific populations associated with ALWC.

Analysis of the different layers of biofilm-deposit complexes indicated the presence of an oxygen gradient within the biofilm/deposit complexes. Green rust and iron sulfide detected with SRB in the inner layers of ALWC samples indicated the occurrence of SRB activities.

Further results and their interpretation will be discussed in the future to improve ALWC diagnostics and prediction.

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Influence of microfouling on sea corrosion and destruction of sheetings

Karpov V.A.[1], Kovalchuk J.L.[1], Kharchenko U.V.[2], Beleneva I.A.[3],
[1]*A.N. Severtzov Institute of Ecology and Evolution RAS, Moscow, Russia*
[2]*Institute of ChemistryFEB RAS, Vladivostoc, Russia*
[3]*A.V. Zhirmunsky Institute of Marine Biology FEB RAS, Vladivostoc, Russia*
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On an example of carbonaceous and stainless steels it is shown, that microfouling, developing on a surface of metals, possesses high corrosion activity and stimulates corrosion processes. Adapting for changes of conditions of environment, aggression of sea microflora increases. By us it is established, that in the polluted port waters speed of corrosion of many materials several times above, than in rather pure waters and the basic contribution to this process belongs to microorganisms. Local corrosion stainless steels can be made active ability to live anaerobic microorganisms under the basis of small houses barnacles. Pitting corrosion under them develops at hit under their small houses sulfate-reducing and iron-bacteriums. In absence of microorganisms (sterile conditions) corrosion on metals practically does not develop.

In sterile conditions we observed similar process at test protective paint and varnish coverings (ЛКП). In sterile sea water from modelling antifouling coverings with the biodamaged basis, containing rosin and copper(II), allocation of ions of copper was defined by only chemical dissolution of rosin and made 3-5 mkg/sm^2 a day. In sea water with microorganisms the curve going out ions copper has peak (60mkg/sm^2 a day) with the subsequent exit on a plateau with value (to 23mkg/sm^2 a day). In sterile conditions the given dependence looks like a direct, parallel axis of abscisses. Thus, the bacterial film (microfouling) influences the expense biocide from the sheetings which organic basis is for them the power supply. The biofilm concentrates in itself copper connections, it accumulates superfluous quantity of copper and liberates in the sea environment only its part. Viability in a biofilm is kept adapted for ions of copper by microorganisms. In sterile conditions efficiency antifouling paints with copper coverings sharply decreases.

Biological corrosion of the metals applied in the atomic power station

G.V.Zhdanova, J.L.Kovalchuk
A.N. Severtsov Institute of Ecology and Evolution, Russian Academy of Sciences, Moscow, Russia

Influence of corrosion of constructional materials on reliability and safety of work of atomic power stations are studied insufficiently full. Research of a biocorrosion situation in pipelines of the heat-carrier of the atomic power station at lay modes was the purpose of the present work.

Kinetic characteristics of corrosion of steels 08X18H10T and st20 are analysed. In industrial neutral electrolit before infection with microorganisms. The estimation of influence of microorganisms and products of their metabolism on corrosion of the steels protected biocide by connection is spent.

For revealing of a role of microorganisms on corrosion of constructional materials of system chemical water clearing and a constructional steel of the process equipment, on the infected samples and processed biocide, studied kinetic electrode processes. Curves of cathodic and anode polarisation removed in potentiodinamic a mode on potentiostat ПИ-50-I. It is shown, that in the presence of bacterial flora speed of cathodic polarisation of metal sharply increases, braking cathodic and activation anode processes takes place. So, it is established, that speed of corrosion st20 in the presence of microorganisms increased in 2-3 times, and a steel 08X18H10T lost ability to passivation.

It is established, that corrosion-active microflora, getting to the heat-carrier through ionic-exchange installations, blocks functional groups ionic-exchange pitches. Thus speed of an exchange of inorganic ions from processed water decreases. There is an increase falling through ions to increase in degree of pollution of pitch. Getting to pipelines crude water creates in addition corrosion-dangerous situation. For prevention of the given phenomenon it is offered before regeneration ionic-exchange pitches in addition to include an endurance stage (15-20 minutes) ionit in 1.5 % a solution $Na_2B_4O_7 \cdot 10H_2O$ with the subsequent washing of the water.

Consequences of biodeteriorations of objects of an infrastructure and engineering structural materials in the metropolis

V.A. Krylenkov
Biology and Soil Department of the St. Petersburg State University,
Saint-Petersburg, Russia
O.P. Poltarukha,
A.N. Severtsov Institute of Ecology and Evolution (RAS), Moscow, Russia

Biogeocenosis violation as a result of technical progress constitutes a very difficult biological problem of coexistence of humans and a huge range of organisms and microorganisms communities that inhabits the biosphere. Genetically diverse organisms (various genera and species of prokaryotes and eukaryotes) have to interact and survive in the artificial (urban) environment and closed (isolated) environment created by humans. For their joint survival they form strong microbial communities. A pronounced polymorphism and rapid change (plasticity) of nutrition ways are characteristic of such microbial communities (bacteria and microscopic fungi). The processes of biological corrosion of inorganic materials and building (products) and other forms of biogenic destruction (in the form of biofilm and «blood clots» out of different microorganisms) have been revealed even in the severe conditions of the Antarctic and other extreme zones of intense human activity. Sensitivity and high indicator ability of these microorganisms enable to choose the methods of microbiological analysis as a tool for monitoring of human-induced changes in the biosphere, biodeterioration of materials and building (products). The processes of biological corrosion and other biodeterioration forms of building materials and building (products) adequately reflect the negative influences of any kind regardless of how profound these influences have been investigated. The speed biodeterioration development is an indicator of sustainability (bioresistantance) and, accordingly, durability of inorganic materials, products and engineering structures.

Nuclear Corrosion

Stress corrosion cracking of Alloy 600 in secondary water of PWRs

Hong Pyo Kim, Dong-Jin Kim, Seong Woo Kim
Seong Sik Hwang, Youn Soo Lim and Joung Soo Kim

Nuclear Materials Research Division, Korea Atomic Energy Research Institute,
1045 Daedeok-daero, Yuseong-gu, Daejeon, Korea
E-mail : *hpkim@kaeri.re.kr*

Abstract

Stress corrosion cracking (SCC) of Alloy 600 in steam generator of pressurized water reactors (PWR) has been issues in nuclear industry. Most of steam generators with low temperature mill annealed alloy 600 tubing was replaced to steam generator with thermally treated Alloy 690. However, steam generators with high temperature mill annealed Alloy 600 and thermally treated Alloy 600 are still working in nuclear industry even though these are more resistant to SCC than low temperature mill annealed Alloy 600. In this work, SCC of Alloy 600 was studied in high temperature solution with and without addition of lead oxide or nickel boride using slow strain rate test and C-ring specimen. Characterizations of oxide layer on Alloy 600 were analyzed with the electrochemical impedance spectroscopy, the Auger electron spectroscopy, the x-ray photoelectron spectroscopy and the transmission electron microscopy, equipped with the energy dispersive x-ray spectroscopy. SCC resistance of Alloy 600 and impedance of the oxide layer on Alloy 600 was dramatically reduced with addition of lead oxide. The oxide layer on Alloy 600 was changed from double layer structure to single layer structure with addition of lead oxide. The change in oxide layer structure with addition of lead oxide seemed to be related with SCC resistance and impedance of oxide layer. Lead was incorporated into the surface oxide in a metallic state and as an oxide state of PbO, which causes a degradation of the passivity leading to a PbSCC susceptibility. The NiB inhibitor reduced the lead incorporation level into the oxide layer, thus substantially improving the oxide passivity, and decreasing its susceptibility to a PbSCC.

UNDERSTANDING OF CORROSION MECHANISMS OF HYDRIDED ZIRCONIUM ALLOYS DURING OXIDATION IN PWR CONDITIONS

Caroline BISOR-MELLOUL, Marc TUPIN, Philippe BOSSIS, CEA/DEN, Service d'Etudes des Matériaux Irradiés, CEA/Saclay, 91191 Gif-sur-Yvette cedex, France, marc.tupin@cea.fr
Jacques CHENE, CNRS-CEA/DEN, SCCME, CEA/Saclay, 91191 Gif-sur-Yvette cedex, France, jacques.chene@cea.fr
Jean-Luc Béchade, CEA/DEN, Service de Recherche en Métallurgie Appliquée, CEA/Saclay, 91191 Gif-sur-Yvette cedex, France, Jean-Luc.BECHADE@cea.fr
François JOMARD, CNRS UMR 8635, Groupe d'Etude de la Matière Condensée, 92195 Meudon cedex, France, francois.jomard@cnrs-bellevue.fr
Arthur MOTTA, Departement of Mechanical and Nuclear Engineering, 227 Reber Building, The Pennsylvania State University, University Park, PA 16802, atm2@psu.edu

Zirconium alloys are widely used as fuel claddings in Power Water Reactors. As they represent the first confinement barrier to fission products, their mechanical integrity is essential for nuclear safety. During their corrosion in primary water, a fraction of the hydrogen released ingresses into the alloy. In the metallic matrix, once the solid solution limit is reached at the irradiation temperature, hydrogen precipitates as Zr hydrides mainly located just under the metal/oxide interface due to the thermal gradient across the cladding. As these hydrides may contribute to larger oxide thickness and to a more fragile behaviour of the cladding, the minimization of hydrogen pick-up is required. Consequently, the Zircaloy-4 cladding (Zr-0.2Fe-0.1Cr-1.3Sn) is progressively substituted by the other alloys which are less sensitive to hydriding phenomenon. As it is frequently suggested that hydrides may also contribute to an increased corrosion rate of Zircaloy-4, the understanding of the influence of hydrides on corrosion is thus a question of interest. This paper deals with the microstructure of the oxide formed on pre-hydrided materials compared to that of the scale on the Zircaloy-4 matrix without hydrides and with the future of the hydrogen of the hydrides during the corrosion process. To fulfil the last objective, SIMS analyses have been performed on cathodically pre-hydrided samples corroded in PWR conditions with heavy water (D_2O) in order to study the hydrogen distribution after oxidation. Concerning the microstructure, cross sections of oxides formed on pre-hydrided sheets and Zircaloy-4 matrix (without hydrides) have been analysed by micro X Ray Diffraction in Argonne National Laboratory to determine the phases formed in these layers.

An additional phase indexed as the sub-oxide Zr_3O have been evidenced by this last technique on the oxide film formed on the rim of massive hydrides, whereas it was not observed on reference specimens corroded in the same conditions. Moreover, the hydrogen of the hydrides is clearly not integrated in the oxide during the corrosion of the hydrides but penetrates in the hydrided matrix, which could result in the transformation of the δ–$ZrH_{1.66}$ in ε–ZrH_2, as shown by the μ-DRX results.

These results lead to support the hypothesis of a change in oxidizing mechanisms of hydrides containing samples.

Application of polymer coatings for repair and restore of heat-exchange equipment in power engineering

N.V. Pechnikov[1], V.A. Golovin[2], A.B. Ilin[2], V.A. Shchelkov[2]
[1] R&D ROCOR Ltd, Moscow, Russia
[2] Institute of Physical Chemistry and Electro Chemistry, Russian Academy of Science, Moscow, Russia

Keywords: heat-exchange tubes, corrosion, pitting, polymer coatings, eddy current testing.

The examples of types of corrosion destruction of heat-exchange tubes of main steam condensers on the Russian nuclear power stations are given. The special attention is concentrated on local types of corrosion of tubes from copper-nickel alloys. It was found that a quantity of tubes having local pitting distributed in a random way on all their length increases in time. A pitting depth can reach 50 % of a thickness of a tube's wall. The single pits are through. Through-hole formation is especially dangerous in case of using high-mineralized water or sea water as a cooling agent.

High heat-conducting polymer coatings are offered to apply on an internal surface of the tubes. These coatings can be applied for repair and restore of corroded tubes, including tubes with through holes. These coatings can also be applied for prevention of further corrosion. This engineering decision is covered by the patent № 2186633 of the Russian Federation and the patents of other countries and includes:

- The special polymer materials are able to form the polymer "rivets" in through holes, to fill other corrosion pits and to form a thin (30-70 mkm) non-flowing down coating on the undamaged tube surface;
- The diagnostic automatic complex combined the eddy current analyzer with video system. The complex can be applied to analysis of corrosion-and-mechanical damages of tube's wall, also for a control of scale thickness on the tube walls, a control of descaling quality, a control of thickness and quality of coating application. The speciality of the complex is carrying out high-speed eddy current testing of corrosion damages and tube wall wear and automatic changing to video shooting of the most dangerous parts;
- The special application equipment providing an application of polymer coating on an internal surface of tubes 20 m long and 20 – 35 mm in diameter.

Many years' application experience of this technology for repair of tubes on Leningradskaya, Kolskaya, Tverskaya, Balakovskaya, Rostovskaya and Yuzhnoukrainskaya nuclear power stations was analysed. More than 200 thousand heat-exchange tubes on NPS have been repairing and protecting by this technology since 2004.

Development of new kind of corrosion protection coatings in lead at temperature of 500°C

M. Utili [a,*], R. Scarfiello [b], A. Gessi [a], P. Agostini [a]

[a] ENEA CR Brasimone, Camugnano (I)

[b] Università degli studi di Bologna, Facoltà di Chimica, Bologna (I)

One of the critical issues for the Lead cooling Fast Reactor development is the material compatibility and corrosion in the coolant, pure lead. With the aim to select and qualify new kinds of coatings to be able to prevent any corrosion attack of the martensitic steel T91 in the liquid metal, different kinds of coatings (FeAl based) were selected and tested in CHEOPE III loop at 500 °C under controlled oxygen atmosphere. Coatings analysed are: FeAl-DC sputtering, SS39L and BLUE. T91 specimens coated by FeAl-DC sputtering was provided by the university of Trento, instead the other two new kinds of coatings have been selected in the commercial market with the aim to find a well developed coating technique. The first kind of commercial coating, named SS 39-L, is a Titanium and Zirconium Carbides instead the second one, BLUE coating, is a Titanium and Aluminium Nitrides. The three kinds of FeAl-coated T91 specimens were characterized in fluent lead at 1m/s with a test section temperature of 500°C. Oxygen control and monitoring is performed by means of gas bubbling and Oxygen electrochemical sensor in order to keep Oxygen concentration at 10-6 wt%. The specimens after a exposure to flowing lead for 2000 and 4000h were observed by means of microscopy and EDX spot microanalyses. The coatings behaviour has been analysed and FeAl-DC sputtering has shown the better corrosion resistance in pure lead.

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[*] Corresponding author. Tel.: 0534801203 Fax.: 0534801250
E-mail address: marco.utili@enea.it (M. Utili)
ENEA Brasimone
Camugnano (BO) 40032,
Italy

Electrochemical study of uranium metal corrosion and dissolution in neutral solutions and nitric acid based electrolytes

***A. Maslennikov*, V. Peretrukhin**

A.N.Frumkin Institute of Physical Chemistry and Electrochemistry
of Russian Academy of Sciences, Moscow, Russia

Corrosion and dissolution of the reactor grade uranium metal in neutral solutions (0.1 M $NaClO_4$, pH 3.0 – 9.0) and HNO_3 based electrolytes was studied using conventional electrochemical techniques. Corrosion potentials ($E_{corr.}$) and corrosion rates ($v_{corr.}$) of uranium metal in the region of passivity as well as transpassivation potentials were determined. In neutral electrolytes at the potentials between – 0.5 to 0.4 V / Ag/AgCl uranium metal is found in a passive state. With the increase of the electrolyte pH from 4.0 to 9.0 its $E_{corr.}$ decreased slightly from -249 to -277 mV / Ag/AgCl with corresponding increase of $v_{corr.}$ from 1.28 to 2.77 $\mu g \cdot cm^{-2}h^{-1}$. The increase of HNO_3 concentration from 0.05 to 2.0 M caused the shift of the $E_{corr.}$ towards positive direction, achieving 390 mV / Ag/AgCl in 2.0 M HNO_3. The corresponding values of $v_{corr.}$ increased from 0.6 to 3.12 $mg \cdot cm^{-2}h^{-1}$.

Transpassivation potentials ($E_{tr.}$) of uranium metal (430-450 mV / Ag/AgCl) were found to depend weakly both on H^+ and NO_3^- concentration in the solution. The potential controlled electrolysis (PCE) at the potentials E> $E_{tr.}$ resulted in the accumulation of soluble U(VI) species in the electrolyte. The rate of uranium metal anodic dissolution increased with the increase of PCE potential. The electrolysis current efficiency was about 6.0 F/mol U in all the studied electrolytes, proving the oxidation of uranium to (+6) oxidation state. Uranium metal dissolution was accompanied by the spallation of insoluble particles from metal surface, especially noticeable in neutral and weakly acidic electrolytes. The observed particle spallation along with the character of the I – t curves registered during PCE proved the pitting mechanism of uranium metal dissolution at $E>E_{tr.}$

The introduction of the carboxylic acids, in particular, HCOOH to the nitric acid electrolyte resulted in the 200 -300 mV decrease of uranium metal $E_{corr.}$ relatively its value determined for the fixed concentration of HNO_3. The $v_{corr.}$ estimates for HNO_3 – HCOOH solutions were 2 – 3 times higher in comparison with the $v_{corr.}$ values for HNO_3 solutions of the same concentrations The $E_{tr.}$ in presence of carboxylic acids in nitric acid electrolyte decrease 150 – 200 mV, thus narrowing the region of potentials, corresponding to uranium metal passivity. The latter observation may serve as a fundamental for the development of uranium metal and uranium based alloys dissolution technique for the reprocessing of the metal based spent nuclear fuel.

Corrosion of ^{238}Pu and ^{239}Pu metals in contact with air

V.F. Peretrukhin, A.G. Maslennikov
Institute of Physical Chemistry and Electrochemistry of RAS, Moscow, Russia

PuO_2 or hydrated Pu(IV) dioxide are known to form as the principal products of Pu metal corrosion in contact with atmosphere. The process of corrosion of ^{238}Pu is complicated by the occurrence of the (α,nγ) reactions on the oxygen atoms included to the surface oxide film. The accumulation of oxygen on the metal surface results in the increase of neutron and photon fluxes from the metal samples. The present study is aimed to determine the rate and mechanism of ^{238}Pu metal corrosion, to find out the correlations between the corrosion rate and radiation characteristics of ^{238}Pu metal and the comparison of corrosion rates of ^{238}Pu ($E_{1/2}$=87.7 years) and ^{239}Pu ($E_{1/2}=2.4\cdot10^4$ years).

^{238}Pu metal was prepared using electrochemical amalgam technique, including electrochemical reduction of Pu(III) to Pu^o(Hg) in aqueous acetate solution at mercury pool cathode followed by the thermal decomposition of the amalgam in Ar and ingot melting in vacuum at 1100°C [1]. The pellets (d = 0.6 cm, m ≈ 1.0 g) for corrosion study were prepared by cold pressing of the ingots. The mass gain as well as the neutron and photon fluxes from ^{238}Pu metal samples were measured during ^{238}Pu metal sample atmosphere corrosion test. It was found that the measured value of neutron flux included the spontaneous fission neutron component which did not change during the experiment. The components of neutron flux presented by induced fission neutrons and the neutrons formed due to $^{18}O(\alpha,n\gamma)^{21}Ne$ и $^{18}O(\alpha,\alpha'\gamma)\,^{18}O$ reactions were increasing in course of corrosion. The symbatic increase of the neutron flux ΔN from the sample and mass gain Δm were revealed. Three steps were found to be characteristic for ^{238}Pu metal corrosion in contact with air. The first step (620 hours) related to the germination process occurring according linear law [2]. The second step (620-1200 hours) was characterized by the significant increase of the corrosion rate. This increase was caused by the germs oxidation to $PuO_2{\cdot}2H_2O$ occurring at the intercrystallite surface and resulting finally in the pellet destruction, followed by the significant increase of its specific surface. At the third step (after 1200 hours) the ^{238}Pu corrosion rate decreased due to the increase of the surface $PuO_2{\cdot}2H_2O$ film thickness. At this step the corrosion rate is limited by the diffusion of the oxygen or water molecules to plutonium metal surface. The values of the effective corrosion rate constants and corresponding reaction orders were determined for all three steps of corrosion process using the principal equation for the heterogeneous reactions kinetics. The reaction order while passing from step II to step III was found to decrease from 4.0 to 1,0. The determined value of maximum corrosion rate for ^{238}Pu metal $(3.1\pm1.8)\ 10^{-3}$ $mg\cdot cm^{-2}\cdot h^{-1}$ was found the order of magnitude higher in comparison with the corrosion rates reported for ^{239}Pu metal [3]. This difference is accounted for the higher specific a-activity and local temperature of ^{238}Pu sample in comparison with ^{239}Pu.

The study of ^{238}Pu metal corrosion showed that the metal samples with a mass about 1 g may be handled in dry atmosphere at room temperature during 25 days without considerable increase of neutron flux. It was found that the neutron and photon flux from freshly prepared ^{238}Pu metal was about 4 times lower than that for PuO_2. This observation increases the interest to ^{238}Pu alloy as an energy source instead of $^{238}PuO_2$ for the man-piloted space ships.

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A method for determining safe concentrations of chloride ions in pitting corrosion of steels in nitrate media

V.P.Rasygraev, M.V.Lebedeva, A.I.Shcherbakov
Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, Moscow, Russia

As is known, in the operation of nuclear power plants, large amounts of liquid radioactive wastes (LRW) accumulate. The base component in such solutions, which are accumulated and stored in stainless steel containers, is sodium nitrate with a large number of various admixtures, in particular, chlorine ions; these are the most dangerous from the standpoint of corrosion. LRW solutions carry the high potential risk of local pitting corrosion, in which case the LRW container wall becomes perforated despite insignificant loss of metal in terms of general corrosion.

As is known, the pitting corrosion is effectively inhibited by NO_3^- anions, in the presence of which the permissible concentration of Cl^- ions significantly increases. However, the clarity of pitting manifestations sharply decreases in the potentiostatic regime, where only a relatively small maximum of dissolution in the passive region is observed instead of the characteristic avalanche growth in the anode current. For this reason, usual electrochemical methods do not always reveal pitting corrosion in solutions containing both NO_3^- and Cl^- ions.

We propose a new approach for this, which stipulates the artificial initiation of pitting under definitely aggressive conditions, followed by gradual dilution of the solution until the complete suppression of the pitting focus. This method is based on the assumption that the operation of a pitting focus is accompanied by the continuous exchange of solution between the inner volume, where the local dissolution proceeds, and the outer volume of the medium (outside the cavity). Then, in the case of variation of the solution composition in the cell (a decrease in concentration of Cl^- ions and/or increase in the concentration of NO_3^- ions), this exchange will eventually lead to suppression of the anodic reaction in the volume of pitting. By changing the solution composition in the cell at a sufficiently slow rate, we can almost synchronously vary the composition of medium inside the cavity. Retardation of the anodic process inside the cavity is reliably manifested by decreasing current. When all foci of local dissolution in the cavity are suppressed by the inhibitor, the current ceases to display random oscillations, becomes stabilized at a certain low level, and only exhibits weak smooth fluctuations.

Using the method of continuous mixing dilution, we have studied the process of local corrosion suppression (i.e., of the limiting surface filling by ions) depending on the final concentration of chloride. Analysis of these data show that the nitrate concentration necessary for the complete suppression of pitting on 18/10 stainless steel increases with the concentration of Cl^- ions present in the dilute solution. However, the other parameter that also characterizes the conditions of local corrosion inhibition—the [NO_3^-]/[Cl^-] ratio—sharply decreases with increasing chloride concentration. This behavior is related to the fact that the complete displacement of adsorbed chlorine ions from the surface is determined by the limiting coverage of ions, which depends very weakly on the chloride concentration.

Of course, the proposed method for determining protective ratios of the inhibitor (NO_3^-) to activator (Cl^-) concentrations gives somewhat overstated values of this ratio, which is related to more rigid conditions of accelerated testing. Indeed, the material in such tests is artificially given a potential corresponding to the maximum rate of pitting, which ensures determination of the guaranteed conditions for its suppression. However, the preset potential is always more positive than the corrosion potentials realized in practice.

Corrosion experiments of reference steels in flowing LBE at 450°C

A. Gessi [a], M. Agostini,[a] P. Agostini [a]

[a] ENEA CR Brasimone, 40032 Camugnano, Bologna (I)

The definition of the corrosion behaviour of reference steels like T91 and AISI 316L in contact with HLM, as far as Pb and LBE are concerned, is a fundamental topic in the development of GenIV LFR.

At ENEA Brasimone, several loops and HLM facilities have been devoted to corrosion studies since the second half of the 90s. The LECOR loop (Lead CORrosion) was designed with the goal to perform corrosion tests in flowing LBE with extremely low Oxygen concentrations, in order to characterize reference materials in extreme environments.

This paper describes the experimental data, EDX imaging and elemental analyses, gathered form the LECOR loop, after 5000 hours of exposure of T91 and AISI 316L steels' specimens in flowing LBE at 450°C, with a speed of 1m/s. This environment was chosen as representative for relatively high temperature areas in the LFR reactor concept.

Also, the experiment was carried on in the frame of the DEMETRA EUROTRANS FPVI of the E.U.

Keywords: corrosion, LBE, coolant chemistry.

[a] Corresponding author: Alessandro Gessi, ENEA Brasimone, 40032 Camugnano (BO) Italy.

Alessandro.gessi@enea.it

Oil fuel based protective liquids application in tanks of hot water-supply

Tatur I.R., Musalov Y.A., Sharafutdinova D.V., Tonkonogov B.P., Gubkin State Oil and Gas University/Moscow

Protective liquids are used in energetic industry for anticorrosion protection of metal surface of hot water-supply tanks. Water reserve stored in that 100 – 20 000 cubic metres volume tanks. It is necessary for levelling of hot water streams in open systems of centralized communal heat supply and for uninterruptible heat-transfer feeding to consumers.

Protective liquids are viscous solutions of high molecular polymers with mineral oils and anticorrosion additives.

Generally high molecular polyisobutylene (molecular weight 200 000) are used as a thickening agent and industrial oil И-20А or И-12А are used as a base.

Protective liquids are used in tanks for 4 years at the temperature conditions 80 - 90 ^{O}C.

Due to high adhesion ability protective liquid cover inside tank with thick layer, which prevent contact between metal surface and water.

The application of protective liquids results in corrosion speed carbon steel decrease until 180 and 1200 time in steam-gas phase and on interphase accordingly**.** Moreover, high quality of drinkable and circulating water is achieved.

Protective liquids provide longer life time of metal surface then lacquering or zinc-silicate films. In addition, It is excluded operations, connected with prime preparation of equipment surface for covering that liquids.

Now more then 50 % of Russian energetic concerns use protective liquids as a means of anticorrosion protective. Also their widely spreading is connected with their ability to prevent of hot water evaporation from tanks.

AGEING EXPERIMENT OF IRON WITH MARKER IN CLIMATIC CHAMBER IN ORDER TO ACHIEVE LONG TERM ATMOSPHERIC CORROSION PREDICTION

E. Burger [1,2], M. Fénart[2], S. Perrin[2], D. Neff[1], P. Dillmann[1]

[1] Laboratoire, Archéomatériaux et prévision de l'altération, SIS2M/LAPA, CEA Saclay, France
[2] CEA, DEN, DPC, SCCME, LECA, F-91191 Gif Sur Yvette, France

Nuclear waste could be packaged in low alloy steel containers for interim storage for about 300 years. In the storage conditions, the condensation on the containers walls can conduct to atmospheric corrosion caused by a succession of wet and dry periods. In order to predict the corrosion effect for such a long period, a mechanistic modeling of atmospheric corrosion of iron has been developed. One important element to integrate to this modeling is the place of formation of the rust during the corrosion process. Consequently, experiments have been performed in climatic chamber. Iron samples with a non continuous gold deposit have been corroded with a succession of wet dry cycle. Afterward, the gold marker is located compared to the rust layer by using SEM-FEG analysis. Theses localizations of the gold marker are related to the microstructure of the corrosion layer, previously finely characterized by micro-Raman spectroscopy. These experiments show, in most of the cases, an internal development of the rust layer. As a consequence, formation of the rust layer takes place near the metal-rust interface. Considering this result and the Pilling-Bedworth ratio superior to one, it is possible to conclude to the presence of compression stress in the rust layer. This mechanical stress can evolve the formation of fissures and as a consequence of porosities in the rust layer. As the modeling is based on a limiting step which is diffusion in the pores, the modeling evolution, taking into account these new data will be discussed.

Tribocorrosion

Methods of detecting hydrogen stress corrosion cracking and its protection in tribochemical environments

Xiaobo Zhou, Bo Han, SKF Engineering & Research Centre,
Postbus 2350, 3430DT Nieuwegein, The Netherlands, Bo.xiao.zhou@skf.com

Objectives: Development of techniques to investigate the hydrogen stress corrosion cracking and to valid solutions in both water and oil lubricated conditions

Background: Tribocorrosion or tribochemical attack becomes an increasing important issue in contact mechanics and mechanical engineering as many critical failures could be attributed by the mechanism, such as in oil industry and windturbine applications. Hydrogen stress corrosion cracking is one of the major failure mechanisms in the tribochemical attack. Research techniques to measure the process of hydrogen stress corrosion cracking are crucial for understanding the mechanism and more importantly to verify solutions.

Development and results: In this article, two major techniques are presented for this purpose: 1) An electrochemical method (the so-called Devanathan method) to measure hydrogen uptake and permeation, and 2) A newly developed C-ring test rig. In the Davenathan method, electrochemical principle was used to generate hydrogen on the charging side of a thin specimen and the amount of hydrogen was measured on the evaluation side of the specimen. With this method, the resistance of various steels and coatings to hydrogen uptake and permeation can be measured. The flux (amount) of hydrogen can be detected. The effect of additives can also be evaluated.

In the newly developed and home-made C-ring rig, the C-ring is made of a cylindrical roller bearing inner ring in which one part is cut open, and is loaded with a static load. The C-ring is submerged in a lubricant oil. The C-ring can be made with various steel grades or covered by different protective coatings. Various additives such as water, anti-wear (AW) and extreme pressure (EP) were added in the oil. A tribo-wear mechanism is applied on the location of the C-ring surface where the maximum tensile stress is located to facilitate the trobochemical process. This tribo-wear mechanism will remove any passive layer formed on the C-ring steel surface. The C-ring will be fractured under the combination of the tensile stress and tribochemical attack. The time to the fracture is the measure of the attack of the lubricant additives or the resistance of coatings. This test method can be used as a research tool to evaluate aggressive of water and AW/EP additives as well as a validation method to rank solutions such as steel grades and protective coatings.
The development has also been validated by other methods such as pin-on-disc sliding wear test and rolling contact fatigue test.
Several experiments have been done and the results confirmed that the methods are powerful tools for the tribochemical research and solution technology development.

In **conclusion**: the new methods have been developed to investigate the hydrogen stress corrosion cracking process in both water and oil lubricated conditions. The methods can also be used to rank solutions.

WEAR, EROSION- AND CORROSION-RESISTANT COATINGS FOR EXTREME APPLICATIONS OF OIL-GAS INDUSTRY

Lakhotkin Yu.V., Kouzmin V.P., Goncharov V.L., Dushik V.V., Rozhanskii N.V., Rybkina T.V., A.N. Frumkin Institute of physical chemistry and electrochemistry RAS, Moscow, Russia.

Most components of oil-gas equipments are using in extreme-heavy abrasion, erosion and corrosion environments. Three new classes of hard nanostructural W-C coatings deposited from gaseous mixture of tungsten hexafluoride, propane and hydrogen at low temperatures (370-600) ^{0}C and pressures (1-10) kPa are presented in [1,2]. The CVD method allows to synthesize individual tungsten carbides WC, $WC_{(1-X)}$, W_2C, W_3C, $W_{12}C$ with a hardness of (27-40) MPa and thickness of 14-25 microns. These super hard carbides are nanostructured with a grain size (3-20) nm. The CVD technology allows solving the fundamental problem of superhard coatings that is a brittleness of the coating material. Decisions of the problem are connected with the formation of multilayered coatings as well as bulk nanocomposite layers. Multilayered coatings consist of the alternated thin layers of tungsten carbides and tungsten. The nanocomposite coatings represent the tungsten matrix with dispersed fine tungsten carbide particles (2-5) nm in size.

The nanocomposite coatings can be produced on carbon, tool and stainless steels, Ni-, Co- and Cu-based alloys with a controllable coating thickness in the range from 30 to 100 microns and hardness from 11 to 20 GPa. As a nano-structured material, it demonstrates outstanding toughness, crack and impact resistance. There is no damage after 3000 microstrain deformations. The data of abrasive and erosion resistance of W-C coatings in comparison with the properties of industrial hard coatings are shown.

W-C coatings are pore free due to surface growth mechanism. They have higher chemical resistance in comparison with HVOF and hard chrome coatings (traditionally used coatings) and protect the substrate from attacks by the aggressive media. Corrosion resistance of W-C coatings in H_2S, H_2SO_4, HCl solutions at different concentrations and temperatures is presented it this study.

Some applications are also demonstrated in the paper. We mean down-hole tools, piston and rotation pumps, ball, gate and control valves. Traditional hard materials were too brittle, so it was difficult to use them in machine parts with a complex shape. It was also not possible to use other deposition technologies to coat hidden surface areas. So, CVD W-C coatings appear to be only available solution for this application. The unique W-C coatings have protective properties, wear and erosion resistance, needed toughness, hardness, as well as impact- and crack-resistance.

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Tribocorrosion Properties of PM Duplex Stainless Steel

F.Martin, C. García, Y. Blanco, Universidad de Valladolid/E.I.I., Valladolid/Spain

The combined wear-corrosion degradation of stainless steel obtained by powder metallurgy has been investigated. Base materials and duplex stainless steels obtained by mixing ferritic and austenitic powders in several proportions have been studied under pure wear, pure corrosion and wear-corrosion conditions. The AISI 316L, 430L and mixtures of powders have been sintered in nitrogen atmosphere and in a vacuum furnace. The tribocorrosion behaviour sliding against alumina ball was analyzed using a tribometer with a pin-on-disk configuration by electrochemical techniques. Such techniques were the open circuit potential measurements and the potentiodynamic polarization measurements in 1 M H_2SO_4 + 5 N NaCl solutions. The effects of composition of mixtures and sintered atmosphere were determined. The obtained results are interpreted and related to microstructural features.

CORROSION AND TRIBOCORROSION BEHAVIOUR OF THERMALLY SPRAYED CERAMIC COATINGS ON STEEL

C. Monticelli, A. Balbo, F. Zucchi
Centro di Studi sulla Corrosione "A. Daccò" - Università degli Studi di Ferrara – Italy

Wear is the major cause of material wastage and loss of mechanical performance and friction is the principal cause of wear and energy dissipation [1]. The concomitant presence of corrosion processes usually induces a synergistic stimulation of material degradation. Thermally sprayed ceramic coatings on steel represent an efficient and economic way to improve the wear resistance of mechanical components, but they result often inadequate if the components operate in aggressive environments .

This research aims at investigating the corrosion and tribocorrosion behaviour of thermally sprayed ceramic coatings deposited on steel specimens and exposed to a 3.5% NaCl solution. The coatings have been prepared by plasma spraying Cr_2O_3 and Al_2O_3-13TiO_2 powders on Ni20Cr bond coatings. Combined wear-corrosion conditions have been achieved by sliding an alumina antagonist on the lateral surface of coated steel cylinders, during their exposure to the aggressive solution.

Polarization curves recorded after 3 days of immersion and polarization resistance values monitored during 3 days exposures showed that in the presence of both coatings the corrosion rates (connected to the steel substrate corrosion) are unaffected by sliding conditions, when sliding rates vary in the range 20-100 mm/s and loads span in the range 2-10 N. These results suggest that the steel corrosion process depends on the defect population of the coatings which is not modified under the applied sliding conditions. However the corrosion rates depend on the coating type as Cr_2O_3-coated specimens are much more corrosion resistant than Al_2O_3-13TiO_2-coated specimens. The reason for these differences have been investigated by coating defect analysis and by SEM and EDS investigation.

By profilometry measurements wear rates have also been measured. These data depend both on the coating type and on the sliding conditions.

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Corrosion and Tribocorrosion of Electrodeposited CoW-WC Nanocomposite Coatings

S.K. Ghosh[a,b] and J.P. Celis[b]
[a,b]Materials Processing Division
Bhabha Atomic Research Centre
Trombay, Mumbai-400085, India
[b]Department MTM, Katholieke Universiteit Leuven
Leuven, B-3001, Belgium
Email: Subir.Ghosh@mtm.kuleuven.be, Jean-Pierre.Celis@mtm.kuleuven.be

Research for alternatives to electroplated hard chromium coatings is still on-going because of their environmental and health hazard concerns. Among other possibilities, electroplated Co-W alloys showed recently promising properties like an abrasive wear and corrosion resistance close to and even better than the ones of electroplated hard chromium. In this study, the Co-W alloy was further strengthened by incorporating nano-size WC particles via an electrochemical codeposition technique. The cobalt matrix bounds the WC particles while these particles strengthen the matrix along with tungsten codeposited as an alloying element.

In order to understand the corrosion resistance of these composites, potentiodynamic polarization tests were carried out in 0.5 M NaCl solution at room temperature, and compared to electrodeposited CoW alloys with similar composition. The morphology of corroded surfaces and their composition were analyzed. Based on these data the corrosion process is discussed.

Attention was also given on the corrosion behavior under simultaneous mechanical loading, known as tribocorrosion. This was investigated in a 0.5 M NaCl solution. The open-circuit potential of these coatings was measured under mechanical loading and unloading conditions. The material loss under mechano-chemical test conditions was determined. The tribocorrosion behavior of these coatings is discussed based on information gathered on the wear scar morphology and on open circuit potential evolutions.

Tribocorrosion behaviour of ferritic and ferritomartensitic stainless steels

N. Mary[1], B. Normand[1], L. Peguet[2]

[1] Institut National des Sciences Appliquées, INSA, Laboratoire MATEIS, groupe RI2*S*,
7 avenues Jean Capelle, 69621 Villeurbanne, France.
[2] ArcelorMittal Stainless Europe Research Center, rue Roger Salengro BP15, 62330
Isbergues, France.

Abstract

Ferritomartensitic stainless steels have a two-phase structure ferrite/martensite which improves abrasion resistance and toughness. They are widely used as structural elements, machine frames or conveyor belts where resistance to creep deformation, wear and corrosion are critical materials properties.

In this study, a method is developed to characterize the electrochemical and mechanical behaviors of a electrochemical and tribological behaviors a single-phase ferritic 430 (1.4016) type SS. This approach it then applied to a 17%Cr (1.4017) ferritomartensitic SS to assess to the role of this specific dual microstructure. Tests with an inert pin have been performed in sulfate containing solutions as well as in chloride containing media. The aim is to estimate the influence of both mechanical stress and chemical aggressive agent on passivity, corrosion rate and surface damage. Specific attention is paid to current and potential evolutions in relation with passive film breakdown and repassivation.

Keywords : Ferritomartensitic stainless steel, tribocorrosion, passivation and depassivation

Influence of the carbon content on the tribocorrosion performance of DLC coatings for artificial joints

R. Bayon1), A. Igartua1), X. Fernández1), U. Ruiz de Gopegui1)

1Fundación Tekniker, Spain www.tekniker.es. rbayon@tekniker.es

In artificial joints, like hip and knee prosthesis, corrosion and wear phenomena coming from the hostile environment of the body and friction process respectively, can result in an adverse reaction of the body due to corrosion products and wear particles, causing in many situations the failure of the implants. In these cases, a hard, wear-reducing and corrosion-reducing coating, which is also biocompatible, would reduce the mentioned problems. Diamond-like carbon (DLC) are excellent candidates for use as biocompatible coatings on biomedical implants, not only for their excellent mechanical and tribological properties but also their chemical composition containing carbon, nitrogen and titanium, which are biologically compatible.

In this work, five PVD coatings based on metallic-DLC composition and applied on Ti6Al4V biomedical alloy, have been studied attending on their tribological performance as well as their corrosion and tribocorrosion behaviour in simulated body fluids. The coatings carbon composition and therefore, their mechanical properties, were modified by changing the concentrations of reactive gases, nitrogen and acetylene involved in the deposition process. Excellent tribocorrosion response has been found especially in case of coatings with high carbon content. A significative reduction of friction and wear has been obtained in comparison to the substrate response. Friction coefficient has been reduced from 0.473 (uncoated Ti6Al4V) to 0.172 (DLC-5). On the other hand, no measurable wear was found in case of DLC 4 and DLC 5 in contrast with the material loss measured in case of the substrate (0.45 mm^3) under tribocorrosion conditions.

Keywords: Tribocorrosion, artificial joints, DLC coatings

Workshop: Corrosion and Corrosion Protection in the Aerospace Industry

Ion-plasma coating salt corrosion protection of compressor GTE steel blades

Muboyadzhyan S.A., Aleksandrov D.A., Gorlov D.S.
FSUE "VIAM", Moscow (Russian Federation)

VIAM has recently developed a protective ion-plasma coating of СДП-1+ВСДП-20 (SDP-1+VSDP-20) composition for compressor blades gas turbine engine protection from salt corrosion at sea conditions operation. The deposition process of the coating is made by means of a PVD-method (Physical Vapor Deposition) with the help of advanced VHEPT-technology (Vacuum High Energy Plasma Technology).

The process of ion-plasma deposition of SDP-1+VSDP-20 (systems Ni-Co-Cr-Al-Y+Al-Co-Si-Y) coating is carried out on MAP (МАП) industrial-scale ion-plasma plant. The SDP-1+VSDP-20 coating considerably enhances corrosion resistance of not only steels (ЭИ961, ЭП866) but ЭП718ИД alloy as well.

The accelerated cyclic corrosion tests have shown, that ЭП866 steel with SDP-1+VSDP-20 coating of 6-10 microns thickness makes GTE compressor blades possible to operate at 650°C maximum with high protective effect. The long-term sample tests (for six month) of the coating in salt fog chamber (CSF-35) and in tropical climate chamber (CTC) have confirmed the corrosion cyclic tests results. There were discovered no even minor defects on the samples after corrosion tests.

The steel-coating composite heat resistance was estimated by means of quiet air atmosphere furnace tests at 650°C (ЭП866 steel samples) and at 700°C (ЭП718 alloy samples). The coating SDP-1+VSDP-20 deposited on the above-mentioned materials considerably enhances heat resistance of the material. There was an 0.3 mg/sm^2 increase in specific additional weight for 300 hours exposure.

The corrosion crack test of ЭП866 steel samples covered with SDP-1+VSDP-20 coating results in (3-4) crack-formation time increase. The influence SDP-1+VSDP-20 coating on steel (ЭП866) samples long term and fatigue durability has also been investigated and it was shown, that the SDP-1+VSDP-20 coating with the thickness of 10 micron does not decrease base material mechanical characteristics.

Advanced SDP-1+VSDP-20 coating and the technology of its deposition was successfully implemented at public corporation "Klimov" (ОАО «Климов») in the technology of production gas turbine engine compressor blades and components for deck located fighters aircraft.

Fatigue-Oxidation Interaction for a Nickel-Based Superalloy

A. Karabela, L.G. Zhao and J. Tong, University of Portsmouth, UK

N.J. Simms and J.R. Nicholls, University of Cranfield, UK

M.C. Hardy, Rolls-Royce plc, UK

The alloy under consideration is RR1000, produced via powder metallurgy by Rolls-Royce plc. Recently, studies of oxidation kinetics and damage have been carried out for RR1000 at temperatures between 700°C and 800°C (Encinas-Oropesa et al., 2008), but without the influence of fatigue. The aim of this work is to investigate the fatigue-oxidation interaction for RR1000 at high temperatures. Specifically, two fatigue experiments have been undertaken on hour-glass test pieces to examine the effects of exposure temperature and cyclic stress on oxidation damage. These test pieces were exposed to cyclic stresses at 700 and 750ºC for approximately 200 hours. Post-test Focused Ion Beam (FIB) microscopy of these test pieces revealed surface oxide scales and, micro voids and modified microstructure beneath the oxide scales. As expected, the test piece exposed at 750ºC showed more severe oxidation damage when compared to that exposed at 700ºC, in terms of the depth of oxide scale and sub-surface damage, with a greater frequency and size of voids.

To examine the effects of cyclic stress level on oxidation damage, three points located on the surface of the hour-glass test piece were selected for the FIB examination. These points were located at the narrowest section of the test piece, which experiences the highest stress level, and at distances of 15 mm and 30 mm, respectively, from point 1, which show reduced stresses that were predicted to be at levels of 50 and 15% of the peak stress. The measured oxidation damage from these 3 locations has indicated that increases in cyclic stress level have enhanced the extent of oxidation damage. However, at 700°C, the influence of cyclic stress appeared to be insignificant.

To complement the experimental work, a finite element (FE) method has been explored to evaluate the influence of fatigue on the diffusive transport of oxygen into the material as a result of the gradient in hydrostatic stress. Flux of oxygen into the material was assumed to follow the parabolic law obtained from oxidation kinetics that were reported by Encinas-Oropesa et al. in 2008. Similarly, oxygen diffusivity and mobility parameters were calculated from the reported oxidation damage. The results of these FE analyses showed that the influence of fatigue on oxygen diffusion depends on both temperature and load level, which is consistent with the experimental results.

Acknowledgements

The project is funded by the EPSRC (Grant EP/E062180/1) of the UK. The specimens were provided by Rolls-Royce plc. AK acknowledges the support from Dr Adriana Encinas-Oropesa and Mr Andrew Dyer in the use of the FIB facilities at the University of Cranfield.

Microstructure oriented fatigue and damage analysis of Al/Al and Al/steel friction stir weldings (FSW) considering corrosive effects

T. Tesfu-Zeru, C. Conrad(3), X. Lang (2), R. Noveva,(1), G. Wagner(2), W. Fürbeth
Dechema e.V.: Karl-Winnacker-Institute
Theodor Heuss Allee 25, 60486 Frankfurt am Main/Germany
Mailto: Tesfu@dechema.de

It is verified that FSW of aluminium is becoming an increasingly sophisticated technology with numerous commercial applications [1]. In the course of this talk a comprehensive investigation of microstructure oriented corrosion and fatigue properties of FSW Al/Al (Al-6016T4, Al-5754 and Al-5454) and Al/steel (Al-6016T4/DC01) weldments will be presented.

The corrosion properties of FSW Al/Al and Al/steel were evaluated by different methods: Standard intergranular corrosion test (ASTM G110-92), open circuit potential measurements (OCP), potentiodynamic polarization measurements, Scanning Kelvin probe technique and salt spray tests. The microstructure of the specimens was analyzed by optical microscopy and SEM/EDX and correlated with the results of corrosion test.

The results of the corrosion immersion test according to ASTM G 110-92 reveal intergranular corrosion for the Al/Steel (Al-6016T4/DC01) weldings with distinguishable failures in the advancing welding side. However, FSW weldings of Al/Al (Al-6016, Al-5754 and Al-5454) without steel did not show intergranular corrosion, but pitting corrosion was found on the alloy surfaces.

OCP and Potentiodynamic measurements reveal significant differences between the different FSW weldments in the electrochemical response with respect to corrosion susceptibility and breakdown potential of the materials respectively.

The results of the Scanning Kelvin probe investigations also demonstrate that the Volta potential of the working material depends on alloy composition and microstructure development due to the welding process.

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Project Partners:

1. R. Noveva, University of Stuttgart/Germany, IMWF
2. X. Lang and G. Wagner, University of Kaiserslautern/Germany, WKK
3. C. Conrad, Fraunhofer Institute for non-destructive metrology, Saarbrücken /Germany IZFP

STRESS-CORROSION CRACKING FAILURE OF SCC RESISTANT AERONAUTICAL MATERIALS: IAF CASE STUDIES

Capt. L. Allegrucci*, Maj L.Aiello,
Capt. F Bagnoli, LT. Vincenzo di Francesco, LT.Col. M. Bernabei
Chemistry Department – Flight Test Center
"M. De Bernardi Airport"
00040 Pratica di Mare (RM) Italy
laura.allegrucci@aeronautica.difesa.it

Abstract

Mechanical and structural components of military aircraft and helicopters are subjected to severe stress and environmental conditions during the normal operations. Frequently stress-corrosion cracking is the cause of progressive failures on Italian Air Force fleet with serious consequences.

The Chemistry Department of Flight Test Center studies the nature and the mechanism of these phenomena to determine the whys and the wherefores of the damage, by both a fractographyc and metallographyc analyses.

The high number of different kind of components and consequently of materials, used to prevent the SCC, allow to have a significant overview on real effects of this progressive mechanism.

The considerations derived from the evaluation of morphological, structural and chemical aspects allow the introduction of new changes in terms of materials selection or surface treatments and maintenance operations, in order to preserve the safety and the requested airworthiness.

Some examples will be presented to explain this aspect.

A problem of fatigue life of structural materials under attacks of corrosive media

A.D. Zhirnov, A. V. Grinevich, S.A. Karimova
All-Russian Institute of Aviation Materials (VIAM), Moscow, Russia

Service life of machines and devices operating under attacks of variable loads is usually estimated on the base of fatigue life of the materials used for manufacturing. Resistance of such materials to the attack of corrosive media is an important parameter of their operational reliability, because environmental parameters, such as temperature and moisture, affect machines and devices in the course of their operation. By now, a number of procedures based on fatigue life of specimens tested under laboratory conditions have been developed for estimation of service life of real structures. However, there are no similar techniques taking into account the attack of corrosive media. At the same time many techniques intended for estimation of corrosion resistance of materials are available. A number of procedures mean an exposure of structural material not only to corrosive media, but also to permanent or variable loads, as it is in the course of corrosion fatigue tests.

However, the developed techniques allow one to range materials in terms of their sensitivity to corrosion medium attacks, but are unable to estimate real fatigue life of materials. Therefore, these techniques should not be used for prediction of structure service life.

In spite of the fact that mechanical failure produced in the course of laboratory tests is similar to damages induced during real operation, laboratory simulation of corrosion attack in real scale of operation time and loads is an open problem.

The authors propose a number of new approaches based on principles of verification of similarity of real corrosion attacks during operation to those produced in the course of laboratory tests.

A number of test techniques for determination of service life under exposure to corrosive media are described in the report. The developed techniques based on an assumed criterion of corrosion damage allow one to estimate residual fatigue life after rated corrosion damage and to define fatigue life under exposure to corrosive media in real time scale.

Initiation of localized corrosion in AA 2099-T8 aluminium alloy

Y. Ma, X. Zhou, G.E. Thompson
Corrosion and Protection Centre, School of Materials, The University of Manchester,
Manchester M60 1QD, UK

Novel Li-containing aluminium alloys are promising substitutes for conventional aluminium alloys in aerospace industries in seeking for improved payload and fuel efficiency of aircrafts [1-2]. AA 2099 aluminium alloy has overcome many shortcomings of its previous generations and exhibited superior physical and mechanical properties over traditional 2xxx and 7xxx series aluminium alloys [3-5]. However, previous work [6] revealed that AA 2099-T8 aluminium alloy had relatively low resistance to localized corrosion in a chloride-containing environment. The mechanism for initiation of such localized corrosion has not been fully understood. In present work, mechanically polished bulk alloy and ultrathin sections (15 nm in thickness) were immersed in a 3.5% NaCl solution and deionized water, respectively, to initiate localized corrosion in the alloy. Surfaces and cross-sections of the regions containing localized corrosion were examined using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Orientations of individual grains and misorientation angles between the grains in localized corrosion-containing regions were decided using either electron backscattered diffraction (EBSD) or TEM. It is revealed that both high angle grain boundaries (HAGBs) and low angle grain boundaries (LAGBs) are susceptible to intergranular corrosion, with susceptibility probably being stronger at HAGBs relative to LAGBs. Besides, individual grains also exhibit strong susceptibility to intragranular corrosion, with transient crystallographic corrosion morphology characterized by small straight steps at the corrosion front within the attacked grains. Furthermore, attacked grains and grain boundaries have been found to coexist at sites of severe localized corrosion. Taking into account the high population densities of precipitates, including T_1 (Al_2CuLi) and θ' (Al_2Cu), at crystallographic defects such as grain/subgrain boundaries and dislocations in the alloy, it is suggested that the precipitates at the crystallographic defects play an important role in initiating localized corrosion in AA 2099-T8 aluminium alloy.

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Validation of a Galvanic Corrosion Model for AA2024 and CFRP with Localised Coating Damage

Siva PALANI[1], Theo HACK[2], Andres PERATTA[3], Robert ADEY[4], John BAYNHAM[5], Hubertus LOHNER[6]

[1] *EADS, Germany, siva.palani@eads.net*
[2] *EADS, Germany, theo.hack@eads.net*
[3] *CM BEASY, UK, aperatta@beasy.com*
[4] *CM BEASY, UK, r.adey@beasy.com*
[5] *CM BEASY, UK, jbaynham@beasy.com*
[6] *AIRBUS, Germany, hubertus.lohner@airbus.com*

Abstract: The paper presents the development and experimental validation of a computational model for simulating galvanic corrosion in typical case scenarios appearing in an aircraft environment. The numerical approach is based on the three dimensional Boundary Element Method. Amongst the inputs of the problem are: geometrical description and physical properties of the electrolyte, as well as macroscopic polarisation curves of the active electrodes. The main outcomes of the model are corrosion rates, electric current density and potential distribution.

The case study used for the validation consists of a co-planar pair of Aluminium AA2024 and carbon fibre reinforced polymer (CFRP) immersed in saline solution with variable coating conditions. In particular, the situation of a circular damage ("pinhole defect") of a coating of very high insulating properties on the anodic side of the sample is considered. A comparison between experimental measurements, including potential and total current flowing between anode and cathode, and the corresponding simulation results is presented for different variations of the modelling scenario. Very good agreement has been obtained between observed and simulated results for systematic variations of the case study which consider different locations of the damage in the sample, different surface area ratios between anodic and cathodic regions, and different electrolyte conductivities. The successful validation of the modelling approach has enabled its use for simulating galvanic corrosion in more complex structural components of an aircraft as illustrated in this paper.

Keywords: Galvanic corrosion, AA2024, CFRP, Boundary Element Method, Aircraft

Novel protective Cr-free aerospace coatings based on hybrid sol-gel/conducting polymer systems.

R. Akid, H. Wang and M. Gobara[1],
Materials & Engineering Research Institute
Sheffield Hallam University
Howard Street, Sheffield, S1 1WB. U.K.

[1] now at Military Technical College, Kobry El-Kobba, Cairo, Egypt

Abstract

The most commonly used lightweight metal, and its alloys, used in the aerospace sector is that of Al. A metal that offers great potential, due its low density (60% less dense than Al) and high strength to weight ratio, is that of Mg. Unfortunately, while Al provides a serious challenge in terms of corrosion protection, Mg is significantly less resistant to corrosion; and although many topcoat systems used for Al are quite capable of providing adequate protection for Mg, the pre-treatment/primers being used almost exclusively contain Cr(VI)-based compounds, which are toxic and carcinogenic.

Promising alternative pre-treatment/primers are those based on sol-gel chemistry. However unless formulated correctly these coatings have limited corrosion resistance [1]. A development in this field is that involving the use of sol-gel/conducting polymers (SGCP) systems. This paper will present the results of corrosion tests, notably electrochemical impedance and salt spray tests conducted on SGCP systems applied to both AA2024 and Mg AZ31. A discussion on the self-healing capabilities of these coatings is also given based upon surface analysis using Scanning Vibrating Electrode Analysis, X-ray photoelectron spectroscopy and Fourier Transform Infra Red analysis.

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Development principles of corrosion-resistant magnesium alloys

Inna MUKHINA
All-Russian Scientific Research Institute of Aviation Materials, State Research Center, Moscow, Russia

Magnesium alloys as construction material confidently occupy their position in diverse areas of engineering industry, especially in the areas where it is significant to reduce the product's weight. One of the reasons blocking wider application of magnesium alloys is their inadequately high corrosion resistance. Significant researches in the area of magnesium alloys corrosion were accomplished by M.A. Timonova, V.P. Batrakov, I.K. Marshakov, Hanawaltz, Mauz, Nicozo Endo and others.

It is a very timely task of development of light magnesium alloys with corrosion resistance higher than of existing ones. The essential solution to this problem lies in studying the mechanism of alloy behavior in different media, and the influence of alloying elements on magnesium corrosion properties.

One of the ways to increase the corrosion resistance of magnesium and its alloys in conditions of corrosion behavior with cathodic and mixed controls is alloying with elements decreasing cathode activity of alloys, increasing hydrogen overpotential and reducing micro-cathode area. The systematic research for determination of such elements was executed on the following corrosion characteristics: corrosion rate, electrochemical potentials, hydrogen overpotential, phase composition of binary and more complex magnesium alloys depending on the position of alloying element in Mendeleev chemical periodic system. Present research studies the mechanisms and reveals the patterns of influence of alloying element's atomic number and its phase diagram on corrosion rate.

THE FORMATION OF CHROMATLESS CONVERSION COATINGS ON ALUMINIUM ALLOYS

Oleynik S.V.
Institute of physical chemistry and electrochemistry of Russian Academy of Sciences, Moscow, Russia

To development of technologies of chromateless chemical oxidation of aluminum alloys of different alloying systems the much attention is given. Rather early the capability of obtaining of the protective conversion coatings (CC) on Al - Mg alloys in the alkaline molybdate containing solution, such as IFHANAL-1, modified by different oxidants, was shown. In this paper the influence of physico-chemical parameters of oxidation on the kinetics of formation and protective properties of conversion coatings on aluminum alloys, obtained in the new various solutions IFHANAL was studied.

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The features of oxidation of Al alloy of different alloying systems in dependence of its heat pretreatments in IFHANAL conversion solutions and resistans of the formed CC to pitting corrosion in chloride solution by electrochemical and x-ray spectral microanalysis methods were studied. It was shown a possibility of the directed modification of the composition and thickness of formed CC by addition of complexing and inhibitive agents to converting formulations (CF) IFHANAL. Filling such CC, obtained in modifide CF, in the inhibitor IFHAN-25 solution results to significant increasing of its protective properties in chloride solution and salt spray chamber.

Workshop on Corrosion in Natural Environments

Monitoring of external corrosion of underground steel pipelines

***Andrey Marshakov*, Maxim Petrunin, Vasily Ignatenko**
A.N. Frumkin Institute of Physical Chemistry and Electrochamistry of Russian Academy of Sciences, Moscow, Russia

Several corrosion modes and factors are known to impact the integrity of underground pipelines including general corrosion, pitting, stress corrosion cracking, microbiologically influenced corrosion, stray current. Several technology gaps have been identified to address the issues of overall integrity and operability of pipelines. These gaps include both gaps in our understanding of how various factors influence soil corrosion of steels and how to better detect the onset and extent of pipelines corrosion.

In the paper the methods for monitoring of various types of external corrosion of underground pipelines are observed. The criteria of pipeline external corrosion assessment depending on mechanism and kinetics of soil corrosion of pipeline steels are discussed. The various scenarios where electrical resistance soil corrosion probes can be used for the corrosion damage assessment or for the control of cathodic protection effectiveness are described. The possibilities of using hydrogen probes, electrochemical measurements and chemical analysis of soil electrolyte for prediction of crevice corrosion and stress corrosion cracking of pipelines are discussed.

Corrosion Behaviour of Mg/Al Alloys in Humid and Saline Atmospheres

R. Arrabal[1], A. Pardo[1], M.C. Merino[1], P. Casajús[1], M. Mohedano[1], S. Merino[2], E. Matykina[3]

[1] Departamento de Ciencia de Materiales, Facultad de Ciencias Químicas,
Universidad Complutense, 28040, Madrid, Spain
[*]Corresponding author. Tel: 34 1 3944348; Fax: 34 1 3944357
E-mail: raularrabal@quim.ucm.es

[2]Departamento de Tecnología Industrial, Universidad Alfonso X El Sabio, 28691,
Villanueva de la Cañada, Madrid, Spain

[3]Centro Nacional de Investigaciones Metalúrgicas, Avda. Gregorio del Amo,28040
Madrid, Spain

ABSTRACT

The influence of temperature, relative humidity and chloride concentration on the corrosion behaviour of AZ31, AZ80 and AZ91D magnesium alloys was evaluated in high humidity and salt fog environments. In high humidity environment, the degree of corrosion increased with increasing relative humidity and temperature and was influenced by the aluminium content and alloy microstructure for relative humidity values above 90%. Under the salt fog test, corrosion attack increased with decreasing aluminium content in the alloy and increasing Cl^- concentration and temperature. In both environments, corrosion attack was initiated around the Al-Mn inclusions for the AZ31 alloy, whereas aluminium segregation and β-phase distribution were the main controlling factors for the corrosion behaviour of the AZ80 and AZ91D alloys, the latter revealing lower corrosion resistance than the AZ80 alloy in saline environments.

Keywords: Magnesium alloys; Atmospheric corrosion; Salt fog.

The protection effect mechanism of the metallic aluminium coat in the humid tropical climate

Kharina I. L., *Joint stock company Scientific and production association “CNIITMASH”, Moscow, Russia, kharina@cniitmash.ru*
Tupikov R. A., *Experimental design office “GIDROPRESS”, Podolsk, Russia, tupikov@grpress.podolsk.ru*

In connection with aggregates which are operated in the atmospheric conditions the main factor of the operation features decrease is corrosion of the external surface.

Intensity of atmospheric corrosion is determined with degree of corrosive power and environmental parameters. The most negative combinations of these parameters you can encounter in the humid tropical climate region.

The choice of a protective coat besides severe environmental conditions is determined by the shape and steel intensity of the protected surfaces, high operating temperature of the equipment, providing of thermal conductivity, manufacturability and repairability of the coat.

It is know that metallic aluminium is atmospheric corrosion-resistant in the processes which are controlled both anodic and cathode polarization.

The research which was made in the environmental camera (the Institute of Physical Chemistry the Academy of Science) at 37,8ºC in the atmosphere with constant relative humidity – 98% and with simulation of the touch with the sea atmosphere by the immersion method in 1% NaCl solution (VOLVO-VICT method) determined high protective properties of the aluminium coat, which was deposited by the gas-flame metalizing method: after 2160 h exposure the damage of the surface was not above 1% in environmental with chlorides and 0,1% in environmental without chlorides.

Metallographic observation, raster electronic microscopy, micro X-ray spectral analysis allowed to determine that aluminium (95%) and oxygen (5%) are found in the coat. Porosity doesn’t overshoot 15%, particles of the coat are round with various degree of dispersion. Based on the type of coat deposition it was supposed that each particle consists of metallic aluminium and aluminium oxide which is on the surface.

Corrosive processes in the aluminium coat-humid chloride containing environmental system progress according to pitting corrosion mechanism in common with corrosion of metallic aluminium.

Electrochemical characteristics of the cover (equilibrium potential, type of anodic polarization curves in the 3% NaCl solution) authenticate that starting from some critical thickness (more than 50 micrometers) autolysis current of the coat becomes less than of metallic aluminium. It is because of protective film formation similar to the firm on the alumimium. Protective properties of the metalized coating are determined by the “cure” of the pores mechanism that are formed by corrosion products and it is provided by anodic polarization of the process and thermodynamic characteristics of the coat external surface.

Effects of Geomagnetic Disturbances on pipelines

Ya. Sakharov
Polar Geophysical Institute KSC RAS, RUSSIA
L. Trichtchenko, D.H. Boteler
Geomagnetic Laboratory, Geological Survey of Canada, CANADA

Variations of geomagnetic field induce telluric currents in pipelines, lead to change of pipe/soil voltage and can affect on corrosion conditions. The impact of geomagnetically induced currents and fields depends on the level of disturbance, pipe location and orientation, local ground conductivity. We present the review of measurements and modeling the geomagnetic induction in pipelines, discuss the possibility of investigation induction effects in pipelines in Russia.

The carbonaceous steel and copper protection in atmosphere with the high SO_2 content impact conditions

N.V. Schel, O.G. Chetyrina, A.Y. Osetrov.
Tambov State Technical University, Tambov, Russia

The metal conservation materials protection in strict and very strict atmospheric corrosion conditions is a very important technological problem. One of the most simple and effective ways is the oil conservation materials application which contained inhibiting additions. There are represented in report the analysis results of the oil nature influence (industrial oil I-20A, waste motor oil (WMO) contained IFKhAN-29A or superior quality gun lubricant (SQGL) additions as the inhibiting products on the carbonaceous steel and copper corrosion in the air containing 10^{-3} – $6{,}7\cdot10^{-2}$ vol.% SO_2 (relative humidity (H) is 71 – 100 % (airproof desiccators).

The real specified C_{SO_2} value is appreciably different from the initial one, what is determined by the SO_2-solubility in the liquid phase. Besides the thermodynamic factor their correlation depends on gaseous (V_{GP}) to liquid phase volume (V_{LP}) ratio. The pH value in the liquid coating condensed on the barrier oil coating and also in solution entered into its capillaries and discontinuity flaws is about 2 and varies to a little degree (ΔpH~0,7) by the SO_2 26-fold concentration changes.

The carbonaceous steel corrosion rate (K) decreases appreciably already by the 1 wt. % IFKhAN-29A content in oil and SO_2 concentration ~ 10^{-3} vol.%. By the C_{SO_2} increase the K of the steel rises and by the $C_{IFKhAN\text{-}29A}$ increase up to 10 wt. % decreases substantially. The protective efficiency by the H = 70 – 80 % does not practically depend on the $C_{ADDITION}$ (5÷10 wt. %). By the H = 100 % its protective action reduces sharply. At the same time K rises with the C_{SO_2} increase. The $C_{IFKhAN\text{-}29A}$ optimal value is 5 wt. % (I-20A, WMO).

The copper corrosion rate also rises with the C_{SO_2} in gaseous phase increase and recedes with the C_{SQGL} in the protective coating increase from 7 up to 40 wt. %. The oils themselves and less C_{SQGL} in the protective coating lead to the corrosion acceleration (C_{SO_2} =10^{-3}÷5,48 vol. %). By the relative humidity increase from 70 up to 90 % K_{Cu} rises to little degree. By the further H increase up to 100 % there is the sharp K_{Cu} -increase. Generally speaking the SQGL-additive put into the oils is promising enough for the copper corrosion protection in the SO_2-contained atmosphere. The such compositions protective effect amounts to 86 % (H=71%, C_{SO_2} =0,4 vol. %).

Corrosion Fatigue Of AZ91C Magnesium Alloy In Aqueous Solutions

[*]M.A. Shoeib,[**]M.M.Aldarwish and [**]Y.F.Barakat
*Surface Treatment & corrosion Control Department, Central Metallurgical Research and Development Institute (CMRDI), Cairo, Egypt.
** Tebbin Institute for Metallurgical Studies (TIMS), Cairo, Egypt
mshoeib@yahoo.com

Abstract

Corrosion and fatigue studies are an important element to prevent many industrial and commercial disasters. Many researchers undertook specific analysis for which a clear determined conclusion is adhered to in order to provide a meaningful path to industrial issues.

This study, AZ91C Mg-alloy is used as the substrate material. Corrosion fatigue and corrosion behavior were subjected to 3.5% NaCL (pH=1, 2, 6, 7, and 9), 3.5% NaCL+$Na_2B_4O_7$ (Concentrations are: 0.05, 0.1, 0, 15 and o.2N) and $Na_2B_4O_7$ (Concentrations were: 0.05, 0.1, 0, 15 and o.2N)

The study of Corrosion Fatigue behavior was determined through the use of plane-bending corrosion fatigue machine with stress ratio R=0.5 and under constant frequency of 10 Hz. Preliminary results show that in 3.5% NaCL fatigue life (N_f) decreases with an increase of pH from 1 to 6 and was constant at pH=7,9. In 3.5% NaCL+$Na_2B_4O_7$, the highest N_f was observed at concentration of 0.05 N. N_f in $Na_2B_4O_7$ increased till 0.1 N then decreased from 0.15 till 0.2 N. The investigated alloy developed a CrO_3 coating on the surface by chemical conversion coating in chromating bath. Coating layer film on AZ91C alloy is used to improve corrosion and corrosion fatigue of this alloy. The composition and microstructure of the coating layer was analyzed using X-ray diffraction (XRD), and the surface morphology of the film is investigated through optical microscope and scanning electron microscope (SEM). Immersion and electrochemical tests are being applied to study the corrosion protection of the alloy coating in the above mentioned environments. Measurements performed on coated specimens showed that the CrO_3 coating provided considerable protection against corrosion. Corrosion fatigue tests are being carried out on coated alloy in the mentioned environments.

The number of failure cycles (N_f) increased at 0.05and 0.2 N $Na_2B_4O_7$ solution, improving efficiency were: 32%, 39% .In 3.5% NaCl, N_f increased at pH=1, 2, 6, improving efficiency were: 27.2%, 9%, 63.4% respectively.

The improvement efficiency corrosion resistance through the use of chromating bath increased from 11% and reaches 92%.

Key words: Corrosion fatigue, AZ91C alloy, Chemical conversion coating, chromating bath

Workshop on Nanotechnologies

OXIDATION/CORROSION RESISTANCE OF NANOCRYSTALLINE Fe-Cr ALLOY

R.K. Gupta, R.K. Singh Raman and C C Koch#

Department of Mechanical and Aerospace Engineering
Department of Chemical engineering
Bldg 31, Monash University (Melbourne), Vic 3800, Australia
Raman.singh@eng.monash.edu.au
Ph: (+61) 3 9905 3671, Fax: (+61) 3 9905 1825

Dept of Materials Science and Engineering
North Caroline State University, Raleigh, NC 27695-7907, USA

It was hypothesised that it may be much easier to develop a protective film on nanocrystalline Fe-Cr alloys. However, successful processing of nanocrystalline alloy samples suitable for oxidation/corrosion testing is a non-trivial task. This paper will present description of the processing of nanocrystalline Fe-Cr alloy powders by mechanical alloying and their successful compaction while retaining nanocrystalline grain size. The paper will also discuss the most recent findings to address the Validation of the hypothesis will have highly attractive economic/industrial implications.

Triggered release of intercalated organic inhibitors from Layered Double Hydroxide nanocontainers: a systematic study

J. Tedim, A. Kuznetsova, S. Kallip, A. Salak, M. L. Zheludkevich, M. G. S. Ferreira.
Department of Ceramics and Glass Engineering, CICECO, University of Aveiro
Universidade de Aveiro, Campus de Santiago, 3810-193 Aveiro, Portugal

The development of anti-corrosion protective coatings based on the self-healing effect has been attracting considerable interest among academia and industry researchers. Oppositely to traditional coating formulations where the corrosion inhibitors are directly incorporated, the concept associated with anti-corrosive self-healing coatings is based on the storage of inhibitors within inert nanocontainers for undefined periods of time, with the active species being released only when certain conditions in the surroundings are verified [1]. In this respect, the major challenge for material scientists is to find ‘host’ nanostructures and modified them in such a way that the triggering conditions for the release of inhibiting species match those corresponding to coating degradation and corrosion initiation.

Layered Double Hydroxides (LDHs) are structurally derived from brucite ($Mg(OH)_2$), in which some divalent metal cations are replaced by trivalent cations. The excess of positive charge generated in these hydroxides is compensated by the intercalation of anions between hydroxide layers [2]. In the corrosion field they have been used as receptacles for anionic inhibitors and sensors for water uptake [3, 4].

In this work, we report the synthesis and characterization of LDHs loaded with different organic inhibitors (Figure 1). A thorough investigation on the conditions influencing the release of the organic species and the kinetics of release is inferred using spectroscopic and chromatographic techniques. The effect of possible release-triggers such as pH and presence of corrosive anions is evaluated. The anti-corrosion efficiency of the resulting systems is assessed by Electrochemical Impedance Spectroscopy (EIS), and the Scanning Vibrating Electrode Technique (SVET). The results provide guidelines for the optimization of nanocontainer/inhibitor systems and effective implementation into industrial coatings.

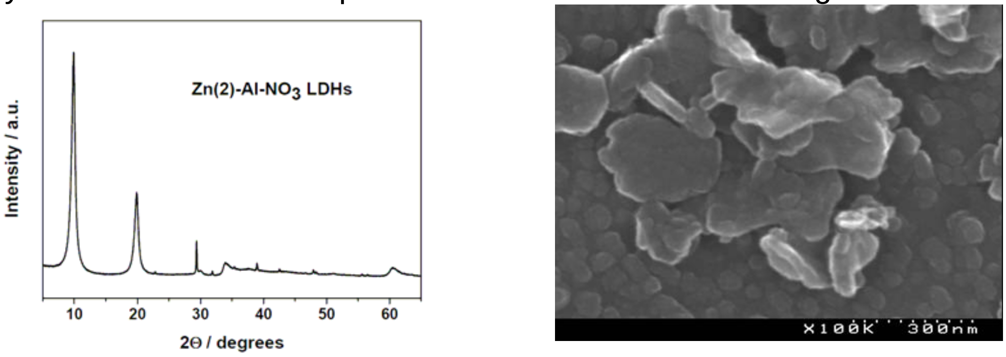

Figure 1: XRD diffractogram and SEM image of Zn-Al LDHs.

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Nanotechnologies fighting against corrosion and other complications in extraction and transportation of water-cut oil

***Dmitry BUGAY*[1], *Rustem AKHIYAROV*[1], *Anatoly LAPTEV*[2]**
[1]Ufa state petroleum technological university; Ufa, Russia,
[2]JSC “Company Nalko”; Moscow, Russia

The corrosion of metallic equipment of oil fields is determined mostly by the composition of the aggressive environment which is in contact with its surface. In this case the mechanism of metal destruction, as a rule, is based upon the peculiar behavior of such nanoparticles of the electricity conducting media as ions, molecules and bacteria nuclei.

We have developed a number of technologies which allow to cardinally decrease or completely prevent metal corrosion of oil and gas equipment by means of purposeful impact upon separate nanoparticles of the environment. This impact is based upon utilizing devices on permanent simple construction magnets which are placed into the pipeline and give opportunity to realize magnetic hydrodynamic treatment (MHDT) of the charged particles of the environment. As a result these particles are expelled from the corrosion process. Besides, by means of MHDT the nanostructures required are being formed in the environment which exclude the exposure of a number of important complications in oil extraction and preparation.

Particularly, the nanotechnologies developed have been used for:

1) reducing corrosion activity of the water substratum of the oil and water flow as a result of forming carbocations, which allows to increase pH of the environment and, by this way, to reduce the speed of metal equipment corrosion 8-12 times;

2) increasing the effectiveness of corrosion inhibitors as a result of protoning their molecules in introducing reagents into the oil and water flow which allows to increase adsorption capacity and effectiveness by 30-50%;

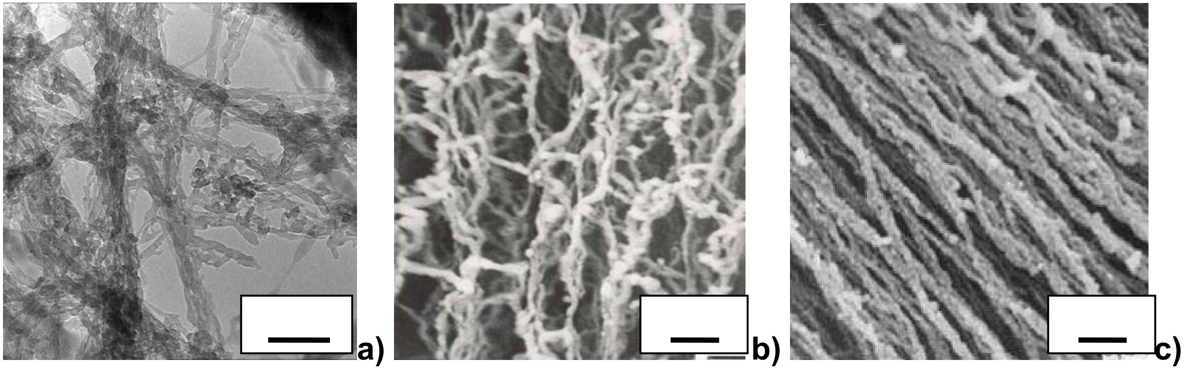
3) introducing hydroxonium ions into the bacteria nuclei with the aim of restraining their vital activity. The number of vital nuclei of aerobic bacteria is reduced by 2-3 times and aerobic bacteria nuclei, sulphate-reducing ones among them, are completely destroyed;

4) obtaining nanocrystals of salts with poor dissolubility in the flow of water media at the expense of replacement of oppositely charged ions into the local flow that prevents salts sediment on the pipe walls and the equipment. The nanocrystals obtained interact actively with each other and the organic inclusions without causing abrasive wear of the pipelines.

Physical and chemical properties of the oxides formed at the surface of liquid metallic alloys

A.N.Khodan, A.N.Frumkin Institute of Physical Chemistry and Electrochemistry Russian Academy of Sciences, 119991 Moscow, Russian Federation.

The oxidation of some liquid-metal alloys under the certain environment results in the formation of porous oxides with 2D and 3D nanostructure. In particular, the oxidation of Hg, Ga or Bi melts, containing small amount of Al, allows synthesizing a porous monoliths of nanostructured oxyhydroxide of alumina (NOA) [1]. The structure and the physicochemical properties of NOA materials synthesized in a humid air or gas at the surface Hg or Ga alloys are the most studied. Typical growth rate of NOA monoliths in a humid air is about 1 cm/hour at the temperatures 25 – 30 °C. Using of the different alloys provides quite similar results and the properties of NOA materials: small density (0,02 – 0,04 g/cm^3), high porosity (99 %vol.), large specific surface (300 m^2/g, and up to 800 m^2/g with sublimation drying). The structure of NOA consist of the three-dimensional network of the amorphous nanofibrils, with 5 – 7 nm diameter and 120 – 150 nm length, and having the composition $Al_2O_3 \cdot 3{,}6H_2O$. An annealing in the temperature range 900 – 1700 °C does not destroy solidity and porous structure of NOA samples, but the linear sizes of the samples are decreasing proportionally, the density increase from 0,02 up to 3 g/cm^3, and the porosity and specific surface decreases: (99,3 – 25 %) and (800 – 1 m^2/g) respectively. All these transformations accompanied by structural and phase transitions – from the supramolecular amorphous and amorphous states to the crystalline γ- θ- and α-Al_2O_3.



Morphology of the NOA samples: a) – oxidation at the surface of submicronic Hg layer on Al plate (TEM, negative); b) – oxidation of the surface of Ga-Al alloy (SEM); c) – oxidation of the inside surface of a bubble in the volume of Ga-Al alloy (SEM).

The structure and chemical composition of the products of Al selective oxidation at the Hg and Ga melts surfaces have been studied in details by the TGA, IR, XRD and TEM methods; the kinetics of the composition and structure evolution of NOA materials under isochronous annealing in the temperature range 25 - 1700 °C also were studied. Obtained results allows to develop the methods of solid state synthesis of the porous monolithic nanocomposites using chemical and/or structural modification of NOA materials.

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Interrelation of surface composition and corrosion behavior of nanosized multicomponent cathodic catalysts for fuel cells

Tarasevich M.R., ***Bogdanovskaya V.A.***

Istitution of Russian Academy of Sciences, A.N. Frumkin Institute of Physical Chemistry and Electrochemistry RAS (IPCE RAS), E-mail:bogd@elchem.ac.ru

The development and investigation of nanosized multicomponent catalysts based on platinum and its alloys with transition metals are the most important direction of activities in the area of fuel cells. The composition and structure of nanoparticle surface define activity in oxygen electroreduction reaction and corrosion stability. The behavior of multicomponent systems synthesized on carbon supports PtM_1/C and PtM_1M_2/C (M=Co, Fe, Ni, Cr) substantially is distinguished from monoplatinum catalyst. Electrocatalytical activity of platinum in alloy is increased into several times upon simultaneous enhancement of stability.

In terms of di- and threemetallic catalysts, the analysis of main phenomena proceeding in course of the alloy-formation and subsequent corrosion action (chemical and electrochemical) was carried out in accordance with the findings of structure and electrochemical studies of the catalyst surface. The corrosion treatment has the double influence, namely, there are the dissolution of smaller particles and their agglomeration and also the formation of core-shell structures in the case of multicomponent systems. The enhancement of particle size results in lowering mass activity (A/g of precious metal) and, on the other side, specific activity (A/cm^2 of surface precious metal) is increased owing to dimensional effects. There is the formation of core-shell structures upon the alloy-formation and subsequent treatment as the result of surface segregation and dissolution of nonplatinum components of alloy. The core is an alloy (PtM) but the surface (a shell) is enriched by platinum which forms the clusters. The properties of platinum in shell are distinguished from the properties of monoplatinum systems having the sizes familiar to metallic phase owing to ligand influence of core and depend on nature of alloy components. The role of ligand influence of core consists in that the potential of formation of oxygen-containing species from water on platinum clusters is shifted into positive side in comparison with monoplatinum catalyst. This provides the enhancement of catalytic activity in oxygen reduction reaction owing to the lowering of surface blocking effect for adsorption of molecular oxygen. On the other hand, the decrease of surface coverage by oxygen-containing species results in the lowering of platinum dissolution rate as platinum oxidation by water is the start of corrosion process which is accelerated at high value of steady-state potential and in the presence of complexing anions.

Thus, corrosion treatment may result in creation of catalyst with higher parameters in comparison with initial one due to treatment ensuring the creation of core-shell structures and achievement of optimal relation between mass and specific activities.

Antiscale Plasma Electrolytic Oxidation Coatings

Alexander Minaev, Sergey Gnedenkov, Sergey Sinebyukhov,
Dmitry Mashtalar/ Institute of Chemistry Far Eastern Branch of the Russian Academy of Sciences, Vladivostok/ Russia, aminaev@mail.ru

In this paper the results of the research of scale formation processes for marine power equipment are presented. The scale formation influence on heat exchange at boiling of large volume of the seawater is intensive studying now in the word science. But, unfortunate, the reliable antiscale protection has not been created up to date. In presented investigation the scale formation research at the seawater forced motion was carried out on the experimental complex intended for testing of different types of the heat-exchange apparatus which function on seawater in ship conditions.

Different ways of the control of the process of the scale formation are considered. One of the perspective methods is plasma electrolytic oxidation technology (PEO). PEO method is based on the anodic or asymmetric alternating pulsed reversed voltage polarization of processing metals and its alloys under plasma microdischarges on the processing surface. These discharges arise after exceeding of the critical polarization potentials. As a result of this processing on the surface of the metals and alloys the coatings possessed by important for practice physical-chemical properties are formed.

PEO-process permits to form on metals and alloys surfaces the multifunction coatings having the complex of practically important physical-chemical properties: 1. The anticorrosion coatings on the titanium and its alloys (decreasing the intensity of galvanic corrosion of the heterogeneous materials for constructions (e.g. steel/titanium) exploited as galvanic couples in the seawater in the construction of the ship's energetic system, deep-sea apparatuses, etc.). 2. The antiscale coatings (decreasing the scaling intensity on the heat-exchangers surface working with a thermal flow from 0,2 MW/m^2 up to 0,5 MW/m^2 and using the seawater as a cooling liquid). Antiscale coatings may be formed in the electrolyte, which containes phosphate-ions. The treatment of the PEO-coatings by the superdispersed polytetrafluoroethylene (SPTFE) Forum® was made for creating of the hydrophobic layer on the surface, decreasing its roughness. The processing of non-oxidized surface by polymer powder is not effective because the powder has not good adhesion to metal. The PEO-coating possesses some roughness and guarantees fine adhesion.

Workshop: Standards and Regulations in Corrosion Protection of Oil and Gas Production Equipment and Pipelines

Requirements to corrosion-resistant products

A.P. Shalin, Certification Centre "CONTSTAND", Moscow, Russia

At the present time in the forming process of requirements to corrosion-resistant products designers proceed from possible percentage of hydrogen sulfide and carbonic acid in extractive liquid. For example, GOST 13846-89. The Christmas tree and discharge fittings. Typical circuits, main parameters and technical requirements to the construction, to the corrosion execution of wellhead equipment (K2 – application in mediums till 6% of H_2S, K3 – till 25%)

Depending on different real pressure on wellhead partial pressure will be different. Therefore the corrosion effect of extractive liquid will be different. That's why the application of partial pressure H_2S as a corrosive activity index of the medium demonstrates conditions of material running, simplifies the materials selection procedure for the specific running conditions.

This index is applied in standards under the corrosion resistance assessment of steel and alloy in laboratory conditions (NACE TM 0177-2003) and also at the materials selection (GOST R 51365-99. Oil-field mining wellhead equipment. General technical conditions. NACE MR 0175-2003).

Nevertheless supervisory bodies (Rostechnadzor) require the conformity assessment under K1-K3 after the results of laboratory corrosive testing though it would be better to estimate the materials resistance during the work in the medium with the specific partial pressure.

It is necessary to change the method of standards forming in the process of standardization and equipment designing and to work out the normative basis for corrosion testing and inspection corrosion.

Standard costs of corrosion management and sustaining of pipelines operability

I. S. Sivokon, OJSC TNK-BP, Moscow, Russia

From 2005, TNK-BP has been pursuing a target policy to mitigate oilfield pipeline leaks and extend the time of their no-failure operation.

As is known, the key cause of oilfield pipelines deterioration is external and internal corrosion which implies various mechanisms subject to specifics of the oil field. Accordingly, the operability sustaining costs are related to corrosion management and replacement of failed pipeline sections.

In 2004 – 2009, the Company used various approaches to implementation of the integrity management program:

From complete replacement of the leaking pipelines (control of current leaks and risks, industrial safety expert review to remove the claims of the controlling public authorities);

To stage-wise implementation of key instruments for leak mitigation and improvement of spending efficiency:

1. Risk prioritization and assessment for each pipeline;
2. Individual assessment of pipeline technical condition based on detailed instrumental inspection in compliance with strict internal requirements. Switch to selective pipeline repair and replacement.
3. Restructuring of integrity costs with growing role of corrosion protection measures, repair and maintenance.

Enforced requirement for tough cost saving in Q4 2008 and 2009 has led to implementation of the anti-crisis program within which a well thought-over experiment was staged to assess the sensitivity of the indicators against various actions (inhibition, electrochemical protection, replacement, and repair)

The accumulated experience and lessons learned review helped achieve as follows:

1. Within 5 years, leak rate in the pipelines reduced more than 2.5 times
2. In 2009 the pace of leak reduction did not decrease with significant reduction of costs

Analysis of leak rate, costs of corrosion management and sustaining of pipelines operability has shown that, with various strategies in 2005 – 2009 across TNK-BP, the level of costs for leak reduction and the leak rate have fundamental association that can be described by a simple formula in which variables and constants have a clear physical meaning.

The formula is good to describe both, previous profile of costs and leaks and also predicted indicators which were obtained as consolidated opinion of the Company's experts based on statistics.

The derived LAW has two implications which should be considered in planning of actions focused on leak mitigation:

Implication 1:

- Costs of sustaining the achieved integrity level are inversely proportional to the leak rate, i.e. the lower leak rate, the higher costs for its sustaining.

Implication 2:

- To mitigate the leak rate against the achieved level, **one-off costs** are required.

Alteration of physico-mechanical properties of sealing composite materials at influence of excited environments, characteristic for oil-and-gas branch

Yu.S. Ryabets, N.V. Sorokina, V.G. Antonov, “GAZPROM VNIIGAZ”,Moscow, Russia,

In activity influence of ageing of strong polymeric composite materials (PCM) new generation [1] in four types of modelling corrosive-excited environments, characteristic for gas branch is researched, at various temperatures and exposure times on change of physical parameters and strength parameters of hundred kinds of seals from PCM a various design and a structure.

Seals from nonasbestos strong materials seals on the basis of various rubbers, termoexpanded graphite (TEG) or the graphite foil, filled or reinforced are considered by various materials are:

- Metal;
- Fibres Kevlar (aramide);
- Ceramic fibres;
- Mineral fibres;
- A cotton thread;
- Fibres from fluoroplastik.

The basic requirements to strong materials at the control of process of ageing:

- Small permanent distortion of compression;
- Resistance action of the transported environment at the corresponding temperature of operation;
- Insignificant value of a relaxation of pressure;
- Resistance ageing;
- Migratory resistance a material of pipes.

Criteria of an estimation of quality [2] were used for classification of strong materials or products from them on resistance (in not strained) to the accelerated ageing in special corrosive-excited environments accordance with tabl.1.

Table 1- Technical requirements on resistance for PCM

Type of plastic	Changes of a parameter,%	The Designation of group of resistance
Thermo-plastics and materials on their basis	from 0 up to 10,0	1
	from10,0 up to 15,0	2
	from above 15,0	3
Thermo-setting plastic and materials on their basis	from 0 up to 15,0	1
	from 15,1 up to 25,0	2
	from above 25,0	3
The note: 1-Good; 2-Satisfactory ; 3-Bad		

Results of the conducted researches have confirmed a conclusion that

- The set conditions of the accelerated ageing modelling operational parameters in the gas industry and trial and error methods and definitions of characteristic criteria of an estimation of resistance of materials in environments are chosen methodically correctly since answer on a brought attention to the question - whether the material is proof in the given environment;

- Techniques of definition of quality PCM after effect of corrosive-excited environments were a means of an estimation of resistance of materials and the results of tests received on them reflect relative change of controllable parameters at action of corrosive-excited environments.

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Hydrogen charging of carbon and low alloy steel by electrochemical methods

F. Bolzoni, P. Fassina, G. Fumagalli. L. Lazzari,*
Politecnico di Milano, Dipartimento di Chimica, Materiali e Ingegneria Chimica "G. Natta", Milano, Italy
**ENI, Exploration & Production Division, San Donato Milanese, Italy*

In the presence of H_2S, metallic materials, such as carbon and low alloy steels, may suffer hydrogen damage and hydrogen embrittlement. Sour service materials must be used in compliance with international accepted standards, used worldwide in oil & gas activities, when fluids are classified as sour.

There is evidence from field and laboratory experiences that reduction of toughness and ductility due to hydrogen damage could be enhanced by low temperature in arctic applications.

The present study has been carried out in order to set up an electrochemical method to charge with hydrogen steel specimens to be mechanically tested at low temperature. The electrochemical method has been proposed with the purpose to obtain charging conditions in an environment not particularly critical from the point of view of preparation, safety and disposal.

Hydrogen charging on API 5L X65 specimens has been carried out in acetic acid and sodium acetate solution with 200 ppm $S^{=}$ added, aerated, at room temperature; applied cathodic current density was 0.6 mA/cm^2 for 20 h.

After hydrogen charging, specimens have been plated with nickel and copper plating (total thickness 30 μm approx.) in order to guarantee that the hydrogen penetrated into the specimen should remain confined in the material for a time long enough to carry out mechanical tests.

Hydrogen content in the specimens has been measured by two different methods: hot glycerol bath and LECO hydrogen determination. Although the high scattering of the results even when the specimens have been charged in identical conditions, the results of the two methods are in good agreement. Hydrogen content in the CV specimens is about 1-3 ppm; these specimens have been tested by Charpy resilience test and CTOD (results are presented in the paper "Materials behavior in extreme conditions: influence of large amounts of H_2S on steel toughness in arctic environments" by *P. Fassina, R. Morana, L. Alleva, G. Mortali, L. Vergani* in this conference).

Comparison of Two Methods for Determination of Pipeline Steel Resistance to SSC According to Nace Standard TM0177-2005

Petr Jonšta [1]**, Karel Matocha** [2]
[1] VSB – Technical University of Ostrava, Czech Republic
[2] RESEARCH & DEVELOPMENT, Ltd., Ostrava, Czech Republic

Abstract

Failure due to cracking under the combined action of tensile stress and corrosion in aqueous environments containing hydrogen sulfide (H_2S) at room temperature is generally termed sulfide stress cracking (SSC). SSC of steels exposed to oilfield environments containing H_2S was recognized as a materials failure problem by the beginning of eightieths of the last century. Room temperature failures in high strengths micro alloyed steels are generally believed to result from hydrogen embrittlement. The presence of H_2S tends to cause hydrogen atoms to enter the metal rather than to form hydrogen molecules that cannot enter the metal. In the metal, hydrogen atoms diffuse to regions of high triaxial tensile stress or to some microstructural configurations where they become trapped and decrease the ductility of the metal.

NACE Standard TM0177-2005 covers the following testing methods used for for determination of pipeline steel resistance to Sulfide Stress Cracking:

- Method A – Standard Tensile Test
- Method B – Standard Bent-Beam Test
- Method C – Standard C-Ring Test
- Method D – Standard Double-Cantilever-Beam Test

The evaluation of pipeline steel X65 for resistance to sulfide stress cracking (SSC) was carried out using both Method A and Method B of NACE Standard TM0177-2005. Constant-strain loaded round bar tensile test specimens, 3 mm in diameter, were loaded in stressing frames according to ASTM G49 applying tensile stress $\sigma = 0{,}7.R_{p0,2}$, $\sigma = 0{,}8.R_{p0,2}$ and $\sigma = 1{,}0.R_{p0,2}$. The bent-beam test specimens 26 mm wide, 2 mm thick and 130 mm long were loaded using four point bending stressing jigs according to ASTM G39 at the same stress levels. Loaded test specimens were exposed for 720 hours in test solution B according to NACE Standard TM0177-2005. The paper summarizes the results obtained by these two methods.

Keywords: sulfide stress cracking (SSC), metals, testing methods

Poster Programme

Corrosion and Scale Inhibition

COMPARISON OF CHEMICAL AND PLASMA REMOVAL OF OXIDE SCALE FROM DUPLEX STAINLESS STEEL

Črtomir Donik[1], Irena Paulin[1], Aleksandra Kocijan[1], Miran , Monika Jenko[1]
[1]*Institute of metals and technology, Lepi pot 11, SI-1000 Ljubljana, Slovenia*
[2]*Jožef Stefan Institute, Jamova 39, SI-1000 Ljubljana, Slovenia*

Abstract

A tightly adhering oxide scale is formed on all types of stainless steels when they are annealed. The removal of the oxide scale and chromium-depleted under layer is one of the most important processes during the stainless steel production. Their removal of oxide scale from duplex stainless steel has shown to be even more difficult than normal austenitic or ferritic stainless steels. While it is well known that electrolytic pickling in neutral sodium sulphate is widely used for oxide scale removal the amount of energy and the composition of the container is quite complex so we tried another approach with reductive plasma in comparison with simple chemical scale removal. This study describes the different stages of the oxide scale removal on duplex stainless steel DSS 2205 in HNO3/HF mixtures and removal by reductive plasma. The dissolution is proposed to proceed by the chemical reactions of the scale in successive stages. At the beginning of the pickling process chromium and manganese of the outer oxide layer were preferentially dissolved. When the chromium content of the outer layer decreased, the scale and oxide/metal interface was enriched of iron. The comparison of elemental composition of the residue oxide layer on the top has been investigated by surface sensitive techniques XPS and AES.

Keywords: duplex stainless steel, reductive plasma, scale removal, XPS, AES

e-mail: crtomir.donik@imt.si

The partial contributions of the phase coating and inhibitor as the united system to its protective action estimate method

L.E. Tsygankova, V.I. Vigdorovich, A.I. Fedotova, C.A. Zakurnaev.
Tambov State Technical University, Tambov, Russia

By the hydrosulphuric, carbon dioxide and some other kind of corrosion there is the different nature coating on the surface. At the initial time the inhibitor efficiency is specified by conjugated electrode reactions rate reduce by the inhibitor's sorption onto juvenile metal surface or generated oxide coating. Then the structure and nature of such coating and also the corrosion rate change. At the same time the conditions of the inhibitor's fit onto the surface and the protective efficiency Z_i of the inhibitor and surface film change. The nonstationary processes run up to coating-inhibitor system steady state formation onto metal/solution-interphase.

There is the theory of the introduced by the authors the coating (Z_{COAT}) and inhibitor (Z_{INH}) as the united system contributions to the $Z_{\sum}$ estimate method represented in report (picture).

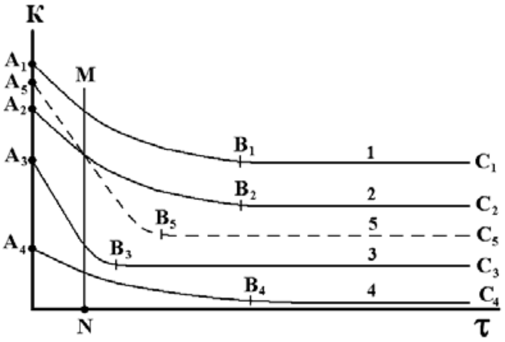

Figure. Schematic relationship of K value in time in solutions that cause coating formation on the corroding surface. 1 – noninhibited, 2…5 – inhibited solution.

Curves 1 and 2 (Figure) conform to the same stationary surface state attainment time τ_{ST} and K without and in inhibitor presence. The protective coating (PC) formation acceleration in inhibited solution is by the curve 3 described, the A_3B_3 segment length and τ_{ST} decrease and dK/dτ value rises at that. The changes counter motion is by the curve 4 described, particularly by the A_4B_4 segment length and τ_{ST}. They rise respectively and dK/dτ value decrease.

On the B_iC_i curves segments the protective system's formation retards in time or stops at all, then $K \neq f(\tau)$. There K and Z measurements shell be carried out.

By the such interpretation the A_1 and B_1 (K_{A_1} - K_{B_1}) points coordinates difference ratio to the A_1- ordinate (Figure) is the coating's protective action in noninhibited solution and B_1 and B_1 ordinates difference ratio to the A_1- ordinate is the Z_{INH}. ($Z_{INH,2} = K_{B_1} - K_{B_2})/K_{A_1}$, $Z_{INH,4} = (K_{B_1} - K_{B_4})/K_{A_1}$). The same approach can be used by the corrosion stimulant put, by the metal mechanical characteristics reduce inhibiting, in passive state attainment (in time) conditions. There are in report Z_{COAT}, Z_{INH} and $Z_{\sum}$ of some systems by the hydrosulphuric and carbon dioxide steel corrosion as the inhibitor's nature, C_{H_2S}, P_{CO_2} and corrosion duration function.

Zinc- and carbon-modified oil compositions for atmospheric steel corrosion protection

V.I. Vigdorovich, A.O. Golovchenko, M.V. Vigdorovich.
Tambov State Technical University, Tambov, Russia

The zinc- and carbon-loaded oil compositions protective action is researched against the carbonaceous steel corrosion in 3%- saline solution (NaCl) by the pH 7, 4 and 3 also at the humidistat by the periodic relative humidity H (70 – 100 %) and temperature 20 – 40 ^{0}C variation. The micromeritic graphite and the activated by the high-temperature acid processing multilayer carbon nanotubes (MCNT) with external diameter 10…20 nm and average effective pore size about 7 nm were put into waste motor oil as the carbon material (0,01 – 1,0 wt. %). The zinc powder content were 40, 50 and 60 mass percent.

The barrier zinc-loaded (50 wt. %) coating application reduces the steel E_{CORR} in neutral solution from -0,50 down to -0,71 V. The micromeritic graphite (MG) compound (0,01 – 1,0 mass percent) does not change the E_{CORR} or increases it up to -0,68 V and 1,0 mass percent MG compound up to -0,57 V. The steel dissolution rate calculated by the polarization measurements decreases up to 850 – 470 times. The C_{MG} reduce or growth by 10 wt. % leads to insignificant changes only. The MCNT put instead of MG does not influence the E_{CORR} or increases it up to -0,62 V(40% Zn). By the 60% Zn content the steel E_{CORR} reduces down to -0,72 V, but there is no MCNT concentration factor.

The pH reduce down to 4 does not practically influence the E_{CORR} (50 % Zn), the MCNT put reduces it down to -0,72 V. The same is by the pH = 3. For the first 10 days of the corrosion tests the iron does not transgress from the protected steel to the solution (the $K_4[Fe(CN)_6]$ qualitative reaction) and protector's anodic dissolution from the barrier coating is retarded comparison with the solid zinc.

The zinc-loaded compositions contained micromeritic graphite protective action amounts to 80 (40 % Zn) – 89 % (50 % Zn). The MG by the MCNT replacement leads to the protective action reduce.

The coatings protective action amounts to 91 (40 % Zn) – 99 % (60 % Zn) by the 30 day test at the humidistat by the periodic relative humidity H and temperature variation. The MG by the MCNT replacement does not practically change it (60 % Zn) or frequently decreases it for 4 – 13 % (40 % Zn).

There is the detailed description of the zinc, MG and MCNT concentration and pH value influence on the researched composites by the steel corrosion protective action in report.

Concepts and practice of the hydrosulphuric and carbon dioxide corrosion universal inhibitors preparation

V.I. Vigdorovich, L.E. Tsygankova, A.V. Ryasanov, A.N. Mozharov.
Tambov State Technical University, Tambov, Russia

One of the inhibitory protection numerous problems solutions is the universal products application. Their engineering and application allow to eliminate many processing complications and to expand the domestic raw materials sources. The universality means the inhibitors ability to retard several kind corrosive actions and react negative impacts of the different kind corrosion stimulant at once. As the universal inhibitors can be considered individual compounds and homological mixes which are effective at the same time against the hydrosulphuric, carbon dioxide and complex corrosion (CO_2 + H_2S) and also by the hydrogenation in pH wide-ranging; active bactericides which preserve structural materials mechanical properties. Such materials existence is undoubtedly feasible. In the report is the EM-9 product represented which is the tetraethylene pentamine and tall oil acids interaction resultant technological mixtures. Its carbonaceous steel corrosion protective effect (Z) reaches up to 90 % in mineralized (50 g/l NaCl) hydrosulphuric (up to 400 mg/l H_2S) media with the pH reference value = 2…6; it is high enough (≥ 80%) in carbon dioxide solutions by the $P(CO_2)$ – (0,5 – 2) · 10^{-5} Pa and rises up to 85% in such oxygenless solutions. The corrosion stimulant combined attendance: H_2S (100 mg/l) and CO_2 (equilibrium pressure (P_{CO2} - 10^5 Pa) keeps the Z value on the top limit. The 25…200 mg/l inhibitor injection increases the hydrogen diffusion retardation through the carbonaceous steel membrane factor $\gamma = i_{H,0} / i_H$ ($i_{H,0}$ and i_H are hydrogen diffusion fluxes in uninhibited and inhibited solutions respectively) in the range (oxygenless solution):

C_{INH}, mg/l	pH	γ in the presence of			
		H_2S*	H_2S**	CO_2***+H_2S*	CO_2***+H_2S**
25	2	1,5	1,8	32,0	6,5
	4	1,8	-	1,0	-
200	2	2,2	7,5	3,2	30,0
	4	9,2	6,4	1,6	-

* - 25 mg/l, ** - 100 mg/l, *** - CO_2 pressure,10^5 Pa.

The sulfate-reducing bacterium amount rejection in Postgate nutritient solution by the C_{Inh} = 25, 50, 100 and 200 mg/l schedules appropriately 73, 75, 77 and 82% and correlates well to mycotas H_2S-producing, the steel firmness loss factor reduce (stretch for carbon steel and bend for spring steel) amounts to 98 – 99% in observable solutions.

Drinking water containing Cu^{2+} ions is a boon in dentistry

S Rajendran [1,2*] and B Shyamaladevi [3]

1.Corrosion Research Centre, Department of Chemistry, GTN Arts College,
Dindigul – 624005, India. Email: srmjoany@sify.com
2. Corrosion Research Centre, Department of Physical Sciences, Servite College of
Education for Women, Thogaimalai-621313, Tamilnadu, India
3. Department of Chemistry, Vivekanandha Institute of Engineering and Technology for
Women, Elayampalayam, Tiruchengode, Tamilnadu, India
Email: shyapranesh@yahoo.com

Abstract

Copper is usually present in fresh water in low amounts, but the concentration can increase substantially when water travels through copper pipes within residential homes. The effect of copper on the corrosion behaviour of three metals, namely, mild steel (MS), mild steel coated with zinc (MS-Zn) and SS 316 L in artificial saliva (AS) has been investigated by polarization study and AC impedance spectra. In the absence of copper and also in the presence of copper, the order of corrosion resistance is SS 316 L > MS-Zn > MS. The corrosion resistance of all the three metals is higher in the presence of Cu^{2+} than in its absence. Drinking water traveling through copper pipes is a boon to the people who make use of the above metals in dentistry. SS 316 L is a better candidate than MS-Zn and MS, in dentistry.

Keywords : Artificial saliva, metals, dentistry, effect of Cu^{2+}, SS 316 L

The effect of corrosion stimulation of inhibitors on trial in relation to Varandey field conditions

***L.S. Moiseeva*, E.S. Uglova**
United Research and Development Centre, Moscow, Russia

The goal is to carry out comparative tests of corrosion inhibitors №1 and №2 on media of Varandey field to estimate their efficiency.

Physical-chemical analysis of water probes was carried out; corrosion activity is caused by watering of extractive emulsion, presence of dissolved CO_2, O_2 и H_2S.

The corrosion rate of Ст10, Ст20 in mineralized water, water-oil emulsion, oil and vapor phase was determined by gravimetric and polarization resistance methods at 20°±2°C and 80°±2°C in steady-state and dynamic conditions.

The dependence of corrosion rate and protection rate of two inhibitors ИК №1 and ИК №2 on concentration in the range of 10 - 60 mg/l was obtained in the oil-water emulsion sample of composite probe of two oil wells products. It was found that inhibitor's efficiency is associated with concentration. ИК №1 and №2 decrease corrosion rate of steel in water-oil emulsion at 20º C. The protective effect of ИК №1 increases continuously with the increase of concentration and has maximum when concentration is equal to 60 mg/l (Z=100%). Inhibitor №2 efficiency is maximal when concentration is equal to 40 mg/l (Z=96%). Further increase of concentration of ИК №2 leads to decrease of protective effect. ИК №1 is more effective. The nature of inhibitors changes at 80°C. The efficiency of ИК №1 vary from stimulation to inhibition, protective effect is maximal when concentration is equal to 40 mg/l and it is minimal at 60 mg/l. ИК №2 slightly inhibits the corrosion rate of steel at 10 mg/l (Z+ 11%). Further increase of concentration lead to stimulation of corrosion process which reaches considerable amount at 60mg/l. The effect of stimulation was not observed earlier when inhibitors were tested in water-oil emulsion. The nature of ИК №1 and ИК №2 stimulation of steel corrosion may be different. Reasons which cause stimulation effect are considered in the report.

Comparative tests of inhibitors at operation concentration 40 mg/l and temperature 20°C and 80°C in mineralized CO_2 saturated and acidated to pH 4.82 water which was separated from water-oil emulsion showed that there was no stimulating effect, inhibitors showed high performance.

Investigation of transport properties of ИК №1 and №2 in three-phase media «oil-stratal water of well №03В – vapor phase» at concentration equal to 60 mg/l and temperature equal to 20°C and 80°C showed that in oil fraction ИК №1 and №2 inhibit corrosion process and stimulate corrosion in stratal water fraction and vapor phase. The mechanism of the effect observed was suggested.

Results obtained was used for development of corrosion protection system for equipment and pipes in Varandey field.

Corrosion of 304SS in H_2SO_4 Containing Molybdates and tungstates as inhibitors

Ahmed S. Alshamsi, Department of Chemistry, UAE University, Al-Ain, UAE

The electrochemical behavior of 304 stainless steel has been thoroughly investigated in H_2SO_4 as a function of H_2SO_4, chloride ions, and molybdate ions concentrations at room temperature. In addition, the effects of other ions such iodide, bromide, and tungstate ions have been studied. Standard corrosion techniques that have been used include Tafel measurements, R_p *vs*. time measurements, cyclic polarizations measurements, and the critical pitting potential measurements. Initial results indicate that the addition of molybdate ions at sufficient concentrations enhances both the resistance to general corrosion and to pitting corrosion in the case of chloride ions presence. It is suggested that molybdate ions inhibit pitting by lowering the current densities in the active and passive range, enhancing repassivation in the process, making it difficult for metastable pits to grow into stable ones.

Investigation of POD - Oil Steel Corrosion Inhibitor as Surfactant

G. Ostapenko[1,2], P. Gloukhov[1], and S. Sadivskiy[3]

[1]*Department of Chemistry & Ecology,*
Togliatti State University, Russia
[2]*Moscow State University of Food Production,*
Togliatti Division, Russia
[3]*Joint-Stock Company KuibyshevAzot,Togliatti, Russia*

The organic wastes of the caprolactam production (POD-oil) were investigated as acid corrosion inhibitor of steel [1, 2]. The basic inhibiting component of the POD-oil is dimer of hexanon (dianone).

All effective inhibitors are strong surfactants. Generally a surface activity of the nonionic surfactants can be determined by interaction of surfactant molecules with metal or the interaction of these molecules with a solution. However overwhelming majority of works on the adsorption mechanism relates the adsorption just to interaction of surfactant and metal.

Here the mechanism of nonionic surfactant adsorption is investigated, as an example, dianone adsorption on iron in acid chloride solution and dianone acid chloride solution – air interface. Adsorption on the solution – steel interface is investigated by Electrochemical Impedance Spectrscopy technique. The maximum bubble pressure technique is applied for investigation of surface tension on solution – air interface.

Inhibitor adsorption isotherms for air – solution and steel – solution interfaces well agree to Langmuir equation:

$$\theta = \frac{K_{ad}C}{1 + K_{ad}C} \quad \text{or} \quad \frac{C}{\theta} = \frac{1}{K_{ad}} + C,$$

where θ is the surface coverage, C is the inhibitor concentration and K_{ad} is the adsorption constant. The slopes direct (0.92 and 0.97) well agree with a theoretical (unit) slope. Hence the Langmuir adsorption take place both on the steel surface and on the air – solution interface.

The values K_{ad} for air – solution (0.16 mass %) and steel – solution (0.15 mass %) interfaces practically coincide. Therefore it is possible to make the guess that the dianone adsorption does not depend on an adsorbent nature, but depends on the interaction of dianone with solution. It is possible to explain this effect by a solvofobic solvation of surfactant organic molecules and entropic tendency of displacement of the adsorbate from solution volume to the phase interface [3]. The basic criterion for this phenomenon is the low surfactant solubility [3] that occurs for POD – oil and dianone in acid solutions.

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Combating with corrosion and scaling - a complex problem in the fields of PB “Rosneft”

Khairullin I. I., Gubkin State University of Oil and Gas, Moscow/Russian Federation

The main factors contributing to corrosion of the aqueous phase on the PB “Rosneft” fields:

- Type, pH and salinity;
- Content of oxygen (O_2), hydrogen sulfide (H_2S), carbon dioxide (CO_2);
- Contents of iron ions (Fe^2 +, Fe^3 +);
- Content of mechanical impurities and oil.

Analysis of the harvested waters of the Priobskoe deposit showed that the concentration of dissolved carbon dioxide is in the range 100 - 200 mg/L, the mineralization of 5.10 g/l, pH 6,5-7,5. Such water on the degree of aggressive exposure related to much aggressive. The actual rate of local corrosion more than 8 mm/year. Gusts on pipelines leading to oil spills, which is extremely negative impact on the ecological situation of the Priobskoe field, especially its right-bank part, located in the floodplain of the Ob.

At the same time a more significant problem in the fields of PB “Rosneft” is the fight against scaling, which is capable to stop well work in just a few days. Salification represent deposits that fully block lifting pipe, valves, pumps, and the inner surface of the downhole equipment, littering, so well and impeding the flow of liquid. To remove the salt deposits is being used multiple acid treatment (AT), which accelerates the corrosion of downhole equipment. The resulting corrosion products change the structure of the surface of the impellers and tubing and are centers of crystallization of carbonates. In this connection, corrosion control can be considered as part of the anti-scaling.

In 2009, on the deposits of PB “Rosneft” was carried out treatment on producing wells by impulse-wave impact (IWI). Cardinal changes in the reservoir has been achieved only after the treatment of wells by IWI + AT. These changes affected the following aspects:

- Firstly, the layer no longer initiate scaling, despite the high salinity of fluids flowing out from the formation;
- Secondly, the flow rate of wells not only achieved the targets, but in some cases, multiply exceeded the maximum flow rate obtained in the history of the borehole.

The activities undertaken have to exclude up to 9 months the treatment of wells with acid and thus significantly increase the lifespan of underground equipment. Therefore I think corrosion and scaling on the fields of PB “Rosneft” is the problem requiring a comprehensive approach.

Application of Vapor Corrosion Inhibitors in Hydro-testing

Alla Furman, *Andrea Hansen, Rita Kharshan, Elizabeth Austin*
Cortec Corporation, White Bear Lake, MN, USA

Objective

Hydro-testing of metal equipment is an important method for quality control of its production and use. Corrosion of the metal during and after this test is a concern. The goal of this study was to evaluate and find effective vapor corrosion inhibitors for protection of metal equipment against corrosion during its hydro-test and also transportation or storage.

Significance of Work

Vapor corrosion inhibitors are low toxic, mainly biodegradable and often bio-based materials. Their effectiveness in corrosion inhibition was studied and confirmed on the most often used metals such as carbon steel, cast iron, galvanized steel and aluminum. Use of vapor corrosion inhibitors is economical, environmentally responsible and labor reducing option of corrosion protection of machinery, storage tanks and piping systems during and after hydro-testing.

Results

Vapor corrosion inhibitors with different mechanism of action were studied.

VCI A is a combination of film formers and vapor corrosion inhibitors. VCI B is a vapor corrosion inhibitor based on salt of aromatic acid. VCI C is a synergistic blend of organic and inorganic salts and alkalinity builders, it acts as a film-former/ passivator. VCI D is a combination of biodegradable surface modifiers, chelating agents and oxygen scavenger. VCI E is a vegetable oil based corrosion inhibitor. Because of its high surface activity, when added to hydro-test water VpCI E attaches to the metal and protects them from corrosion. This product contains ~91% bio-based material and is applied as a float coat.

Laboratory Studies include weight loss and electrochemical tests. Tests were also set up to verify the “after-action protection”, protection of the metal after hydro-testing.

Field Applications include:

- Addition of water soluble corrosion inhibitor to hydro-test water. In this case the residual film formed by the inhibitor on the metal should be effective enough to protect from corrosion during the storage. This is recommended when the volume of hydro-test water is relatively small, or water can be reused for hydro-testing several time, because the concentration of corrosion inhibitor should be relatively high.
- Addition to hydro-test water of a low dose of the corrosion inhibitor, which will prevent corrosion mostly only during hydro-test time, and the when water would be drained, addition of VCI powder or spray to provide corrosion protection during the storage.
- Oil soluble bio-based ‘float coat’ application for hydro-test of large systems filled with salt water.

Summary

Use of vapor corrosion inhibitors is effective, economical and environmentally friendly way of preventing corrosion during and after hydro-testing. They can be used in various water chemistries including salt water.

EVALUATION OF INHIBITOR EFFECTIVENESS ON AA 2024 SUBSTRATES BY IMAGE ASSISTED ELECTROCHEMICAL TECHNIQUES

Rosero-Navarro N.C.[2], Curioni M.[1], Bingham R.[1], Durán A.[2], Aparicio M.[2], Cottis R.[1], Thompson G.E.[1]

[1] Corrosion and Protection Centre, School of Materials, The University of Manchester, United Kingdom
[2]Ceramic and Glass Institute (CSIC), Spain, karolrosero@icv.csic.es

High strength aluminium alloys are susceptible to localized corrosion and protective measures, i.e. chromate based surface treatments, are required for demanding aerospace applications. Here, the inhibition mechanism of cerium nitrate is examined and compared to benzotriazole (BZT) and a sodium chromate reference by the use of image assisted, Electrochemical Noise (EN) and Electrochemical Impedance Spectroscopy (EIS). The previous techniques provide information on the interaction between the inhibitor and the corroding surface, with minimal perturbation to the corrosion process. EN analysis overcomes the limitations of traditional EIS (frequency sweep), where natural potential and current noise during the early stages of immersion prevent recording of smooth spectra. Impedance has been calculated from the natural current and potential noise, and the data manipulation enables a satisfactory time resolution. Correlation of the previous with images of the corroding surface provides a powerful tool for comparative evaluation of the inhibitor effectiveness. By examination of accelerated motion videos and electrochemical data, it has been confirmed that cerium nitrate behaves as a cathodic inhibitor, limiting corrosion propagation.

REACTIVITY AND INHIBITION OF COLD ROLLED STEEL IN 1M HYDROCHLORIC ACID: AN ATOMIC EMISSION SPECTROELECTROCHEMICAL INVESTIGATION

Polina Volovitch[1], Ilyas Gazizullin[2], Kevin Ogle[1]

[1]LPCS, CNRS UMR7045, Ecole Nationale Supérieure de Chimie de Paris, 11 rue Pierre et Marie Curie, 75231 Paris Cedex 05, France
E-mail: polina-volovitch@chimie-paristech.fr
[2] Department of Chemistry, Lomonossov Moscow State University, MGU Vorobievy Gory Moscow, Russia

The spontaneous reactivity of cold rolled low carbon steel in 1 M hydrochloric acid was studied by atomic emission spectroelectro-chemistry (AESEC). The dissolution rates of Fe, Mn and P were monitored as a function of time for samples with varying concentration of alloying elements (C, P, and Mn) and the effect of small concentrations (10^{-7}M– 10^{-1}M) of hexamethylene tetramine (HMTA) was investigated. In the absence of inhibitor, a quasi-steady state was obtained, characterized by the simultaneous dissolution of Fe, Mn and P. The fraction of Mn dissolving in the steady state regime is shown to be in very good agreement with that of the bulk sample. The initial transitory period shows a significant enrichment of Mn dissolution. Phosphorus dissolution was also clearly detected, P emission intensity varies directly with the %P elemental composition and that it is reasonable to assume that P dissolution is simultaneous with the Fe dissolution. Because of P segregation on grain boundaries, the simultaneous dissolution of P can be in favour of selective dissolution of near grain boundary areas. A clear inhibitive effect of HMTA on Fe dissolution is observed between 10^{-3} and 10^{-2} M for all samples. A very strong effect was observed for the most reactive steel and a weaker effect on the less reactive steel. Interestingly, although the two samples showed a difference in reactivity of a factor of 10 in the absence of HMTA, approximately identical dissolution rates were observed for the highest concentration (0.1 M) of HMTA. These results may be interpreted in terms of the electrostatic nature of interaction between the surface and protonated form of HMTA. The microstructure sensibility of the inhibition can be related with adsorption mechanism because the higher reactivity indicates the high concentration of structure or chemical inhomogenities which play the role of active centres for adsorption. Mn dissolution is not affected at all for HMTA concentrations at and below 10^{-2} M. A simple interpretation of these results is to assume that inhibition is selective for the Fe dissolution reaction. Therefore, the inhibition of cold rolled steel pickling in 1M HCl by HMTA can involve two mechanisms:
(1) the conventional inhibition mechanism involving selective blocking of the cathodic sites by the adsorbed molecules;
(2) the selective dissolution of the segregated elements that enhance dissolution reactivity.

As both mechanism lead to a decrease in the open circuit potential, they cannot be distinguished on the basis of “normal” electrochemical experiments.

Corrosion inhibition of Ni, Fe and their alloys by chemisorbed CO

Gema Cabello[a] and Ángel Cuesta[a]*

[a]Instituto de Química Física "Rocasolano", CSIC, C. Serrano, 119, E-28006 Madrid, Spain
**Corresponding Author. E-mail: a.cuesta@iqfr.csic.es*

In UHV or at the gas–metal interface CO tends to chemisorb dissociatively on the transition metals at the left-hand side of the periodic table, and molecularly on those at the right-hand side, the dividing line running between Fe and Co, Tc and Ru, and W and Re[1]. It has been shown that, at the metal–electrolyte interface, CO chemisorbs strongly on Fe, Co and Ni electrodes[2-4]. As a consequence of the strong chemisorption bond between CO and the surface atoms of ferrous metals electrodes, surface oxidation or dissolution is impeded, a well–known fact since Uhlig described carbon monoxide as a corrosion inhibitor for stainless steel in 1940[5].

We report here corrosion inhibition by CO chemisorbed on Ni, Fe and three of their alloys (UNILOY 420, N80 and INCOLOY 825), and the interaction of CO with two usual corrosion inhibitors (cinnamaldehyde and propargyl alcohol) in very aggressive conditions: 7.5, 15, 20 and 28% (w/w) HCl solutions, i.e., very acidic solutions with a high chloride concentration. The inhibitors behavior was characterized using electrochemical (cyclic voltammetry), spectroscopic (Fourier-transform infrared spectroscopy (FTIRS) and surface enhancement raman spectroscopy (SERS)) and proximity microscopy (electrochemical–STM and AFM) techniques.

From our measurements, we conclude that carbon monoxide chemisorbs strongly on UNILOY 420, N80 and INCOLOY 825 alloys, inhibiting corrosion, and that, when used in combination with cinnamaldehyde or propargyl alcohol, an enhancement of corrosion inhibition occurs.

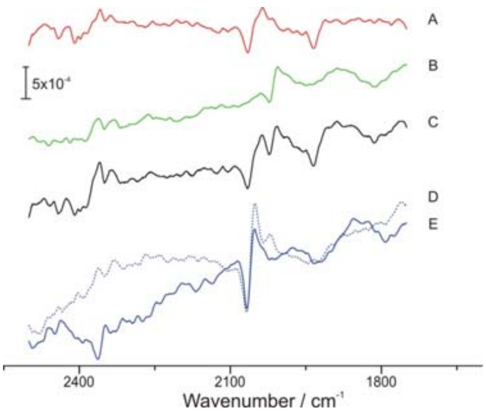

Figure 1. FTIR spectra in 7.5% HCl of CO chemisorbed on Ni (A), Fe (B), I825 (D), and passivated I825 (E). Spectrum labeled (C) is the result of adding (A) and (B).

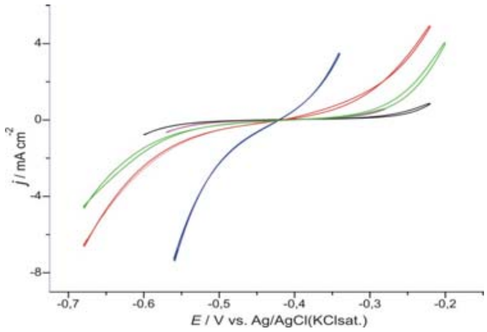

Figure 2. Cyclic voltammgrams of N80 in 7.5% HCl. (blue) N_2. (red) CO. (green) CO + TCA. (pink) N_2 + TCA. (black) TCA + CO.

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The inhibited turbine lubricating oils for defence of crude oil and gas equipment against hydrogen sulphide corrosion

V. Spirkin, M. Silin, I. Tatur, B. Tonkonogov, Gubkin State Oil and Gas University/Moscow

For protection against corrosion and deterioration of the oil and gas equipment working on hydrogen sulphide containing natural and following gases, the inhibited turbine oil is developed. The composition includes corrosion inhibitor, antiemulsion, antiwear and antioxidizing additives. Tests of a composition are conducted with positive results on the Complex of methods of a qualifying estimation. At use the inhibited composition of turbine oil speed of corrosion of a steel in the presence of hydrogen sulphide decreases at 3-6 times.

PHYSICAL AND CHEMICAL ASPECTS OF CHOICE OF INITIAL PRODUCTS, REACTIONS OF SYNTHESIS AND FORECASTING OF VOLATILE INHIBITORS OF ATMOSPHERIC CORROSION EFFICIENCY (SCHIFF AND MANNICH BASES BEING THE EXAMPLE)

Alla I. ALTSYBEEVA, Vladislav V. BURLOV, Tatyana M. KUZINOVA,
Nadezhda S. FEDOROVA, Galina F. PALATIK
All-Russian Scientific Research Institute of Petrochemical Processes, Saint-Petersburg, Russia

Considering Schiff and Mannich bases as the example, physical and chemical aspects of choice of initial products and reactions of synthesis of volatile inhibitors of atmospheric corrosion (VIACs) of both ferrous and nonferrous metals and issues of interrelation of physical and chemical and electronic characteristics of metals of various nature and molecular parameters of the inhibitors are discussed, allowing to predict their efficiency.

It is shown, that the general concept of estimation of substances' adsorbability on metals and, as consequence, their inhibiting properties on the basis of the electronic characteristics of substance and metal (the potential of ionization and electron work function) does not allow to unequivocally predict the inhibiting efficiency of substances in relation to metals of various nature. It is shown, that the concept of the inhibiting activity estimation on the basis of concurrence of the first adiabatic potentials of substances' ionization and "resonant" potentials of metals and their oxides can be used only for forecasting of possible forms of adsorptive bonds of a molecule with metal and explanation of the return phenomenon – stimulations of metals' corrosion facts.

High efficiency of Schiff and Mannich bases as VIACs – commercial inhibitors of the VNC-L group is validated. It is shown, that the basic molecular characteristics of products of complex condensation of nitrogen containing compounds with aldehydes provide the basis to predict their high inhibiting efficiency as VIACs. The basic physical and chemical parameters characterizing VIACs, commercial inhibitors of the VNC-L group and new inhibitors – products of complex condensation of nitrogen containing compounds with aldehydes are determined.

Dependence of drag coefficient of steel atmospheric corrosion (γ) and physical and chemical properties of the synthesized compounds is discussed and the opportunity of forecasting of substances' inhibiting efficiency is also shown on the basis of correlation between γ and the estimated parameters – saturated vapors pressure, total electronic density on heteroatoms and the inhibitors' constant of hydrophoby. The predicted and experimental corrosion drag coefficients of new inhibitors have coincided with accuracy of ±10 % rel.

THE CORROSION BEHAVIOUR OF AUSTENITIC AND DUPLEX STAINLESS STEELS IN ARTIFICIAL SALIVA WITH THE ADDITION OF FLUORIDE

Aleksandra KOCIJAN[1], **Darja KEK MERL**[2], **Monika JENKO**[1]

Institute of metals and technology, Lepi pot 11, 1000 Ljubljana, Slovenia, e-mail:
aleksandra.kocijan@imt.si
Jozef Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia, e-mail: darja.kek@ijs.si

The 2205 duplex stainless steel was investigated as a material for orthodontic bracket fabrication. Orthodontic brackets are essential component of modern fixed appliances. Duplex stainless steels are balanced with two phases, ferrite and austenite. The combination of both phases has a beneficial influence on the corrosion characteristics in various aqueous environments, thus gradually displacing the stainless steels of the AISI 300 series. The aim of the present study was to compare the electrochemical properties of duplex stainless steel 2205 and AISI 316L stainless steel in artificial saliva and with the addition of sodium fluoride, in order to assess the influence of fluoride mouthwash products on the corrosion resistance of orthodontic brackets. The evolution of the passive film formed on duplex stainless steel 2205 and AISI 316L stainless steel in artificial saliva and with the addition of sodium fluoride was studied using electrochemical impedance spectroscopy and potentiodynamic measurements. The extent of the passive range significantly increased comparing duplex stainless steel 2205 and AISI 316L stainless steel in both solutions. The passive layers were studied by X-ray photoelectron spectroscopy, and their compositions were analysed as a function of depth. The passive films were formed at open-circuit potential for 168 hours. The passive layers on the surface of both materials predominantly contained Cr-oxides, whereas Fe-species were markedly depleted compared to the bulk concentration. The alloying elements improve the corrosion resistance of duplex stainless steels; however, their content within the passive layer was negligible.

Protection of bronze by an environment friendly corrosion inhibitor

Katarina Marušić, Helena Otmačić-Ćurković, Ema Stupnišek-Lisac

Faculty of Chemical Engineering and Technology, University of Zagreb, Croatia
Marulićev trg 19, 10 000 Zagreb, Croatia

Bronze is one of the oldest alloys. It has been used for a very long time for sculptures and for building structures such as roofs, facades, and gutters. Many copper roofs have lasted for centuries on castles and other monumental buildings. Because of the increasing air pollution all these artefacts are endangered by dissolving.

In this work we propose the use of 1-(*p*-tolyl)-4-methylimidazole (TMI), an innoxious imidazole compound, as a corrosion inhibitor for bronze.

1-(*p*-tolyl)-4-methylimidazole was investigated on the Cu-6Sn bronze. To gain a condition similar to the urban environment the electrochemical measurements were performed in a solution consisting of 0.2 g L^{-1} Na_2SO_4 + 0.2 g L^{-1} $NaHCO_3$ at pH 3 and 5, which simulate very strong and mild acid rain in urban environments. Corrosion studies were performed by potentiodynamic measurements and electrochemical impedance spectroscopy (EIS) to determine optimal concentrations of 1-(*p*-tolyl)-4-methylimidazole at both pH values. The results have shown that 1-(*p*-tolyl)-4-methylimidazole protects the bronze at both pH values.

The adsorptive behaviour of TMI in the sulphate / carbonate solution may be approximated by the Langmuir type isotherm at pH 3 and by the Freundlich type isotherm at pH 5. The free energy of adsorption of bronze at pH 3 was found to be - 11.3 kJ/mol and at pH 5 it is - 21.3 kJ/mol. This indicates that the inhibitor adsorbs to the surface by physisorbtion at both pH values.

Corrosion inhibitors for bronze protection in polluted atmosphere

Amela Keserović[1], Helena Otmačić Ćurković[2], Ema Stupnišek-Lisac[2], Katarina Marušić[2] , Alla Furman[3], Margarita Kharshan[3]

[1] GlaxoSmithKline Research Center, Zagreb, Croatia
[2] Faculty of Chemical Engineering and Technology, University of Zagreb, Croatia
[3] Cortec Corporation, St.Paul, MN, USA

The aim of this work was to investigate the possibility of bronze protection in atmospheric conditions by three protective systems. Two of them were based on environmentally friendly corrosion inhibitors: 4-methyl-1-(*p*-tolyl)imidazole, and a vapor phase corrosion inhibitor. The third protection method was the use of water-based acrylic primer containing the mixture of non-toxic corrosion inhibitors.

The research was carried out in the solution of 0.2 g dm^{-3} $NaNO_3$, 0.2 g dm^{-3} Na_2SO_4 and 0.2 g dm^{-3} $NaHCO_3$ at pH 3. This electrolyte simulated the composition of acid rain characteristic for polluted urban environment. Measurements were performed by the means of electrochemical methods - Tafel extrapolation method, linear polarization method and electrochemical impedance spectroscopy. Stability of applied protection was also tested in humidity chamber at two temperatures.

Results of the investigation showed that each of applied corrosion inhibitors provided protection to bronze in the tested conditions. However the maximum inhibiting efficiency of 4-methyl-1-(*p*-tolyl)imidazole was about 68%, that of vapour phase inhibitor about 98% while acrylic coating containing corrosion inhibitor had an efficiency of almost 100% .

The inhibition effects of some Schiff bases as corrosion inhibitors of aluminium in HCl

Aylin Aytaç [a], Semra Bilgiç [b], Nilgün Ancın [c], Gül Öztaş [c]

[a]Department of Physical Chemistry, Gazi University, Ankara,Turkey
[b]Department of Physical Chemistry, Ankara University, Ankara,Turkey
[c]Department of Inorganic Chemistry, Ankara University, Ankara,Turkey

Aluminium and its alloys are extensively used in various industries such as pipes, machinery, batteries and particularly aircraft industry. Due to their importance, several investigations focus on the corrosion of aluminum and its alloys. On the other hand, hydrochloric acid is used for pickling, chemical and electrochemical etching of aluminum. Therefore, to reduce the corrosion rate of these materials in HCl solutions several organic compounds are used as inhibitors. Recently, Schiff bases are chosen as corrosion inhibitors of aluminium and its alloys in such media.

In this study, the inhibition effects of the new synthesized two tridentate Schiff bases, namely, N-(3-hydroxypyridine-2-yl)-salicylideneimine (S1) and N-(3-hydroxypiridine-2-yl)-3,5-dichlorosalicylideneimine (S2) have been investigated in 0.5 M HCl for aluminium, respectively. The corrosion experiments were performed in three compartment cell. Working electrode is aluminium which has a surface area of 1.33 cm^2 and purity of 99.99%. As reference electrode Ag/AgCl and as counter electrode Pt wire were used. Bidistilled water was used to prepare the solutions. Corrosion current densities have been determined by Tafel polarisation and impedance spectroscopy methods. Tafel plots have been obtianed with a scan rate of 1 mV s^{-1}. In order to obtain Nyquist impedance curves, electrochemical impedance measurements were carried over the frequency range from 20 kHz to 50 mHz at open circuit potential.

The inhibition efficiency of S1 at the 2.5 x 10^{-4} M and 1 x 10-^{3} M concentrations in 0.5 M HCl, is found to be lower than that of S2 in the same concentrations. Furthermore, In the range of 2.5 x 10^{-4} and 5 x 10^{-3} M concentrations, it has been found that the corrosion current densties decrease with decreasing concentrations of S2. In other words, there is an increase in the inhibition efficiencies in terms of the decrease of S2 concentrations.

CORROSION PERFORMANCE OF THE N_2-H_2 RADIOFREQUENCY COLD PLASMA NITRIDED CARBON STEEL: AC IMPEDANCE AND XPS STUDIES

Michel TRAISNEL[1], **Fatima Zahra BOUANIS**[1], **Charafeddine JAMA**[1],
Fouad BENTISS[2]

[1]Laboratoire Procédés d'élaboration de revêtements fonctionnels (PERF), France,
michel.traisnel@ensc-lille.fr, fatima.bouanis@pop.ensc-lille.fr,
charafeddine.jama@ensc-lille.fr,
[2]Laboratoire de Chimie de Coordination et d'Analytique, Morocco,
fbentiss@enscl.fr

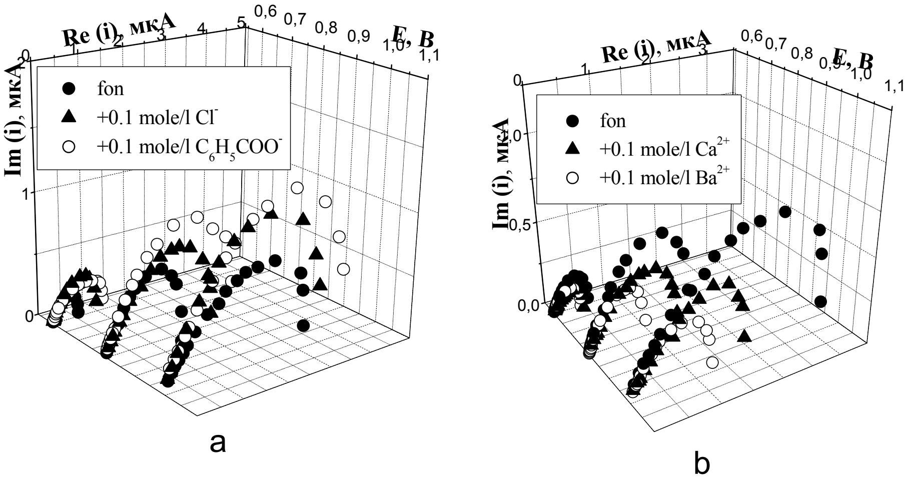
Plasma nitriding is one of the widely used surface modification plasma process. The properties of the plasma nitrided surface can be influenced by process factors such as time, temperature, chemical composition of the treatment gas, working pressure, electrical power and the geometry of the chamber. The purpose of this work is to contribute towards understanding the effect of hydrogen addition to nitrogen in radiofrequency (RF) cold plasma on the corrosion resistance performance of C38 carbon steel nitrided substrates.

C38 carbon steel have been plasma-nitrided using a radiofrequency cold plasma discharge treatment in order to investigate the influence of gas composition on corrosion behaviour of nitrided substrates. The investigated C38 steel was nitrided by a RF plasma discharge treatment using two different gas mixtures (75% N_2/25% H_2 and 25% N_2/75% H_2) at different times of plasma-treatment on non-heated substrates. Electron Probe Microanalysis (EPMA) showed that the nitrided layer formed using 75% N_2/25% H_2 gas mixture was thicker compared to those formed in the case of 25% N_2/75% H_2 or pure N_2. The modifications of the corrosion resistance characteristics of plasma-nitrided C38 steel in 1 M HCl solution were investigated by weight loss measurements and ac impedance technique. The results obtained from these two evaluation methods were in good agreement. It was shown that the nitriding treatment in both cases (75% N_2/25% H_2 and 25% N_2/75% H_2) improves the corrosion resistance of investigated carbon steel, while the better performance is obtained for the 75% N_2/25% H_2 gas mixture and attains 98.5 % for 8h of plasma-nitriding. X-ray photoelectron spectroscopy (XPS) was carried out before and after immersion in corrosive medium in order to establish the mechanism of corrosion inhibition using N_2/H_2 cold plasma nitriding process.

Complex ions treatment of water supplies systems revealed cost efficient approach to rust removal

Zabenkina E.O.[1], Baryshnikova E.A.[1], Rusakova S.M. [1], Artamonova I.V. [1], Batrakov V.V. [2]
1 Moscow State Technical University (MSTU), Russia
2 Moscow State Pedagogic University, Russia
zabenkinno@list.ru

Rust removal from the industrial water supply systems is the major problem of their maintenance. As a consequence of rust accumulation, water mineralization decreases thereby leading to the expedited deterioration and energetic burdening of the system. We assume that the photoprocesses, which take place in the inert films on the iron surface, might have an implication for the development of antirust means. Particularly, the effects of additives on the kinetics of iron dissolving have never been investigated. Following this thought, we studied the absorption of (1) surface-active ions (Ba^{2+}, Ca^{2+}, Cl^- и $C_6H_5COO^-$) on anode-oxidized iron electrode at neutral pH and (2) the complex ion oxyethylen diphosphoric acid (OEDP) on powdered magnetite Fe_3O_4 in sulphuric acid. The iron electrode was covered with hydrated oxide γ-Fe_2O_3. For the first time Intensity Modulated Photocurrent Spectroscopy (IMPS) has been applied to monitor ion absorption on passivated iron surface. The main advantage of IMPS is that it enables detection when the film capacitivity is much smaller than capacitivity of DES. Anions absorption was found to increase the photocurrent while kations absorption rather decreased one (Fig.1).



a

b

Fig.1. Frequency Spectra of Photocurrent running through the possivated iron electrode in 0.5 M $NaNO_3$ in the presence 0.1 M concentrations of anions (a) and kations (b) at and pH 6.9. Voltages were set at 0.6, 0.8 and 1.0 V (relatively to the saturated AgCl electrode).

Using the modeling of magnetite dilution, the favorable conditions for scale removal were established. Accordingly, the effective antirust treatment relevant for industrial application was 0.1-0.3 M OEDP solution in the presence of 0.01 M FeH_2Y at pH1.5-2.5 and T 363 K.

In addition, the ions absorption on the scale was qualitatively assessed revealing its moderate antirust activity. At last, OEDP was shown to be a descaling agent with minimal impact on the intact iron.

Influence Of Alkamine Cyclic And Acyclic Derivatives Chemical Structure On Their Corrosion Inhibition Properties

Kovalyuk E.N., Angarsk State Technical Academy, 665835 Russia, Angarsk, Chaikovskiy str., 60.
Kuharev B.F., Irkutsk Favorsky Chemistry Institute of 664033 Russia, Irkutsk, Favorskiy str.,1.
Negoda A.J., Angarsk State Technical Academy, 665835 Russia, Angarsk, Chaikovskiy str., 60.
Matvienko M.A. Angarsk State Technical Academy, 665835 Russia, Angarsk, Chaikovskiy str., 60.

The significant part of industrial inhibitors is nitrogenous organic compounds. The balance between efficiency and structure of inhibitors is a subject of the numerous scientific researches now. These theoretical works will allow to forecast availability of inhibitive properties of groups of compounds and individual substances, and also to reduce expenses for syntheses and testing of unefficient inhibitors.

We have researched anticorrosion properties of vinyl ethers of alcohol amines, imidazolidines, oxazolidines, azines, 2-pyrazolines and N-N- acetales, containing pyrazoline fragment. All compounds were received and identified at Irkutsk Chemistry Institute of CA Russian Academy of Sciences.

The “Technology of Electrochemical Industry department” of Angarsk State Technical Academy have estimated the defensive effect of inhibitors. The defensive effect was calculated through corrosion gravimetric factor, received in accordance to All-Union standard (GOST) 9.505-86 in 20% chlorohydric acid at inhibitor concentration of 0,01 moths/l. Test was carried out on platelike specimen (Steel 20), at the temperature 20 ^{o}C and at free ventilation of solutions.

For determination of physicochemical properties of the inhibitors’ molecules, the MORAS program for quantum-chemical analysis (the MNDO method) was used.
It was determined that the defensive action of nitrogenous organic compounds increases with increase of electronic density on nitrogen atom.

The defensive effect of azines of acetone and methyl-ethyl ketone is not more than 36%. Pirazolines (derivants of acetone azine) are more active than derivants of azine of methyl-ethyl ketone. The defensive effect of these groups of compounds is 15-79%, depending on structure. The separate representatives of vinyl ethers of alcohol amines protect steel for 90%.

We determined, that injection of aromatic substituents into molecule of imidazolidine, can slightly reduce the corrosion-preventing activity. The maximal defensive effect among researched compounds have oxazolidines and N-N- acetales (up to 89-95%).

Thereby, further inquiry of oxazolidines and N-N- acetales as inhibitors of steel corrosion in acidic medium is highly perspective.

Corrosion performance of alloy 625 exposed in $ZnCl_2$-KCl mixtures at 250 and 350ºC

*C. Cuevas Arteaga, A. Alfantazi
Department of Materials Engineering, Faculty of Applied Science, University of British Columbia, 6350 Stores road, V6T 1Z4, Vancouver, B.C., Canada.

This work presents the evaluation of the corrosion behavior of the Ni-based alloy 625 exposed in three different compositions of zinc chloride and potassium chloride, $52ZnCl_2$-48KCl, $70ZnCl_2$-30KCl, and $30ZnCl_2$-70KCl (wt. %) at 250 and 350ºC. In this study, potentiodynamic polarization (PC), electrochemical current noise (ECN), and electrochemical impedance spectroscopy (EIS) were applied. From PC, the corrosion mechanisms were obtained together with key parameters such as corrosion potential, corrosion current density and Tafel slopes. The qualitative behavior of the pattern current noise time records and the localization index were determined based on the ECN. From EIS, the Nyquist, Bode and Phase plots were obtained. This technique could provide qualitative and quantitative information on corrosion phenomenon. From the Nyquist plots, it was possible to determine the values of the solution resistance (Rs), and the charge transfer resistance (Rct), parameters that could be also determined from the Bode plots. In addition, from the Nyquist plot, information about the controlled corrosion process could be obtained, observing that this plots presented an unfinished semi-circle followed by a straight line, which indicates that the corrosion process of studied systems was in general a mixed controlled corrosion process.

Corrosion inhibitors containing imidazolin for the protection of gas and oilfield equipment

*Frolov V.I., Gubkin Russian State University of Oil and Gas, Moscow, Russia,
Ivanov E.S., Egorov V.V.Society with limited liability «Technochim», Kolomna, Russia*

The majority of industrial corrosion ingibitors, applied to protection of the gas and oilfield equipment, which is in contact with aggressive high mineralized water containing hydrogen sulphide, are the nitrogen containing surface-active substances of amphiphilic structure. They are capable to be strongly adsorbed on a metal surface and to form strong protective layers. On technology of synthesis, anticorrosive efficiency and industrial availability a wide circulation for protection of gas and oilfield equipment ingibitors containing imidazoline have received.

The data on research of anticorrosive efficiency of imidazoline-2 derivatives (a trade mark is “Olazol”), containing various functional groups (double bonds, primary, secondary and tertiary amino groups, oxy-. imino-, carboxy-, cyanogroups) in various aggressive environments (highly mineralized water at presence and absence of hydrogen sulphide) are presented.

The data on research of anticorrosive synergism of imidazolines and amidoamines mixtures, with the data on their polarity, basicity, a superficial tension and their colloidal chemical state in water is cited also.

It is established that addition amidoamines to imidazoline-2 leads to sinergetic effect of anticorrosive action in the environment of NACE in the hydrogen sulphide presense. The maximum effect is reached at the amidoamine concentration of 10 % of weights. It is shown that inhibitors containing imidazoline suppress sulfate reducing bacteria (SRB), actively reducing hydrogen sulphide. On an example of Open Company «Lukoil-Komi» oilfields, where waters are highly aggressive (H_2S 20-83 mg/dm^3, SRB 10^5 cell/ml with an index of activity 33-50), the general speed of corrosion in system of pressure maintenance is 4,86 mm/year, local to 18 mm/year. Protection with «Olazol» inhibitor reduces corrosion speed to 0,1-0,4 mm/year.

New low-alloyed steels corrosion firmness in the aggressive environment modelled water of Usinsk oilfield and «Olazol» inhibitors influence on their ability to suppress corrosion is studied. It is shown that «Olazol» inhibitor effectively suppresses both the general and local corrosion of these steels, reducing it to the minimum values of an order 0,01-0,015 g/m^2·h.

MILD STEEL CORROSION IN CHLORIDE ENVIRONMENT: EFFECT OF SURFACE PREPARATION AND INFLUENCE OF INORGANIC INHIBITORS

F. ATMANI[1.2], M. POELMAN[3], D. LAHEM[3], C. BUESS-HERMAN[2], M. OLIVIER[1]

[1] Université de Mons (UMONS), Service de Science des Matériaux, 20, Place du Parc, 7000 Mons, Belgium, fouad.atmani@umons.ac.be
[2] Université Libre de Bruxelles, Service de Chimie analytique et Chimie des Interfaces, Bd. du Triomphe, 1050 Bruxelles, Belgium
[3] Materia Nova ASBL, Rue de l'Epargne 56, 7000 Mons, Belgium,

Abstract:

Mild steel is the most worldwide used material for industrial and domestic applications. One of the most common protection methods for steel is provided by metal coating with zinc. The zinc coating gives a galvanic protection to steel in damaged areas of the coating. However, the use of zinc has some drawbacks: the zinc price and its availability. Moreover recycling galvanized materials have a high cost and may cause environmental problems. For these reasons, other alternatives must be considered to protect steel. Self healing coating is one solution considered to protect mild steel against corrosion. The protection of mild steel may be assured by a barrier layer containing corrosion inhibitors to provide self-healing if mechanical or chemical damage occurs.

The aim of the present work is to study the effect of surface substrate preparation on its electrochemical behavior in chloride solution. Various surface preparations are studied: industrial alkaline degreasing with Ridoline® C72, acid pickling and mechanical preparation (polishing). Open circuit potential measurements and potentiodynamic polarizations are used as corrosion monitoring techniques. The electrochemical-AFM is used to investigate the interaction of corrosion inhibitors with mild steel. The effect of chloride concentration is evaluated.

The ability of inorganic inhibitors (Na_2MoO_4, $NaNO_2$, Na_2WO_4, Na_2VO_3, $Ce(NO_3)_3$) to stabilize the passive state of steel in chloride-containing solutions is studied by electrochemical and surface analysis techniques.

Keywords:
Mild steel, substrate preparation, inorganic inhibitor, chloride environment NaCl.

An investigation on corrosion behaviors of two types of commercial stainless steels after plastic deformation

E. Jafari, Islamic Azad University, Shiraz/IR

ABSTRACT

The influence of plastic deformation on corrosion resistance of two types of stainless steels sink was studied. A tensile machine was employed to give plastic deformation at room and elevated temperatures. Degrees of plastic deformation were given by deep drawing tests at various strain rates. The effect of plastic deformation on the steels were analyzed by X-ray diffraction tests, electrochemical tests (potentiostatic and cyclic polarization works), and optical metallography and scanning electron microscopy. Results show that chromium, nickel and copper have a significant effect on the corrosion resistance of the steels after plastic deformation. It was observed that the corrosion resistance after plastic deformation is a function of deformation temperature, strain rate and alloying elements.

SOME THEORETICAL CALCULATIONS ABOUT THE CHELATING ABILITY OF AN IMINO COMPOUND TOWARD SOME METAL IONS AS ANTICORROSION MATERIALS

Iran Sheikh Shoei, Ozra Farsi, Batool Sheykhshoaiee

Chemistry Department, Shahid Bahonar University of Kerman, Iran
E-mail: ishoaie@gmail.com

In recent years, different trapped organic compounds on a variety of solid matrix have been successfully used for preconcentration and separation of trace metal ions. Schiff bases derived from the condensation between of aldehyde and amine is an important class of coordination ligands with a high absorption capacity in the presence of trace metal ions. Chelating agents with moderate coordination sites like nitrogen in C=N group. In this work we have been calculated some structural parameters for some symmetrical tetra dentate Schiff bases ligands with N_2O_2-coordination sites. All calculations have been done by AM1, PM3 and MNDO quantum chemical methods by using Hyperchem 7.0 and ADF program packages.

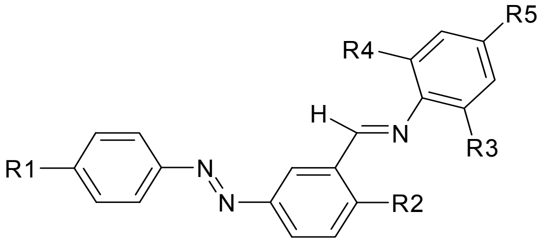


Fig. **1**

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Some Quantum Mechanical Study on the Molecular Structural Properties of a Group of Symmetric Imino Compounds with Tetra Donor Set Atoms Az Anti-Corrosion Compound

Iran Sheikhshoaie
Chemistry Departmen, Shahid Bahonar University of Kerman, PO. Box: 76177-133, Kerman, Iran

Abstract

Quantum chemical studies on corrosion inhibitors are usually chosen for use in an environment of interest from empirical considerations based on macroscopic physico-chemical properties. The inhibitors, found to act as electron donors to the metal atoms, block the corrosion reaction by the formation of a bond. The HOMO energies obtained were correlated with the inhibition efficiency of the inhibitors. In this work the linear combination of atomic orbitals (LCAO) self-consistent field (SCF) molecular orbital (MO) semi-empirical method was used to study for some imino compounds. The HOMO energies obtained were correlated with the inhibition efficiency of the inhibitors. The data show that the corrosion inhibition is high when the molecule is planar and has a high energy value for HOMO. Theoretical study were shown, that the relation between the inhibition efficiency, the net charges on hetero atoms and the HOMO-LUMO gap energy have an important role in the inhibition factor for these imino compounds.

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Corrosion by Hot Gases and Combustion Products

Investigation of hot corrosion resistance of plasma sprayed YSZ-Ceria TBC in Na_2So_4+V_2O_5 at 1050 °C

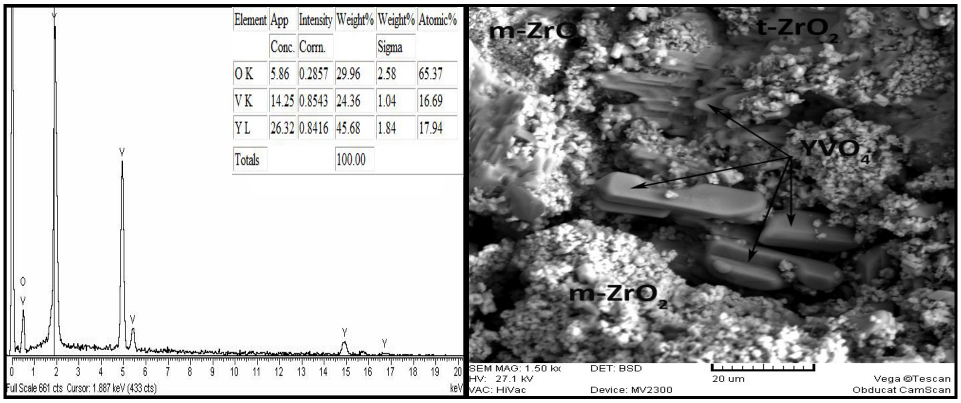
M.Saremi[1], M.H. Habibi[2]

Corrosion Laboratory, School of Metallurgy engineering and materials, University of Tehran, North Kargar, Tehran, Iran, P.O. Box: 11155-4563

Abstract

Thermal Barrier Coatings are used in the hot section of gas turbine engines in order to increase operation temperature with better efficiency. The TBCs are consisted of a MCrAlY band coat (M=Ni,Co) over the super alloy substrate that can provide oxidation resistant layer and yttria-stabilized zirconia (YSZ). Low quality fuels usually include impurities such as S and V. The salts of these elements (Na_2SO_4, V_2O_5) react with yttria to form YVO_4, which depletes the Y_2O_3 stabilizer from ZrO_2 matrix. As a result, transformation of tetragonal and cubic zirconia to monoclinic phase occurs upon cooling. In this research, the hot corrosion behavior of three types of coatings was investigated: (1) Normal YSZ, (2) YSZ+CeO_2 (the composite layer of Ceria and YSZ), (3) CeO_2/YSZ (The over layer of Ceria on YSZ). Hot corrosion tests were carried out on the surface of the coatings in molten salt (Na_2SO_4 + V_2O_5) at 1050 °C for 36 hours. The microstructure, morphology and chemical composition of the surface and the cross-section of the coatings were examined by scanning electron microscopy (SEM) equipped with energy dispersive spectrometer (EDS). X-ray diffraction (XRD) was used to determine the crystalline structure of the coatings and hot corrosion products. With regards to microscopic observations (YVO_4 crystals (Fig. 1) formation and YSZ spallation) and amount of phase transformations (Tetragonal ZrO_2 to monoclinic ZrO_2), YSZ/CeO_2 provides the best hot corrosion resistance and usual YSZ provides the least among three coatings.

Keywords: Hot corrosion; TBC; yttria stabilized zirconia(YSZ) ; Cerium Oxide (CeO_2)



Element	App	Intensity	Weight%	Weight%	Atomic%
	Conc.	Corrn.		Sigma	
O K	5.86	0.2857	29.96	2.58	65.37
V K	14.25	0.8543	24.36	1.04	16.69
Y L	26.32	0.8416	45.68	1.84	17.94
Totals			100.00		

Fig. 1-SEM image from the surface of normal YSZ TBC after Hot corrosion and EDS Analysis from Rod crystals on image.

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[1] saremi@ut.ac.ir

[2] hamedhabibi@ut.ac.ir

Oxidation and Hot Corrosion Properties of Composite Al_2O_3-YSZ Thermal Barrier Coatings

M.Saremi,A.Keyvani, A, Afrasiabi and M.Kazemi

Faculty of Metallurgy and Materials Engineering, University of Tehran, Tehran, Iran,
E-mail: saremi@ut.ac.ir

Thermal barrier coatings, based on stabilised zirconia (YSZ), have been used to reduce the thermal effect on the components of combustion chamber and to increase the efficiency of gas turbines. However hot gases on the combustion chambers components. However, the durability of the YSZ is affected by many parameters including oxidation and hot corrosion coming from the corrosive hot gases which results destabilisation and separation (spallation) of the coating.

Alumina was added to the YSZ in three different ways as follows:

1-Sprayed as a top coat on YSZ(Al_2O_3/YSZ)

2-Alumina particles mixed with YSZ particles and plasma sprayed over the bond coat.

3-Sparyed on the bond coat as an interface between bond coat and YSZ(YSZ/Al_2O_3).

Fig. 1 shows the microstructure of the three composite coatings. The coatings were subjected to cyclic oxidation at 1050 C and hot corrosion at 1050C in a fused salt mixture of Na_2So_4 and V_2O_5.

The results showed that normal YSZ was degraded and finally spelled off the surface due to destabilisation and formation of a thick thermally grown oxide in the bond coat-YSZ interface. It is also shown that destabilisation came as a result of the formation of YVO_4 crystaline compound as a by-product of the reaction between V_2O_5 and yttrium of the YSZ causing its phase transformation and destabilisation. While the presence of alumina layer as a top layer over YSZ prevented the infiltration of oxygen and corrosive salts toward YSZ and bond coat and consequently more stable YSZ.

The mixture of alumina-YSZ was also beneficial while presence of alumina layer over the bond coat was not helpful.

It is concluded that the presence of a thin alumina layer over YSZ can improve the stabilisation of the YSZ by infiltration of oxygen and corrosive compounds.

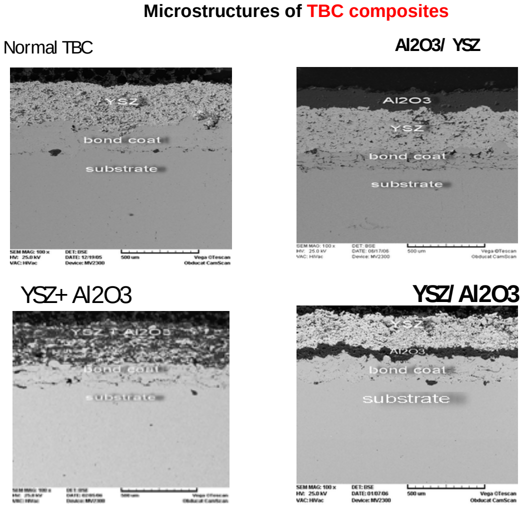

Fig.1 Microstructures of normal and composite Al_2O_3-YSZ coatings

Functional and structural particularities of diffusion barriers in high-temperature coatings for heat-resistant composite materials

Kasatkin A.V.**, **Andriushin S.G.
A.N. Frumkin Institute of Physical Chemistry and Electrochemistry of Russian Academy of Sciences, Moscow, Russia.

Some new investigations have been realized to create scientific basis of functionally gradient antioxidizing protection of structural elements of high-temperature equipment heat-loaded by high-velocity high-enthalpy gas flows. Two groups of functionally gradient materials have been investigated: I – based on solid solutions of metals of IVa group (like Mo-Zr) modified by silicon and (or) boron; II – compositions based on boride-silicide mixtures ($TiSi_2$-TiB_2/ZrB_2; $MoSi_2$-ZrB_2/$TiSi_2$ etc.). For the I group of materials some perspectives of using of heat-resistant FGM and heat-resistant coatings' components on the basis of refractory alloys and C-C-compositions have been investigated. The compositions of the II group have been tested for using as the principal component of multilayer heat-resistant coatings for all-carbon and other composites subjected to high-temperature oxidation (HTO). A problem of definition of forming principles of heat-resistant during HTO materials by self-organization of surface oxide compositions including refractory oxide (Al_2O_3, ZrO_2, SiO_2) and comparatively plastic component like the fusible oxide or compound oxide and oxinitride mixture has been formulated. The parameters of chemical balance in MeI-MeII-(Si;B); MeI-MeII-(Si;B)-(O;N); C-Me-(Si;B)-O systems, where MeI – Mo, Ti, Nb; MeII – Ti, Zr, Al, and thermodynamics of phase transitions in these systems have been analyzed. Based on these results the most perspective FGM to use as high-temperature protection have been found and the technologies of its' forming have been proposed and tested. The metallization, siliconizing, boronizing, phase and structure forming of FGM kinetics, physical and chemical mechanisms have been investigated, such as the mechanisms of HTO in different conditions for each FGM group. The oxiding when the temperature is between 900 and 1800^{o}C the FGM based on solid solutions Zr-Mo (I group) has proved that these compounds have good perspective as heat-resistant coatings for refractory alloys under the temperature 1300-1800^o C. In this situation the heat-resistant protection is realized by forming of the compound oxide film based on ZrO_2-SiO_2 composition modified by boron and yttrium oxide inclusions. These compounds are ineffective to protect carbon-based FGM and when the temperature is below 1100^{o}C.

Al-Si CVD-FBR PROTECTIVE COATINGS FOR STEAM CORROSION APPLICATIONS

S. Mato, P. Hernández, M.P. Hierro, H. Santos and F.J. Pérez

*****Grupo de Investigación de Ingeniería de Superficies - Dpto Ciencia de los Materiales, Universidad Complutense Madrid, Avenida Complutense s/n, Facultad de Ciencia Químicas, 28040 Madrid, Spain

Abstract

Ferritic steels are usually used in boiler or supercritical steam turbines which operate at temperatures between 600-650ºC under pressure. Protective coatings are often applied in order to increase their oxidation resistance and protect them against degradation. In this study new Al-Si protective coatings were deposited by CVD-FBR on P92 ferritic steel. The initial process parameters were optimized by thermodynamic calculations using Thermo-Calc software. Then, those parameters were used in the experimental procedure to obtain Al-Si coatings at low temperature and atmospheric pressure. Co-deposition was achieved at moderate temperatures in order to maintain the substrates` mechanical properties. The coatings` microstructure and phase constitution was characterized. Fe-Al intermetallic coatings containing Cr and Si were obtained. The phase constitution is discussed with reference to the Fe-Al-Si ternary phase diagram. The effect of diffusion heat treatment on the phase transformations as well as the steam oxidation resistance of these coatings at 650ºC and 800ºC was investigated.

Keywords : Thermocacl simulation, Al-Mn coating, CVD-FBR, steam oxidation

Hot corrosion of new HIPIMS nanostructured coatings on gamma-TiAl

I. Lasanta, M. Tejero, A. Rey, A. Fernandez S. Mato, M.P. Hierro, J. Nieto and F.J. Pérez
Grupo de Investigación de Ingeniería de Superficies. Universidad Complutense de Madrid. Departamento de Ciencia de los Materiales. Facultad de Ciencias Químicas. 28040 Madrid. Spain

ABSTRACT

Molten sulphates are formed in most of the energy production devices, such as gas turbines. There are different attemps in the use of electrochemical techniques in this environments, but the corrosion of the testing samples do not allow to go more than hours of corrosion testing. Based in this problems, and tanking into account the new development of micro and nano-structured coatings for high temperature applications under INNOVATIAL EU project, a new kind of testing sensors with the nano-structured coatings have been develop to monitor their corrosion process in real time. It will allow to know different corrosion mechanism in real time and the expected behaviour in the steady state. Electrochemical impedance spectroscopy is the base analysis for this systems, and the development of reference equivalent circuits for the interpretation of results will be explained in detail. Another aspects of the corrosion mechanism (effect of protective spinels) will be discusses for further materials design. Based on the monitoring results a new oxidation mechanism will be shown. The results will provide a general overview of the oxidation behaviour of each coating and also a semi-quantitative comparative analysis in real time for different nano-structured coatings on γ-TiAl. Some of the coatings developed in this project have shown an excellent result, comparing with some traditional protective systems. Comparative results will be shown

Effectivity of new heat-proof silicide coatings protecting heat-proof carbon composite materials from high-temperature gas corrosion and erosion

Terentieva V.S.*[*], *Kasatkin A.V.*[**], *Eremina A.I.*[*], *Astapov A.N.*[*]

[*] *Moscow Aviation Institute (MAI), Moscow, Russia.*

[**] *Physical Chemistry and Electro-Chemistry Institute, Russian Academy of Sciences, Moscow, Russia.*

Heat-proof carbon-based composite materials (C–C, C–SiC, SiC–SiC) having high strength-to-weight ratios are widely used in high-temperature machinery, especially in heat-loaded structure elements of hypersonic flight vehicles. However carbon composites subjected to oxygen-containing high-temperature gas flow impact have low corrosion and erosion strength and can be modified by siliconizing only up to 1800-1900 K, so that the protection problem is now actual and cannot be solved completely, primary in space vehicles design. An aero capturing hypersonic flight vehicle is subjected simultaneously to aggressive plasma flow, limit heat and mechanical loads. An ambient air in the wave front is almost completely dissociated and the vehicle is by chemically active oxygen and nitrogen atoms, ions and excited particles mixture streamlined. Flow and surface temperatures during capturing are extremely high and reduce to the intensive gas corrosion and erosion, thus it is quite essential to use both volume protection by siliconizing and surface heat- and erosion-proof protection. Here some multifunctional protective coatings designed in MAI using a new self-healing heterophasic protection's conception are considered, particularly the most investigated MAI D5 Si-Ti-Mo-B-Y coating and its repair modification. The presented MAI D5 coating is the microscopic composite material with refractory disilicides' dendritic pattern and the cells filled by cilicon-containing eutectics. This structure provides the random volume and surface defects' self-healing under high-temperature thermal load; especially eutectics presence into structure provides quick forming and restoration of the consumable during coatings operation extra-thin protective amorphic silica layer. MAI D5 coating is a thin-layer one forming at one stage out of powder Si-Ti-Mo-B-Y micro-composition material under high-temperature processing, during operation or high-temperature stand testing in oxygen-containing medias with self-organized multilayer of functional micro-, sub-micro- or nanoscopic layers. In the paper some experimental methods and complex investigations results of MAI D5-coated carbon composite specimens in VAT-104 and VTS TsAGI wind tunnels are presented. The MAI D5 coating secure low surface catalytic activity values (heterogeneous recombination speed of nitrogen and oxygen atoms is K_w = 3-5 m/s) and satisfactory emittance value ($\varepsilon \approx 0.7$-0.8). All specimens have stand the test modeling hypersonic vehicle aero capturing with surface temperature up to 2100 K and simultaneous hypersonic dissociated air flow and mechanical tensile stresses up to 80-90 MPa with surface temperature up to 1800-1900 K. Multi-parametrical tests of MAI D5-coated specimens in the temperature domain 300-2100 K have shown that the presented coating protects effectively carbon composites in the indicated above temperature domain with admissible mass carry-over for considered structural elements' classes.

The presented investigation was supported by RFBR (Project No 08-01-13507 ofi_c).

Protection of simple cast cobalt-based alloys by pack-cementation Cr-deposit and study of their behaviour in high temperature oxidation

Grégory Michel, Patrice Berthod, Michel Vilasi and Pierre Steinmetz
Institut Jean Lamour (UMR CNRS 7198), department CP2S, team "Surface and interface, chemical reactivity of materials", Faculty of Sciences and Techniques, University Henri Poincaré Nancy 1,
B.P. 70239, 54506 Vandoeuvre-lès-Nancy, France

Cobalt alloys are often less resistant against high temperature oxidation than nickel alloys. The resulting necessity for the formers to contain high amounts in chromium (e.g. 30wt.%) to sufficiently delay their catastrophic oxidation leads to increase fabrication costs and decrease solidus temperatures and then creep resistance. Fortunately it is possible for cobalt alloys, as currently done for other refractory alloys, to enrich their surface in chromium by chemical vapour deposition, notably with the pack-cementation process, even if this is not yet very frequent in the case of cobalt-based alloys. The aim of this work is to study the enrichment in Cr of the alloy's surfaces and the obtained improvement for their resistance against high temperature oxidation.

Results

Several cobalt-based alloys with low chromium contents (less than 20wt.%Cr), carbide-free binary alloys or carbides-containing ternary alloys were synthesized by high frequency induction melting in inert atmosphere, then covered by chromium deposition using the pack-cementation technique. The coating adhesion and inward diffusion of chromium were realized by applying a heat treatment for different durations, and the coated samples were thereafter subjected to high temperature oxidation.

The initial microstructures of the alloys, the coated samples and the coated-then-treated samples were metallographically characterized. Thermogravimetry curves recorded during the oxidation tests were compared to the ones of the same alloys but without any coating, as well as to the same type of alloys but with 30wt.%Cr.

Conclusions

As observed for the low-Cr uncoated alloys, the impoverishment in chromium logically induced a severe decrease in resistance against high temperature oxidation. But the surface enrichment in chromium conferred by the pack-cementation treatment followed by the diffusion heat treatment, the temperatures and durations of which influence the Cr-content on surface and the depth of Cr-enrichment, significantly improved the behaviour in oxidation at high temperature.

Behaviour in high temperature oxidation of chromium-rich cobalt alloys reinforced by different types of MC carbides

Patrice Berthod, Grégory Michel and Lionel Aranda
Institut Jean Lamour (UMR CNRS 7198), department CP2S, team "Surface and interface, chemical reactivity of materials", Faculty of Sciences and Techniques,
University Henri Poincaré Nancy 1,
B.P. 70239, 54506 Vandoeuvre-lès-Nancy, France

MC carbides are among the most stable hardening particles which may appear in an eutectic form with matrix in the interdendritic spaces of equiaxed chromia-forming alloys destined for high temperature applications. The most known is likely the tantalum carbide TaC but there are other MC carbides which can be candidates for the strengthening of such refractory alloys and superalloys. However, since their metal is generally very easy to oxidize, it is important to verify the resistance to oxidation at high temperature of alloys reinforced by such carbides.

Results

Several 30wt.%Cr-containing cobalt-based alloys with different contents in carbon and in MC-forming metallic elements (Ta, Nb, Hf, Zr) were elaborated under inert atmosphere by high frequency induction melting, metallographically characterized and tested in oxidation in hot air (T > 1000°C) for several tens hours, either in a simple resistive tubular furnace or in a thermo-balance with thermogravimetric measurements for the most oxidation-resistant alloys.

The alloys display a microstructure composed of a dendritic matrix (containing a part of the M element in some cases) and of eutectic script-like MC carbides mixed with matrix, which favour good interdendritic cohesion.

If the microstructures are quite similar for all the alloys, there are significant differences concerning their behaviour in high temperature oxidation: the TaC-reinforced alloys oxidized slowly, with a parabolic kinetic (Kp of about 30×10^{-12} g^2 cm^{-4} s^{-1} at 1200°C) and a rapid protection of the surface with a continuous chromia layer, while the oxide thickness and/or mass gain rates tend to be especially high.

Conclusions

The good behaviour in high temperature oxidation of TaC-reinforced cobalt alloys is not reproduced if tantalum is replaced by one of the other MC-forming elements tested in this work. The spinel oxides which rapidly grew on surface of these alloys clearly show that 30wt.%Cr is not sufficient to guaranty a long-term resistance against oxidation, and let think that they need to be enriched in chromium on surface, for example by a pack-cementation coating.

High temperature oxidation and intermetallic phase formation of galvanized steel sheet during austenitisation

Robert Autengruber, voestalpine Stahl Linz, Austria
Gerald Luckeneder, voestalpine Stahl Linz, Austria
Siegfried Kolnberger, voestalpine Stahl Linz, Austria
Josef Faderl, voestalpine Stahl Linz, Austria
Achim Walter Hassel, Johannes Kepler University Linz, Austria

In recent times ultra high strength steels (UHSS; Rm > 1400 MPa) with enhanced corrosion protection properties become more and more common in car bodies. Due to the lack of formability of these materials at ambient temperature, hot forming processes have to be implemented. By now it is possible to produce UHSS components with classical cathodic corrosion characteristics, starting from a galvanized steel sheet in a patented hot forming process.

The present work focuses on oxidation processes and reactions within the coating during this manufacturing process. For this purpose specimens of a hot-dip galvanized steel sheet, provided by voestalpine Stahl Linz, were heated up to 400, 450,…, 900°C without soaking and up to 900°C with soaking, and then quenched in water. All experiments were done with a radiation furnace and in ambient atmosphere.

The annealed samples were examined analytically with SEM, EDX, XRD and Auger spectroscopy as well as electrochemical methods and laboratory corrosion tests.

From these examinations, it was deduced that when the Zn coating melts iron-zinc phases are formed consistent with the Fe-Zn phase diagram. After annealing at 900°C for several minutes, zinc saturated α-iron with Γ-phase regions are formed. This created coating shows excellent corrosion protection according to the cathodic protection effect.

Zinc oxidation on the surface started at 600°C and becomes intensive at 900°C. The oxide scale consists of successively arranged wrinkled layers of Al_2O_3 and ZnO, containing some oxidised alloying elements.

Modified reactive elements additions and heat treatment procedures for obtaining higher emission coefficients of alumina surface layers on FeCrAl alloys

S.G. Gopalakrishnan, P. Huczkowski, L. Niewolak, R. Iskandar,*
D. Naumenko, J. Mayer, L. Singheiser, W.J. Quadakkers*

Research Centre Juelich, Institute of Energy Research (IEF-2), 52425 Juelich, Germany
**RWTH Aachen University, Central Facility for Electron Microscopy (GFE), 52074 Aachen, Germany*

Abstract

It is well known that the formation of thin, slow growing alpha alumina scale makes FeCrAl alloys an excellent material for high temperature applications (e.g. 900 – 1300 °C). One of the main applications of this alloy includes the ultra thin foil like heating elements. Despite the outstanding stability of the oxide scale, the life time of the component is limited by the rapid consumption of the aluminium reservoir from the bulk alloy. It could be possible to overcome this problem by modifying the alumina surface scales to obtain a high emission coefficient so that the heating element temperature can be decreased resulting in extended life times of the component.

By using a specific internal oxidation treatment, a new type of in-situ growing alumina base surface scale was achieved which leads to the increase in emission coefficient of the surface oxide scale. The internal oxide precipitates formed on the material act as template for the incorporation of particles and micropores in the growing alumina layer thus altering the emission coefficient.

Present investigations focus on the role of reactive elements (RE) in FeCrAlY model alloys. FeCrAlY alloys doped with different reactive elements (Zr, Hf) as well as variation in reactive element content were oxidized in air at various temperatures between 1050 and 1200 °C. Two different thicknesses of specimens were investigated at all the temperatures. In addition, a selected batch was studied in different atmospheres and two stage pre-oxidation exposures at different temperatures. The oxide scale characterizations were performed by optical microscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM), sputtered neutrals mass spectrometry (SNMS) and glow discharge optical emission spectroscopy (GDOES). Oxidation kinetics of the investigated materials were compared with the initial specimen thickness, scale composition and scale morphology.

CONCEPTION FOR THERMODYNAMICAL MODELING OF WASTE SYSTEMS IN THERMAL TREATING

Oleg Chizhko, Moscow environmental center, Institute for environmental high-technologies,
Post-Box 88, 369000 Cherkessk, Russian Federation
E-mails: Oleg.Chizhko@alumni.uni-karlsruhe.de, Chizhko.Olegg.@vdi.de

Mathematical modeling is the method of a theoretical research for complex actual problems of science and technology. In this aspect the empirical objects were investigated as abstracts, which could be transferred from the real experiment, but the theoretical ones as idealizations and the logical schemas of reality. Deducted from fundamental definitions the theories and their postulates were interpreted with help of the theoretical schemas, which were subordinated to the fundamental ones, but in an autonomic state [1]. After analyzing of these partial entities we evaluated the specifications and implanted them in the fundamental revelations.

In this work we paid an attention to the conserved models, which had no exterior influence and included not only the thermodynamic formalisms but also the kinetics of real processes. In the numerical algorithms we used the property of homogeneity for the program dimensions with aim to optimize the operational memory for computations. Inventions were made together with the natural investigations for metal rest species in the plant for the thermal treating of municipal solid waste and this fact gives us a possibility to converge the calculated dates with the TAMARA measures [2]. And the continuous comparison with experimental results allowed us to correct and to reconstruct the coefficients and parameters in the approximation terms, which at the same time were being fulfilled with a physical sense of routing events.

From the point of view of a correct task the single solution of a differential equation is necessary. The difference schemas should be stable and be continuously dependent on the start conditions. We understand an equilibrium state of the thermodynamic system as the finite element for the agglomerate of condensed phases or the mixture of pure gaseous substances. The gas is ideal and described with $pv = RT$. The solid state is approximated with the model of “huge molecules” [3]. In our calculations the co- existence both mobile species with solid particles is simulated.

The numerical investigations show that calcium has the more energetic efficiency than magnesium. But according to the existing racket fuel mixes, which are the most on the basis of Al and Mg, we refuse aluminum because of its less corrosion stability for the condensed phase of Al_2O_3 and choose MgO-CaO coatings. The conditions for the vaporization of calcium oxide, which is inherited from the waste species, we support during the dissipation of electric current in the form of Joul’s heat. After the treating we reach slag pellets with the plasma spraying thing film, which is used as the high temperature resisting cover for the hazardous substances during a contact with aggressive environments. This method of detoxification for thermal and water mobile essences is an alternative one and substitutes the 3-R ***glass***ification of bottom ash with SiO_2 at 2000 K [2].

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COORAL − Safety and Reliability of CCS using Screening Corrosion Tests

S. Simon, D. Bettge, S. Bohraus, A. Kranzmann
Federal Institute of Materials and Testing, Berlin, Germany

The increasing concentration of CO_2 in the Earth's atmosphere is one of the main factors for global warming and climate change. One third of the anthropogenic CO_2 emissions originate from fossil fuel combustion in power plants. The reduction of CO_2 emissions into the atmosphere is a major goal in limiting global warming. Technologies for efficient combustion of coal and subsequent CO_2 separation from the flue gas are under development. The separated CO_2 must be transported and stored into appropriate geologic formations such as saline aquifers. Before the technologies can be implemented, a number of technological, economic, environmental and safety issues are to be investigated.

The COORAL project (German acronym for "CO_2 purity for capture and storage") deals with the level of impurities in the CO_2 stream acceptable for carbon capture and storage (CCS). . The impurities will dominate the probability for corrosion failure within the CCS process chain. Therefore, the interactions between several steels and gas mixtures were evaluated using a factorial experimental design to limit the number of experiments. These experiments were performed using gas mixtures of different compositions and concentrations of CO_2 and the impurities H_2O, CO, SO_2, NO_2, and O_2 at three temperatures representative for the different steps in the process chain as there are separation, transport and injection. Carbon steels were used for transport conditions at 281 K and alloyed steels at 333 K and 443 K for injection and compression conditions, respectively. A screening test was developed to investigate the corrosion under atmospheric pressure. We present first results of a test series run to identify the most adequate materials for the different applications. These materials will be further investigated in long-term experiments.

Preliminary corrosion results from Vattenfall's 30 MW oxyfuel pilot plant

Anders Hjörnhede, Vattenfall Power Consultant, Goteborg, Sweden
Melanie Montgomery, Vattenfall Heat Nordic/DTU Mekanik, Lyngby, Denmark
Martin Bjurman, Vattenfall Research and Development, Avlkarleby, Sweden
Pamela Henderson, Vattenfall Research and Development, Stockholm, Sweden
Alexander Gerhardt, Vattenfall Research and Development, Berlin, Germany

Several material related issues may arise from oxyfuel combustion of coal due to the presence of CO_2 but also as an effect of the partial recirculation of the flue gas, which increases the sulphur levels. Such examples are increased corrosion and carburization in the boiler which may limit steam data and problems with low temperature corrosion in preheaters/economisers.

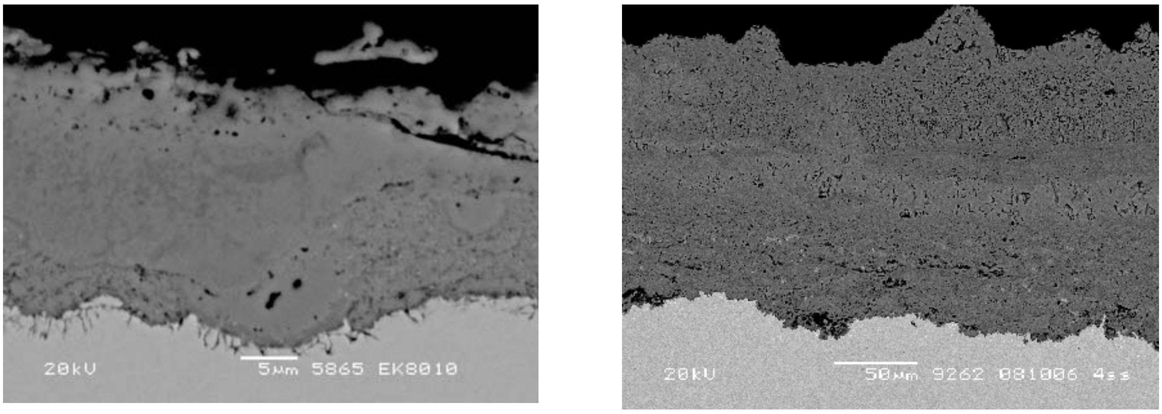
A number of corrosion tests, in both air-firing and oxyfuel mode, have been made in Vattenfall's 30 MW oxyfuel pilot plant located in Schwarze Pumpe, Germany, which runs on lignite. Internally cooled corrosion probes, equipped with ferritic, austenitic, super austenitic steels as well as Ni-based and FeCrAl alloys, simulating superheaters, economisers and "air" preheaters were exposed for up to 1600 hours. Flue gas analyses and deposit chemistry and growth rate analyses have also been made.

The analyses show an indication of higher material wastage for some alloys in oxyfuel compared to air combustion especially at low exposure temperatures. The differences in corrosion will be discussed with reference to the flue gas and deposit chemistry. The differences in corrosion resistance and microstructural stability between the different types of alloy will be discussed in terms of the ability of the alloys to form protective oxide layers.

Steam Oxidation of X20CrMoV121: Comparison of laboratory exposures and in situ exposure in power plants

M. Montgomery, DTU Mekanik/Vattenfall/Dong Energy, Lyngby, Denmark
A.N. Hansson, DONG Energy, Copenhagen, Denmark;
T. Vilhelmsen, Vattenfall Heat Nordic, Odense Denmark
S.A. Jensen, DONG Energy, Copenhagen, Denmark;

X20CrMoV121 is a 12% Cr martensitic steel which has been used in power plants in Europe. Many specimens have been removed from X20CrMoV121 superheater tubes: These tubes have been exposed for various durations from 5000 hours up to 135,000 hours at various power plants in Denmark at steam temperatures varying from 450°C-560°C. At the higher temperature region, thinner oxides have been observed. This paper will collate the data, compare oxide morphologies and assess to what extent a parabolic rate kinetic can be used to describe the oxidation rate.



a) Steam temperature 450°C:
Exposed at Avedøre 2 superheater 1 for 11 000 hours

b) Steam temperature 540°C:
Exposed at Amager 3, Superheater 4 for 135 000 hours.

Figure 1: Comparison pf the oxide morpholgy from specimens removed from two different plants.

A disadvantage with plant data is that oxide growth is also under the influence of temperature fluctuations during operation as well as thermal cycling due to start-up and shutdowns. Thus laboratory data can be used to understand the kinetics of oxidation at various temperatures. The steam oxidation behaviour has been investigated in the laboratory in an Ar-46%H_2O mixture at 500°C, 600°C and 700°C for 336 hours[1] and it was observed that the morphology of the oxide layers was strongly influenced by temperature. This paper will seek to compare the plant data with the laboratory data both with respect to oxide morphology and parabolic rate constants.

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STEAM CORROSION STUDIES OF FE-AL BASED ALLOYS

Dirk VOGEL, Martin PALM, Frank Uwe RENNER

Max-Planck-Institut f. Eisenforschung, Germany, renner@mpie.de

While chromia- or silica-forming stainless steels suffer from evaporation at elevated temperatures especially in the presence of water vapour, alumina passive films are chemically stable up to very high temperatures. In steam alumina-forming stainless steels and also iron-aluminides are therefore a possible cheaper alternative to expensive Ni-based superalloys. Although there has been considerable progress in the optimisation of mechanical (bulk) properties of iron-aluminides [1], corrosion phenomena have been less frequently studied. The corrosion behaviour of binary, ternary and quaternary Fe-Al-based alloys with Al contents ranging from 10 to 45 at.% Al has been investigated in steam. Saturated water vapour produced by a “steam generator” was passed over the samples in a reaction tube [2]. The tests were conducted at 700 °C for 672 h without employing a carrier gas. The weight changes of the samples were determined after the experiments, and the formed scales were characterised by optical microscopy, X-ray diffraction (XRD), and scanning electron microscopy (SEM). The results for the different alloys vary quite markedly. Corrosion resistance for the binary alloys improves with increasing Al content, while the corrosion attack of ternary and quaternary alloys is less predictable based on composition. Corrosion attack e.g. on Fe-Al-Ti alloys is more severe.

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Effect of testing parameters on the lifetime of EB-PVD thermal barrier coatings with conventional and Zr-modified MCrAlY bondcoats

D. Naumenko, M. Subanovic, P. Song, R. Vassen, L. Singheiser, W.J. Quadakkers

Forschungszentrum Jülich GmbH, Institute for Energy Research,
52425, Jülich, Germany

Abstract

Electron beam physical vapor deposited (EB-PVD) thermal barrier coatings TBC's with a conventional and a Zr modified MCrAlY (M = Ni, Co) bondcoats were tested until macroscopic TBC failure in two cyclic furnace tests at 1000°C in laboratory air. It is shown that during discontinuous testing (hot dwells of one week and still air cooling) the TBC system with Zr modified bondcoat outperformed the system with conventional bondcoat by a factor of four. In contrast during cyclic temperature exposure (hot dwells of 2 hours and cooling with pressurized air) only a minor lifetime improvement with Zr-addition to the bondcoat was found. This result could be explained in terms of differences in the microstructure and associated failure mechanisms of the thermally grown oxide (TGO) formed on the two bondcoats. In the system with the conventional bondcoat a flat, dense alumina TGO formed and failure occurred at the TGO/bondcoat interface at a critical TGO thickness independent of the cyclic parameters. With the Zr-modified bondcoat heterogeneous, rapidly inward growing TGOs formed, whereby the failure path was shifted to the TBC/TGO interface. For the latter TBC system the lifetime was mainly limited by the number of temperature cycles. By reducing the Zr reservoir in the bondcoat, however, the cyclic lifetime can be significantly increased. The lifetime extension compared to the conventional MCrAlY bondcoat requires an exact control of the Zr-reservoir, which is determined by the Zr content, bondcoat thickness and processing parameters.

Nuclear Corrosion

Corrosion of stainless steels in nitric acid service: corrosion degradation issues and control measures

Vivekanand Kain, K. Chandra, M Kiran Kumar, Sneha Rhode, Raghav Gupta**
Materials Science Division, Bhabha Atomic Research Centre, Mumbai, India
** PEC University of Technology, Chandigarh, India*

Abstract

This paper highlights the corrosion degradation modes for stainless steels in applications that use nitric acid. Though the use of nitric acid grade stainless steels has ensured freedom from intergranular corrosion of welded components, other degradation issues have to be addressed to avoid corrosion related failures in plants that operate with nitric acid as the main process fluid. End grain corrosion is a major form of degradation that affects all grades of stainless steels including NAG stainless steels. Controlled solution annealing, laser surface remelting, weld overlay and welding of a material over the expose end faces have been shown to be highly effective in avoiding end grain corrosion. Other factors that are of concern are the presence of halide ions in nitric acid streams. It has been shown in exposure tests in boiling nitric acid solutions of concentration ranging from 0.5 M to 12 M for 48 h that when the nitric acid concentration was 3 M or higher, the stainless steel did not show any influence of the presence of chloride ions up to 6000 ppm. These corrosion rates remained acceptably low and there was no localized corrosion observed on the samples. For the 1 M boiling solution of nitric acid (for the 48 h exposure), there was no influence of chloride level addition upto 1000 ppm and the corrosion rate increased at 3000 ppm level. As the nitric acid concentration decreased to 0.5 M, the corrosion rate increased appreciably when 3000 ppm chloride ions were added. Electrochemical anodic polarization tests in nitric acid containing various levels of chloride ions have been used to corroborate the results from boiling immersion tests. The free fluoride ions in nitric acid on the other hand are shown to accelerate the dissolution rate of stainless steels. The influence of cold work in fabricated components on the corrosion behaviour of stainless steels in nitric acid service has been established after giving different levels of cold working (bending and cold rolling) to stainless steel. It was shown that strain hardening takes place and martensite forms upon cold working but it does not deteriorate the corrosion behaviour in cold worked condition in nitric acid. Presence of highly oxidizing corrosion products/simulated fission products in the process stream causes even the solution annealed stainless steel to corrode by intergranular corrosion. Concentrations of many of these oxidizing ions to cause severe intergranular corrosion of even solution annealed stainless steel type 304L in 6M boiling nitric acid, in 48 h exposures has been established. This is attributed to shift in the operating potential to transpassive regime for stainless steel. Therefore chemical plants using nitric acid as the process stream have to take all these aspects in to consideration to avoid degradation and ensure long plant life. Implementation of these degradation control measures, related to fabrication and process chemistry, would ensure trouble free operation of these plants.

Keywords : Zirconium alloy, Hydrogen, Creep, Anisotropy

Hydrogenation of cladding tube in Zirconium alloy and effect on creep behaviour.

D. Poquillon[1], P. Rublon[1,2], J.-M. Cloué[2]
[1] CIRIMAT, Université de Toulouse, France
[2] AREVA, Areva NP, Fuel Business unit, Lyon, France

The cladding tubes are very important structural parts in nuclear plants, which are subjected to complex thermo-mechanical loads under complex chemical environment. So, in order to better know their mechanical behaviour, an innovative creep device and an analysis method specially adapted to multi-axial loads of such tubes have been developed in the CIRIMAT. The present work focuses on the effect of hydrogen on creep behavior. Different tests under hydrogenated Argon are carried at 400°C. The purpose is to prevent cladding oxidation out in order to let hydrogen diffusion occurs. In situ measurement of cladding tube deformations are carried out. A method is the proposed to prevent cladding oxidation and to promote hygrogen diffusion in the zirconium cladding tube. Creep tests are carried out on hydrogen-enriched (but non-hydrided) claddings. The results are compared with those obtained without hydrogen enrichment

Impact of water chemistry operations on the deposit of corrosion products in the fuel assemblies at Paks Nuclear Power Plant

Árpád Doma
Chief Technologist, Paks Nuclear Power Plant
7030 Paks Pf 71, Telephone: 75-507-541, doma@npp.hu

A large number of Steam Generator decontamination operations were carried out prior to feedwater header replacement work for three of the four VVER-440 type Units of Paks Nuclear Power Plant. The internal surface of the Steam Generator heat exchanger tubes had not been sufficiently passivated after the decontamination, which caused the release of excess corrosion products into the main coolant loop.

The deposited corrosion products had reduced the flow cross section within the fuel rod bundles and, as a consequence, increased the hydraulic resistance of the fuel assemblies. Decision was made to remove the deposit from the fuel assemblies with the use of a chemical cleaning method. During these cleaning operations carried out in a separate tank at the reactor, 30 fuel assemblies have seriously damaged as a consequence of insufficient cooling due to a design error of the cleaning tank.

To minimise the rate of deposit, a new, originally not used water regime was developed for the start-up/shut-down operation conditions, for which we have a two year long operational experience now. The water regime parameters used for normal operation conditions have also been revised and international experts were requested for expert opinion on the established modifications. The introduction of the modifications is in progress now.

Heat Transfer Corrosion of Stainless Steel in Nitric Acid

Ben Cordner, University of Manchester, UK;
Dr Nicholas Stevens, University of Manchester, UK.

In nuclear reprocessing plants, interest is focused on the behaviour of stainless steels in nitric acid solutions, the principal heated process vessels being spent-fuel dissolvers and evaporators.

The corrosion of stainless steels by nitric acid is known to be complex, being affected by a host of metallurgical and environmental factors. Amongst the latter, temperature exerts a strong effect, the corrosion rate being subject to activation control, typically doubling for a temperature increase of 7-10 °C depending on the exact liquor composition. The type of corrosion which occurs is intergranular whereby grain boundaries between individual stainless steel crystals are subject to attack. This is due to differing local concentrations of alloying metals and interstitial contaminants at the grain boundaries and eventually causes entire crystals to detach from the bulk steel. Less well understood is what, if any, effect a temperature gradient between the liquor and the stainless steel vessel exerts on this corrosion mechanism and therefore the corrosion rate of the vessel. Possible effects include changing mass transport mechanisms to the surface of the steel, a temperature gradient could also influence what corrosion products are formed at the surface which in turn has a considerable affect on the passivity of the steel.

This project will investigate the corrosion rate of stainless steel heat transfer surfaces contacted by nitric acid solutions and compare this with corrosion rate data obtained isothermally at the effective surface temperature in order to test whether additional effects occur. A wide range of heat transfer conditions will be tested using a variety of nitric acid liquors.

Using weight loss and electrochemical techniques it is possible to deduce the corrosion rate as a function of time. Various microscopy techniques will also be employed to provide a qualitative understanding of the corrosion mechanisms involved.

IN-SITU ELECTROCHEMICAL CHARACTERIZATION OF ZIRCONIUM ALLOYS CORROSION IN HIGH TEMPERATURE POWER CYCLE ENVIRONMENT

Jan MACÁK [1], Petr SAJDL [1], Radek NOVOTNÝ [2], Veronika RENČIUKOVÁ [1], Věra VRTÍLKOVÁ [3]

[1] *Institute of Chemical Technology, Prague, Czech Republic; jan.macak@vscht.cz*
[2] *Institute for Energy, Joint Research Centre, Petten, The Netherlands*
[3] *UJP Praha a.s., Prague, Czech Republic*

Zirconium alloys are used as fuel cladding materials in nuclear reactors. Their stability in reactor coolant depends on the characteristics of oxide, formed on cladding surface under high temperature conditions. Currently, the only method that enables in-situ characterization of corrosion processes at high temperatures and pressures is Electrochemical Impedance Spectroscopy (EIS). As long as it operates in wide enough range of frequencies, it provides information of both dielectric properties of oxide layers growing on the zirconium alloys surfaces during the exposition in nuclear reactor coolant as well as the kinetics of the corrosion process and the associated mass transfer processes.

In the presented paper, corrosion of different types of zirconium alloys was investigated in-situ under high pressure high temperature conditions using electrochemical impedance spectroscopy (EIS) and polarization measurements. Chemical conditions were those applied in WWER type of reactor coolant (boric acid, potassium hydroxide, lithium hydroxide). Experimental impedance spectra were approximated by equivalent circuits (EC) based models. Optimal model was selected and parameters characterizing time evolution of oxide parameters and kinetic and mass transfer parameters of zirconium alloys corrosion were obtained. Kinetic parameters (Tafel constants) were derived from in-situ measured polarization curve. Applicability of Stern-Geary approximation for high temperature corrosion of zirconium alloys was discussed. Electrochemical corrosion parameters were correlated with those obtained by independent methods (weight gain, electron spectroscopy, kalotest).

Environment Sensitive Fracture

Stress-corrosion damages of steels and welded joints of gas-main pipelines

K.M.Dzioev “Stroygazkonsulting” Ltd, Moscow, Russia,
K.D.Basiev, North Caucasian Institute of Mining and Metallurgy, Vladikavkaz, Russia,
S.K.Dzioev “SpetsRemGazdiagnostika” Ltd, Moscow, Russia

For the development of effective methods of protection against stress-corrosion cracking as well as for the development of new grades of pipe steels resistant to such kind of damage, it is necessary to create a model, allowing explanation of mechanisms of processes proceeding in materials of pipelines. It is possible to develop procedures and to ground scientifically the necessary amount of inspection of pipe metals and the ways of its effective protection on the basis of such model.

The explanation of stress-corrosion cracking will allow solving the problem of pipeline work resource prolongation, as the conclusion of work resource prolongation should be accepted on the basis of analysis of an actual state of the parent metal and welded connections.

Stress-corrosion attacks are registered in many countries of the world. Especially often it occurs in Russia, Canada, the USA and the countries of the European Union.

Despite intensive research of this problem, the reason and mechanisms of stress-corrosion damages of pipe steels are not found yet. This is concerned with a variety of factors that lead to stress-corrosion damages of the main pipes.

The main factor is the hazard evaluation of discovered cracks in an active gas pipeline and making well-founded decisions.

Stress corrosion cracking detection of sensitized stainless steel 304 in chloride media by using electrochemical impedance spectroscopy (EIS)

B.Adib * (1), *J.Neshati*(2),*A.Sardashti*(1)

(1)Department of Chemistry, Islamic Azad University, North Tehran Branch
(2)Corrosion Department,Research institute of Petroleum Industry,Tehran,Iran

Electrochemical impedance spectroscopy (EIS) was used to detect stress corrosion cracking (SCC) in stainless steel 304 alloy exposed to an aqueous environment at 120 ^{0}C. Stainless steel 304 alloy as u-bend was tested in the solution that contains 40 weight percent magnesium chloride. U-bended samples were prepared according ASTM G30.EIS measurements were always performed simultaneously on u-bend under stress and without stress samples.

Results indicate that changes phase shift versus time could be related to the stress corrosion cracking process. Stress corrosion cracking is detectable in frequency 23.95 Hz.EIS measurement can be used for SCC monitoring in u-bend samples.

Analysis of the fracture surface by using metallographic and SEM confirmed EIS results.

Keywords: Stress corrosion cracking, Stainless steel 304, U-bend, Monitoring

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* Email:B_adibb@yahoo.com , Fax: (98)(21)22222512 ; P.O.Box 1913674711 Tehran Iran

Long-range surface forces in liquid environment-induced cracking

Fyodor Kulikov-Kostyushko[1], Alexander Malkin[2]
[1] *Faculty of Chemistry, M. V. Lomonosov Moscow State University, Moscow, Russia*
[2] *A. N. Frumkin Institute of Physical Chemistry and Electrochemistry, RAS, Moscow, Russia*

Stress-corrosion cracking is often manifested in a form of *brittle fracture* so that plastic deformations are localized in a small vicinity of a crack tip. Under such condition, the crack growth rate for a given ‘material–environment’ system and condition of testing is usually treated as a function of only stress intensity factor (SIF, K_I). For example, the crack starting condition under slow uniaxial strain can be formulated as $K_I > K_{Iscc}$ where the threshold value of SIF K_{Iscc} is considered to be independent of the crack length.

A well-known solution gives $K_I \sim \sigma_\infty L_c^{1/2}$ where σ_∞ is applied stress and L_c is crack length; crack starting stress and the crack length are hence related by simple formula $\sigma_\infty \sim L_c^{-1/2}$. However, besides the external loading there exist internal forces acting between crack faces and altering SIF. When these forces appear to be sufficiently strong the above simple relation for crack starting stress needs to be modified. The important kind of such forces (as applied to stress corrosion cracking) are long-range surface ones which are usually described in terms of disjoining pressure.

The objective of our work is to qualitatively estimate the impact of the surface forces between crack faces on the process of stress-corrosion cracking. The evaluation is based on a calculation of the actual SIF at the crack tip taking into account the presence of the surface forces. In such calculation, several types of surfaces forces are considered: van der Waals, electrostatic (double-layer), electron, structural ones, *etc.* It is shown that the magnitude of disjoining pressure inside corrosion crack can mount to 10^6...10^7 Pa.

In this work, we mostly focus on liquid-filled cracks and restrict consideration to a slow crack growth rate when hydrodynamic effects are negligible. Cracks in silicate solids (*e. g.* glass) filled with solutions of surfactants and/or electrolytes, and ‘solid metal–liquid metal’ systems are two points of interest.

Using the known relations for disjoining pressure as a function of crack opening displacement we obtain the relations for actual SIF as the function of applied stress, crack length and various constants of a given ‘material–environment’ system, including those related to surface forces.

The results obtained show that disjoining pressure inside a crack leads to a marked difference between the ‘geometric’ and the ‘actual’ SIF value. For lengthy cracks with large opening displacements that difference usually gives only minor correction to the crack starting stress and kinetic characteristics. This correction can, however, be particularly large in the case of small (micron-sized) cracks, thus radically changing the kinetics of their growth. The disjoining pressure can specifically be the cause of non-zero crack opening displacement observed in the absence of an external loading of an ideally brittle solid.

Hydrosulphuric and hydrogen cracking of steel structures

Kushnarenko V.M., Chirkov Y.A.
Orenburg State University, Orenburg, Russia

As of rolled steel, used to produce pipes and vessels operated under the action of hydrogen sulfide gas environments that are often observed in the middle part of the wall construction of disk-shaped sulfide inclusions in length from a fraction to tens of millimeters. Formed by the contact of steel structures with hydrogen sulfide, hydrogen environment, getting in the zone of the interface matrix - non-metallic inclusions, the formation of molecules, causing the hydrogen cracking of the metal. Cracks nucleate hydrogen cracking in the middle of the wall structure at the boundaries of the matrix-inclusion and distributed, usually intergranular in the direction parallel to its surface. The interaction of these cracks-bundles arises Trunk step crack cutting across some or all of the metal cross section.

In contrast to hydrogen cracking in hydrogen sulphide cracking of steel structures cracks originate from the surface in contact with hydrogen sulfide environment, or in the surface layers and are distributed mainly perpendicular to the surface, i.e. normal to the current operating voltage. Main crack hydrogen sulfide cracking in the development connects individual microcracks, caused by formation of hydrogen molecules in the reservoirs and oriented along the rolling parallel to the applied voltage.

Found that hydrogen sulfide cracking of steel structures exposed to hydrogen sulfide environments, and occurs as hydrogen cracking, intergranular separation. Hydrogen is the metal in the form of ions, which are entering the microcavity through the grain boundaries and from the crystal lattice, capture of the electron cloud of the metal electrons and become atoms, reducing the strength of these sections of the border and, with increasing concentration of the hydrogen atoms form a molecule, leading to intergranular fracture of steel wall construction.

It seems that not only the engines are identical to hydrogen sulphide and hydrogen cracking, but also by the same mechanism is formed in the steel rolled steel bundles and the so-called cold cracking when welding steels, as well as the emergence and development of cracks and other damage during the action of hydrogen sulfide on steel structures environments. Thus, the nature of the fracture of steels with hydrogen is the same, while controlling sorption processes are metal ions of hydrogen and the formation of hydrogen molecules in a microcavity (channels vacancies) located at the grain boundaries and interfaces between the matrix - non-metallic inclusions.

MODELLING OF STRESS CORROSION CRACK GROWTH IN DUPLEX STAINLESS STEELS DURING CLT EXPERIMENTS PERFORMED IN HYDROGEN SULFIDE – CHLORIDE ENVIRONMENTS AT 120 AND 80°C

Boleslav Eremias, **Vladimir Cihal, Eva Kalabisova,**

SVUOM Ltd., Czech Republic, eremias@svuom.cz

During the "Eurocorr 2008" we presented results on possibilities of modelling of stress corrosion crack growth in duplex stainless steels (DSS) during SSRT experiments in hydrogen sulfide – chloride environments at 120°C. It was shown that for calculation of the average near crack-tip strain rate detailed mathematical treatment of the stress – strain curves relating the depth of the deepest crack to the maximum stress value is necessary. By using this approach the initiation stress value corresponding to the time for the initiation of the crack is possible to find when we combine the analysis of stress – strain curves with metallographic evaluation of the surfaces of the ruptured specimens.

Similar approach can be used for modelling of stress corrosion crack growth in DSS during CLT experiments performed in hydrogen sulfide – chloride environments at 120 and 80°C. In this case the detailed analysis of elongation – time curves combined with metallographic evaluation of the surfaces of the rapture specimens is necessary. This idea was verified in our CLT experiments performed in 20% NaCl – H_2S (pH=4) at 120 and 80°C. To rationalize the received data for several DSS and material/medium combinations we have used a mathematical model based on the approach of Santarini. Briefly, this approach facilitates calculation of time to failure in relation to the applied stress and the depth of the deepest crack in CLT experiments.

It was demonstrated that for modelling of stress corrosion crack growth in DSS during CLT experiments performed in hydrogen sulfide – chloride environments at 120 and 80°C also environmental and temperature effects became important for given type of DSS.

Operating experience of gas pipelines from pipes of the various assortment in the conditions of stress corrosion cracking

A.S.Kuzbozhev, Open Company branch «Gazprom VNIIGAZ – Severnipigaz», Ukhta, Russia, a.kuzbozhev@sng.vniigaz.gazprom.ru
V.O. Solovey, Open Company «Gazprom transgas Ukhta» Ukhta, Russia,
I.V. Rayhovsky, Open Company «Gazprom VNIIGAZ», Moscow, Russia,
Yu.V. Aleksandrov, Open Company «Gazprom transgas Ukhta» Ukhta, Russia

In corridors of the main gas pipelines are in operation of a pipe of three generations of release (depending on time of release and a way of manufacture). Steels of the first generation which 17G1S manufactures of the Chelyabinsk pipe-rolling factory (ChPRF), and also pipes 1020×8,5 manufactures of Sweden concern the normalised steel 17GS and its updatings 17G1S, are let out in 70th years and earlier. The thermoimproved steels concern steels of the second generation – 14G2SAF manufactures ChPRF and a steel 17G2SF for pipes with a spiral seam, let out by the Volga trumpet factory during the period with 1970 for 1975. The third generation are steels supervised proskating rinks a class of durability X60-X70, are made at Hartsyzsky trumpet factory and in Italy, Japan, Germany France in 80th years.

There are given statisticans of emergency destructions because of stress corrosion cracking (SCC) on Open Company «Gazprom transgas Ukhta» on pipes of different generations.

The greatest number of emergency destructions of gas pipelines is fixed on the pipes made of the normalised steel, – 27 failures. On pipes from a steel supervised proskating rinks – 23 failures, including 8 failures on pipes in diameter 1420×16,5 mm from steel X70 of manufacture of Japan and Italy (a pipe of manufacture at Hartsyzsky trumpet factory), 15 failures - on pipes 1020×9 mm from steel X60 of manufacture of France. On the thermoimproved pipes from steels of the second generation there were 20 failures: on pipes from a steel 14G2SAF 1220×11 mm – 7 emergency destructions, on the spiral seam pipes 1220×10,5 mm from a steel 7G2SF – 13 failures. On specific number of emergency destructions emergency destructions are distributed as follows: on pipes from the normalised steel 17G1S – 0,0078 failures/km, on the thermoimproved pipes – 0,014 failures/km, on pipes from a steel supervised proskating rinks – 0,0075 failures/km.

It is recommended at researches of stability of metal of pipes to SCC to consider the data of the comparative analysis of steels of different generations of the under abnormal condition-destroyed pipes on a chemical compound, characteristics of mechanical properties, features of structure, presence and impurity nonmetallic inclusions, to quantity of defects. It is expedient to consider data on the established preconditions to development of processes SCC put at stages of melt of a steel, proskating rinks of sheet, heat treatment and manufacture of pipes.

Effects of electrolyte composition and potential on near-neutral pH stress corrosion crack propagation

Roman Bogdanov, **Vasily Ignatenko, Andrey Marshakov**
Institute of Physical Chemistry and Electrochemistry of Russian Academy of Sciences, Moscow, Russia, mar@ipc.rssi.ru

The first cases of near-neutral pH stress corrosion cracking (SCC) of the buried pipelines were occurred about 20 years ago. Nevertheless the study of its mechanism continues to be of current interest because of present multiplying pipeline accidents due to SCC. The paper describes the influence of electrolyte composition and potential on crack growth rate in pipeline steel X70 to estimate the leading mechanism of near-neutral pH SCC.

The crack growth rate was determined using resistance test of samples with pre-grown fatigue crack. The rate of hydrogen absorption was measured in membrane tests. Citrate buffer (pH 5.5) and mixture of ground electrolyte NS-4 and borate buffer with pH 6 – 8 were used as background solutions under static and cyclic loading correspondingly. Various substances were added to the work solutions to change anodic dissolution and hydrogen absorption of iron. The tests both under static and cyclic loading demonstrated that SCC propagation corresponded to visual information and metallographic analysis of the walls of gas pipelines.

The effect of electrolyte composition on crack growth rate depends on anodic dissolution of iron (AD) and hydrogen absorption (HA) processes. Thus, sulfide and phosphate ions, which stimulate the both processes, accelerate crack propagation. AD and HA inhibitors such as benzothriazole decrease the crack growth rate. The influence of AD promoters (rhodanide- and iodide – ions, thiocarbamide) may be diverse. This fact could be connected with their different effect on AD rate: rhodanide- ion decelerates significantly this process, while iodide-ion does not practically influence it. The addition of thiocarbamide slows down crack propagation in the citrate buffer but accelerates it in the borate solution. This fact is conformed to the different effect of thiocarbamide on AD rate in these media.

It was shown that anodic polarization of iron increases the SCC propagation in all studied electrolytes. The potential shift into negative region from the corrosion potential decelerates the crack growth, if HA rate does not exceed the critical value. Only in solutions containing HA promoters, the significant negative potential shift increases crack growth rate.

The data obtained testify that the SCC leading mechanism of pipe steel X70 under near-corrosion potential is the anodic dissolution of the metal in the crack tip. The influence of HA promoters on the crack propagation could be connected with the activating effect of atomic hydrogen on the anodic dissolution of iron.

The necessity of Stress Corrosion Cracking (SCC) prognosis on gas mains to reduce the breakdown rate and overhaul expenses

E.A.Spiridovich, V.N.Lisin, OAO “Giprogazcenter”, Nizhny Novgorod,
Russia, spir@ggc.nnov.ru

In the late nineties of the last century and the beginning of the 2000-s on the main gas pipelines of the United system of gas supply of the Russian Federation there began to develop rapidly the so-called stress corrosion cracking (SCC). This manifestation was expressed by the failures of gas mains in the northern and center areas of the country. OAO "Gazprom" developed the program on prevention of emergencies of SCC manifestation at the stages of search of the reasons of localization of the sites, creation of the devices and techniques. Special development was gained in the area of in-line fault detectors passing, determining the specific manifestation in the crack form with their reference to the terrain and the ground methods of the search of manifestation and localization of cracks, grids of cracks in short and extended pits.

The Register of SCC potentially dangerous gas pipelines sites for 17 000 km was elaborated by OAO "Giprogazcenter". The Register was developed on the base of the “Technique on inspection of SCC-sensitive gas pipeline sites. The base of the “Technique…” is represented by main provisions of RF patents No 2120079 “Method of SCC prevention of pipelines” and No 2147098 “Method of revealing of SCC-sensitive gas mains sites.”

The experience of the usage of the “Technique” and the Register, in the aggregate- “The Predictive Technique”, showed the convergence of the Register with superimposed emergency failures of gas mains, the results of in-line diagnostics up to 80-90%.

The Predictive Technique permits:

-to determine the first-priority passing of expensive SCC tool (in-line fault detector), having excluded idle passing;

-to reduce SCC overhaul expenses of gas mains by the method of pipe screening on all potentially dangerous site, thus having excluded the initiation of the failures on it in the future operation period;

-to conduct the inspection of GM sites for SCC manifestation in the so-called “dead zones” for passing of in-line fault detectors and also for process gas loops;

-to determine the quantity of necessary pipes while screening in the process of overall re-insulation

Hydrogen diffusion and trapping in austenitic stainless steels studied with thermal desorption spectroscopy

O.Todoshchenko, Y.Yagodzinskyy, H. Hänninen,
Aalto University School of Science and Technology, Espoo, Finland

Hydrogen solubility and diffusion in austenitic stainless steels, namely, AISI 310, AISI 301LN, AISI 201 and duplex stainless steel LDX 2101 are studied with thermal desorption spectroscopy (TDS) after electrochemical potentiostatic hydrogen pre-charging. Temperature dependencies of hydrogen desorption for all studied steels manifest a complex main peak caused by hydrogen releasing from the steel lattice by diffusion. Depending on the steel and heating rate the peak is situated from 350 to 500 K and its shape reflects a specific of hydrogen diffusion in stainless steels which are multicomponent and multiphase alloys.

Analysis of the TDS curves is based on the hydrogen diffusion model taking into account trapping of hydrogen atoms in the energetically deep interstitial positions in the steel lattice and difference in the hydrogen diffusion mobility in different phases of the steels. Effects of pre-strain of the steel and heating rate during TDS measurement on the peak shape and position are discussed.

Diffusion coefficient of hydrogen and its total content after the same charging procedure are obtained from the TDS curves and compared for all the studied steels.

Influence Of Environmental Factors On The Susceptibility to Stress Corrosion Cracking Of High-Strength Al-Zn-Mg Alloys

[1]H . A . Jawan,

[1]Department Of Mechanical Engineering
University Of Al-Margep
Alkhoms , Libya
Tel – 00218-926312605

Abstract : Stress corrosion cracking (SCC) is the result of the Combined action of Metallurgical , Mechanical , and environment factors. While the letter two factors are governed by the service conditions. The effect of the environment on crack initiation and propagation has been shown to depend on the aggressiveness of the environment. The experiments performed on this factor during the last decades enhance our knowledge of the mechanism of SCC of wrought aluminum alloy. The present paper describes the environmental factors such as composition of environment, PH of solution, electrochemical potential and temperature which may influence on crack initiation and propagation.

Corrosion Mechanisms & Methods

Oxidation Induced Tin Whisker Growth on the Surface of Rare Earth Containing Solders

T.H.Chuang and C.C.Jain

Addition of rare earth (RE) elements in solder alloys gas been reported to have improved effects on their physical and mechanical properties. However, Chuang and Yen observed that long fiber- and hillock-shaped whiskers grew on the surface of a Sn-3Ag-0.5Cu-0.5Ce solder after air storage at room temperature and 150℃, respectively. It has been proposed that the mechanism for the rapid whisker growth in this Ce-doped solder is the predominate oxidation of rare earth containing CeSn3 intermetallic phase existing in its alloy matrix, which leads to a compressive stress that extrudes the tin atoms out of the specimen surface. Further metallographic observations and chemical analyses on the cross sections of the oxidized RE-intermetallic phases $NdSn_3$ in the air-exposed Sn-3Ag-0.5Cu-0.5Nd alloy, a "successive compressive stress model" for the tin whisker growth on the surface of rare earth containing solders has been proposed: During the air-storage, the outer surface of RE-intermetallics oxidizes to release Sn atoms beneath the first RE-oxide layer and induces a compressive stress to extrude small amounts of Sn atoms out of the RE-intermetallics phase from the weak spot of the first RE-oxide layer. The outward extruded Sn atoms appear as a tin sprout on the surface of the first RE-oxide layer, releasing the compressive stress in the oxidized RE-intermetallics. Subsequently, owing to the higher chemical activity of RE-element than Sn, the RE-intermetallics beneath the first Sn layer oxidize predominantly and release additional Sn atoms beneath the second RE-oxide layer, which induces a further compressive stress that extrudes the Sn atoms out of the first RE-oxide layer and leads to the growth of the tin sprout. Further oxidations of the RE-intermetallics beneath the RE-oxide/Sn multilayer result in the successive supply of compressive stress, which acts as the driving force for the continuous growth of Sn whiskers.

LOW-CYCLE CORROSION FATIGUE OF STAINLESS STEEL 316L

Yakov B. Unigovski, Emmanuel M. Gutman, Yurii Shubov,
Dept. Materials Engineering, Ben-Gurion University of the Negev, Beer-Sheva, Israel.
Gobboon Lothongkum,
Dept. Metallurgical Engineering, Chulalongkorn University, Bangkok, Thailand

Corrosion fatigue in structures is caused by high-frequency vibration as a consequence of the rotation of structural parts or fluid motion, or by low-frequency strain cycling as a result of start-and-stop operations. High-cycle corrosion fatigue has been studied much more extensively than low-cycle corrosion fatigue (LCCF), although the latter is much more dangerous because of the presence of plastic strain.

LCCF of stainless steel 316L was investigated in doubly deionized water and 3.5% NaCl at the strain ratios R of –1 and 0.1. A detrimental action of corrosion on the lifetime of steel in comparison to that in air was estimated using the environmental factor $EF = (N_a - N_s)/ N_a$, where N_a and N_s are numbers of cycles to failure in air and in the solution, respectively.

With pH values of NaCl solutions decreasing from 6 to zero, *EF* increases in the range from about 0.3 to 0.7. At the strain ratio of 0.1, the detrimental action of corrosion is markedly below that for R = –1, e.g., in 3.5% NaCl solution with pH 0, *EF* values amount to 0.48 and 0.65, respectively. During a short initial time period of the test, the sample temperature increases very intensively up to the temperature saturation. After the time corresponding to 0.7- 0.8 of fatigue life, a marked decrease in the temperature is found due to steel softening.

Experimentally found coefficients in the equation of Coffin-Manson type can be used for predicting the lifetime of steel. Changes in cyclic ductility parameters with changing pH reflect the changes in mechanochemical interactions, which can result either in additional plasticization (chemomechanical effect) or in the embrittlement (microcracking) during cyclic loading.

Effect of pH on the electrochemical behaviour of CoCrMo biomedical alloy in phosphate buffered solutions

C. Valero Vidal; A. Igual Muñoz

Departamento de Ingeniería Química y Nuclear
Universidad Politécnica de Valencia E-46071 Valencia, Spain

Abstract

CoCrMo alloy are widely used as biomaterial for manufacture of prosthetic devices due to their good corrosion resistance and biocompatibility. The pH in biological systems is modulated mainly by phosphate buffering and is kept around 7.4 under normal conditions. Nevertheless, pH may be modified by several factors such as wound-healing process after surgery (reaching values from 5.5 to 9 with infection) or hematomas and corrosion in some local sites where the pH may drop to approximately pH 1 or even lower. Therefore it is important to evaluate the influence of pH on the corrosion behaviour of CoCrMo alloy for biomedical applications.

Open Circuit measurements (OCP) and potentiodynamic curves were employed to characterize a CoCrMo alloy in Phosphate Buffered Saline solution (PBS) at different pHs (3, 7.4 and 10) with and without addition of Bovine Serum Albumin (BSA). N_2 (deoxygenated) and O_2 (oxygen saturation) were purged into the solutions in order to analyze the influence of aeration conditions on the CoCrMo electrochemical behaviour.

In all tests, the current density of the cathodic domain is determined by the reduction of water and/or reduction of oxygen. This current measurements vary depending on the pH and O_2 content. Furthermore, the O_2 reduction takes place according to two reactions steps, clearly distinguishable on the current-potential curve as two successive diffusion plateaus.

The results show that the general corrosion behaviour of CoCrMo alloy depends on the pH media. Thus, the effect of BSA and the aeration conditions are related to pH. At pH 3 no influence of BSA was observed in deoxygenated solutions which imply that BSA acts over the oxygen reduction reaction in acidic media. On the contrary, a noticeable influence of BSA was observed at pH 7.4 (independently on the gas content). In this case, a small effect of oxygen was detected in the potentiodynamic curves. Finally, at pH 10, the influence of BSA was significant in oxygenated solution, being less significant in the deoxygenated one. The aerated conditions do not affect passive and transpassive domains in acidic and neutral media, but in basic electrolytes important differences in those domains were observed due the metal complex formation.

Keywords: CoCrMo alloy, Biocorrosion, Bovine Serum Albumin (BSA), passivity, pH.
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Influence of Ca ions and temperature on the corrosion behavior of WC-Co hardmetals in alkaline solutions

Florian Kellner, University of Erlangen-Nuremberg, Erlangen/Germany
Sannakaisa Virtanen, University of Erlangen-Nuremberg, Erlangen/Germany

The effect of temperature and Ca ions on the corrosion behavior of hardmetals was investigated in 0.1 M NaOH and 0.05 M $Ca(OH)_2$ alkaline electrolytes using impedance spectroscopy, potentiodynamic polarization and surface analytical techniques. It was found that calcium containing alkaline solutions efficiently decrease the anodic currents up to 5 times by forming a calcium containing deposit on the top of the WC-Co hardmetal surface, which remains stable even at higher temperatures (40°C and 60°C). This positive influence of Ca ions is predominant under polarization in the range from 0 to +0.85 V (Ag/AgCl) but is not apparent under OCP conditions. In NaOH, however, the corrosion resistance strongly decreases at higher temperatures as compared with the room temperature. At the slightly elevated temperature in 0.1 M NaOH the Co binder phase loses its passivity and is almost completely washed out of the compound material. A WC skeleton remains on the surface and hence the ductility in the hardmetal is lost. In the end, the material could completely fail under such operating conditions. Also the Ni alloyed binder loses its strong passivation ability at the elevated temperatures.

Influence of thermal conditions on local activation of iron in hydrocarbonate-halide media

S.A. Kaluzhina*, N.G. Nafikova**, T.V. Vlasova*
*Voronezh State University 394006 University Sq. 1
**Voronezh State Technological Academy 394019 pr. Revolutsii, 19
Voronezh, Russia
E-mail: kaluzhina@vmail.ru

Local fracture of heat-exchange equipment made of iron-based alloys determined by heat carrier corrosive power and thermal conditions substantially reduces reliability of its operation. In this context the present work describes the comparative analysis of influence of the stated factors on local activation (LA) of iron in soft water.

Experiments were conducted on a device with a rotating disc heat exchange contact heating electrode [1] of armco iron (electrode rotation speed - 350 r/min) over the disc surface temperature range - 20-80 ^{o}C and metal-solution oriented positive heat currents - $Q=(7,3\text{-}21,6)\cdot 10^4$ W/m^2. Comparative data were obtained on thermal equilibrum solution electrode (TSE) and on heat transfer electrode (HTE) in supporting hydrocarbonate solutions with addition of Cl^--, Br^-- and I^-- ions with use of electrochemical methods. Metal surface condition before and after the experiment was under microscopic control.

Factual findings showed that introduction of halide ions in the ground electrolyte under all thermal conditions causes LA of iron in the area of potentials 0,35-1,20 V (N.H.E.). General regularity lies in the fact that at low temperature metal surface is covered with multiple shallow pitting corrosion ($d=5\cdot 10^{-5}$ m) The number of pitting corrosion reduces with TSE temperature growth at simultaneous growth of local destruction diameter (up to 10^{-4} m). Similar effect is not observed on HTE where takes place only increase of pitting corrosion number in the disc periphery.

Conducted research showed that the LA process flows in accordance with the adsorbtion mechanism [2] and remains constant in all studied systems. The role of anions-activators is limited to adsorbtion displacement or substitution to passivating particles on metal surface, with formation of complex able to transfer into solution. At the same time the activating ability of halide ions reduces in the row $Cl^- \rightarrow Br^- \rightarrow I^-$, what is confirmed by the growth of their critical concentration from which iron is subject to LA.

Surface temperature increase reduces LA hazard for TSE and THE of iron by various reasons. On TSE this effect is connected with formation of a thicker protective layer, which makes the electrode more tolerant to local fracture. On THE the decisive role is played by the difficulty of ion-activator delivery to the near-electrode zone due to strengthening of primary thermal diffusion of passivating particles to the THE surface.

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Correlation between a scale of one to ten for corrosion resistant metallic packing materials and classification of canned food ranking in terms of its corrosion activity

Shavirin V. A., Tovstokora N. S., Chavchanidze A. Sh., Timofeeva N. Yu.,

Bazarkin A. Yu.

All – Russian Research Institute of Canning and Vegetable Drying Industry, 124703, Russia, Region of Moscow, Vidnoe, 78 st. Shkolnaya

Email: tchavtcha@yandex.ru

To establish correlation between a one to ten scale for corrosion resistance of metallic packing materials basing on corrosion depth index K_{dep} (mm/year) and classification of canned food in terms of its corrosion activity using gravimetric corrosion rate index K_{gr}^{-} (g/m^2 per hour) is critical to detection and prediction of corrosion in metallic packing materials for canned food. Interrelation between K_{dep} and K_{gr}^{-} taking the form: $K_{dep} = (8.76\ K_{gr}^{-})/\rho_{Me}$, where ρ_{Me} is metal density (g/cm^2) , is reliable only in case of uniform corrosion. However tinplate corrosion in fruit and vegetable juices and standardized organic acid test solutions is nonuniform in its nature and corrosion rate varies between different surface areas. To establish interrelation between K_{dep} and K_{gr}^{-} in case of nonuniform corrosion we have carried out tinplate corrosion tests in juices and test solutions using such corrosion measuring devices as «Expert-004» and «UISK-2». As a result of processing of the experimental data arrays of K_{dep} and K_{gr}^{-} stationary values by means of mathematical statistics we obtained Person correlation coefficient $r_{xy}= 0.98$ to be higher than statistical criterion $r_{xy}^{tabl}=0.92$. This fact indicates to a high correlation degree between these two indexes. We have also calculated coefficients of linear regression equation.

Based on the regression equation we have established correlation between a one to ten scale for corrosion resistance of metallic packing materials and classification of canned food in terms of its corrosion activity which is of great value for detection and prediction of corrosion in metallic packing materials for canned food since in course of corrosion process heavy metal salts pass into canned food resulting in deterioration of its taste and nutritional qualities while release of hydrogen leads to can blowing.

Quick electrochemical corrosion test for metallic cans and a test operation board

Shavirin V. A., Kvasenkov O. I., Chavchanidze A. Sh., Timofeeva N. Yu., Bazarkin A. Yu., Chavchanidze Sh.A.

All – Russian Research Institute of Canning and Vegetable Drying Industry, 124703, Russia, Region of Moscow, Vidnoe, 78 st. Shkolnaya

Email: tchavtcha@yandex.ru

A new quick electrochemical corrosion test of the inner surface of the metallic cans by potentiostatic method has been developed. The advantages of the test involved namely : high sensitivity (10^{-3} mcm/year) and a wide range of the corrosion depth index ($10^{-2} \div 10^{7}$ mcm/year) values have been achieved by using universal portable corrosion measuring device «Expert-004».

The corrosion tests of the metallic cans were carried out on a new test operation board. The main characteristics of the board include : compactness, portability, multisite arrangement, automatic register of experimental data in periodic operation mode and original component arrangement including special electrochemical unit for carrying out corrosion test of the inner surface of cans. The approbation of the given quick electrochemical test method were performed on the electrodeposited tinplates which inner surface had been in contact with standardized test solutions imitating vinegar containing canned food.

The application perspectiveness of the new quick electrochemical corrosion test and test operation board both for laboratory and performance tests has been established as far as a shift has been produced from testing metallic packing materials to testing finished product – metallic cans.

Study of the behaviour of different dental alloys in case of exposure to high and very high potentials

Pascal De March[1,2], Patrice Berthod[2] and Maxime Helfer[1,3]
[1]Faculty of Dentistry, Department of Prostheses, U.H.P. Nancy 1, 96 avenue de Lattre De Tassigny, B.P. 50208, 54000 Nancy, France
[2]Institut Jean Lamour (UMR CNRS 7198), Faculty of Sciences and Techniques, U.H.P. Nancy 1, B.P. 70239, 54506 Vandoeuvre-lès-Nancy, France
[3]Laboratoire de Thermodynamique des Milieux Polyphasés (EA 3099)
École Nationale Supérieure des Industries Chimiques
1 rue Grandville, B.P. 20451, 54001 Nancy, France

Most of the dental alloys used in prosthetic dentistry are composed of noble elements as gold, platinum, palladium, ... Other ones are also generally very resistant against corrosion in the buccal milieu although they are based on nickel and chromium, thanks to their easiness to become passive. However, exposed to high potentials in a three-electrode cell, they can know significant anodic currents, as it can be seen near the end of the anodic parts of polarisation runs in artificial saliva. Since high potentials can be sometimes achieved in reality (e.g. intensive aeration of saliva), it can be interesting to extrapolate such situations in order to see how these alloys can be significantly deteriorated in some extreme situations.

Results

Several dental alloys, with various nobilities, were prepared as working electrode and immersed in an acidified Fusayama's artificial saliva (pH=2.3) heated at 37°C and subjected to a potentiodynamic polarisation up to high values of potential (solvent's wall). By considering the polarisation curves obtained, several specific potentials were chosen where an anodic current locally maximal was detected. In a second type of experiment, the alloys were polarised at each of these potentials, in the same conditions of solution and temperature as before. During the 72 hours of constant potential applied, the current was recorded while, at the end of experiment, the surface of the electrode was examined using a Scanning Electron Microscope. In addition, a part of the solution was used in order to qualitatively analyse by ICP the possible presence of the elements belonging initially to the alloys.

Conclusions

The anodic currents recorded during the polarisations at constant potential generally well correspond to the current initially measured at this same potential during the potentiodynamic polarisation. For the constant polarisations at moderate potential (e.g. +1000mV / NHE), which can be achieved in real conditions but in extreme cases, one saw that either no metallic species were detected in the artificial saliva, or only several hundreds ppm of some metallic elements of the concerned alloys. The surfaces of the electrodes after this first polarisation seemed still intact. In contrast, polarisations at higher potentials led both to a visible deterioration of the alloy and to significant concentrations of metallic elements in the artificial saliva. Fortunately, such very high potentials (e.g. +1470mV / NHE) cannot be achieved in practice in usual conditions, of course.

Influence of the chemical composition of nickel & chromium – based dental alloys on their corrosion behaviour in an artificial saliva

Laurent Kedinger[1], Leslie Janiaut[1], Anne-Sophie Corroy[2], Ludivine Clément[2],
Pascal De March[2,3] and Patrice Berthod[1,3]
[1]Faculty of Sciences and Techniques, University Henri Poincaré Nancy 1,
B.P. 70239, 54506 Vandoeuvre-lès-Nancy, France
[2]Faculty of Dentistry, Department of Prostheses, U.H.P. Nancy 1, 96 avenue de
Lattre De Tassigny, B.P. 50208, 54000 Nancy, France
[3]Institut Jean Lamour (UMR CNRS 7198), Faculty of Sciences and Techniques,
U.H.P. Nancy 1, B.P. 70239, 54506 Vandoeuvre-lès-Nancy, France

The frameworks for fixed partial dentures are often composed of noble dental alloys which can be based on gold, platinum or palladium. Alternatively less noble metallic materials can be chosen to replace these expensive parent alloys, as example nickel-based alloys containing around 25wt.% Cr and 11wt.% W or Mo, and also other elements in smaller quantities. Such alloys are almost as resistant as the formers since they can easily enter they passivation domain, which allow them to resist efficiently against corrosion. However their chemical composition needs to be carefully chosen to achieve such good behaviour. The aim of this study is to electrochemically characterize the corrosion behaviours of ternary alloys which are simplified versions of commercial alloys, for comparison with the latter ones, and also to study how the Cr-, W- and Mo-contents can be important for the corrosion behaviours of these model alloys.

Results

The work began with the synthesis, by high frequency melting of pure elements in inert atmosphere, of all the ternary alloys which are simplified versions (ternary Ni(bal.)-22Cr-11W and Ni(bal.)-26Cr-11Mo) of the commercial alloys “Pisces Plus” (62Ni-22Cr-11W-2Al-3Si) and “4ALL” (61Ni-26Cr-11Mo-2Si) as well as the same ternary alloys but with half Cr content and/or W (or Mo) content divided by 2. Their electrochemical behaviours were studied in an acidified Fusayama’s saliva heated at 37°C in a three-electrodes cell. The runs performed were linear polarisations for Rp measurements and potentiodynamic polarisations (E_{corr}, I_{corr}, conditions of passivation). These measurements showed that the commercial alloys displayed the best behaviours, by comparison to the simplified versions, although the latter were themselves very resistant against corrosion. However, decreasing the amount of an alloying element tend to significantly deteriorate the corrosion resistance, particularly when this alloying element is chromium.

Conclusions

The contents of the elements present in these not noble alloys are to be respected. It is already (and logically) true for chromium, the content of which can be probably slightly decreased without loss of resistance but obviously not in the proportion applied here. It is also true for the minor elements present in the commercial alloys and which are usually known to be active elements.

DEALLOYING OF Ag,Au-ALLOYS IN ACIDIC NITRATE ELECTROLYTE AT THE ANODIC POTENTIODYNAMIC POLARIZATION

Oleg A. KOZADEROV, Oksana V. EVTEEVA, Alexander V. VVEDENSKII

Voronezh State University, Russia, ok@chem.vsu.ru

Selective dissolution (dealloying) of homogeneous metallic A,B-alloys consists in ionization and transition into electrolyte of only component - electronegative metal A. Investigation of dealloying kinetics promotes development of the anodic dissolution theory and ways of protection against corrosion of multicomponent metal systems.

Dealloying leads to enrichment of dissolving alloy surface layer by the second component B and to its saturation by nonequilibrium vacancies. Non-stationary character of the process determines a choice of chrono-methods for the establishment of its rate and mechanism. In the present work selective dissolution of binary alloys is investigated at potentiodynamic (chronovoltammetric) polarization.

The problem of anodic selective dissolution in the assumption that rates of diffusive mass-transport of ions in a solution and atoms in an alloy are comparable is theoretically solved. Expressions for voltammograms calculation of A,B-alloy selectively dissolving in a mixed-kinetic mode are obtained. Realization conditions of especial solid-phase diffusion transport are found.

Kinetics of Ag,Au-alloys (atomic fraction of gold x_{Au} = 0.15-0.60) anodic dealloying in acidic nitrate environment is experimentally studied. It is found that at high potential scan rate (v) and initial concentration of silver ions in a solution (c) the kinetic mode of the process is mixed. Decrease of v and c, as well as increase of x_{Au} promote the transition of the process from mixed into the solid-phase diffusion mode. The role of the surface segregation, initial electrode roughness and nonequilibrium vacancy subsystem relaxation in Ag,Au-alloys selective dissolution kinetics is discussed.

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Corrosion studies on piping steels exposed to CO_2 and artificial brines

O. Yevtushenko, R. Bäßler

BAM - Federal Institute for Materials Research and Testing, Unter den Eichen 87, 12205 Berlin, Germany

The reduction of carbon dioxide emissions from fossil fuel combustion into the atmosphere is a widely discussed issue. One of the possible solutions is its separation from flue gas and subsequent geological storage of CO_2 (Carbon Capture and Storage, CCS), e.g. in depleted gas reservoirs, or in saline aquifers. Carbon dioxide, however, may induce corrosion on the piping steels during separation/compression/transportation/injection. Therefore, selection of appropriate piping steels is the key factor in order to increase the safety and reliability of the CCS technology, and to keep the processes cost-effective.

Within the project COORAL (German acronym for "CO_2 purity for capture and storage") first studies on piping steels exposed to CO_2 and artificial brine have been carried out. The suitability of heat treated (AISI 4140, 1.7225), martensitic (AISI 420, 1.4034), and austenitic (alloy 31, 1.4562) steels possibly suitable for an onshore CCS site in Germany, is investigated in a corrosive environment (artificial brine with high chloride concentration, T = 60°C, CO_2-flow rate 3 – 5 L/h, different exposure times) using electrochemical and metallographic techniques. Depending on experimental conditions and materials investigated different corrosion kinetics were observed and compared with results obtained from exposure tests (700 – 8,000 h) in the same environment.

Investigations of electrochemical processes on metal surfaces beneath organic coatings

Y. Xu , J. M. Sykes

Department of Materials, University of Oxford, Parks Rd, Oxford OX1 3PH, U.K.

Abstract

With DC measurements it is impossible to distinguish the resistance of an organic coating from the polarisation resistance of the underlying substrate. More information on the coating and the corrosion process can be obtained by using Electrochemical Impedance Spectroscopy (EIS) in the frequency domain or some form of time-domain measurement. Various groups have used methods based on potential-time transients, but current-time transients offer an alternative.

In previous work we studied composite steel-Zn samples coated with paint. This method establishes a well-defined galvanic cell. When the samples were exposed to NaCl solution, the couple current was directly measured by a zero-resistance ammeter (ZRA). Coating behaviour for two individual electrodes was monitored by EIS and found to be different. Potentiostatic current measurements were also made on each metal at different overpotentials to plot polarization curves with the ohmic potential drop corrected. Evans diagrams were then plotted, to make a quantitative assessment of Mayne’s resistance inhibition model.

In this work we compare these results with steel-noble metal samples coated with the same paint, so the steel piece will act as anode. Together these quantify electrochemical behaviour at both anode and cathode, giving a fuller understanding of galvanic cell behaviour on painted steel.

Modification of localized corrosion resistance of AA7075 aluminium alloy by molybdenum implantation

C.M. Abreu, M.J. Cristóbal, R. Figueroa, G. Pena.

Department of Materials Science, University of Vigo, 36310 Vigo, Spain
**corresponding author: mortega@uvigo.es*

High strength aluminium alloys are widely employed in aerospace industry due to their attractive properties such as high specific strength, ductility, toughness and resistance to fatigue. However, 7xxx series are sensitive to localized corrosion (pitting, intergranular, exfoliation). It is well known, that localized resistance is dependent of the intermetallics constituent particles that present a strong galvanic coupling with the matrix [1-2]. Moreover, the susceptibility of these alloys is also affected by the aging treatments that modify their microstructure to obtain the optimal mechanical properties [3].

Ion implantation can be used to modify and improve surface properties, such as wear and corrosion resistance. With regard to the implantation of Mo in aluminium alloys some bibliographical references exist that indicate a substantial improvement in the resistance to the pits corrosion in chlorine solutions in pure aluminium [4-5]. Nevertheless, very few works exist that report the effect of molybdenum on aluminium alloys. [6]

The aim of this work is to analyze the effect of molybdenum implantation on the composition and structure of the passive layers generated on AA7075 aluminium alloy and in its resistance to the local breakdown in presence of aggressive ions. The effect of implanted element is considered under two different metallurgical conditions: artificial aging treatment (T6 temper), that produces the highest values of mechanical resistance and hardness in this alloy, and T73 hardening treatment, specifically developed to improve the resistance to SCC of alloy AA7075.

To evaluate the effect of the surface modification in the localized resistance different immersion tests (EXCO, exposition to chlorinated solutions), have been performed. The obtained results have been interpreted after the characterization of the molybdenum-induced passive layer by X-ray Photoelectron Spectroscopy (XPS) and Glancing Angle X-ray Diffraction (GAXRD) and the analysis of the effect of intermetallics particles (LOM and SEM). Our results demonstrate that the susceptibility of the 7075 aluminium alloy to exfoliation resistance is greatly depending on the aging treatment and the electrochemical activity between second phases and the matrix, even under a more resistant surface film formed after implantation.

Keywords: AA 7075,Mo Implantation, EXCO test, XPS, GAXRD

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EFFECT OF CRYOGENIC TREATMENT ON THE AA2017-T4 ALLOY

M. Cabeza [1], I.Feijoo [1], P.Merino [1], X.R. Novoa [1], S.Trillo[2]

[1] ENCOMAT Group, University of Vigo, E.T.S.E.I., Campus Universitario Lagoas Marcosende, 36310 Vigo
[2] Technology Centre AIMEN, Relva 27 A Torneiros, 36410 Porriño, Pontevedra
[3] University of Vigo, C.A.C.T.I., Campus Universitario Lagoas Marcosende, 36310 Vigo

Abstract

Stress corrosion cracking (SCC) is the phenomenon caused by the combined action of an environment and a tensile load. The occurrence of SCC can lead to loss of ductility of the material, causing brittle fracture. The susceptibility to stress corrosion cracking differs from one material to another. The aluminium alloys used as structural material in the aeronautical industry, in particular the 2XXX alloys, are susceptible to this phenomenon. In this work, the AA2017-T4 alloy has been studied. This alloy presents good mechanical properties, however it suffers of fatigue failure. Moreover, when the AA2017-T4 alloy is exposed to aqueous environment containing Cl^-, it suffers stress corrosion cracking, which involves a reduction of the service life of the material. Recent studies on other materials show that resistance to SCC can be improved through cryogenic treatment [1].

The aim of this work is twofold. First, finding the optimal parameters to perform the cryogenic treatment, and second to study the effect of those cryogenic treatments on the AA2017-T4 alloy. With that aim, micro-structural characterizations were carried out by optical microscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffractometry (XRD) and differential scanning calorimetric (DSC). The residual stress, fatigue life, and stress corrosion cracking (SCC) resistance were also studied.

The results obtained show that the microstructure has not been affected by the cryogenic treatments; however the compressive residual stress of the treated samples was higher than the residual stress of the untreated samples. That increased resistance can be at the origin of the improved the fatigue life of the AA2017-T4 alloy [2] as well as its resistance to SCC [3] after thermal treatment.

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Coulometry at controlled potential for evaluation of corrosion kinetics

Alexander E. Kuzmak, **Alexander V. Kozheurov**
IFCE RAS, Moscow, Russia

In the given report the results of corrosion kinetics investigations by a direct method of CCP (Coulometry at Controlled Potential) on glass-carbon electrode-indicator (electrode cell) are presented. In *microampere range* of measured currents of an electrolysis the effect of a quantitative unbalance between the total charges of ions *injected* into a background solution and *founded* in result of registration *) is observed.

For determination of the physical nature of the mentioned phenomenon and for more measurements informativity the process of a surface modification of a GC-electrode in a background electrolyte (under the influence of strong electric field) is investigated in the given work.

Results of an electrolysis on electrode surfaces gained *without of discharged ions* have shown presence *of discrete* kinetic areas of a current of electrolysis $\mathbf{I\tau}_i$ (i = 1 ÷ 6) instead of *monotonous* "classical" dependence.

The mentioned kinetic areas (further, ***k***-zones) differed one from another in following parameters: initial current $\mathbf{I_{0i}}$; a rate of electrolysis current changes $\mathbf{dI_i/d\tau}$ and life time interval $\Delta\tau_i$ (of i^{th} ***k***-zone).

Use of the gained values of electrode process parameters in experiment technology has allowed reliably to estimate the following characteristics:

- *Charge Rate of ions* - ν_i, discharged in the interval - $\Delta\tau_i$.
- Number of surface conditions $\mathbf{N_i}$ - "traps" for a part of discharged ions.
- Part of the charge spent for reaction of electro-transformation of defined substance.

Thus, began possible to identify *reliability areas of measurements,* having provided high experiment informativity at observance of necessary conditions of implementation of method CCP (as an etalon-free method of registration of corrosion products):

- 100 % current efficiency;
- Accuracy and selectivity of definition of a ions charge of registered substance;
- Reliability of an estimation of the moment of measuring process completion.

*) The similar phenomenon also is known at use of indicators from other materials.

The effect of electron structure of metals on the rate of electrochemical corrosion and the choice of corrosion resistant iron-based surface solid solutions

Chavchanidze A.Sh.[1], *Galushkina Yu.I.*[1], *Timofeeva N.Yu.*[1], *Bazarkin A.Yu.*[2]

1 - Moscow State University of Food Industry, 125080, Russia, Moscow, 11 road Volokolamskoe
2 - All – Russian Research Institute of Canning and Vegetable Drying Industry, 124703, Russia, Region of Moscow, Vidnoe, 78 st. Shkolnaya

E mail: tchavtcha@yandex.ru

The influence of electron structure of metals on the rate of electrochemical corrosion with hydrogen depolarization has been studied. The mathematical description of the interrelation between corrosion rate in acid media and electron work function has been analyzed using statistical analysis. This description corresponds closely to Tamman`s « n/8 » rule.

The results of quantum mechanics calculations of electron density oscillations parameters as well as calculations of potential energy of electrons around impurity atoms in iron-based substitution solid solutions have been presented. The interrelation between the parameters and electron configuration of impurity atoms has been established. The choice of chemical composition of corrosion resistant surface solid solutions was made taking into account changes of electron structure of iron in the formation of solid solution.

The choice of the type of corrosion resistant surface solid solutions is based on the analysis of possible variations of substitution impurity atoms distribution in relation to the distance between the surface and matrix, on the analysis of phase diagrams of iron-based alloys with unlimited solubility.

Impurity concentration profile curves in α-iron have been made. They represent a combination of two zones. One zone involves corrosion resistant solid solution with constant melting point (nanoquasimetal), the other presents solid solution with gradual changes of chemical composition, physical and chemical properties.

ELECTROCHEMICAL NOISE OF SCC IN AUSTENITIC STAINLESS STEELS: A COMBINED MACRO- AND MICRO-ELECTROCHEMICAL APPROACH

Mathias BREIMESSER[1,2], Stefan RITTER[1], Hans-Peter SEIFERT[1], Thomas SUTER[2], Sannakaisa VIRTANEN[3]

[1]Paul Scherrer Institute PSI, Nuclear Energy and Safety Research Department, Lab for Nuclear Materials, 5232 Villigen PSI, Switzerland, mathias.breimesser@psi.ch
[2]EMPA – Swiss Federal Laboratories for Materials Testing and Research, Lab for Corrosion and Materials Integrity, 8600 Dübendorf, Switzerland
[3]Friedrich-Alexander University, Department of Materials Science, Institute for Surface Science and Corrosion (LKO), Martensstrasse 7, 91058 Erlangen, Germany

The electrochemical noise (EN) technique is a promising tool for continuous in-situ corrosion monitoring in technical systems, which has the potential to detect stress corrosion cracking (SCC) initiation, although a limited number of systematic studies were performed so far. The basic and quantitative understanding of EN during SCC is currently rather limited. The theoretical treatment of the EN phenomenon is incomplete, which further exacerbates the interpretation of experimental results. An ongoing PhD thesis at the Paul Scherrer Institute (PSI) and Swiss Laboratories for Materials Testing and Research (EMPA) focuses on two aspects: achieving a basic understanding of the EN signals during intergranular SCC initiation on a microstructural level and the identification of noise patterns on a macroscopic level that can be correlated with the onset of SCC. A comprehensive understanding is essential and of utmost importance for the correct interpretation and modelling of macroscopic EN signals and the qualified application of the EN method in the field for the early detection of SCC initiation.

The combination of the electrochemical microcapillary technique developed at EMPA, and the EN measuring technique applied at PSI, is selected to identify and isolate the relevant microscopic sources that contribute to the macroscopic EN signal during the SCC process. This twofold approach, applied to the model system of thermally sensitized austenitic stainless steel (AISI 304) in aqueous solutions of potassium tetrathionate at room temperature, is introduced briefly. Furthermore, preliminary results of macroscopic EN measurements during loading tests, as well as measurements of discrete initiation events of intergranular cracks, using the microcapillary technique, are presented.

On the Initial Stage of Galvanodynamic Voltametry Polarization (GVP) of Pure Al-foil in 3N HCl

J. C. Lin[a b *], G. H. Zeng[b], T.P. Teng[b], C.H. Chang[b]

[a]Institute of Materials Science and Engineering, National Central University, Jhongli City, 320, Taiwan
[b]Department of Mechanical Engineering, National Central University, Jhongli City, 320, Taiwan
[*]corresponding author E-mail: jclincom@cc.ncu.edu.tw

Abstract

Galvanodynamic voltametry polarization (GVP) was used to investigate the electrochemical behavior of a commercial pure Al-foil in 3.0 N HCl solution. Triangular pulse waveforms with a constant current density of 0.15 A/cm^2 were employed in this work. The triangular pulse consisting of a symmetrical negative triangle and a positive triangle varying in different symmetries on the current peak (i.e., prior peak on the left of triangle, PPLT; peak on the left of triangle, PLT; standard triangle, ST; peak on the right of triangle, PRT; and post peak on the right of triangle, PPRT). In the performance of GVP, especially at the initial stage, the potential of the aluminum foil was measured and the dependence of potential variation on the symmetry of positive current peak was explored. The morphology on the Al-foil electrochemically etched by different triangular pulse waveforms was examined by field emission scanning electron microscope (FESEM). The size of surface pores on Al-foil etched by different waveforms was evaluated. In the GVP diagram, each E-i curve reveals a characteristic anodic peak (i.e., $E_{b,}$ the breakdown potential of the anodic film) that is useful to estimate the feasibility in etching. The magnitude of breakdown potential and the corresponding breakdown current decreases in the order PPRT > PRT > ST > PLT > PPLT. When PPLT Triangular waveform was employed to etch Al-foil, less quantity of charges was consumed to form anodic film (Q_f) but higher quantity of charges was consumed to dissolve aluminum (Q_d). Thus the pores caused by PPLT Triangular waveform are big then by other ones.

Keywords : Al-foil, GVP, etching, anodic film, breakdown potential

Wear of metals of the cathode during electrolytic hydrogen-enrichment

SURANOV G.I.
Ukhta State Technical University, Ukhta, Russia

Long-live hydrogen-enrichment of a material of the cathode causes its intensive destruction. Tested samples from steel (40XHMA), cast-iron (turned and cut out of the cylinder barrel of compression ignition engine), coppers, zinc and aluminium. Hydrogen-enrichment carried out in a U-shaped test tube in 1 %-water solution of sulfuric acid at a current magnitude 20...50 мA (current density 27,5...1,88 мA/sм^2) during 30...40 h. Wear of samples defined weighing to within $1 \cdot 10^{-4}$g.

During hydrogen-enrichment steel, cast-iron and zinc samples wear out most intensively. Their surface in electrolyte becomes covered by bubble of gas which fractionally expand and then, coming off a surface of a sample, precipitate out on a surface of electrolyte.

Surfaces of steel and cast-iron samples becomes covered black layer for in which the carbon deleted from a material of samples contains, and on them numerous and deep cavities are formed. In bottom of samples branchy dendrite crystals which float in electrolyte grow, sometimes collapse and drop out in a deposit. In a cathode part of electrolyte and on its surface precipitate out various color of a micelle with the advent of which the size of a current fractionally drops and gassing is practically stopped.

At hydrogen-enrichment a zinc sample the crack is audible, and at the bottom of a test tube settle large-size particles of products of destruction of zinc that is related with high absorption capacity (occlusion) of hydrogen.

Speed of wear (destruction) of copper and an aluminium samples approximately on two sequences is less, than steel, cast-iron and zinc. At hydrogen-enrichment Cu and Al-samples a precipitating out hydrogen is not late on their surface and intensively precipitates out from electrolyte. Such behaviour of hydrogen and the minimal wear of a copper sample can explained in positive potential of copper in electrochemical series (more positively hydrogen).

During hydrogen-enrichment cast-iron samples collected the gas which is precipitating out in a cathode part of a test tube in container with the locking liquid (an aqueous saturated solution of sodium chloride) and determined its composition. The analysis of gas has shown presence of methane, ethane, propyl hydride, *n*-butane and other hydrocarbons that specifies passing of chemical reactions of hydrogen with carbon of metals, and also on pyrolysis of methane during hydrogen-enrichment.

Destruction of a material of the cathode at hydrogen-enrichment can be explained by transformation of singlet, as diffusive-active hydrogen in molecular, and formation of methane which collect in structure of metal under high pressure. Besides as a result of chemical interaction of hydrogen with elements and impurities of metals, and also pyrolysis of methane in electrolyte micelles are formed, and in a precipitating out gas various hydrocarbons contain.

About the nature of anode processes at the initial stage of copper corrosion in solutions of haloids

V.P. Razigraev, M.V. Lebedeva, V.A. Golovin, S.A. Dobriyan.
A.N.Frumkin Institute of Physical Chemistry and Electro Chemistry, Russian Academy of Science, Moscow, Russia
E-mail: razygraev@ipc.rssi.ru

From the analysis of the concentration dependences of the potentials of copper corrosion in haloid ions solutions follows that in concentrated solutions the values of corrosion potentials are established much more negative than the potentials of formation of known substances CuH, Cu_2O, $[CuH_2]^-$. In neutral medium with oxygen depolarization the potentials of copper corrosion have inverse dependence from agitation in other words they are displaced in negative direction. It is caused by primary stimulation of anode reaction. The last fact can be used for determination of the equilibrium potential of anode reaction which coincides with the potential of removal of concentration restrictions for anode process. Dependences of φ_{equil} for investigated anions are experimentally determinated:

$\varphi^{Cl^-} = -0{,}057 - 0{,}057 \cdot \lg a_{Cl^-}$; $\varphi^{Br^-} = -0{,}108 - 0{,}063 \cdot \lg a_{Br^-}$; $\varphi^{I^-} = -0{,}260 - 0{,}062 \cdot \lg a_{I^-}$.
From these dependences follows that the anode process has the first order on anions for all solutions.

A stimulation of anode reaction on copper by agitation at low dissolution speeds is not corresponding with the conceptions about usual diffusion restrictions. The anode process runs locally. This fact was presumed and experimentally confirmed at microscopic researches.

Probable anode processes with haloids participation on copper can be represented by following sequence:

$$\begin{tikzcd}
 & & & \mathrm{CuH_{solid}} \\
\mathrm{Cu^0 + H^-} \arrow[r, shift left, "\{1\}"] & \mathrm{Cu^0(H^-)_{adsorb} - e^-} \arrow[l, shift left] \arrow[r, "\{2\}"] & \mathrm{(CuH)_{adsorb}} \arrow[ur, "\varphi>\varphi_{equil}^{CuH}"] \arrow[dr, "\varphi<\varphi_{equil}^{CuH}"'] & \{3\} \\
 & & & \mathrm{CuH_{aqua} + n\,H^- \rightarrow [CuH_{(n+1)}]^{n-}.}
\end{tikzcd} \qquad (5)$$

The initial stage of copper corrosion with haloid ions is independent of end products properties and includes two obligatory stages: haloid ion adsorption {1} and subsequent electrochemical stage of surface adsorbed $(CuH)_{adsorb}$ complex formation {2}. The subsequent changes of $(CuH)_{adsorb}$ complex at the stage {3} depend on electrode potential:

- the low soluble surface sediment of copper haloid is the only product of anode reaction at potentials more positive than the equilibrium potential of CuH_{solid} (φ_{equil}^{CuH}) formation;
- the surface $(CuH)_{adsorb}$ complex is desorpted in solution with the subsequent formation of products of type of $[CuH_n]^{(n-1)-}$ in the rage of the potentials located more negatively than the equilibrium potential of CuH_{solid} (φ_{equil}^{CuH}) formation but more positively than the equilibrium potentials of reactions of soluble products formation.

Effect of hydrogen and anodic dissolution on the promotion of stress corrosion cracking in pipeline steel

J. X. Li, B. W. Pan, Y. J. Su, L. J. Qiao
Center of Corrosion and Protection, University of Science and Technology Beijing,
Beijing 100083, China

Abstract: The effect of hydrogen and anodic dissolution in stress corrosion cracking (SCC) in API X-60 pipeline steel in soil of containing water with 8.5 pH value under open circuit and catholic polarization conditions has been investigated. The results indicated that both hydrogen-induced plastic loss and the hydrogen-induced additive stress for recharged samples all increase linearly with increasing the logarithm of hydrogen concentration. Hydrogen atoms can enter into the sample during SCC in the soil solution under open circuit and catholic polarization, thus the plastic loss and the additive stress are due to hydrogen, anodic process and coupling of hydrogen and the anodic dissolution process. The plastic loss during SCC at various potentials increases with increasing the additive stress. For SCC at open circuit, there is no coupling of hydrogen and anodic process. And hydrogen and anodic dissolution through the additive stress play an almost equal important role during SCC in the soil solution at open circuit.

Corresponding author:
Jinxu Li (J. X. Li)
Tel: 86-10-62334493
Fax: 86-10-62332345
Email: jxli65@ustb.edu.cn

Nitrogen implantation on aluminium alloys: Effect on the electrochemical properties

C.M. Abreu, M.J. Cristóbal, R. Figueroa, G. Pena.
University of Vigo, E.T.S.E.I., Campus Universitario Lagoas Marcosende,
36310 Vigo, Spain. cabreu@uvigo.es

Engineering aluminium alloys attain their desirable mechanical properties, such as high-strength/weight ratio, as a result of heterogeneous microstructures developed by specific alloying conditions and heat treatments. Unfortunately, the corrosion resistance of these alloys is highly influenced by the presence of second phases, since the intermetallic particles exhibit different surface film characteristics, and, in contact with an electrolyte, local galvanic cells ca be easily formed on the surface, leading to a accelerated local corrosion attack.

The use of aluminium alloys is restricted in applications by their low surface hardness and wear resistance, so different techniques of surface modification are used to overcome this limitation. N^+ implantation has proved to be an efficient way to increase mechanical resistance of the surface. But its effect on the local corrosion resistance is not clearly established (since it is highly dependent on the implantation conditions, type of selected alloy and test media).

In this work, we present the results of an electrochemical study of 2024-T3 and 7075-T6 alloys performed in aerated Na_2SO_4 solutions, to clarify the influence of N^+ implantation on their corrosion properties. The implantation conditions were selected after simulation according to SRIM computational code, in order to achieve the highest level of nitrogen in the outermost surface of both alloys. The electrochemical behaviour of the base and modified alloys was analyzed using EIS and potentiodynamic polarization techniques. The characterisation of the passive layers formed after implantation on both alloys (X-ray Photoelectron Spectroscopy (XPS) and Glancing Angle X-ray Diffraction (GAXRD) and the microscopic study (LOM and SEM) of the surfaces after the tests, allowed the interpretation of the obtained results.

The important increase of the impedance registered in both implanted alloys, after the initial immersion in the solution, reflects an improvement in the passive films formed on the surface. However a displacement in the OCP values towards more active potentials is detected after N-implantation, indicative of an activation of the surface as a consequence of the ionic bombardment. During the anodic scan in the potentiodynamic polarization tests, the oxidation and dissolution of the anodic second phases (mainly AlCuMg) and the dissolution of the aluminium matrix surrounding the cathodic phases (Al-Cu-Fe phases) is detected. After the polarization measurements, the impedance of the surface decreases, although it still higher in the implanted than in the unimplanted alloys. In order to elucidate the initial breakdown of the passive films Z vs. was recorded, showing clear differences between both alloys in both conditions.

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Assessing the residual lifetime of district heating network

By Lone Mathiesen, Technical coordinator, Municipality Kalundborg;
Asbjørn Andersen, Søren Klinggaard, Lisbeth Richel Hilbert, FORCE Technology

Abstract

Assessing the condition of district heating systems can be a very important task e.g. when a municipality decides to carry out urban renewal projects.

Based on the assessment it can be decided whether the district heating system has a residual lifetime similar to the expected life of the urban renewal. Or if - within the foreseeable future - an increased number of leakages or other errors are to be expected: Incidents that could necessitate excavations in order to change or repair part of the pipe system.

In the following case story we will describe an assessment of the lifetime of the district heating system of Municipality Kalundborg, Denmark.

To establish the present state of the district heating system visual inspection is used, which necessitates excavation. Further we assessed the material thickness by use of long range ultrasound measurement. By this method only a minor excavation is necessary in order to get an assessment of the material thickness in the piping for an extended part of the system.

The article sums up the results leading to an assessment of the residual lifetime of the district heating system in Municipality Kalundborg.

NICKEL INFLUENCE TO THE STRESS CORROSION AND STACKING FAULT ENERGY ON MANGANESE-CHROMIUM STAINLESS STEELS

Vladimir Cihal[1], Marie Blahetova[2], Eva Kalabisova[1], Stanislav LASEK[2], Libor Turek[1]

[1]SVUOM Ltd., Czech Republic, biba@svuom.cz
[2]VSB-TU Ostrava, Czech Republic, vladimir.cihal@vsb.cz

The orientation of the work addresses the characteristics of the stainless manganese-chromium grades 03Mn18Cr16N and 03Mn18Cr16MoN based on the initial testing made on the austenitic manganese –chromium creep resistant steels. The experimental orientation includes steels modified by nitrogen and molybdenum aiming at improving the resistance to stress corrosion cracking.

Nickel content exceed 0.5 wt.% level is detrimental to stress corrosion cracking resistance. When nickel content rises to more than 5% Ni, resistance to the stress corrosion cracking begins to seemingly rise with increasing stacking fault energy.

When the nickel content is around 2% and/or below, the stacking fault energy is so low that it causes transformation of the austenite →stacking faults → έ phase → α martensite type, strengthening and probably increases the resistance to stress corrosion cracking of steel.

Molybdenum in addition to chromium increase the resistance to the general, pitting and intergranular corrosion.

The mechanical properties show that all the experimental heats had higher strengths properties and/or yield point levels than the austenitic CrNi steels with a comparable carbon content.

Aluminum anodic behavior at neutral electrolytes with inorganic and organic additives

Svetlana Kaluzhina, Tatiana Borisenkova,
Voronezh State University, Voronezh, Russia

Aluminum forms various composition and thickness oxide-hydroxide films, therefore anodic behavior aluminum is complicated. It assumes obtaining of correct data in each concrete case of aluminum application. At the present work this question was analyzed in Al (99,9 %) anodic polarization conditions at mediums, close to neutral (pH = 4,0-8,5), with inorganic (Na_2SO_4, KNO_3, NaCl) and organic (glycine, α-alanine) additives. The working solutions concentration range varied from $0,7x10^{-4}$ M to $1,7x10^{-1}$ M.

Complex of independent physic-chemical methods (voltammetry, chronoamperometry, optical microscopy (MBS-2 and MIM-7), scanning electronic microscopy (SEM) with JEOL-6380LV and energy-dispersive X-ray analysis (EDXA) with INCA Energy-250) were used for receiving reliable experimental results.

The obtained data have shown differently aluminum behavior in the studied electrolytes. Aluminum was in a passive condition under anodic polarization in systems with additives SO_4^{2-} and NO_3^- - ions and water solutions with glycine (pH = 5,0-5,8) and α-alanine (pH = 4,6-5,7) additives. On the contrary, metal was exposed to local activation (LA) under anodic polarization in the solutions, containing Cl^- (pH =4,0-6,0), Gly^- (pH = 8,5), α-Ala^- (pH = 8,5) – ions. On the basis of experimental and literary data mechanisms of the studied processes were suggested at interpretation of the obtained results. So, it has shown that passive layer was formed without electrolyte anions participation due to aluminum high chemical affinity in relation to oxygen. Opposite, electrolyte anions (Cl^-, Gly^-, α-Ala^- - ions) interact with passive metal during LA process and form the surface adsorption complexes, with further transfer into electrolyte volume. Research results of aluminum anodic behavior are confirmed by kinetic analysis data, SEM and EDXA results and are interpreted on the basis of nucleophilic substitution theory and of "hard and soft acids and bases" conception.

The Negative Difference-Effect in the anodic oxidation of zinc in sodium hydroxide solution

Protasova I.V., Gorlov A.S., Aleshina L.A., Vvedenskii A.V

protasova@chem.vsu.ru, Voronezh State University, Voronezh, Russia

Numerous researches of the anodic process of zinc in alkaline solutions show the complex nature of its kinetic dependencies which is caused by the multi-step electrode reaction, stage of products diffusion aside from an electrode surface, phase formation and mass transfer in the solid phase. It is experimentally established by authors of this work for solutions 0,1 -2 M NaOH and it is shown by a number of other authors that anode zinc oxidation in alkalis is complicated multi-step process, ratio of speeds of various its stages varies with changing the anodic area.

This work attempted to estimate the partial reactions of anodic processes on a stationary zinc electrode in 2 M NaOH. In the given research by results of the solution analysis on zinc ions the anode curve of dissolution of zinc is received.

On current-potential curve, as on the curves received by other methods, are observed the area of fast growth of speed of anode process with polarization, area of sharp braking of anode process and its independence of potential.

The kind of current-time curves obtained during potentiostatic dissolution of zinc varies with polarization. Their character well illustrates that passivation processes are absent or negligible at small displacement of potential to anode area (the current practically does not vary), and at the further increase potential, at the potentials of the ascending branch of peak, an insoluble products of oxidation of zinc on electrode surface are formed (characteristic peaks nucleation are observed), and at displacement in area of zinc passivity the anode current for split accepts constant value. Comparison of speed of anode process on the zinc, received of the analysis of a solution taking into account corrosion current and average speed of process in time dissolution with controlled potential, has shown that total speed of transition of zinc in a solution exceeds the speed of anode process answering to the charge passed through an electrode in all investigated area of potentials. Thus, in unstirred air-free 2 M NaOH on a stationary zinc electrode in all investigated area of potentials the Negative Difference-Efect (NDE) takes place.

It is necessary to notice that the Effect size on zinc in alkaline solution depends on anode potential. Thus, at little displacement of potential in anode area (to 40 мВ) the Difference-Effect practically is absent, the anode dissolution of zinc in the field of an ascending branch (-1220 мВ-1150 мВ) is accompanied by growth NDE. At the further increasing of potential, in peak potentials and in potentials of pull-down branch of the current-potential curve, Difference-Effect decreases. The complicated character of electrochemical behavior of zinc at various anode potentials testifies to a difficult parity of the thermodynamic and kinetic factors defining speed of separate interfaced reactions, proceeding on an electrode. So increase NDE at small anode potentials can be caused increase in speed of self-dissolution of metal as a result of chemical interaction of zinc with solution components. The reason of this growth can be local depassivation zinc. The further reduction NDE with polarization is probably connected with growth of passive layer on zinc and, accordingly, its stability to local destruction. Thus in the field of passivity zinc self-dissolution, most likely, proceeds from the oxidized condition with constant speed, apparently, a little exceeding corrosion current. Research supported by the RFBR project 08-03-00194.

The Passive behavior of magnesium alloys containing rare-earth elements in alkaline media

*R. Pinto[1], M.G.S. Ferreira[1,2], M.J. Carmezim[1,3], M.F. Montemor[1]**

1 – ICEMS, Instituto Superior Técnico, Technical University of Lisbon, Portugal
2 – CICECO, Universidade de Aveiro, Portugal
3 – Instituto Politécnico de Setúbal, ESTSetubal, DEM, Portugal

Abstract

The passive behaviour of magnesium alloys ZK31, EZ33 and WE54 was studied in alkaline media (NaOH pH13) in the presence and absence of chloride ions. The electrochemical properties were investigated by potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and capacitance measurements.

X-Ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and atomic force microscopy (AFM) were employed for the study of the chemical composition and surface morphology of the surface films, respectively.

The electrochemical impedance results revealed that the film formed on the surface of the three alloys is characterized by an increasing resistance, which stabilized with time. In the absence of chloride the film resistance was identical for all the three alloys. However, in the presence of chloride, the resistance of the film formed on the EZ33 alloy dropped nearly one order of magnitude comparatively to the other alloys. Generally, in the presence of chloride there was a decrease of the conductive character of the film.

The films are homogeneous and, according to the XPS results, the outer layer seemed mainly composed of Mg(OH)2 and the internal layer composed of MgO, independently of the presence of chloride. The AFM study revealed that the presence of chloride affected film morphology, namely nano-crystallites dimensions and aggregates size, which were increased.

Keywords: Mg-Zr alloys, Rare earths, Impedance, Passivity

Acknowledgments: Project PTDC/CTM/72223/2006

Interference of in common proceeding electrode processes at dissolution low-carbon steels in the acidified solutions containing nitrate ions

Zartsyn I.D., Fedjanin D.O., the Voronezh State University, Voronezh

According to the modern electrochemical theory of corrosion anodic reaction of metal dissolution and cathodic - oxidizer reductions can be interfaced at the expense of electrons of conductivity of metal. Such linking is realized in the conditions of an open circuit and in galvanostatic conditions. In potentiostatic conditions the external chain is a source and an outlet of electrons of infinite capacity. Therefore electrons of conductivity of metal any more are not the general intermediate particles for anodic and cathodic reactions. The yielded reactions in potentiostatic conditions should be independent parallel processes.

However linking of partial electrode reactions can be realized at the expense of other particles, besides conductivity electrons. For example, the intermediate reactive particles formed in cathodic process, can take part in anodic then partial electrode processes will appear are interfaced and in potentiostatic conditions. One of the vivid examples - interference of collaterally proceeding reactions of ionization of metals of iron’s subgroup and chrome, and nitric acid reduction in the diluted solutions. It has appeared, that in the diluted nitric solutions iron dissolves and at cathodic polarization with a speed much exceeding the size received by extrapolation of the partial anodic curve from area of positive potentials. Thus and the anodic polarizing curve is displaced towards the big currents in the presence of hydrogen nitrate.

Other example - increase in ionization rate of metals of iron’s subgroup in the presence of oxygen-containing oxidizers. It is offered to name interference of collaterally proceeding reactions of ionization of metal and oxidizer reduction chemical linking. Purposeful influence on law of chemical linking can be considered as a recent trend in protection of metals against corrosion. In particular, it is possible to assume, that presence at electrolyte of substances, capable to supersede from a surface anodic-active intermediate particles, should suppress chemical linking.

Kinetic and thermodynamic aspects of interference of collaterally proceeding anodic and cathodic reactions have been analyzed by application of a method of kinetic graphs (diagrams). Physical and chemical models of influence of processes of nitric acid reduction, oxygen-containing oxidizers on law of iron ionization and low-carbon alloys on its basis have been offered. Influence of an anion adsorption and other components of electrolyte on laws of this phenomenon have been analyzed.

It has experimentally been positioned, that adsorption chloride - and sulphate-ions, organic phosphonic acids really suppresses chemical linking of processes of iron ionization and nitric acid reduction, and also other oxygen-containing oxidizers both at anodic, and at cathodic polarization. Semi quantitative conformity of theoretical and experimental results has been received.

CORROSION CHARACTERISATION OF VARIOUS STAINLESS STEELS EXPOSED TO ELEVATED FLUORIDE SOLUTIONS

Josias VAN DER MERWE[1], **Zulaika HALIFA**[1]

[1]*University of the Witwatersrand, South Africa, Josias.vandermerwe@wits.ac.za*

The corrosion characteristics of three duplex stainless steels as well as type 316L stainless steel were evaluated in elevated fluoride solutions. The objective of the investigation was to determine the performance of various duplex stainless steels when exposed to a variety of fluoride concentrations and pH levels. The duplex stainless steels evaluated were: types 2101, 2205 and 2507, in order to get a spectrum of results from the lean to the super duplex stainless steels. Exposure and electrochemical tests were performed at 3 different fluoride concentration as well as 3 pH levels. Polarisation characteristics and chrono-potentiometry/amperometry measurements were performed as well as scanning electron microscopic evaluation. The LDX2101 duplex stainless steel in most instances showed the lowest corrosion resistance in fluoride solutions followed by 316L austenitic stainless steel. The duplex stainless steels 2205 and 2507 presented the best corrosion resistant properties from all the steels investigated. Increased sodium fluoride concentrations at the same pH and temperature caused lower corrosion rates.

EFFECT OF LASER-REMELTING AND AGEING TREATMENT ON THE ELECTROCHEMICAL BEHAVIOUR OF A LOW NICKEL MARAGING STEEL

M. Cabeza[1], G. Castro[2], P. Merino[1], G. Pena[1], M.Román[1], R.Figueroa[1], P. Vázquez[2]
[1] Vigo University, E.T.S.E.I., Campus Universitario Lagoas Marcosende,
36310 Vigo, Spain. gpena@uvigo.es

[2] Technology Centre AIMEN, Relva 27A Torneiros,
36410 Porriño (Pontevedra) Spain

Precipitation-hardening maraging steels are well known for their combination of high strength and high toughness, which are among the highest attainable in general engineering alloys. Because of these attractive properties the use of these alloys is in continuous growth in important high-tech areas, especially in thermo-mechanically loaded parts of tools for pressure die casting of Al and Mg alloys.

Laser-remelting process of the surface is proving to be a good option to repair the damaged components made of maraging steels, due to the fact that the selection of adequate parameters provides a thin remelted surface with very fine dendritic microstructure and high chemical homogeneity, preventing local stress concentrations [1]

Since the parameters of the isothermal ageing treatment and the surface remelting process are selected to improve the mechanical properties of the steels [2], little attention is paid to other characteristics as corrosion resistance of the surface.

This paper is focused on the electrochemical study of a new class of low nickel maraging steel, the 14Ni(200) in chlorinated media, by means of potentiodynamic polarisation and electrochemical impedance spectroscopy. The behaviour of the super-saturated martensite present in the annealed condition and the effect of the precipitation of $Ni_3(Mo,Ti)$[3] nanocompounds in the ageing treatment at 525ºC for 6 hours were analyzed. The laser-remelting treatment was carried out with a Nd-YAG laser and the operational parameters were optimised to obtain an overlapped remelted surface with the best hardness values (Power: 2kW; speed: $50 mm\cdot s^{-1}$; laser-beam diameter on the surface: 3mm; energy density: $13.33\ J\cdot mm^{-2}$; 25% overlapping). The effect of this repairing treatment in the electrochemical behaviour of the maraging steel is considered alone and combined with a final age hardening treatment.

Acknowledgements: This work is supported by the Xunta de Galicia under the program INCITE (07TMT001304PR)

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Electrochemical testing of inhibition efficiency some types of anticorrosive pigments for pitting corrosion of carbon steel at ambient temperature

Boleslav Eremias, Hana Geiplova, Jaroslava Benesova,
SVUOM Ltd.,Prague/Czech Republic

It is well known that the presence and concentration of chloride as well as temperature play key role in determining whether localized corrosion of carbon steel occurs. The effect of chloride concentration on E_{pit} of carbon steel for water extracts of anticorrosive pigments has not yet been however examined. It can be due to the fact that sufficient concentration of chloride for pitting of carbon steel can be low in this type of environments. In addition to it water extracts of anticorrosive pigments are environment where carbon steels typically do not undergo deep penetration by pitting corrosion and exhibit rather weak protective passive films.

All these facts make necessary to test applicability of E_{pit} approach for carbon steel and the conditions under which passivity and localized corrosion are possible in this type of environment.

This work describes cyclic voltametry method for the rapid screening of inhibition efficiency of some anticorrosive pigments for pitting corrosion of carbon steel. The chosen method is able to determine E_{pit} value of carbon steel for given type of tested extract during the first scan as well as possible pitting initiating within occluded regions during the reverse scan. Possible loss of pH control within occluded regions, such as matrix-inclusion interfaces, is discussed.

Electrochemical noise of AA2024 in solutions promoting IGC

J.M. Sánchez-Amaya[1]*, L. González-Rovira*[2]*, K. El Amrani*[2]*, M. R. Amaya-Vazquez*[2]*,*
and F.J. Botana[2]*.*

[1]*Titania, Ensayos y Proyectos Industriales S.L. Puerto de Santa María, Cádiz.*
[2]*LABCYP. Departamento de Ciencia de los Materiales e Ingeniería Metalúrgica y Química Inorgánica. CASEM. Universidad de Cádiz.*
Avda. República Saharaui s/n, Apdo. 40, Puerto Real, 11510. Cádiz. SPAIN.

Abstract.

In different industrial sectors, as in aeronautic, standardized tests are usually employed to control the quality of the materials used. In the case of metallic components, various restrictions must be satisfied, among them an appropriate corrosion resistance. There are a lot of standardized tests that allow the evaluation of the corrosion behaviour of metallic samples. Some of them have the aim of determining the susceptibility to Intergranular Corrosion (IGC). The latter tests are based on immersion treatments of the samples in aggressive solutions, with the damage being evaluated later by means of metallographic analysis.

In the present contribution, the influence of different variables of these tests (such as the immersion time, the temperature and the composition of the solutions) on the damage suffered by the samples has been studied. The obtained results have showed that both the morphology and the depth of the attacks are different when these variables are modified. Additionally, Electrochemical Noise (EN) of both potential and current were simultaneously measured during the immersion period of the tests. The main objective of this work has been to analyse the correlation of the results obtained from the analysis of the EN signals generated during the tests with the results obtained from the metallographic analysis performed after the tests.

Keywords:

Electrochemical Noise, Shot Noise, AA2024, Metallographic analysis, Intergranular Corrosion.

The method and practice of corrosion inhibitors true solutions and emulsions integral toxicity estimation

V.I. Vigdorovich, S.V. Romanenko, M.V. Vigdorovich.
Tambov State Technical University, Tambov, Russia

The request uniform system to the corrosion inhibitors regardless to their purpose and functional universality level should include the requirements to the toxicological characteristics. But the limited permissible concentration (LPC_i) estimate of such products, also including their criterial values relative to the water (LPC_W) or proper approximate safe influence level ($ASIL_W$) is extremely difficult because of the technological complications and its cost. Moreover it is hardly possible because such products are usually the mixtures with the different levels of these values.

In these cases the most toxic component even by its lowest concentration can determine the product total toxicity or its aqueus system. In similar cases two ways seem effective enough:

1) Integral toxicity values (ITV) application: chemical (CCO) and biological (BCO_i, usually BCO_5) consumption of oxygen.

2) The experimental method usage which is based on the system biotesting. To that end it is necessary to use no less than two test-objects (daphnids and infusorian, ceriodaphnids and bacteria or aquatic plants). The system biotesting method allows to estimate its danger class (represented in report). But the first way is more simple and available.

There are in report received in that way aqueous systems ITV containing inhibitors compositions EM- and AMDOR-lines combined with their components formulas. As an example there is the row of such relationships for 3 compositions below (EM-12, EM-13 and EM-14).

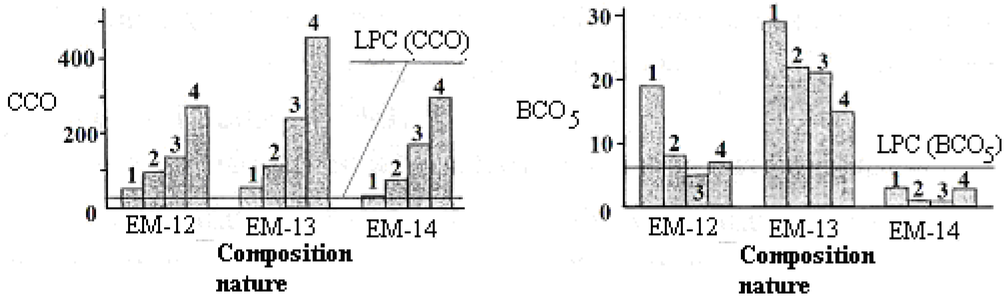

Figure. The CCO and BCO_5 values (mg O_2/l) of the aqueous systems containing inhibitors. C_{Inh}, mg/l: 1 – 25, 2 – 50, 3 – 100, 4 – 200. The horizontal line characterizes the LPC_i.

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Duplex Steel S 32304 – A Low Cost and Corrosion-Resistant Alternative to Molybdenum Containing Austenite

Ralph Bäßler, Margit Weltschev and Kathleen Weidauer
BAM - Federal Institute for Materials Research and Testing
Unter den Eichen 87
12200 Berlin/Germany

In Germany the "BAM-List – Requirements for Tanks for the Transport of Dangerous Goods" is the basis for substance-related prototype approvals for tank containers given by the BAM - Federal Institute for Materials Research and Testing. Compatibility evaluations of selected metallic materials as well as polymeric gasket and lining materials under the influence of approximately 7000 dangerous goods have been published in the BAM-List since 1989.

Duplex steel S 32304 was originally developed as a substitute for the austenitic grades 316L and 316Ti. Due to its characteristic profile this steel was qualified for applications requiring high strength values and concomitant adequate corrosion resistance. Due to the lower content of the alloy elements nickel and molybdenum this duplex steel is a cost-efficient alternative to molybdenum containing austenite.

Only a limited number of corrosion test results of S 32304 under the influence of dangerous goods have been published in the BAM-List. Therefore, test specimens of this steel were exposed to selected corrosive substances.

Due to the reduced alloy content, the corrosion resistance of the duplex steel S 32304 was reduced in acidic substances, such as formic acid, acetic acid and sulphuric acid, in comparison to austenitic CrNiMo-steels. Tests in an alkaline medium showed sufficient resistance.

These tests were performed to complete the BAM-List in order to provide the user a comprehensive base for materials selection.

Determination of the corrosion current density in low conductivity media: the use of microelectrodes to minimize the ohmic drop in Diesel oil

Paulo César A. de Oliveira, Rodnei Bertazzoli*
State University of Campinas, Faculty of Mechanical Engineering,
13083-970, Campinas- São Paulo, Brazil

The gravimetric and electrochemical tests are the most common techniques used in determining the corrosion rate when a material is exposed to an aggressive solution. However, the use of electrochemical polarization is limited to electrolytes with sufficient conductivity. For low conductivity media, the ohmic drop changes the linearity of the Tafel plot, preventing an accurate extrapolation and the determination of the corrosion rate. In this study, we investigated a technique in which working microelectrodes were used to obtain the Tafel curves. The strategy was to reduce the electrode area and hence, the ohmic drop. The microelectrodes were made by wire drawing followed by thermal annealing of AISI 1020 steel. The wires, with diameters ranging from 1000 µm to 35 µm, were encapsulated in glass Pasteur pipets with epoxy resin. The electrochemical cell was a two electrode cell in which an AgI coated Ag plate played a double role as reference and counter electrode. Polarization curves were recorded using a 1mL drop of Diesel oil on the surface of the Ag/AgI plate. Working microelectrodes tip were positioned inside the oil drop by keeping a 0.5 mm gap over the Ag/AgI plate. This experimental set up was placed in a Faraday cage. The electrical resistances as a function of electrodes diameter were obtained from polarization curves and then, used for IR drop calculations. Figure 1 shows values of IR drop for the electrodes diameter as shown, for the range of potentials used for the potential scans. The insert of figure 1 shows that IR drops are smaller than 10^{-5} V for the smaller diameters. The results showed that, for electrodes with diameters below 40 µm, the IR drop tends to a minimum and independent of the microelectrode diameter. For these diameters, the error in determining the corrosion current density from the uncompensated curve was less than 10% compared to the figure from the compensated data.

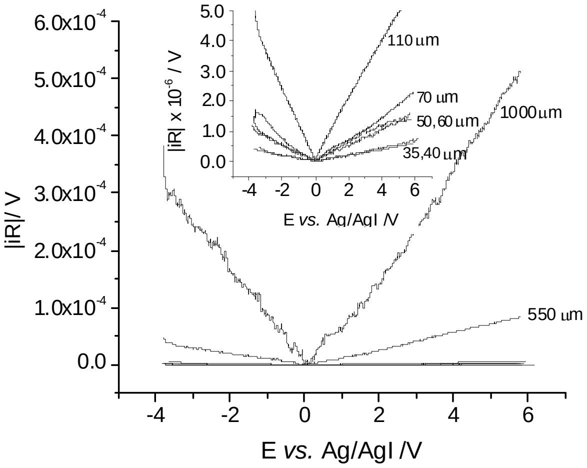

Figure 1. Ohmic drop as a function of electrode diameter during polarization of AISI 1020 microelectrodes in Diesel oil.

*rbertazzoli@fem.unicamp.br

Corrosion studies in low conductivity media: carbon steel in ethanol media

Panossian, Z.[1]; Santos, C. A. L.[1]; Pimenta, G. S.[2]

The corrosion studies in aqueous media, by means of electrochemical techniques, are well established and the situations that limiting its use are also known. The electrochemical techniques, in turn, are very useful and make possible to verify the susceptibility of the materials in media of interest, beyond allowing the attainment of kinetic data on the corrosion. The use of these techniques is sufficiently desirable, however, in low conductivity media of ($\leq$ 1.0 μS/cm) the same ones are not applicable due to being raised resistivity media. Currently, ethanol combustible has been arousing the scientific, technological and commercial interest, due to its ample use in the national market and to its great potential as renewable energy source, in international scope. The present work goals to verify the ethanol corrosivity, by means of electrochemical impedance tests, using carbon steel as working electrode and 316 L stainless steel as auxiliary electrode and reference electrode. Ethanol anhydrous P.A was studied as well as ethanol anhydrous P.A increased of, in the maximum, 1.0 % of water with and without impurities foreseen for norm ASTM D 4806 (2009). The results had indicated that ethanol anhydrous or contend until 1 % of water were little aggressive and the presence of the impurities had raised its aggressiveness.

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[1] IPT – Instituto de Pesquisas Tecnológicas do Estado de São Paulo S.A. Institute for Technological Research – Brazil

[2] CENPES – Centro de Pesquisas e Desenvolvimento Leopoldo Américo Miguez de Mello. PETROBRAS Research Center– Brazil

Effect of plastic deformation on surface reactivity of 316L stainless steel

Yamina Boudinar, Marie Touzet*, Olivier Devos*, Monique Puiggali*,**
*Laboratoire de Mécanique Physique, Université Bordeaux 1, 351 cours de la Libération, 33405 Talence Cedex, France
**Université de Skikda, Faculté des Sciences et des Sciences de l'Ingéniorat, route d'el-hadaiek BP 26 Skikda21000 Algérie.

Numerous studies have shown that processes of corrosion (dissolution, passivation) were modified with the increase of plastic strain. In order to study these processes, an experimental investigation was carried out on a 316L stainless steel in acidic chloride solution. The effect of the strain hardening on polarisation curves was studied for various values of plastic strains corresponding to the three stages of strain hardening. After the specimen pre-straining, polarisation curves were performed before and after polishing the surface in order to analyse the competition between the passive film behaviour and the dissolution processes with or without surface roughness effects.

An investigation on corrosion behaviors of two types of commercial stainless steels after plastic deformation

E. Jafari, Islamic Azad University, Shiraz, Iran

The influence of plastic deformation on corrosion resistance of two types of stainless steels sink was studied. A tensile machine was employed to give plastic deformation at room and elevated temperatures. Degrees of plastic deformation were given by deep drawing tests at various strain rates. The effect of plastic deformation on the steels were analyzed by X-ray diffraction tests, electrochemical tests (potentiostatic and cyclic polarization works), and optical metallography and scanning electron microscopy. Results show that chromium, nickel and copper have a significant effect on the corrosion resistance of the steels after plastic deformation. It was observed that the corrosion resistance after plastic deformation is a function of deformation temperature, strain rate and alloying elements.

Effect of ternary element addition on the corrosion behaviour of NiTi shape memory alloys

E. Kassab[1]*, L. Neelakantan[1], M. Frotscher[1], J. Ponciano Gomes[2], G. Eggeler[1]

[1] Ruhr-University Bochum, Institute for Materials, Universitätsstr. 150, 44780
Bochum, Germany
[2] Federal University of Rio de Janeiro, Dept. of Metallurgy and Materials, Cid.
Universitária-Centro de Tecnologia-Bloco F, 210, Ilha do Fundão 21941-972,
Rio de Janeiro, Brazil
* corresponding author, E-mail: Elisa.JanzenKassab@rub.de

Nickel Titanium (NiTi) shape memory alloys are widely used in biomedical applications due to their special mechanical properties, good biocompatibility and corrosion resistance [1, 2]. Despite the wide range of applications, the corrosion properties of NiTi-based alloys have not been examined in detail. This is especially true for ternary alloys, where a third element has been added in order to improve certain properties such as phase transformation temperatures or mechanical properties. Therefore, these ternary alloys have the potential for a wide range of new applications. With regard to potentially corrosive environments, knowledge about the corrosion resistance becomes very important. The goal of this study is to systematically compare the corrosion behaviour of selected ternary NiTi-based alloys ($Ni_{45}Ti_{50}Cu_5$, $Ni_{40}Ti_{50}Cu_{10}$, $Ni_{47}Ti_{50}Fe_3$, $Ni_{49.8}Ti_{35.2}Hf_{15}$, and $Ni_{39}Ti_{50}Pd_{11}$) with a binary, pseudoelastic $Ni_{50.7}Ti_{49.3}$ alloy. These alloys offer promising mechanical behaviour and can be produced by means of hot- and cold working processes, which is important with regard to the processing of components. We examine the influence of the ternary elements on the corrosion behaviour of NiTi, using standard electrochemical measurements such as OCP and anodic polarization in a physiological solution (0.9% NaCl) simulating a body temperature of 37 ±1°C []. Initial results for NiTiCu alloys indicate that Cu has a negative influence on the breakdown potential, when compared with a binary NiTi alloy. We also discuss the influence of other ternary elements, such as Hf, Fe, and Pd on the corrosion properties.

Keywords:

NiTi shape memory alloys, pseudoelasticity, NiTiCu, NiTiFe, NiTiHf, NiTiPd, corrosion, OCP, anodic polarization, biomedical applications

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Passivation of magnesium at elevated potentials

J. Porto Borba, G. Knörnschild, UFRGS, Porto Alegre/BR

Magnesium alloys are passive in alkaline solutions up to +3V. Above this potential the dissolution current of magnesium rises strongly. A new passivation can be observed at about +10V. Although this observation is of minor relevance for the behavior under free corrosion conditions it has an influence on anodization of magnesium alloys. The behavior of pure magnesium and of the Mg-Al-Zn alloy AZ91 was studied in the active region in NaOH solutions. The current densities in the active region rise proportional to the applied potential, reaching the order of A/cm^2 in the case of pure Magnesium. The overall dissolution current is smaller in the case of the alloy because it is restricted to the magnesium rich phase. Magnesium dissolution is a function of OH^--concentration and is accompanied by oxygen evolution. The observed behavior was interpreted as magnesium dissolution under ohmic control in the defects of an $Mg(OH)_2$ film and can be related to the morphology of the film.

Preparation and physicochemical characterization of natural phosphate and kaolin coatings in Stainless steel

R. Najih[2], A. Chtaini[1,*], H. Oulfajrite[1]

[1] *Equipe d'Electrochimie Moléculaire et Matériaux Inorganiques, Faculté des Sciences et Techniques de Beni Mellal,*

[2] *Laboratoire Valorisation et Sécurité des Produits Agro-Alimentaires, Faculté des Sciences et Techniques de Beni Mellal*

Abstract The inhibition efficiency of natural phosphate and kaolin systems in controlling corrosion of stainless steel in $HClO_4$ (0.1M) solution has been evaluated by electrochemical polarization methods, and electrochemical impedance spectroscopy. The electrochemical data show that the corrosion resistance in greatly enhanced after surface modification. The best protection is obtained with natural phosphate. The uniform coatings of phosphate and kaolin on iron substrates were obtained by electro deposition.

Keywords Electrodeposition, Natural phosphate, Kaolin, Square wave, stainless steel.

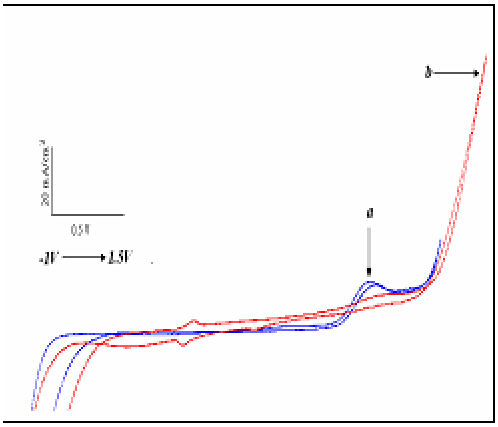


Fig. 2. Cyclic voltammograms of
-a- Stainless steel electrode,
-b- kaolin/stainless steel, in $HClO_4$(0.1M). at 50 mV/s.

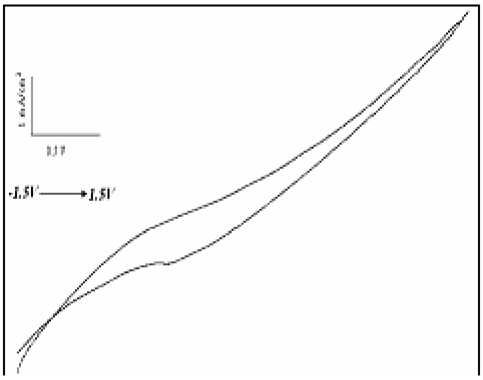


Fig. 3. Cyclic voltammogram of NP/stainless steel electrode in HClO4, at scan rate of 50 mV/s.

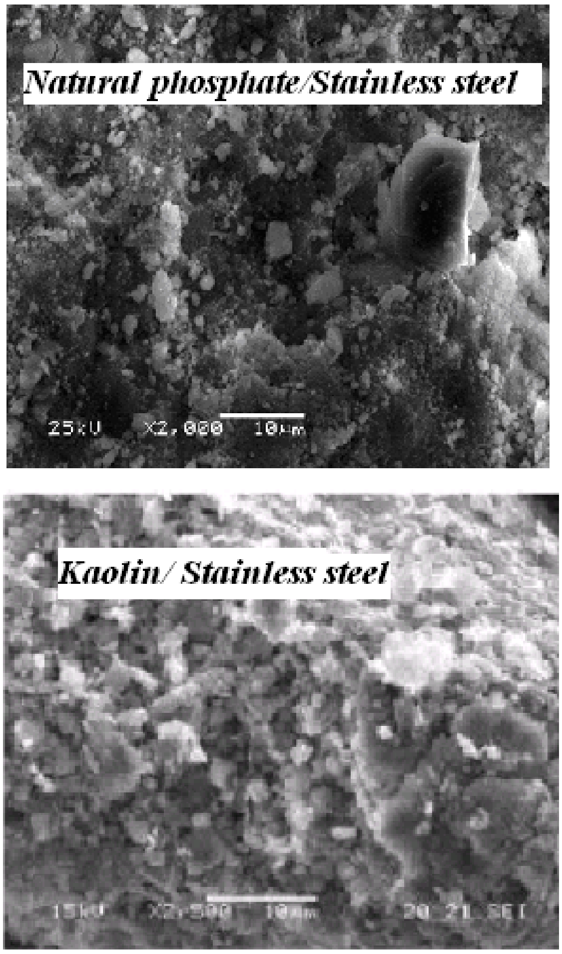


Fig. 1. SEM of modified electrodes

Corrosion Education and Computer Applications

Training corrosion engineers in oil and gas profile higher educational establishment

Dmitry Bugay, *Ufa state petroleum technological university, Ufa, Russia*

In 1981 in "Material science and corrosion protection "chair (MZK) of Ufa state petroleum technological university (USPTU) the specialization "techniques of equipment and constructions' anti-corrosion protection" was opened. The motivating moment was the absence of specializations in the higher educational establishments of the Soviet Union providing corrosion engineers' training in the field of oil and gas equipment anti-corrosion protection. At the same time the period being considered was characterized by the increasing number of failures and accident destructions of oil and gas pipelines and equipment of the branch the main reason of which had been metal corrosion and non metallic materials' efficiency loss in aggressive corrosion media.

From the first days of the specialization existence the main emphasis in teaching students was put on forming engineering skills based on a deep study of such important theoretical disciplines as "Theory of corrosion and metal protection", "Corrosion resistant materials", "Oil and gas and oil chemical equipment anti-corrosion protection", "Experimental technique in chemical strength of materials", "Corrosion mechanical destruction of oil and gas pipelines and the methods of its prevention" and others. Besides, a great attention was paid to laboratory and practical classes which allow to consolidate the knowledge acquired in the process of studying theoretical disciplines effectively. A very important part was given to various kinds of practical classes as a result of which the students from the first year of studies began to get familiar with the real state of affairs in the sphere of equipment and pipelines' anti-corrosion protection in conditions of the enterprises of the branch in operation.

Since 1993 I, as a teacher having a great experience of work as a technical translator, was entrusted by the university authorities to conduct profound teaching of English with the students of this specialization beginning from the first year. The main objective of the studies is to impart the students to oral speech habits and the ability to translate technical texts on the speciality with the dictionary. The teaching experience in this direction has shown that the students with good school training in English considerably progressed during the course of studies and in future passed the interviews for employment in various foreign oil and gas companies successfully.

Selected from the beginning as a studies' criteria a balanced combination of theoretical and practical disciplines immediately gave weighty results: the students of specialization "Technique of equipment and constructions' anti-corrosion protection" found great demand in annual assignment into Russian and foreign companies. At present a considerable part of corrosion services at the enterprises of Volga-Ural and Western Siberian regions has been completed by corrosion engineers, the USPTU graduates.

It should be also noted that qualitative university education obtained by MZK chair graduates, made the basis for their further training in the frames of post-graduate and doctor's courses. It's enough to say that for the time of the specialization existence the former students have defended more than twenty master's and two doctor's theses.

Thus, almost a thirty-year expertise of training corrosion engineers has shown that the presence of such specialization in the branch higher educational establishments is extraordinarily prospective and makes for the timely provision with highly qualified staff of those branches of industry in which technological equipment and pipelines are subjected to destruction due to contacts with aggressive media of different character.

ESTIMATION OF STEEL STRUCTURE CORROSION RISK LEVEL IN CALCULATIONS ACCORDING TO LIMITING STATES

V.Korolov, Y.Vysotsky, A.Gibalenko, P.Korolov
Donbass Centre of Engineering Safety
OJSC "V.Shimanovsky UkrRDISteelconstruction"
44, Fontannaya Str., Makeevka, Ukraine, 86123, center_sts@ukr.net

The paper presents technical approaches and specifies procedures to ensure specified service life of steel structures through sustainable use of primary and secondary protection means and methods. Necessity of development of structure of controllable parameters of quality of structures and their coatings corrosion state on the basis of the process approach of the ISO 9001:2000 quality management system is shown. The problem of conformation of compliance of qualitative and quantitative indices of steel structure corrosion protection reliability to the level of building facility corrosion risk is formulated.

Qualitative and quantitative criteria of technological safety, risk levels according to the alternative features including characteristics of vulnerability and threats in the course of steel structure use in corrosion environments are specified. The technique of determination of the primary and secondary protection reliability indices under the specified service life of steel structures is justified. The developed technical approach allows to estimate the steel structure availability factor by modeling the corrosion protection reliability indices. The table model of steel structure service life in corrosion environments when maintained according to an actual state is generated for the purpose of control of technological safety parameters in the course of structure use.

The problem of modeling of availability factor under corrosive attack includes a design estimation of steel structure maintainability by the limiting states taking into account corrosion resistance and durability of steel structures and their coatings. Results of physicochemical and mathematical modeling of steel structure availability factor, maintainability indices comparative estimation for specification parameter justification by resource taking into account the intensity of corrosive attacks are presented.

Algorithm of analysis of primary and secondary protection measure efficiency according to requirements of technological safety is developed. The levels of corrosion risk for interval values of availability index of steel structures in corrosive environment are specified. Use of corrosion risk criterion gives an opportunity to specify the requirements to the choice of primary and secondary protection measures accounting corrosiveness degree and the preset maintenance system.

Keywords: steel structures, primary and secondary corrosion protection, calculation according to limiting states, corrosiveness degree, durability, maintainability, technological safety, corrosion risk level.

Neural network approach to pipeline SCC and external corrosion integrity assessment

Mashurov S.S., Aerospace Monitoring and Technologies (AMT), Moscow; Mirzoev A.M., AMT, Moscow; Mirzoev A.M., AMT, Moscow; Ivashchenko M.S., AMT, Moscow; Esiev T.S., GAZPROM VNIIGAZ, Razvilka; Ryakhovskikh I.V., GAZPROM VNIIGAZ, Razvilka

External corrosion and stress corrosion cracking (SCC) have long been recognized as major threats to the integrity of buried natural gas pipelines. In the presence of water (from either the product or the external environment) unprotected carbon steel will corrode. Corrosion defects reduce the load-carrying capability of the pipeline and, if they are allowed to continue to grow, may result in leak or rupture failures.

Pipeline operators mitigate against the effects of corrosion and SCC by the removal of water and/or the addition of an inhibitor into the product, the application of an external (or internal) coating and the application of a cathodic-protection (CP) system. If any of these protection systems fail then operators need to be able to identify where corrosion and SCC is occurring along the pipeline and how fast that corrosion is growing in order that appropriate monitoring and mitigation actions be taken.

Unlike internal corrosion, which occurs in a closed system, external corrosion reaction and SCC are influenced by a number of factors including the water content of the soil, the pH level of the corrosion environment, carbon steel characteristics, coating condition, and the degree of oxygenation. Therefore, the prediction of external corrosion rates and determination of pipeline sections that are susceptible to SCC are complex and there is currently no method for estimating these processes using empirical equations.

However, to date, the most part of corroding gas pipelines in Russia have been closely inspected using methods of non-destructive testing, incl. ultrasonic and MFL in-line inspection tools, and corrosion control (resistivity and potential profiles, cathodic protection review, line current and etc.) and a vast database corrosion information has been built up.

This data set formed the basis for the development of a so-called Artificial Neural Network (ANN). The ANN model is a system based on the operation of biological neural networks, in which information is processed in a parallel and nonlinear fashion, leading to a final complex relationship between cause and effect parameters (or input and output values). It has been used successfully in many scientific applications where an accurate mapping of input to output parameters was required.

Due to the rather large amount of parameters that affect corrosion and SCC development on the gas pipeline, it is difficult to describe the effects of all relevant parameters. For such processes in which the interrelationship of parameters is unclear while sufficient experimental data are available, Neural Network modelling may be a suitable alternative.

Thus, results assessed by using neural network can be applied to estimate realistic external corrosion growth rate and to determine potentially dangerous SCC pipeline sections in order to develop effective integrity-management plans for corroding pipelines.

Marine Corrosion

Study of 5083 aluminum alloy for shipbuilding industry after contamination, surface preparation and organic coatings application

M. J. Marques [1], *C. Brites*[1], *I. N. Alves*[1], *R. P. Gonçalves*[1], *T. C. Diamantino* [1]
[1] *LNEG – Laboratório Nacional de Energia e Geologia, LMR – Laboratório de Materiais e Revestimentos, Estrada do Paço do Lumiar, 1649-038 Lisboa, Portugal.*
(Tel.: 351-210924652 Fax: 351 – 217163796, joao.marques@lneg.pt)

A decisive turning point in the growth of the use of aluminum vessels occurs in the early 90´s, decade in which we saw a significant increase in passengers and cargoes. In this scenario arise the category of high speed craft - catamarans – built entirely in aluminum, more precisely, on aluminium alloy.

Currently further studies are needed to enhance the potencial of aluminum in this type of vessels, both in the construction process and in maintenance and repair.

The aluminum - magnesium (Al - Mg) alloy, particularly the AA 5083, is one of the aluminium alloy widely used in shipbuilding industry due to excellent properties for marine applications.

This study, which follows a work previously presented, aims to characterize morphologically and chemically surfaces of AA 5083 – H111. This characterization was carried out before and after contamination with chlorides in artificial environment and subject to different surface preparation techniques. Finally different commercial marine coatings systems were applied.

The panels were contaminated in a salt spray chamber and therefore subjected to surface preparation techniques, e.g. power tool cleaning and waterjetting. Subsequently, the panels were coated with 7 options of commercial marine coatings systems, 4 systems for the ship top side and splash areas and 3 for the ship bottom area.

The evaluation of roughness was performed before and after surface preparation. The morphological and chemical characterization of the AA5083 – H111 surface, with and without marine coatings, was performed using scanning electron microscopy with energy dispersive spectroscopy (SEM/EDS). This characterization was done in order to evaluate the ability of each surface preparation to remove chloride contamination of the aluminium alloy surface and to affect the adhesion at the interface metal substrate / organic coating.

Due to the limited knowledge existing in the scientific field of surface preparation for aluminium, this work has the aim to make an approach to this and other relevant issues affecting the construction and repair in aluminum.

Key-Words: 5083 aluminum alloy, chloride contamination, surface preparation, shipbuilding, SEM/EDS.

Critical pitting temperature of the $Co_{1.5}CrFeNi_{1.5}Ti_{0.5}Mo_{0.1}$ high entropy alloy by chloride ion and its inhibiting effect by nitrate ion

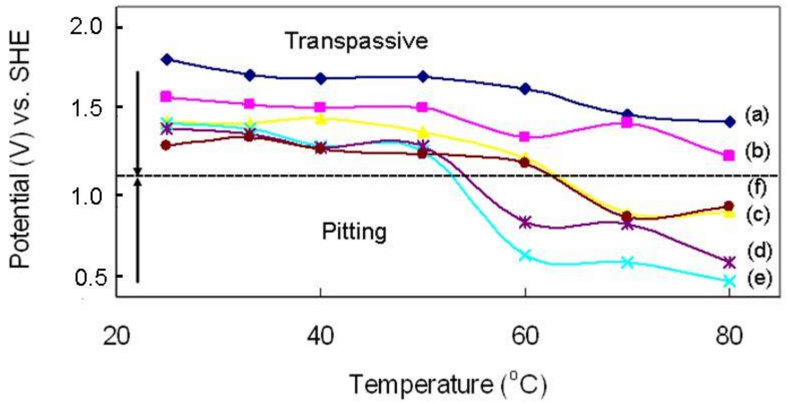
Y. L. Chou [a], *J. W. Yeh* [b], *H. C. Shih* [a, b,]

[a] *Department of Materials Science and Engineering, National Tsing Hua University,*
Hsinchu 300, Taiwan

[b] *Institute of Materials Science and Nanotechnology, Chinese Culture University,*
Taipei 111, Taiwan

Abstract

High-entropy alloys are a newly developed family of multi-component alloys that comprise more than three major alloying elements. Each element in the alloy system is no more than 35 atom %. The $Co_{1.5}CrFeNi_{1.5}Ti_{0.5}Mo_{0.1}$ alloy has simple face centered cubic structure and a high hardness level about HV 380. The purpose of this study is to investigate the effect of temperature from 25 to 80°C on the pitting corrosion of $Co_{1.5}CrFeNi_{1.5}Ti_{0.5}Mo_{0.1}$ high entropy alloy in 0.001 to 1M NaCl and in 1M NaCl containing 0.5M Na_2SO_4 aqueous solutions using the potentiodynamic polarization technique. The results indicated that (1) immunity to pitting corrosion is evident at chloride levels $<$ 0.01M; (2) the increase in chloride concentrations shifts the pitting potential (E_{pit}) of the alloy toward the active direction; (3) the relationship between E_{pit} and logarithm of chloride concentrations in 70 and 80°C is $E_{pit} = 0.65 – 0.23 \log [Cl^-]$ and $E_{pit} = 0.48 – 0.39 \log [Cl^-]$, respectively; (4) the critical pitting temperature (CPT) for the alloy in 0.1, 0.5, and 1M NaCl are 70, 60 and 60 °C, respectively; and (5) the adding of 0.5M Na_2SO_4 to 1M NaCl increases the CPT of the alloy from 60 to 70 °C.



Plot of potential as a function of the temperature for the alloy in (a) 0.001M, (b) 0.01M, (c) 0.1M, (d) 0.5M, (e) 1M NaCl, and (f) 1M NaCl + 0.5M Na_2SO_4.

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Electrochemical characteristics on intergranular and pitting corrosion in welding for austenitic stainless steel

Seong-Jong Kim, Il-Yong Bae, Min-Su Han, Seok-Ki Jang, Seung-Jun Lee, Jae-Cheul Park
Mokpo Maritime University, Republic of Korea

In general, stainless steels (STSs) are widely used under any circumstances such as chemical industry, food industry, machinery industry and building industry due to corrosion resistance is excellent. However, those STSs have fractured possibility at an early stage by pitting, crevice corrosion, galvanic corrosion, stress corrosion cracking, and hydrogen embrittlement. Particularly, austenite STS has also a possibility such as weld decay, knife line attack and several defects. According to G. Lauer et al, the welding of two alloys with small difference in E_{corr} values can lead to increased corrosion of the more active material. In an attempt to provide an indication of which metal or alloy combinations are likely to cause galvanic corrosion in sea water, the International Nickel Company has developed a chart of E_{corr} values of various metals and alloy in sea water. Studies using natural sea water and chlorinated sea water have shown that no galvanic corrosion occurs when the supergrades of STSs are coupled to titanium or the high-molybdenum nickel-chromium alloy such as alloy 625 alloy C-276.

In this study, STSs of double wall gas pipe for duel fuel engine are executed welding. The EPR test(electrochemical potentiodynamic reactivation test) for welded specimen was measured with scan rate 6V/h by using SSCE as reference electrode and Pt as counter electrode. Exposed area of all specimens is 1cm^2. And anodic and cathodic polarization trends were measured from open circuit potential to noble and active directions. At polarization trends of STS 316 and STS316L, current density of STS 316 is higher than that of STS 316L.

Key Words ; stainless steels, corrosion resistance, welding, double wall gas pipe, EPR test

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Estimation of the seawater biocorrosiveness

Kharchenko U.[1], Beleneva I.[2], Karpov V.[3]
[1]Institute of ChemistryFEB RAS, Vladivostoc, Russia
[2]A.V. Zhirmunsky Institute of Marine Biology FEB RAS, Vladivostoc, Russia
[3]A.N. Severtzov Institute of Ecology and Evolution RAS, Moscow, Russia

One of the discussed problem in research of corrosion processes in natural seawater still has an estimation of seawater corrosiveness in relation to concrete materials. Mainly, it is connected by that corrosion aggression of seawater is depended upon all chemical, physical and biological factors, thus the estimation of a role and participation of the biofactor in the general corrosive attack of the sea environment to metal presents certain difficulties.

Recently new biotechnological methods of a microbiological aggression estimation of environments began to be developed. The most perspective among them represent the methods based on a quantitative estimation of microorganisms enzymatic activity one of which is the multysubstrate testings method (MTM). This method is based on the microorganisms isolation from a metal surface and a quantitative estimation of nutrients uptake. The defined value characterises quantitative level of enzymatic activity of all environmental microorganisms and allows to obtain the exhaustive data about a state of microbial community.

Application of method MTM for the characteristic of microfouling communities has allowed us not only quantitatively define levels of microorganisms metabolic activity on a surface of various metals and alloys in different water areas, but also has shown possibility of using microfouling microorganisms activity value as the indicator of seawater corrosiveness.

Influence Of Environmental Factors On The Susceptibility to Stress Corrosion Cracking Of High-Strength Al-Zn-Mg Alloys

[1]**H . A . Jawan**,

[1]Department Of Mechanical Engineering
University Of Al-Margep
Alkhoms , Libya
Tel – 00218-926312605

Abstract : Stress corrosion cracking (SCC) is the result of the Combined action of Metallurgical , Mechanical , and environment factors. While the letter two factors are governed by the service conditions. The effect of the environment on crack initiation and propagation has been shown to depend on the aggressiveness of the environment. The experiments performed on this factor during the last decades enhance our knowledge of the mechanism of SCC of wrought aluminum alloy. The present paper describes the environmental factors such as composition of environment, PH of solution, electrochemical potential and temperature which may influence on crack initiation and propagation.

Microbial Corrosion

Characterization of microbial attachment on metal surfaces by Scanning Kelvin Probe and Epifluorescence Microscopy

A. Heyer[1], F. D'Souza[2], G. Ferrari[2], J.M.C. Mol[3] and J.H.W. de Wit[3]

[1]M2i Materials innovation institute, Mekelweg 2 2628 CD Delft, The Netherlands,
a.heyer@m2i.nl
[2]TNO Science and Industry, Bevesierweg 1781 CA Den Helder, The Netherlands,
fraddry.dsouza@tno.nl, gabriele.ferrari@tno.nl
[3]Delft University of Technology, Department of Materials Science and Engineering,
Mekelweg 2 2628 CD Delft, The Netherlands,
j.m.c.mol@tudelft.nl, j.h.w.dewit@tudelft.nl

Microbiologically influenced corrosion (MIC) is a well-known phenomenon in aquatic environments. The presence of a biofilm on a metal surface often establishes new electrochemical reaction pathways, or promotes reactions, which are not normally favored in the absence of microorganisms, resulting in increased corrosion rates. Limited information is available about the correlation of structural material properties, such as grain boundaries or potential changes on the surface in relation to bacterial attachment.

In this study we investigated the influence of bacterial attachment on the local Volta potential of metal surfaces over a period of 14 days.

By using Scanning Kelvin Probe Microscopy (SKPM) as a high-resolution local technique, we could show that bacterial cell attachment sites are influencing the surface potential. These local attachment sites may result in corrosion initiation to the presence of bacteria. A new combination of AFM-SKPM and fluorescent microscopy additionally allowed us to image the same sample spot with both techniques indicating that potential changes are indeed correlated to bacterial attachment. By using different fluorescent probes it was also possible to indicate active sites within MIC biofilms, which could be proven by SKPM.

Overall, we can summarize that SKPM can be used to indicate biological interactions with metal surfaces, thus allowing a more detailed study of bacterial attachment. This will lead to a better understanding of local MIC processes and possible inhibiting strategies.

Keywords: biofilm, MIC, EFM, AFM, SKPM

A study on the role of inhibitors in protecting against biocorrosion in the water transfer at copper mines

Shakila Motamedi [1*], Reza Marandi [2]

1*-M.s. student of applied chemistry, chemistry department,Islamic Azad
University,NorthTehran Branch, Member of young researchers club.
sh_motamedi@iau-tnb.ac.ir
2-Assistant professor of technical and engineering department,
Islamic Azad University, North Tehran Branch.

Abstract:

Microbial corrosion or a kind of corrosion affected by biological agents could be defined as an electrochemical process, where microorganisms are enable initiate, facilitate or encourage the corrosion process without any change in its electrochemical nature and, of course, the microorganisms attached to the surfaces i.e. biofilms have a principal role in this phenomenon and may be the necessary condition for proceeding the reactions. Damages resulted from biocorrosion lead to allocating high budgets to substitute and fix the equipment and metal installations in most industries per year.

One of the cases of biocorrosion has occurred in the water supply pipes from Khatoon Abad water well to Kerman Sarcheshmeh copper mine (located in southern Iran).In order to control this phenomenon, the water sample from the water supply pipelines was studied from the biological view and it was found that the development of biocorrosion is due to the presence of sulfur corrosive bacteria in the transferred water. Based on the recurrent experiments on the water sample, the identified and separated species was *sulfolobus* bacterium. Then in order to prevent the reduction of sulfate and so controlling the biocorrosion phenomenon, hydrogen peroxide oxidant, glutaraldehyde, hypobromous acid 47%, ozone adding method and a mixture of these two methods were applied and studied and the rate of *sulfolobus* bacteria growth was used as an index to prevent biocorrosion. In the method using hydrogen peroxide, this substance was injected to the water sample in the range of 50 microlitres to 2000 microlitres. Then the samples were incubated in the desired culture medium and it was shown that hydrogen peroxide in the used concentrations has not been able to remove *sulfolobus* bacterium*.* In the ozone adding method, at pressure less than 0.5 bar for 1 hour , 0.5 bar for 1 hour, 1 bar for half of hour , between 1 bar and 1.5 bar for half of hour, 1.5 bar and 2 bar for 20 minutes , the sample was exposed to ozone gas. For each of pressure which exert, each 15 minutes sampling was done and in pressure with less time, each 10 minutes. Then the samples were incubated in the desired culture medium. In method use of glutaraldehyd and hypobromous 47%, from 50 microlitres till 550 microlitres was injected.

Findings are that the most efficient method, considering the time needed for the elimination of the biocorrosion agent bacteria would be applying the biocide hypobromous acid 47%, ozone adding method, biocide glutaraldehyde, and the hybrid method of hydrogen peroxide and ozone, respectively. It is worth mentioning that in the installations where the water transfer or stoppage is less than 24 hours, the abovementioned methods are more effective and efficient.

Keywords: Biocorrosion, Inhibitors, *sulfolobus* bacterium, ozone adding method.

Corrosion-active microflora of water technological environments of the atomic power station

J.L.Kovalchuk, *G.V.Zhdanova*

A.N. Severtsov Institute of Ecology and Evolution, Russian Academy of Sciences,

Moscow, Russia

In the course of atomic power station work in the process equipment with natural water there is a continuous receipt of impurity, in particular the microbiological origin, constructional materials causing biological corrosion. Application of chemical methods for an estimation of quality of technological water not always yields effective result owing to a lack of the information on a biological component of analyzed environments and consequences of its influence on reliability of the systems executed from various materials.

Bacteria of corrosion group get to pipelines of power installations through systems chemic-water-washing (CWW), ionic materials which do not possess bactericidal properties, and on the contrary, are a necessary substratum for microflora ability to live. In large quantities breeding on ionic-pitches (IP), especially at lay modes or in reserve branches of water purification, the microflora blocks IP groups. Without preliminary antimicrobic processing, there can be a fast bacterial poisoning of pitches, frequently the irreversible. Investigated presence of some corrosion-active groups of microorganisms in natural water and systems CWW on the atomic power station. Number sulfate-reducing bacterium (SRB) in ground deposits of the river more than on depth 1,5 m (accordingly, 150 and 50 kl./ml). Amount in water CWW SRB are not revealed. It is connected with adverse conditions for their development (increase pH environments after clarifying agent). The maximum number denitrifying and thiobacterium is revealed in the end of chain CWW (accordingly, $2{,}0\cdot10^6$ and $9{,}5\cdot10^6$ kl/ml), minimum - after clarifying agent ($3{,}0\cdot10^3$ and $9{,}5\cdot10^3$ kl/ml) and in tank of a dirty condensate ($3{,}0\cdot10^3$ and $3{,}0\cdot10^4$ kl/ml).

Quantity thiobacterium in all tests exceeds quantity denitrifying, however both groups of bacteria showed identical law of the development. Number of the given bacteria increased gradually on all chain CWW (denitrifying from $3.0\cdot10^3$ to $2.0\cdot10^6$ and thiobacterium from $9.5\cdot10^3$ to $2.5\cdot10^6$ kl/ml), that speaks about pollution IP materials of filters and development of bacteria on the pitches, being a necessary substratum for their development. Most likely, low firmness ionite is caused by their hydrocarbonic structure. Active reproduction of microflora in IP filters is promoted also by presence in water of the various impurity containing nitrogen, sulphur, phosphorus which microorganisms along with hydrocarbons use as a nutrient medium.

Biocorrosion of P235GH steel in column experiments simulating geological conditions of high-level radioactive waste disposal

Hicham EL HAJJ, **Abdesselam ABDELOUAS, Bernd GRAMBOW**

SUBATECH, UMR 6457 IN2P3/CNRS-Ecole des Mines de Nantes-Université de Nantes
La Chantrerie 4, rue Alfred Kastler B.P. 20722 – 44307 Nantes – France
Hicham.elhaj@subatech.in2p3.fr

We investigated the corrosion of the steel P235 under disposal conditions of high-level radioactive waste in argillite. The objective was to study the role of sulphate-reducing bacteria (SRB) indigenous to argillite that may develop under excess of hydrogen produced by steel corrosion in groundwater flowing through argillite. Batch and column experiments were conducted in serum bottles/diffusion cells with coupons of P235 steel, argillite and synthetic argillite water. This system provided enough nutrients to grow SRB's within two weeks with corrosion of the steel and formation of iron sulphides as corrosion products. The results of the weight loss method showed that the steel corrosion seems to be faster in the presence of SRB's in comparison to sterilized runs. The mineralogical identification of iron sulphides, observed and analysed with the scanning electron microscope, will be conducted with Raman spectroscopy and X-ray diffraction. The corrosion mechanism will be determined by studying steel cross sections and surface observations after removal of corrosion layer. Experiments with column experiments simulating geological conditions showed a decrease of sulphate concentration with production of sulphide ions. The results of the steel corroded in the cell were similar to the batch experiments and showed the precipitation of Mackinawite product in the presence of SRB.

Use of sodium hypochlorite and xanthan as strategy for control of biocorrosion in static system

Maria Alice G. de Andrade Lima[1] ; Sara H. de Oliveira[2]; Pulkra Silva[1]; Diniz R. Lima Junior[2]; Francisca P. de França[3]; Severino L. Urtiga [2].
[1]Departamento de Engenharia Química, UFPE, Brasil; [2]Departamento de Engenharia Mecânica, UFPE, Brazil; [3]Departamento de Engenharia Bioquímica, UFRJ, Brasil.

Biocides are chemical compounds that act by inhibiting microbial growth. Chlorine and its compounds are most commonly industrial biocides used either as dissolved chlorine gas or liquid form through the addition of sodium hypochlorite. Treatment with chlorine may generate products that decrease its antimicrobial effectiveness and could be toxic when discharged through body of water, such as chloramines and organic substances. In addition, chlorine is an oxidizing compound and tends to promote the corrosive processes in industrial systems. On the other hand, it presents several advantages such as low cost and compatibility with other additives. Continuous treatments with chlorine at concentrations from 0.1 to 2 mg/L are often used, as well as periodic treatments in concentrations ranging from 0.5 to 1.0 mg/L. Chlorine is an excellent bactericidal and algicidal agent, though there is reference that the effective concentration of this compound significantly reduced when injected into the bacterial biofilm. The combination of biocide and biodispersant is most effective strategy for the control of biofilms than the application of these chemicals separately, since biodispersant allows the biocide penetration into organic deposits, facilitating its removal by the turbulence of circulating water. Biodispersants neither eliminate the microorganisms nor inhibit their growth, but significantly reduced the concentration of biocide. The aim of this study was to evaluate the effect of xanthan and sodium hypochlorite on the reduction of microbial activity and the rate of carbon steel SAE 1010 corrosion, in a static system using seawater from the SUAPE region in Brazil. In the experiments we used five systems and a test blank. Samples of seawater were analyzed from the microbiological point of view and are subsequently deposited in static systems: system (I) control, sea water without chemical agents (14 and 28d), (II) sea water with 1 ppm of sodium hypochlorite (14 and 28d), (III) sea water with 0,5 ppm of sodium hypochlorite (14 and 28d), (IV) sea water with 2 ppm of xanthan gum (14 and 28d), (V) sea water with 1 ppm of xanthan gum (14 and 28d), (VI) sea water with 0,5 ppm of sodium hypochlorite and 1 ppm xanthan gum (14 and 28d), (VII) sea water with 1,0 ppm of sodium hypochlorite and 1 ppm xanthan gum (14 and 28d), (VIII) sea water with 0,5 ppm of sodium hypochlorite and 2 ppm xanthan gum (14 and 28d) and (IX) sea water with 1,0 ppm of sodium hypochlorite and 2 ppm xanthan gum (14 and 28d).The metal coupons were monitored for a period of 42 days and assessed for corrosion rate and XRD. The results showed that in systems where the sodium hypochlorite was present with xanthan, the corrosion rates were lower than in the system where there was only sodium hypochlorite, indicating that the xanthan had a key role in decreasing rates of corrosion.

Keywords: biocorrosion, biocide, xanthan, carbon steel.

Corrosion of Steel in Concrete

CORROSION DAMAGES OF CENTRIFUGED REINFORCED CONCRETE ELEMENTS IN THE ELECTRIC TRANSFORMER STATIONS

Ioan PEPENAR[1]

[1]*The Research Centre-CERTINCON, Romania, ioan.pepenar@e-altfel.ro*

The paper presents the results of the researches on the service behaviour of the prefabricated centrifuged reinforced concrete elements (columns, beams and supports) for sustaining of electrical equipments in the electric transformer stations of 6…400 kV, after 30-40 years of service, in respect of the damages generated by the corrosive action of aggressive agents.

The corrosion induced damages have been favoured / increased by existence of initial execution malfunctions, deteriorations appeared during the storage, transport and montage of the elements and by absence of efficient intervention measures/anticorrosion protection of these elements.

There were pointed out the corrosive action effects of the aggressive agents on the centrifuged reinforced concrete elements in the electric transformer stations placed both in aggressive environments in power and chemical industries, as well as in electrical network urban units specific aggressive environments. The characteristic aspects on corrosion state of investigated elements are illustrated by colour photos.

Based on the results of the investigations and experiments performed “in situ” and in laboratory, there were proposed intervention measures on centrifuged reinforced concrete elements, differentiated by the nature and intensity of the corrosion damages, as well by the aggressivity degree of environments, in order to assure the resistance, stability and durability of construction elements and the normal conditions of service of electric transformer stations.

Theory and practice of steel reinforcement preservation in concrete structures

V.F. Stepanova,
Scientific R&D Institute for Concrete and Reinforced Concrete, NIIZhB, Moscow, Russia

Peculiarities of the mechanism of steel reinforcement corrosion in concrete structures containing non traditional aggregates and binders are considered. Results of studies of artificial and natural aggregates effect upon the passivation properties of concrete in relation to reinforcement are presented. Assessment criteria for corrosion behavior of reinforcement are established. Scientifically founded practical approach to the design of concrete composition with consideration of properties of hydraulically active aggregates is offered.

Concrete with improved corrosion stability

Rosenthal N.K., *Tchechniy G.V., Liubarskaya G.V. ,*
Scientific R&D Institute for Concrete and Reinforced Concrete, NIIZhB, Moscow, Russia

Results of studies of cement concrete with improved corrosion stability, achieved by introduction of plasticizer C-3, silica fume SF and some other admixtures, are presented in the report. Coefficient of filtration for concrete with C-3+SF can be 10^{-11} ...10^{-12}cm/sec and diffusion coefficient for chloride 10^{-9} cm^2/sec. Concrete is resistant to dealkalisation, stable in acid media up to pH=3,0. When sufficient amount of air is entrained, concrete manifests considerable frost resistance. Alkali-silica reaction could be delayed by introduction of lithium compounds into the concrete.

Proposal of a new indicator to define ductility applied to corroded steel reinforcement on concrete structures

Esther Moreno[a,*], Alfonso Cobo[b], Manuel Fernández Cánovas[c]

[a]School of Technical Architecture, Polytechnic University of Madrid, Spain
E-mail address: esther.moreno@upm.es
[b]School of Technical Architecture, Polytechnic University of Madrid, Spain
E-mail address: alfonso.cobo@upm.es
[c]Faculty of Civil Engineering, Polytechnic University of Madrid, Spain
E-mail address: mfcanovas@caminos.upm.es
Adress: Escuela de Arquitectura Técnica. Avda. De Juan de Herrera, 6. Madrid 28040, Spain

The carbonation of concrete or the chlorides ingress in such quantity to reach the level of bars is triggers of reinforcement corrosion.

One of the most significant effects of reinforcing steel corrosion on reinforced concrete structures is the decline in the ductility-related properties of the steel. Reinforcement ductility has a decisive effect on the overall ductility of reinforced concrete structures. Different Codes classify the type of steel depending on their ductility defined by the minimum values of several parameters.

Using indicators of ductility associating different properties can be advantageous on many occasions. It is considered necessary to define the ductility by means of a single parameter that considers strength values and deformation simultaneously.
There are a number of criteria for defining steel ductility by a single parameter.

The present experimental work study the variation in the ductility of concrete-embedded steel bars when exposed to accelerated corrosion. This paper analyzes the suitability of a new indicator of ductility used in corroded bars.

DESPASIVATION DETERMINATION OF REINFORCING STEEL RODS IN PORE CONCRETE SOLUTION USING THE TECHNIQUES OF LINEAR POLARIZATION RESISTANCE, GALVANOSTATIC PULSE AND EIS

Peña D. 1, Estupiñán H.[1], Vásquez C.[1], Elkin Fernando Mejía[2]

[1]Escuela de Ingeniería Metalúrgica y Ciencia de Materiales.
Grupo de Investigaciones en Corrosión. Universidad Industrial de Santander.
Carrera 27, Calle 9. Bucaramanga. Colombia. dypena@uis.edu.co
[2]Armada Nacional de Colombia ARC. Bahía Málaga. Colombia

ABSTRACT

The corrosion of steel is often a major cause of deterioration of concrete in reinforced concrete structures exposed to seawater. The corrosion of steel in concrete is an electrochemical process that occurs when there is a potential difference between two points on the structure, forming an electrolytic cell in which the anode and cathode are connected through the water in the pores of hydrated cement paste. Tests electrochemical as Electrochemical Impedance Spectroscopy, galvanostatic pulse and linear polarization resistance, were carried out on a flat three-electrode cell, the chloride concentration ranging between 0.5 and 3.5% by weight of a concrete pore solution, where two graphite electrodes were used as counterelectrodes, a working electrode (steel) and a saturated calomel electrode as reference electrode. It was observed the direct influence of the concentration of chloride on steel despasivation, which critical concentration was 2.5%. An analysis of the relationship between the different electrochemical techniques for the analysis of corrosion of reinforcing bars in pore solution was carried out.

Keywords: concrete pore solution, Reinforcing bar, pitting, Galvanostatic pulse.

Corrosion in Oil & Gas Production

IN SITU OPTICAL MICROSCOPY EMPLOYED AT CORROSION STUDY OF CARBON STEEL 1040 IN SULFIDE MEDIUM

Alexsandro Mendes Zimer[1], Emerson Costa Rios[2], Paulo de Carvalho Dias Mendes[3], Ernesto Chaves Pereira[4], Lucia Helena Mascaro[5]

[1]UFSCar, Brasil, amzimer@hotmail.com
[2]UFSCar, Brasil, emersoncostarios@yahoo.com.br
[3]UFSCar, Brasil, pc.dm@hotmail.com
[4]UFSCar, Brasil, decp@power.ufscar.br
[5]UFSCar, Brasil, lmascaro@dq.ufscar.br

This abstract presents a study of the carbon steel (1040) corrosion in aqueous solution containing dissolved H_2S at different pHs in order to investigate the effect of H_2S_{aq} and HS^-_{aq} species. The electrolyte used are acetic acid and phosphate buffer solution in presence or absence of 3,5 wt% NaCl containing 100 and 1000 ppm of Na_2S. The steel corrosion investigation was carried out using potential polarization, open circuit and in situ optical microscopy techniques. The influence of H_2S concentration and the effect of immersion time of metal sample on the corrosion environmental were investigated. Using the in situ optical microscopy coupled with electrochemical measurements we were able to detect the dissolution of ferrite in pearlite region and the formation of iron sulfide films with different colors. The morphological analysis using digital image processing allows the classification of different types of surface corrosion damage, where the observed steel surface reveals the inter-grain corrosion site, pite corrosion and the initial stage formation of the film over pearlitic grains.

Role of Surface Finish on Fatigue Failure of 316L Stainless Steel Coil Tube

A. Abdurrahim, F. Elshawesh, H. Mahfud
Libyan Petroleum Institute,Gergarish St.km7
P. O. Box 6431, Tripoli, Libya

Abstract

Coil tube made of 316L stainless steel and used for the dehydration of wet gas using Tri-Ethylene Glycol showed cracking and premature failure after less than one year of service in the platform gas processing facilities. Detailed metallurgical investigations were conducted on the coil in order to establish the main cause of the premature failure.

These investigations include the chemical analysis, visual examination, macro and microscopic examinations were conducted on as received sample. The results revealed the fact that the cracking of the coil tube can be attributed to the initiation of multiple fatigue cracks at the severe plastically deformed area on the coil external surface. The initiated fatigue crack was extended from the deformed area as a result of vibration of the coil tube during service.

On-site investigation revealed the fact that the coil was installed misaligned within the drum. This results in severe mechanical damage on the external surface of coil during operation where the vibration was reported. High residual stresses as a result of strain hardening or what known by the dislocation interactions is expected at the surface damaged area. This was confirmed by the results of hardness measurements where the undamaged area showed normal hardness value typical for stainless steel (195-210 Hv). In contrast, the deformed area showed high hardness reading (up to 410 Hv), which is typical of severely deformed 316L stainless steel.

THE DEVELOPMENT OF FATIGUE DEFECT IN PIPELINE TRANSPORTATION SYSTEM UNDER CORROSION ENVIRONMENT EXPOSURE AND RESIDUAL STRESS CONDOTIONS

Michael Getmansky, Yuri Zhitnikov
Co Ltd "Intercor Rus", Russia, Moscow

The stable tendency towards the increase of maintainability for the purpose of ensuring trouble-free operation is observed today in pipeline transportation (field pipeline, main line) system. The increase of maintainability is accomplished by the use of pipes made according to technological innovations (tubes with inner and outer insulated coatings and protected welded connections), application of corrosion monitoring facilities (the continuous control of one or more preliminary selected parameters of technical state), the complete control of pipelines along the route (with the use of in-tube intelligent projectile). As a result the pipeline system reliability substantially increases. However, the pressure disturbances, caused by either liquid-gas mixture flow instability or random processes that lead to random change of pipeline parameters, stresses, physical-mechanical characteristics of cargo medium, are typical for pipeline system. Therefore, the loading cyclicity arises that, in conjunction with corrosion stress and residual stresses, may lead to fatigue growth of parent metal and welded joint defects. At the same time the resource loss fatigue mechanism and related to it type of limiting state is not considered in normative literature concerning the lead line and main line construction.

In this work we present the fatigue crack growth under the condition of corrosive attack and residual stresses physical-mechanical calculation model, based on nondestructive examination data. The numerical simulation of limiting conditions regarding loading cyclicities, residual stresses level and corrosive media under which the fatigue crack may develop to critical size, is made. The numerical calculations of fatigue crack growth kinetics up to limiting state of pipelines in which the in-service crack-like defects were located, are made.

UNDERDEPOSIT CORROSION FAILURE OF A COMPRESSOR AFTER STAGE COOLER AT AN NGL PLANT-A CASE STUDY

S.A. Al Dossary, Saudi Arabian Oil Company (ARAMCO), Dhahran/SAR; A.K. Debbert, M.A. Al Mubayidh, Saudi Arabian Oil Company (ARAMCO), Abqaiq/SAR

Premature tube leaks were encountered at a compressor after-stage cooler operating at 100-130°F after three years in service due to under-deposit corrosion. The damage encountered was confirmed by visual, metallurgical examination and chemical analysis of corrosion products. The premature failure resulted from condensation of water containing dissolved carbon dioxide, hydrogen sulfide and possibly oxygen at the center bottom portion of the tube. Moreover, the presence of pitting in the liquid phase area indicates that the injection of the oil soluble water dispersible corrosion inhibitor was not effective. Chemical analysis of the deposits revealed that they comprised mainly of iron sulfide products. Metallurgical examination revealed no manufacturing defects. Mitigation measures of similar failures are discussed in terms of design and inhibition.

Kinetics and thermodynamics of asphaltene adsorption onto rusted metal surface.

Jamilia O. Safieva[1], Yulia S. Shevcova[2], and Rustem Z. Syunyaev[2]

[1] N.M. Emanuel Institute of Biochemical Physics RAS, 4, Kosygina st., Moscow, Russia

[2] Gubkin Russian State University of Oil and Gas, 65, Leninsky prospect, Moscow, Russia

e-mail address: rustem@gubkin.ru

Asphaltene deposition is responsible for many phenomena in the petroleum industry, such as well bore plugging, pipeline deposition, stabilization of water/oil emulsions, sedimentation and plugging during crude oil storage, adsorption on refining equipment. Asphaltene stability depends on a number of factors including pressure, temperature, and composition of the fluid. Acidizing treatment is commonly used to enhance oil recovery, but it has some negative consequences as well. Acidizing job can lead to a corrosion of the metal surface of the wellbore. Acid-induced asphaltene sludging is becoming an increasing cause of oil well stimulation treatment failure. Acid-induced asphaltene deposits are extremely difficult to remove and they can be classified as one of the most severe forms of formation damage. The limited knowledge about asphaltene-metal interactions hinders a development of mitigation techniques.

In this study, the adsorption parameters of petroleum asphaltenes on different metal surfaces were investigated using near-infrared (NIR) spectroscopy. Oilwell tubing metal surfaces which are typically operated in the oilfield were employed. A number of this surfaces were aged under acid conditions and rusted metal surfaces were investigated. Asphaltenes were extracted from West Siberian crude oil and used for the preparation of the model oils in a chosen concentration range. Acid-induced and naturally occuring adsorption processes were investigated. Experimental adsorption data were theoretically modeled using Langmuir adsorption. Maximal adsorbed mass density, adsorption equilibrium constant, and adsorption/desorption rate constants were calculated.

Understanding the mechanism of acid-induced asphaltene adsorption onto different metal surfaces opens a way to a correct selection of appropriate treatment scheme. The knowledge of kinetic and thermodynamic parameters of adsorption opens a way for solvation of deposition problems. A fundamental investigation of the asphaltene adsorption onto metal surfaces will help in a better understanding of a deposit formation process.

An investigation on corrosion failure of cemented carbides of the type (WC, M) M = Ni or Co in some water-glycol hydraulic fluids for subsea applications

Lei Zheng, Anne Neville*
Institute of Engineering Thermofluids, Surfaces and Interfaces,
School of mechanical engineering,
University of Leeds, Woodhouse Lane
Leeds LS2 9JT, UK

Abstract

From BP Amoco's subsea experience, which operates more than 100 subsea wells today, the directional control valves (DCVs) are the most susceptible components to corrosion in an open loop hydraulic system that controlling subsea operations, in particular the pilot-stage valve spindles and the balls that allowed the flow of hydraulic fluid when it was displaced from its seat. Tungsten carbide cermets, both Nickel binder and Cobalt binder ones are used as construction materials of DCV, which suffer from corrosion in such hydraulic fluid/seawater surroundings.

In this work, the corrosion behaviours of both Tungsten Carbide cermets (Ni, Co) are compared in some water-glycol hydraulic fluids and 50% fluid/50% seawater solutions using an electrochemical test methodology. Surface analysis and fluid chemical analysis techniques are involved as well to help understand the corrosion mechanisms. The effects of some factors on the corrosion rates are discussed.

Keywords: Tungsten Carbide cermet, hydraulic fluids, corrosion.

Internal corrosion of pipelines and the gas preparation equipment of JV Vietsovpetro

A.L.Bushkovskiy, Le Cong Thuy, A. N/ Ivanov,T.N.Galljamov
/ JV Vietsovpetro /Vungtau City/SR Vietnam.

The shelf oil and gas recovery of Vietsovpetro is conducted on offshore installations. The gas containing 0,1%об CO_2 and up to 140 ppm H_2S (an average level is 21ppm), is separated from liquid, cleaned, compressed on Central and Small compressor platforms and transported on coast through underwater gas pipeline.The Gas is saturated with water vapour and contains a drop suspension of water with salts (up to 0,42g/l in the condensate). Three-stage compression with cooling interstage provides increase of pressure up to 11,5 - 12,9 MPa with the maximal temperature up to 100^oC. According to Standard NACE MR 0175/ISO 15156 the latent corrosion (pitting, cracking etc.) of carbon steel - the main material of pipes and the equipment can be proceed under such conditions. Schemes of corrosion monitoring with 3 independent methods –probes ER with Corrdata TM devices (accumulation of data), corrosion coupons and residual thickness measurement are created from 2000 to 2010. Results of the monitoring performed by the common techniques have shown reduction of general corrosion rate in a gas phase from 0,0041 up to a 0,0025mm/year during 2001-2009г. Corrosion Rate in the liquid phase (condensate on bottoms of tanks) did not exceed 0,012mm/year, a maximum on inlet separators up to a 0,08 mm/year.

Detailed research of structure and properties of steel samples and products of corrosion after exposition during 3-10years in gas stream with X-ray, metallografic, electronic microscopy analysis, has shown the following:

1. Blistering, Pitting and corrosion cracking are absent at all stages of compression, cooling and transport of the gas completely;
2. Phase structure of steel samples (ratio between ferrite and pearlite 64,3 : 35,7, the size of grain), profile of surface had not changed in comparison with new steel samples;
3. X-Ray analysis has been shown presence of iron oxides (FeO, Fe_2O_3, Fe_3O_4) in a film of corrosion products. Hydrates, sulfides, sulfates were absent;

One of the reasons of low corrosion rate is the waterproof film consist of carbon particles (58%) mixed with heavy hydrocarbons (resins, asphaltens-37 %) with thickness 27-120mcm, covering an internal surface of the equipment. The film possesses high adhesion to steel surface and practically replaces an internal coating. A source of a film - a drop suspension of the oil drops getting with gas stream to the equipment. Carbon particles can be formed at pyrolysis of heteroorganic oil impurities. Growth of the film thickness leads to reduction of the corrosion rate.

Secondly, the real border of dangerous H_2S partial pressure is more than $3{,}5 \cdot 10^{-4}$ MPa according to Standard NACE and exceeds 135ppm for VSP conditions.

As a result of the research Inhibitor Protection of equipment with Cronox 8-999A was stopped since March 2009. There is confirmed low corrosion rate of equipment and absence of attributes of hidden H_2S corrosion after work without inhibitor dosage during 20months.

EFFECT OF AGE HARDENING ON THE CREVICE CORROSION RESISTANCE OF Ni-Cr-Mo ALLOYS

Natalia S. Zadorozne, C. Mabel Giordano, Martín A. Rodríguez and
Ricardo M. Carranza
Depto. Materiales - Comisión Nacional de Energía Atómica
Instituto Sabato - Univ. Nac. de San Martín / CNEA
Av. Gral. Paz 1499, San Martín, B1650KNA Buenos Aires, ARGENTINA
zadorozne@cnea.gov.ar

N. Sabrina Meck
Haynes International, Kokomo, IN USA

Raul B. Rebak
GE Global Research, 1 Research Circle, Schenectady, NY 12309, USA
rebak@ge.com

Ni-Cr-Mo alloys offer an outstanding corrosion resistance in a wide variety of highly-corrosive environments. This versatility is due to the beneficial effects of Cr and Mo in oxidizing and non-oxidizing conditions, respectively. Alloy C-22 (Ni-22%Cr-13%Mo-3%W) is used in harsh environments such as oil and gas applications and it is proposed as a corrosion-resistant barrier of high-level nuclear waste containers in the US. Alloy C-22HS (Ni-21%Cr-17%Mo) provides a corrosion resistance comparable with that of alloy C-22, and it can also be age-hardened to effectively double its yield strength. Alloy HYBRID-BC1 (Ni-15%Cr-22%Mo) has been introduced recently intended for filling the gap between Ni-Mo and Ni-Cr-Mo alloys and applied for reducing acids contaminated with oxidizing species. Aging of Ni-Cr-Mo alloys lead to different microstructure changes depending on the temperature range. A long range ordering reaction occurs between of 350ºC and 600ºC, producing an ordered $Ni_2(Cr,Mo)$ phase. This ordering reaction does not seem to affect the corrosion resistance and produces only a slight loss in ductility. Tetrahedral close packed (TCP) phases precipitate at grain boundaries in the range of 600ºC to 1100ºC. These phases could have a detrimental effect upon corrosion resistance and cause a loss of mechanical ductility. The crevice corrosion repassivation potential of the tested alloys was determined by the PD-GS-PD method. This new technique is a modification of the Tsujikawa-Hisamatsu Electrochemical method (THE) (ASTM G192). The three alloys were tested in the mill annealed condition and in other relevant metallurgical conditions. The thermal aging treatments performed to alloys C-22 and C-22HS led to LRO and/or TCP precipitation. The aim of the present work was to compare the crevice corrosion resistance of mill annealed and thermally treated (aged) Ni-Cr-Mo alloys in NaCl at 90ºC. The crevice corrosion resistance of the alloys increased with the Pitting Resistance Equivalent Number (PREN), which was mainly affected by their Mo content. As the Mo content increased, the resistance to crevice corrosion increased. Thermal aging did not modify significantly the crevice corrosion resistance under the tested conditions.

FATIGUE FAILURE OF 316 STAINLESS STEEL WELDED PIPES

Khalifa Abouswa

LIBYA,abouswa_2002@yahoo.com

Abstract

Failures of small piping connections (2 inch and small) continue to occur frequently at refinery, petrochemical and gas plants. Fatigue can occur in any location where cyclic stresses of sufficient magnitude are functioning. The probability of fatigue failure at a weld is a function of many considerations: type of weld profile, material, weld size, wall thickness, heat treatment, grinding after welding, etc.

Weld seams can be considered as one of the most vulnerable areas to fatigue failure where weld defects such as under cut, misalignment, surface imperfection, corrosion might be found at the weld and will act as a stress raiser.

The 2 inch branch connected to 4 inch process flow line condensate feed stream to stabilizer column in gas plant showed circumferential cracking at weld seams after several years in service.

The operating temperature of the process flow line is 21 to 27°C, the operating pressure is 33 to 37 barg and no chloride in the stream.

Visual examination showed circumferential crack initiated near the circumferential weld and propagated through parent metal.

Detailed investigations include visual observation, hardness measurement, microscopic and metallographic examination of the fracture surface showed that the circumferential fatigue cracks was initiated at drastic change in thickness , poor weld profile on branch connections at the heat affected area and propagate (*grow*) with time during operation particularly when it is under stresses.

Scanning electron microscope (SEM) confirms the finding that the fracture morphology was transgranular and the crack was single non -branching. The tube material was specified as low carbon 316L austenitic stainless steel and the microstructure is not sensitized.

Key words: weld seam, transgranular, fatigue crack, sensitisation, and cyclic stresses.

Resistance of low-carbon pipeline steels to corrosion and corrosion-mechanical destruction in aggressive media of oil and gas fields

Ivanov Ye.S., Brodsky M.L., Timonin A.V.
OAO All-Russia Scientific and Research Institute of Corrosion"
Russia 105318, Moscow, Scherbakovskaya, 3;
e-mail: rcnt1@yandex.ru
ZAO "Objedinennaya metallurgicheskaya companiya"
Russia 115184, Moscow, Ozerkovskaya nab.,28, bld.2
Institute of pipeline industry, China, Xian

Researches of resistance to corrosion, stress corrosion cracking, hydrogen embrittlement, corrosion fatigue of 08ХМФЧА, 07ЩГФБ-У, 06ГБ pipeline steels in model media simulating associated waters of the Northern Russia, Western Siberia oil fields and sulphuretted hydrogen containing media regulated by NACE TM 0177-2006 standard, have been conducted.

It was established that steel corrosion velocity in model media during the 1440-hour testing does not exceed 0.1 mm/per year and decreases in the line 08ХМФЧА>07ЩГФБ-У>06ГБ. Welded seams corrosion velocity is the same as that of the parental metal. All the above steels were tested for hydrogen-induced cracking (HIC) under TM 0177-2006 during 96 hours and for sulfide stress cracking (SSC) under TM 0177-2006 during 720 hours. Spectrum analyses of steels has shown that content of hydrogen does not exceed 2 cubic sm/100g of metal, that is, these steels are not susceptible to hydrogenation.

Researches for corrosion fatigue of large-scale samples of 08ХМФЧА and 06ГБ steels with stress concentrators in the air and in NACE media under TM 0177-2006 showed that these steels are sufficiently resistant to cyclic loads (durability 2.4×10^5 cycles), whereas in NACE media their resistance is a little bit lower ($1.64 +/- 1.8 \times 10^5$ cycles). Parental metal destruction mechanism is tough with elements of quazibrittle fracture.

In general the examined steels are sufficiently corrosion resistant, not susceptible to hydrogen embrittlement, hydrogen-induced cracking, sulfide stress cracking, corrosion-fatigue cracking and they could be recommended for manufacturing of pipes used for transportation of aggressive sulphuretted hydrogen containing media of oil fields.

Corrosion monitoring system

A. Gumerov, L. Khudyakova, Y. Rozdestvensky, A.Faritov
State Company Institute for Power Resources Transportation (IPTER),
Ufa, Russia

State Company Institute for Power Resources Transportation ("IPTER") is staffed with skilled specialists, who have been in the corrosion protection business in and outside of Russia for more than three decades.In order to ensure safe and reliable operation of the pipeline systems, GUP "IPTER" has developed and introduced a pipeline corrosion monitoring system (CMS) for oil producing companies. CMS is a complex of technical and methodical means, software and organizing arrangements, which provide information required for analysis of corrosion hazard, planning of preventive measures and assessment of the effectiveness of protective measures.

CMS includes the following basic elements:

- technical devices of Monicor brand (Monicor-2M corrosion rate indicators, corrosion control units Monicor UKK-240, Monicor UKK-240-GR, Monicor Zond, Monicor UKK-ST and Monicor UKK-NO) complete with software, which allows to get signals from the monitored facilities about the rate of corrosion;
- EXTRA net program complex (Version 6.0) which provides for account, analysis and search of correlation/forecast dependences on the basis of the data obtained by Monicor technical devices;
- methodic materials in corrosion monitoring purposed for putting the planned measures into effect with minimum labor input and maximum reliable results.

CMS is based on the following principles:

- scientific substantiation of the choice of place for mounting corrosion monitoring units, where math models, using the data of flow hydrodynamics and physical-chemical composition of the media, determine the most probable areas of corrosion hazard;
- software application, so that the data obtained from the corrosion monitoring units could be comprehensively analyzed in their interrelation with hydrodynamics of flows, physical and chemical properties of transferred media and actual proneness to accidents, and correlation dependences could be stated to determine optimum corrosion control methods;
- individual approach to each pipeline based on drawing up electronic certificates for all pipelines.

Number of failures in the pipeline systems using CMS reduces 3,4 times, on an average.

Material behavior in extreme conditions: details of the experimental tests

C. Colombo,P. Fassina**, A. Sciuccati*, L. Vergani**
**Politecnico di Milano, Department of Mechanics, Via La Masa 1, 20156 Milano, Italy*
**e-mail: laura.vergani@polimi.it*
*** ENI, Exploration & Production Division, San Donato Milanese,20097 Milano, Italy*

In parallel to two other oral works presented in this conference [1,2], this poster contribute aims to describe in details the experimental tests carried out on two high performance pipeline steels (X65 and F22) in extreme conditions: low temperature and presence of hydrogen. An extensive experimental test was carried out, without hydrogen, and with hydrogen charge. For each test condition Charpy, J_{Ic} and crack propagation tests were carried out by varying the temperature.

The procedure of hydrogen charging is innovative and described in [1]. The verified and measured percentage of hydrogen charged in all the specimens, Charpy and CT, is 2 ppms. All the specimens after the hydrogen charging were put in liquid nitrogen and the experimental tests were carried out in few hours in order not to waste the hydrogen.

The experimental results show a significant effect of the hydrogen on the mechanical behaviour of the steels, in particular, at low temperature, the hydrogen presence prevents the plastic behaviour of both the materials. In the case of X65 the behaviour is more brittle with unstable crack propagation. In the case of F22, on the contrary, the hydrogen reduces the plasticization, but the material is yet ductile.

The fracture surfaces of the hydrogenated specimens are examined and compared to the ones without hydrogen.

In [2] the all the results are described and compared with the ones obtained by an other charging procedure.

In this paper the details of this testing procedure are given and commented.

[1] F. Bolzoni, P. Fassina, G. Fumagalli: “Hydrogen charging of carbon and low alloy steel by electrochemical methods”, Eurocorr2010.

[2] P. Fassina, R. Morana, L. Alleva, G. Mortali, L. Vergani, A. Sciuccati: Materials behavior in extreme conditions: influence of large amounts of H2S on steel toughness in low temperature environments, Eurocorr2010.

WELD OVERLAY SOLUTIONS TO SOLVE CORROSION ISSUE IN EXISTING DISTILLATION COLUMN

Cyril NARJOZ[1], Miguel LARA-CAMACHO[2]

[1]*AQUILEX WELDING SERVICES BV, Netherlands, cnarjoz@wsi.aquilex.com*
[2]*INEOS MANUFACTURING SAS, France, miguellaracamacho@ineos.com*

How to fix corrosion issue on existing equipment?
The presentation will present the most recent overlay technology executed in situ on a distillation column suffering from corrosion on the shell. On the internal the corrosion is due to increase of operating temperature which increases risk of higher corrosion rate. On the external the corrosion under insulation generate localized wall thickness loss.
The specificity of this project is that another area of the same column was suffering also from corrosion and the shell has been replaced by windows in parallel with the overlay during the same turnaround.
The different steps of this project will be explained from identification of the corrosion to selection of repair solution, selection of metallurgy, FEA, execution and safety.

Investigating the factors affect on the corrosion of the two types of commercial stainless steel the 304 stainless steel sink

E. Jafari, Islamic Azad University, Shiraz, Iran

The influence of plastic deformation on corrosion resistance of two types of stainless steels sink was studied. A tensile machine was employed to give plastic deformation at room and elevated temperatures. Degrees of plastic deformation were given by deep drawing tests at various strain rates. The effect of plastic deformation on the steels were analyzed by X-ray diffraction tests, electrochemical tests (potentiostatic and cyclic polarization works), and optical metallography and scanning electron microscopy. Results show that chromium, nickel and copper have a significant effect on the corrosion resistance of the steels after plastic deformation. It was observed that the corrosion resistance after plastic deformation is a function of deformation temperature, strain rate and alloying elements.

Coatings

ROLE OF THE CONFORMATIONAL REARRANGEMENTS OF POLYPYRROLE IN THE CORROSION PROTECTION OF AL ALLOYS

M. Rizzi, M. Trueba, S.P. Trasatti
Dept. of Physical Chemistry and Electrochemistry, Università degli Studi di Milano,
Via Golgi 19, 20133 Milan, Italy
Email addresses: mirko.rizzi@unimi.it, monica.trueba@unimi.it,
stefano.trasatti@unimi.it

Polypyrrole (Ppy) films were deposited on Al alloys of series 2xxx, 5xxx and 6xxx by a two-step procedure: (i) galvanostatic activation (GA) and (ii) galvanostatic deposition (GD). Ppy nucleation inside pits was observed in all cases but the morphology of the polymer surface, as well as its structure, was dependent on the Al alloys nature. In terms of protection performance, anodic polarization in NaCl solution indicated improved behavior of degraded (partially saturated) Ppy/AA6082, with respect to Ppy/AA2024. Conversely, potential-time experiments, carried out under diffusion control rather than being driven by electric fields, gave an inversion of Ppy behavior. Marked undercoating corrosion is observed for Ppy/AA6082, while a well-adhered film with corrosion products entrapped inside the polymer-filled pits is formed with Ppy/AA2024. These results strongly point to the role of the rate at which conformational rearrangements are driven within the polymer matrix.

It is a proven fact that conducting polymers undergo swelling or shrinking as a function of the applied electric potential. Otero et al. proposed the electrochemically stimulated conformational relaxation (ESCR) model to explain anomalous effects of polypyrrole electrochemical behavior [1]. Conformation relaxation is understood as a rearrangement of the polymeric structure with variation in the overall three-dimensional shape adopted by a polymeric segment. Such structural changes linked to corrosion protection of conducting polymers are rarely mentioned in the literature [2]. In this work, the ESCR approach is applied to explain the apparent contradiction described above. Lower free volume due to attractive interactions between neighboring “neutral” chain segments, resulting in a more compact film, should prevail with AA6082. Consequently, more anodic potentials and/or longer times of anodic polarization were required to generate free volume for penetration of aggressive Cl^- species. Conversely, the lower amount of active Ppy segments, as a result of broken conjugation, limits electron hopping in the Ppy network for reduced segments restoring by dissolved oxygen under stationary conditions, this process being stimulated under anodic polarization. In the case of Ppy/AA2024, fixed macroanions as dopants (like CuC_2O_4) stimulates the penetration of cations from solution, delaying the aggressive Cl^- ion attack, despite the more open polymer structure and its swelling upon reduction.

[1] 1. T.F. Otero et al. J. Phys. Chem. B 101 (1997) 3688.
[2] P. Ocon et al., Corr. Sci. 47 (2005) 649.

Corrosion inhibition of pure zinc by new multilayer coating

A. Prună, Dept. Micro and Nanotechnology, Fiat Research Centre, Turin, Italy, alina.pruna@consulenti.crf.it; V. Brânzoi, Dept. Applied Physical Chemistry and Electrochemistry, University Politehnica Bucharest, Romania; F. Brânzoi, Institute of Physical Chemistry, Bucharest, Romania

The corrosion behaviour of pure zinc electrodes modified by polypyrrole (PPy) single layer and polypyrrole/polyphenol (PPy/PPhe) bilayer coating was investigated. Galvanostatic technique as well as the cyclic voltammetry was used for the synthesis of the layers. The corrosion performances of the obtained multilayer (PPy/PPhe) and of the single polypyrrole layer itself (PPy) were investigated in 3% NaCl solution by using electrochemical impedance spectroscopy (EIS), anodic polarization curves and open circuit potential measurements. Scanning electron microscopy was employed for the morphology of the synthesized coatings. From the obtained results it was shown that the multilayer coating had a more protective efficiency with respect to the single PPy layer regarding the corrosion of pure zinc due to the thin polyphenol layer. It was concluded that the very thin PPhe film produced on the surface and within the pores of the PPy coating lowered the permeability of the coating and therefore the mobility of the electrolyte solution within the coating decreased significantly. The best results regarding the anticorrosive properties were obtained in the case of the multilayer films based on galvanostatically electrosynthesized PPy.

Keywords: multilayer coating, polypyrrole, polyphenol, zinc, corrosion

The combined method of protection of an internal surface of steel tanks

Kuznetsov Yu. I., Andreev N.N., Vershok D.B., Oleynik S.V., Sergeev A.V.
A.N.Frumkin Institute of Physical Chemistry and Electrochemistry of RAS, Moscow, Russia

At carrying out of repair work on sea ships or during their construction on shipyard the internal surface of their fuel and ballast tanks is exposed to corrosion. Removal of rust from such surfaces is economically unprofitable and technologically inexpedient because on the cleared of the rust metal surface in conditions of a sea atmosphere the corrosion defeats quickly appear again. It is known, that the rust on a surface of tanks can be converted to a densely linked protective coating. Such coatings are formed as a result of processing a rusty surface became special formulations - rust converters. However, these coatings independently are not capable to prevent for a long time the occurrence of corrosion defeats in conditions of a humid sea atmosphere. In this connection in the given work the efficiency of the combined protection of a rusty steel surface by its processing by the rust converter with additional use of volatile corrosion inhibitors is studied.

It is shown, that the degree of protection of coatings on steel samples with a rust thickness 100-150 microns after processing by the tannin rust converter IFHAN-58PR at tests in the chamber of humidity does not exceed 70 %. Modifying of IFHAN-58PR by corrosion inhibitors raises the degree of protection of received coatings, however does not prevent occurrence of the pitting corrosion on samples during tests. Earlier high efficiency of carbon steels protection by volatile corrosion inhibitor IFHAN-118 was shown. This inhibitor also effectively suppresses corrosion of steel modified by the rust converter. So, during 1000 h of tests of samples with the coatings received in IFHAN-58PR, at presence of IFHAN-118 on their surface, in the chamber of humidity, the occurrence of corrosion defeats was not observed.

The modes of improving of the protective and decorative properties of magnetite coatings on steel

Vershok D.B., Kuznetsov Yu.I., Bulgakov D.S.
A.N. Frumkin's Institute of Physical Chemistry and Electrochemistry of Russian Academy of Science, Moscow, Russia

The ammonium nitrate solution is proposed for the replacing of the ecologically harmful and power-consuming method of blueing of steel in the strong alkali solution at the temperature t = 135-165 °C. It allows to arrive the magnetite coating (MC) with the thickness near 1 μm for the 40 min. It should be modified by some substances which have been added immediately into the blueing bath for the improving of its protective and decorative properties. These substances may be separated in two groups: the inhibitors of the MC formation and the promoters or growth accelerators of MC (GAMC).

The example of the inhibitors usage is the blueing in ammonium nitrate solution with addition of salts of the HEDP acid. The protective properties of MC in this instance increase at the formation of the binary complex of HEDP expense which implement into the magnetite matrix with the decreasing of porosity of it. While this inhibitor decreases the corrosion rate of the steel with MC in the aggressive solutions, but the full protection should be got only with the inhibited treatment of this solution. In this case the inhibitor should be used with the concentration of no more that it's maximum permissible concentration.

The GAMCs also may be separated into the two types. In the first the applying of the ammonium persulfate allows to make the thick coatings which may be impregnated with the passivation solutions easy. In this case the degree of protection of the blued steel in the condition of the atmospheric corrosion extend at the somewhat times. The aluminum nitrate and some amides may be placed into the second type. In the presence of this substances in the blueing solution there is the important increasing of thickness (from 2 to 4 times) of the coating, which is a low-porosity also. As in the case with the salts of HEDP, there is associated with the implementing of some hard-soluble substances, which have been formed during the blueing, into the magnetite matrix. This modified MC may be improved by the impregnation with the passivation solutions also.

The using of GAMC allows to decrease the temperature of the process of the formation of the MC. For example, the using of the aluminum nitrate allows to blue the steel at the t = 70°C. Although the thickness of coating slightly decreases, the resistance to corrosive attack is scarcely changed. The similar to this situation is observed with the blueing of steel in the new-developed solution OKS-9. The new MCs also impregnated by the water-soluble passivated solutions. The accelerated corrosion tests of this MC have shown the exceptional protective properties of it at the conditions of 100% humidity at the periodical condensation of the moisture on the surface of the blued steel.

A comparison between the electrochemical behaviors of some HVOF-sprayed WC-based coatings

M. R. Saghi Beyragh[1], **Sh. Khameneh Asl**[2] , **S. Norouzi**[3]

1. Faculty of Materials Engineering, Sahand University of Technology, Tabriz, Iran,
mr.saghi@gmail
2. Department of Materials Engineering, Faculty of Mechanical Engineering, University of
Tabriz, 51666-16471 Tabriz, Iran, khameneh@tabrizu.ac.ir
3. Electrochemistry Lab, Material and Energy Research Center, 14155-4777 Tehran, Iran

Thermal spray WC-based coatings are widely used in the aircraft industry mainly for their resistance to wear, reworking and rebuilding operations and repair of worn components on landing gear, hydraulic cylinders, actuators, propeller hub assemblies, gas turbine engines, and so on. The aircraft industry is also trying to use thermal spray technology to replace electroplating coatings such as hard chromium. This study compares the electrochemical behavior of some HVOF-sprayed WC-based coatings (including WC-12%Co, WC-17%Co, WC-10%Co-4%Cr, WC-20%Cr-7%Ni and WC-10%Ni). They were produced by High Velocity Oxy Fuel (HVOF) spray technique onto mild steel plates. The microstructure of the coatings was examined by optical microscopy (OM) and scanning electron microscopy (SEM). Polarization and electrochemical impedance spectroscopy (EIS) tests were performed on all of types of coated samples in 3% NaCl solution. Comparative electrochemical test results showed that, the WC-12%Co coat have the highest I_{corr} and was significantly damaged after the electrochemical tests, because its microstructure had lesser metal matrix. On the other hand, the WC-20%Cr-7%Ni coat have shown the lower I_{corr} than the other coats. The most amount of metal binder in the WC-20%Cr-7%Ni coat was found to have a better corrosion resistance than the as sprayed coats.

The effect of the heat treatment on electrochemical behaviors of some HVOF-sprayed WC-based coatings

M. R. Saghi Beyragh[1], **Sh. Khameneh Asl**[2] , **S. Norouzi**[3]

1. Faculty of Materials Engineering, Sahand University of Technology, Tabriz, Iran, *mr.saghi@gmail*
2. Department of Materials Engineering, Faculty of Mechanical Engineering, University of Tabriz, 51666-16471 Tabriz, Iran, *khameneh@tabrizu.ac.ir*
3. Electrochemistry Lab, Material and Energy Research Center, 14155-4777 Tehran, Iran

WC-based coatings (including WC-12%Co, WC-17%Co, WC-10%Co-4%Cr, WC-20%Cr-7%Ni and WC-10%Ni) were deposited onto mild steel substrate using HVOF spray technique. The coated specimens were then heat treated at temperature of 950˚C in a vacuum chamber. The coatings were studied in the as sprayed and heat treated conditions. Metallographic examination by Optical, scanning electron microscopes and XRD analysis indicated that some brittle eta phases were produced at high temperature heat treatment. Generation of these phases increases the coatings hardness. Polarization and electrochemical impedance spectroscopy (EIS) tests were performed on all of types of coated samples in 3% NaCl solution. Comparative electrochemical test results showed that, the heat-treated coatings the lower I_{corr} and was significantly free-damaged after the electrochemical tests, because its microstructure had nano-crystalline phases. Heat treatment of these coatings at high temperature also resulted in partially dissolution of WC particles and formation of new crystalline phases.

Corrosion Properties of Electroless Nickel Composite Coatings by Various particles

A. Farzaneh, Yang Researchers Group, Shahid Bahonar University of Kerman, Iran

M. Mohammadi, Department of Materials Science and Engineering, Sharif University of Technology
S. Velashjerdi Farahani, Razi Metallurgical Research Center, Tehran, Iran

ABSTARCT

Electroless nickel (EN) coatings are widely used in different industries. Various physical characteristics of EN coatings, such as hardness, coating uniformity, wear resistance and corrosion resistance, as well as the ability to plate non-conductive surfaces make this a coating of choice for many engineering applications. In this work, the effects of co-deposition of PTFE, MoS2 and/or nanoSiC particles on corrosion properties of electroless nickel coating (EN) were studied. The influences of heat treatment on the corrosion resistance of EN-PTFE-MoS2 and En-nanoSic composite coatings were also investigated. Scanning electron microscopy (SEM) is used to study the morphology of coatings and the distributions of the lubricant particles in the deposits. potentiodynamic polarization test was used to investigate corrosion properties of the coatings in both salty (3.5wt% NaCl) . Results indicate that co-deposition of PTFE and SiC particles in EN coating improves corrosion characteristics but MoS2 particles decrease the corrosion resistance of EN coating. Simultaneous co-deposition of PTFE and MoS2 particles leads to more reduction in corrosion resistance of EN coating. Heat treatment of coatings has significant effects on microhardness and corrosion resistance of EN-PTFE-moS2 and nanoSiC composite coating.

Keywords: Electroless Nickel, Composite, Heat treatment, Corrosion resistance.

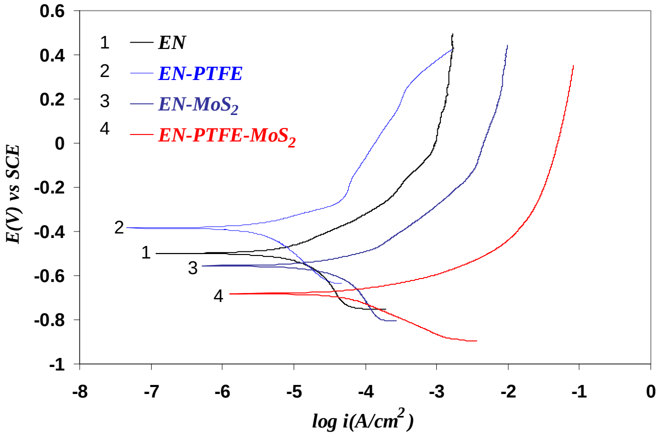

Fig.3. The polarization curves of the coatings in 3.5wt. % NaCl solution

Oxidation of lithium-containing aluminium alloy in chromateless conversion solutions

***Yulia ZIMINA*, Sergey OLEYNIK**

Institute of Physical Chemistry and Electrochemistry of Russian Academy of Science, Moscow, Russia

Lithium doping of aluminium alloys reduces their relative density and raises the modulus of elasticity therefore Al-Mg-Li alloys are highly appreciated in the industry and aircraft engineering. Conversion coatings (CCs) are widely used for protection of aluminium alloys against corrosion. Earlier chemical oxidation carried out in chromate solutions, but currently their application is limited because of their high toxicity. Using of the alkaline conversion solutions containing molibdates and other modifiers was offered as replacement of chromate converting formulation (CF).

Process of oxidation of 1424 lithium-containing aluminium alloy in alkaline converting formulation and protective properties of the obtained coatings were studied.

During the oxidation of 1424 alloy in alkaline IFHANAL-1 conversion formulations well attached to the surface CCs are formed. Polarization measurements data of an 1424 alloy with conversion coatings in chloride-containing environments have shown that addition of modifying additives and complexing inhibitors in converting formulation improves protective properties of obtained coatings. Addition in the CF of modifying additives allows to optimise the content of alloying ingredient oxides and foreign molybdenum dioxide in the aluminum oxide forming the CC, that was verified by the data of the x-ray spectral microanalysis and photoelectron spectroscopy. Such modifying of converting formulation increases efficiency of filling of CCs in IFHAN-25 inhibitor solution.

The further modifying of converting formulation resulted in IFHANAL-3 solution design. During the oxidation of 1424 alloy in IFHANAL-3 conversion formulations well attached to the surface CCs are formed. The filling of the CCs in hot watter and solution of corrosion inhibititor IFHAN-25 results in essential increase of their resistance to local anodic activation in the chloride-containing media.

By results of corrosion tests in the salt spray chamber on the coatings formed in IFHANAL-1 and IFHANAL-3converting solutions corrosion failures was not observed till 500 hours.

Corrosion resistance of plasma sprayed Al_2O_3 with and without Ni-5% Al bond layer on stainless steel substrates

M.A.Shoeib[*] , Sh.Abdel-Samea[**], H.Abdel-Kader[***] & N.Hegaszy[****]

*** Surface treatment and Corrosion control department, Central Metallurgical Research and Development Institute, CMRDI, P.O. Box: 87, Helwan, Cairo, Egypt.**

**** Ministry of Military production, Factory 270,Cairo,Egypt**

***** Faculty of engineering, Helwan University, Cairo, Egypt**

****** Ministry of Military production, Factory 1,Cairo,Egypt**

Abstract:

Plasma sprayed alumina coatings on the surface of metals enhance effectively the corrosion resistance property. In this study deposition of Al_2O_3 ceramic coatings with and without Ni-5%Al as bond layer on substrate of AISI 304 stainless steel using plasma spray technique . In order to enhance the corrosion resistance, a post-treatment has been carried out using polymer sealant. The porosity of the coatings was measured by optical methods (image analyzer) before and after sealing, the graded microstructure of the coatings was examined using optical microscopy (OM) and a scanning electron microscope (SEM). The effectiveness of the type of coatings, bond layer, and sealing treatment on the corrosion behavior of the coatings were determined through static immersion test in 5% HCl . The results showed that a sealed condition of the coated layers lead to higher corrosion resistance, because the through pores in the coatings provided the way for \solution to access the interface. .

Keywords: Coating, porosity; plasma spraying, Al_2O_3 ceramic coating, sealing, bond coat, corrosion resistance.

A Novel method to fabricate nano structured Ni-P composite coatings containing nano scattered Al_20_3.

[*]M.A.Shoeib,[**] Y.F.Barakat,[***] M.A. Hegazy, [***]G. A. Elmahdy and [***]S.S. Abd-El Latif
[*]Central Metallurgical Research & Development Institute (CMRDI), Surface Treatment& Corrosion Control Dept.
[**]Tabbin Institute for Metallurgical Studies (TIMS)
[***]Helwan university, Faculty of Science, Chemical Department
mshoeib@yahoo.com

Abstract

Composite coatings of modified amorphous nickel were prepared by simultaneous electroless deposition of Ni-P and Al_2O_3 on steel, from a solution in which nano Al_2O_3 particles were kept in suspension by stirring. Following short-term heat treatment at 400ºC, the plating acquires chromium equivalent hardness. The deposit surfaces were studied by SEM, profilometry and Vickers microhardness and its structure by X-ray diffraction. The fabricated composite materials were tested under corrosion conditions by linear polarization, Tafel plot & potenchiodynamic measurements. The results show that after the heat treatment at 400ºC for one hour the deposits acquire a crystalline microstructure, with very good adhesion to the substrate. In addition, the micro hardness of heat-treated particle-free Ni-P alloy coatings attained values of 720 HV, while the composite Ni-P– Al_2O_3 coatings acquired an even higher microhardness, exceeding 1200 HV. The corrosion resistance of the fabricated composite layers after heat treatment remained almost unaffected.

Paint and coatings of new generation for anticorrosion protection of metals

I.D. Kuleshova, A.V. Sorokin, ZAO NPP “Spectechnoprocess”, Moscow, Russia

Since the metals are one of the main and prevailing construction materials anticorrosion protection of metal products is one of supreme and important problems. At the same time the requirements for quality and durability of anticorrosion protection of metals and light-metal alloys rise annually.

In the report there were described two ways of coatings of new generation production:

1. Metal containing paints “Vetocor” for prolonged anticorrosion protection forming thin-layer and multi-layer coatings possessing excellent deformation behavior. Semi-gloss flat coatings without any defects are noted for perfect adhesion and cohesive characteristics including application on aluminum and aluminium alloys substrates. Therefore it is significant that application of “Vetocor” does not require a special preliminary surface treatment for the creation of roughness.

Testing of primer coatings 140 µm thicknesses in salt spray chamber during 1440 h in different centers, including Eckart laboratory have shown the absence of any corrosion in the cut. The appearance of coatings after the testing does not change, on the surface there is no the traces of white corrosion. It confirms that the coatings provide good barrier effect.

In consequence of excellent corrosion resistance of primer “Vetocor-103” it is possible to decrease the thickness of primer coating as well as the thickness of the system of coatings. The accelerated testing on GOST 9.401-91, method 6 (open atmosphere of industrial zone of cold-temperate climate) and method 10 (open atmosphere of cold-temperate, tropical and maritime climates) as well as ISO 12944 tests of new materials have shown that the high protective effect possess the new coatings of smaller thickness, than the conventional zinc containing coatings produced by native and foreign manufactures.

For the prolonged exploitation in various climate zones there were tested the systems of metal containing coatings based on “Vetocor” consisting of primers and quick-drying coatings. The predictable life time of coatings systems amount to 15-20 years.

There were considered various fields of application of metal containing materials “Vetocor”, including painting of modern special vehicles (ex. fire engine, produced by “ZIL”).

Thus now on the Russian market offered the new generation of metal containing coatings for the prolonged anticorrosion protection of various steel and light-metal alloys objects surpass in properties conventional native and foreign materials.

2. New paint for the anticorrosion protection of various light aluminium and aluminium-magnesium alloys. After ending of chemical milling (deep hot alkaline pickling) new paint forms antiadhesion (removable) coatings possessing high chemical resistance. Material is successfully used in rocket-space field.

How intelligent software business solutions can improve industrial painting practices, enable real time data management and reduce operating cost

Abd Elaziz M. Salah Eldin
Operation & Integrity Advisor
Abu Dhabi Marine Operating Company ADMA-OPCO
Abu Dhabi, United Arab Emirates
E-mail: aaziz2@adma.ae

Among all the corrosion control techniques, Coatings & Lining receive the least attention from technologists and corrosion focused organization to support and encourage developing software application to serve this sector.

There were always pressing needs to have appropriate database application to serve the industrial coatings business sector which can accommodate inspection reports, audit certificates, contract management reports, QA/QC data, failure analysis reports and many other field generated data while allowing efficient data manipulation and reporting.

Abu Dhabi Marine Operating Company ADMA-OPCO is the largest Offshore Oil producer in the Gulf region has realized this need and was among the first operators who used a Web based Coatings Business solution to manage its daily coating & Lining activities.

The used business solution enable storage of the new as well as the historic inspection reports, provides tools to risk rank facilities, produce management reports, identify overdue facilities and enable measuring the utilization of resources (Workforce & Equipments). The end results are a more efficient way of doing business compounded with a substantial reduction in the annual maintenance coatings expenditure.

This paper reflects ADMA-OPCO experiences while addressing the financial and operation benefits gained over 2 year since the system implementation.

Corrosion Behaviour of AZ31 Alloy with Al/SiCp Thermal Spray Coatings in Saline and Environment Exposure

R. Arrabal[1]*, A. Pardo*[1]*, M.C. Merino*[1]*, M. Mohedano*[1]*, P. Casajús*[1]*, S. Merino*[2]

[1] *Departamento de Ciencia de Materiales, Facultad de Ciencias Químicas,*
Universidad Complutense, 28040, Madrid, Spain
[*]*Corresponding author. Tel: 34 1 3944348; Fax: 34 1 3944357*
E-mail: raularrabal@quim.ucm.es

[2]*Departamento de Tecnología Industrial, Universidad Alfonso X El Sabio, 28691,*
Villanueva de la Cañada, Madrid, Spain

ABSTRACT

The corrosion behaviour of aluminium/silicon carbide (Al/SiC) composite coatings deposited by thermal spray on AZ31 magnesium-aluminium alloy was investigated by electrochemical measurements (DC and AC) in 3.5 wt.% NaCl solution at 22 ºC. Also, the corrosion behaviour was evaluated in neutral salt fog (ASTM B 117) and high relative humidity (98% RH, 50 ºC) environments. The as–sprayed Al/SiCp composite coatings revealed a high number of micro–channels, largely in the vicinity of the SiC particles, that facilitated the penetration of the electrolyte. This resulted in galvanic corrosion at the substrate/coating interfaces and formation of magnesium corrosion products, which eventually led to coating spalling in the case of salt fog tests after protracted times of exposure. The application of a cold–pressing post–treatment reduced the degree of porosity of the coatings and improved the bonding at the coating/substrate and Al/SiC interfaces. This resulted in improved corrosion resistance of the coated specimens. The effectiveness of the coatings slightly decreased with the addition of 5–30 vol.% SiCp compared with the unreinforced thermal spray aluminium coatings. Thus, in high humidity atmosphere, corrosion signs were only visible at the Al/SiC interfaces in the outermost surface of the coatings and, in saline environments; the galvanic corrosion of the substrates was delayed.

Keywords: Magnesium alloys; Composite coatings; Corrosion; Thermal spraying; Salt fog

Functional Surfaces using Fluid Filled Nano-capsules in Metallic Matrix

C. B. dos Santos[a], C. Mayer[b]

[a]University of Stuttgart IFF and Fraunhofer IPA - Germany
[b]University of Duisburg-Essen - Physikalische Chemie - Germany

Abstract

With the development of new technologies and applications the requirements of the materials is changing. Many systems cannot be immediately stopped to suffer an extern repair. An "automatically autonomously repair" can be crucial for critical functions of an equipment. The initial idea is to use the examples of the nature because the most materials in the nature are themselves self-repairing composite materials. This concept offers to designer an ability to incorporate secondary functional materials capable of counteracting service degradation.

The aim of this study is create bio-inspired surfaces with automatically autonomously repair. For this purpose, nano-capsules with a fluid content of diameters between 100 and 500 nm are applied in a modified galvanic process. The capsules are meant to be deposited together with the metal, forming a functional composite coating.

The polymeric capsules were produced at the University Duisburg-Essen. As a basic material for the capsule walls, poly-n-butylcyanoacrylate has been chosen since the resulting structure is relatively stable against mechanical or chemical stress. In addition, poly-n-butylcyanoacrylate nano-capsules can be prepared at low costs on a larger scale. These nano-capsules have been generated in an adapted interfacial polymerization approach. For the electrochemical deposition the chemical composition (salts concentration and additives) of electrolytes was changed and combined with nano-capsules suspension. The mechanical properties were tested by wear testes (linear sliding). The analyses of the electrolyte were carried out on galvanostat / potentiostat system with electrochemical voltametric studies. The small size of the capsules allows for the full embedding of the capsules even in thin coating layers while avoiding significant surface defects. Punctual mechanic load on the surface destroys some of the capsules, leading to a limited local release of the liquid content and initiating its desired activity.

Key words: fluid filled nano-capsules, electrochemical deposition, functional surfaces

Hardfacing of stellite 6 on martensitic stainless steel and evaluation of microstructure and corrosion behavior

Maral Ahmadpour Samani,Isfahan university of technology/pars oil gas company, Tehran/Iran
M. Shamanian*, Isfahan university of technology/ Isfahan university of technology, Isfahan/Iran*
A.Saatchi*,* The Ohio State University */ Isfahan university of technology, Isfahan/Iran*
N.Najari, Isfahan university of technology/ pars oil gas company, Tehran/Iran

Abstract

In this research microstructure, Vickers hardness profile and corrosion behavior in saline conditions of consecutive layers of a cobalt based alloy, Stellite 6, were deposited onto 410 stainless steel, One, two and three consecutive layers and one layer stellite 6 with 309austenitic stainless steel and inconel 617 interlayer were investigated. Gas Tungsten Arc Welding (GTAW) cladding were carried out for depositing. The specimens were investigated by an optical metallogaphy X-ray diffractometer, energy dispersion spectroscopy (EDS), scanning electron microscope (SEM) and hardness test. The microstructure of the clad layer consists of eutectic structure carbides dispersed in the FCC matrix Co with dendritic structure, The carbides are M_7C_3 and $M_{23}C_6$ (M refers to metal), which are mainly compounds of chromium. Interface and dendrites have epitaxial growths. There was a gradual increase in the hardness from the substrate towards clad surface due to the decrease in the size of dendrites and the hardness near the substrate is low because of the dilution of the clad layer with Fe from the substrate. 309austenitic stainless steel Interlayer results dilution of Fe were decreased and hardness were increased. Inconel 617 interlayer cause decrease in hardness. the corrosion rate of 3 layer specimens were low, and the passive region was longer than other specimens, the passive current for stellite coatings with interlayers were lower than 1 and 2 layer but the passive regions were smaller. The corrosion rate of speciments with interlayer were lower than other speciments.

Keywords: stellite 6, martensitic stainless steel, inconel 617, interlayer, microstructure, corrosion behavior, Gas Tungsten Arc Welding

Technology of creation of corrosion resistant nanostructured coatings on metallic surface

Chavchanidze A. Sh., Timofeeva N. Yu., Bazarkin A. Yu.
Moscow State University of Food Industry, 125080, Russia, Moscow,
11 road Volokolamskoe

E-mail: tchavtcha@ yandex.ru

The technology relates to mechanical instrument engineering and can be widely used industrially for technological equipment, different kinds of devices and metallic packaging.

The technology involves galvanic deposition of a metallic layer with subsequent laser treatment in order to obtain two diffusion zones: the first one representing solid solution with constant concentration of deposited metal over the depth of the zone and the second one having variable concentration of the metal over the zone. Having unlimited solubility with the metal of the article the deposited metal forms with it a solid solution with constant melting point (nanoquasimetal).

The use of this new technology allows to improve corrosion resistance of different structural materials and ensures the maximum corrosion protection of the important working components of machines and devices used in food industry as well as protection of the inner surface of tins exposed to the joint action of strong corrosive media and thermo-mechanical cycling.

Application of this technology makes possible to increase durability of the machine components, considerably extends service life of equipment and adds greatly to the storage life of food product in metallic package.

The influence of Cr(III)-based conversion layers on the corrosion resistance of Zn and nano-composite Zn in chloride containing solutions

D. A. Koleva[1], N.Boshkov[2], N. Tsvetkova[2], K. van Breugel[1],
J. H. W. de Wit[3], J. M. C. Mol[3]

[1]Delft University of Technology, The Netherlands, Faculty of Civil Engineering & Geosciences,
Department Materials & Environment; Stevinweg 1, 2628 CN, Delft;
[2]Bulgarian Academy of Sciences, Institute of Physical Chemistry,
Acad. G. Bonchev, Sofia 1000, Bulgaria
[3]Delft University of Technology, The Netherlands, Faculty 3mE, Department Surfaces & Interfaces,
Mekelweg 2, 2628 CD Delft.

This paper reports on the effect of Cr(III)-based conversion layers on the electrochemical behavior of Zn and nano-composite Zn in chloride-containing corrosion medium (5% NaCl). This is a comparative study of four types of coatings: galvanic Zn (Zn) composite zinc (ZnB); chromated Zn (ZnGP) and chromated ZnB (ZnBGP). The main objective was to define if the Cr(III) based conversion layers will additionally improve the corrosion resistance of the Zn and especially the ZnB coatings, the latter previously reported to be with superior properties, compared to pure galvanic Zn.

The nano-composite (ZnB) layer was electrodeposited from slightly acidic electrolyte, as used for the pure galvanic Zn (in mol.dm^{-3}: $ZnSO_4.7H_2O$ – 0.6; $(NH_4)_2SO_4$ – 0.2; H_3BO_3 – 0.5) but containing 1 g/l stabilized $PEO_{75}PPO_{30}PEO_{75}$ core-shell micelles. The solution for obtaining the Cr(III) conversion layers (so called Green Passivation) contains Cr^{3+} ions in the form of a complex salt of chromium with oxalic acid; another component is concentrated H_3PO_4; nitrate (NO^{3-}) ions from nitric acid (in concentration 50%) are used as oxidizers leading to pH values of about 1.5.

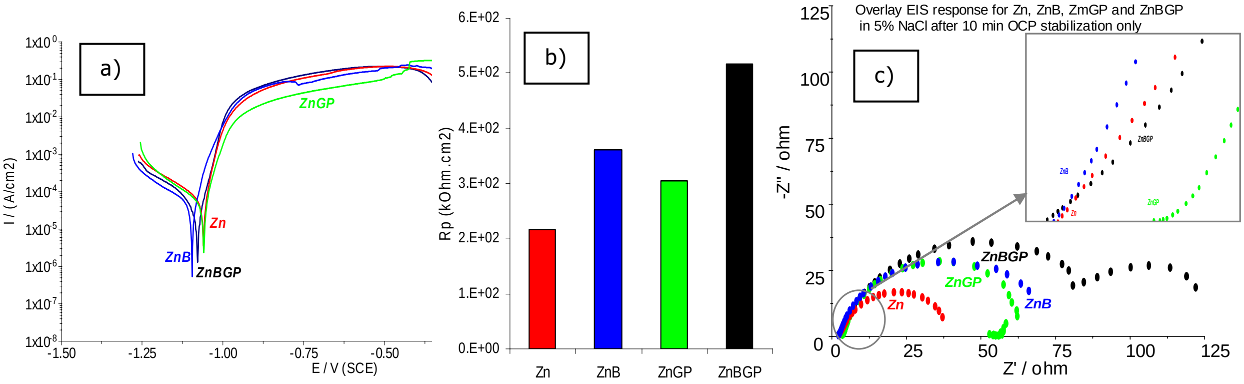

Fig.1 Potentio-dynamic curves (a); summarized Rp values (b); EIS response (c)

This is an on-going test and hereby presented are initial data after OCP stabilization only. Fig.1a) depicts the behavior of all investigated coatings with external polarization in 5% NaCl. Fig.1b) presents the derived *Rp* values. The Impedance response (Fig.1c) is in line with the derived *Rp* values, the chromated nano-composite coatings (ZnBGP) exhibiting the highest magnitude of impedance with a pronounced contribution of the passive layer (as evident by two time constants in the spectrum), whereas the lowest corrosion resistance (as expected) was derived for the pure galvanic Zn. The full paper will further present the corrosion behavior of the coatings after 24h, 90h, 136h and 210h of treatment (involving EIS, SVET and PDP methods) as well as morphology and composition of all coatings before and after treatment in 5% NaCl (defined by SEM, EDX, XPS and AFM).

Specific features of the chemical composition and properties of amorphous (nanocrystalline) protective coatings electroplated from solutions based on Cr(III), Ni(II), Co(II) and Fe(II)

V.A. Safonov[1], L.N. Vykhodtseva[1], L.A. Fishgoit[1], O.V. Safonova[2], P. Glatzel[2]

[1] Department of Electrochemistry, Faculty of Chemistry, Moscow State University, Moscow, 119991 Russia
[2] European Synchrotron Radiation Facility, 38043 Grenoble Cedex, France

Electroplates with the crystallographically amorphous structure that are characterized by several functional properties, particularly, the high corrosion and wear stability attract keen interest. This is largely due to the fact that as compared with amorphous metal coatings prepared by high-energy methods (plasma, electrospark, etc.) of surface treatment, the preparation of deposits in question requires no expensive equipment, the coating thickness is easily controlled by the amount of charge passed in the process and it is much easier to coat samples of intricate shape.

The preparation of such coatings includes the presence of certain organic compounds, hypophosphite ions, boron-, silicon or other metalloid-containing compounds in the electrolyte. As follows from the data of the energy and wave dispersion analysis (SEM EDX, WDX), the prepared deposits contain considerable amounts of metalloids in their composition. The literature contains different views on the chemical state of metalloids in amorphous deposits, which include the assumptions on the presence of elemental (intermediate) carbon and phosphorus in chromium and nickel deposits, respectively. So far, no direct methods were known that would allow one to check these assumptions.

In the present study, one of the versions of the method of X-ray emission spectroscopy, namely, the “valence-to-core” XES is described, which was used by the authors for identification of the chemical composition of amorphous (nanocrystalline) electroplates. High energy-resolution X-ray emission experiments with electrodeposits were carried out at High Brilliance XAFSXES beamline (ID26, ESRF, Grenoble, France). Experimental and calculation details one can find in our publications [1, 2].

The use of this method and the comparison of the obtained data with those obtained by the X-ray diffraction technique allows us to conclude that the original amorphous (according to XRD data) Cr, Ni, Co, Fe deposits contained considerable amounts (up to ~20 at. %) of carbides, phosphides or borides of the corresponding metals. It deserves mention that the amount of these materials remains unchanged at the annealing of samples at temperatures higher than 200°C, which unambiguously points to the absence of metalloids in their elemental state in the deposits.

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Corrosion of as-sputtered and annealed Al-Sc thin films in 5 wt.% NaCl solution

Jing-Chie Lin [a] , Hsueh-Lung Liao [a,b] , Chun-An Tseng [a] , Jian-Jhong Shen [a]*
[a] Institute of Materials Science and Engineering/ Department of Mechanic Engineering, National Central University, No. 300 Jhong-da Rd, Jhongli City 320, Taoyuan County, Taiwan.
[b] Automotive Research & Testing Center, No. 6, Lunkung. S. 7Rd, Lu-Kang Town 505, Changhwa County, Taiwan.
**Corresponding author, E-mail: jclincom@cc.ncu.edu.tw*
Tel: +886-3-4267328 Fax: +886-3-4254501
Institute of Materials Science and Engineering, National Central University, No. 300 Jhong-da Rd, Jhongli City 320, Taoyuan County, Taiwan.

The corrosion of thin Al-Sc solid films, varying the Sc-content in the range from 0 to 0.53wt.%, in 5.0 wt.% NaCl solution was investigated in this work. Most of the films were prepared by direct current magnetron sputtering technique and some of them were prepared by thermal evaporation for comparison. Electrochemical methods and salt spray were carried out to check the corrosion behavior. The corrosion resistance is superior for the sputtered film to the thermally evaporated one. The measurement of corrosion potential (Ecorr) indicated that the film containing higher concentration of Sc reveals higher corrosion potential. The results of polarization resistance demonstrated that the film containing higher Sc-content is more resistant to corrosion in the saline solution. The corrosion current density estimated by Tafel polarization reveals the order: Al-0.19wt.% Sc (153.61 nA/cm2) > Al-0.22wt.% Sc (137.53 nA/cm2) > Al-0.48wt.% Sc (2.27 nA/cm2) > Al-0.53wt.% Sc (1.07 nA/cm2). Salt spray test confirms the order of corrosion rate for the films. The microstructure was examined through high resolution field emission scanning electron microscope (FESEM) and transmission electron microscope (TEM). Alloying of Sc leads to refinement of the aluminum grains into nano scale. The grain size is the greatest (i.e., 185-195 nm) in the pure Al film and it decreases gradually to the smallest (i.e., 50 - 75 nm) with increasing Sc content from 0.19 to 0.53 wt.% Sc. It is interesting that the presence of nano grains in the film may lead to a characterization contrary to the basic concept of corrosion: a film comprising finer grains may expose much more area of the grain boundary to corrosion. All the Al-Sc films were annealed at 450°C for 1 h and then subjected to corrosion test. Worse corrosion resistance was found for the annealed films compared to the as-sputtered ones containing Sc less than0.48wt.% Sc . Hillocks formation in the film significantly deceases the corrosion resistance of the films.

Keywords: Al-Sc films; corrosion; hillock; FE-SEM.

NEW WATER BASED COATING SYSTEM FOR HOLDING & STORAGE TANKS

Margarita Kharsan, Angel Green, Cortec Corporation, White Bear Lake, MN/ USA

Traditional tank lining coatings are costly, have high VOC content and generally require a high film thickness of multiple coats. This abstract presents the results of testing a new type of coating system applied to the inside of holding tanks, exposed to corrosive environments. This new coating system has been extensively tested in the laboratory and field applications. The field applications include several holding tanks, where the products for storage vary from hydrocarbon to high salinity solutions. The coating system consists of a low VOC rust converting water based primer and a low VOC water-based epoxy primer which are applied at a much lower film thickness then the traditional tank lining coating systems, yet provides the same or better corrosion protection.

OBJECTIVE

To prove the new coating system could withstand the harsh environments, it underwent various accelerated weathering exposure tests in the laboratory and field applications.

In order for the coating system to be accepted as an alternative coating system for tank linings, 1000 hours of immersion testing in the listed chemicals below had to be run and show no corrosion.

Table 1 shows the results of the Immersion Resistance Testing. No negative effects were seen on the coating during this testing.

RESULTS

Table 1

Products	Chemical Immersed	Comments
Low VOC rust-converting water-based primer with low VOC water-based epoxy primer	100% Diesel	No effect to the coating
Low VOC rust-converting water-based primer with low VOC water-based epoxy primer	10% Diesel and 10% Gear Oil in water	No effect to the coating
Low VOC rust-converting water-based primer with low VOC water-based epoxy primer	4.5% NaCl and 4.5% $NaSO_4$ with 50ppm $FeCl_3$ in water	No effect to the coating

CONCLUSION

Laboratory and field measurements show that the coating system of a low VOC rust converting water-based primer and a low VOC water-based epoxy primer conforms to the performance criteria for tank lining systems containing hydrocarbon and/or high salinity solutions. Field applications have shown that the coating system is protecting the tanks from corrosion for the last 3+ years.

ORMOSIL coatings containing loaded TiO_2 nanocontainers for protection of AA 2024-T3 against corrosion

A. C. Balaskas, I. A. Kartsonakis, G. Kordas
Sol-Gel Laboratory, IMS, NCSR 'DEMOKRITOS', 15310 Aghia Paraskevi Attikis, Greece, abalaskas@ims.demokritos.gr

Abstract

Organically modified silicate coatings (ORMOSILS) with nanocontainers TiO_2 loaded with 8-hydroxyquinoline and TiO_2 loaded with 2-mercaprobenzothiazole were developed onto aluminium alloy 2024-T3 in order to protect the substrate from corrosion. The properties and structure of the resulting coatings have been evaluated using electrochemical impedance spectroscopy (EIS), Raman spectroscopy, scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX). We observed a significant improvement of the corrosion protection properties of the films by addition of nanocontainers. The total impedance value is increased by more than one order of magnitude in the case of the coatings with nanocontainers TiO_2 loaded with 8-hydroxyquinoline and two orders of magnitude in the case of the coatings with nanocontainers TiO_2 loaded with 2-mercaprobenzothiazole compared to the coatings without nanocontainers. The impedance value at low frequencies for coatings with nanocontainers is increased after long exposure time in corrosive environment suggesting possible self healing effect by releasing the inhibiting ions from the nanocontainers. Also, ORMOSIL coatings with nanocontainers have improved barrier properties.

ORMOSIL Coatings Containing Loaded Nanocontainers for Corrosion Protection of Aluminium Alloy 2024-T3

I. A. Kartsonakis, A.C. Balaskas, E.D. Mekeridis, G.C. Kordas*
Sol-Gel Laboratory, Institute of Materials Science, NCSR "DEMOKRITOS",
153 10 Agia Paraskevi Attikis, GREECE

Abstract

This study focuses on the corrosion protection of aluminium alloy 2024-T3 by applying an Organically Modified Silicate (ORMOSIL) coating that is integrated with a conductive polymer (polypyrrole) and contains ceramic nanocontainers loaded with corrosion inhibitors. The effect of the curing time and temperature parameters to the properties of the formed coating were investigated. Moreover, the ability of the loaded nanocontainers to release the inhibitor upon external trigger (e.g. exposure to aggressive environment) in order to provide self-healing of the surface was studied, too. The anti-corrosion properties of the formed coatings were examined electrochemically via electrochemical impedance spectroscopy (EIS); the composition and structure were investigated via RAMAN, Fourier Transform Infrared Spectroscopy (FT-IR) and Energy Dispersive X-Ray Analysis (EDX), and the morphology was determined with Scanning Electron Microscopy (SEM). It is concluded that the curing temperature and time play important role to the structure of the network and therefore to the properties of the coating system. Furthermore, the choice of the inhibitor plays an important role, too. An increase of the total impedance value is acquired when the curing temperature and time are 80 ^{o}C and 15 min, respectively.

* *Corresponding author. Tel.: +302106503304; fax.: +30210654769*
e-mail address: *ikartsonakis@ims.demokritos.gr*

Effect of guanilthiourea on deposition of the protective Ni-P coatings

O. Dolgikh, N. Sotskaya, L. Sapronova, Vu Thi Duyen, I. Zartsyn
Voronezh State University, Russia
E-mail: dov@chem.vsu.ru

In modern science and technology there are some certain requirements for coatings: they should be decorative, chemically and corrosion resistant and possibly have other attractive physical and mechanical properties. These requirements satisfy nickel-phosphorus coatings, which has long been widely used in various branches of industry. Often during the coating deposition organic additives are used as stabilizers, which besides its main function may influence the structure and properties of the deposit.

The aim of this work was to study the influence of guanilthiourea on the kinetics of deposition of Ni-P coatings, their composition, structure and corrosion resistance. Coatings were formed in two ways: chemical and electrochemical. It was established that the speed of the alloy electrodeposition process increases with increasing of additive concentration in the solution. The electroless deposition, on the contrary, is accelerated by small concentrations of additives ($10^{-7}..10^{-5}$ M) while larger concentrations completely suppress it.

Method of coatings formation also affects their composition and structure. Thus, in the electrodeposited coatings phosphorus content higher than in electrolessly deposited, but the latter more amorphous and are characterized by much smaller grains. Texture of deposit also varies. In the absence of additives in electrolessly deposited coatings faces with orientation (111) predominate, whereas in electrodeposited one - with orientation (200). Addition of guanilthiourea in the solution during electrodeposition promotes change of preferred orientation of faces: the contribution of the (111) increases sharply in comparison with the initial coating.

The effect of guanilthiourea on the porosity of Ni-P coatings, which is the main characteristic determining the corrosion resistance of the material was studied. It was found that the electrolessly deposited coatings, in general, are less porous than electrodeposited. The minimum porosity have deposits, electrolessly deposited in presence of guanilthiourea at C = 10^{-7} M.

This work is supported by RFBR (grant no. 08-03-00194a)

Sol-Gel coatings containing TiO_2 nanoreservoirs loaded with inhibitors for corrosion protection of AA2024-T3

Evaggelos MEKERIDIS , *George KORDAS*

Sol-Gel Laboratory, IMS, NCSR 'DEMOKRITOS', 15310 Aghia Paraskevi Attikis, Greece

Abstract

A novel technic has been successfully developed for corrosion protection of AA2024-T3. Sol-gel coatings were applied on AA2024-T3 substrates via dip coating method. TiO_2 nanoreservoirs were incorporated into the coatings. The first coating was an inorganic polymer of SiO_2 that contains Ce atoms. Then a second coating of epoxy resin was applied. TiO_2 nanoreservoirs loaded with 8-hydroxyquinoline (8-HQ) were incorporated into the second layer. The parameters of the curing temperature and time were studied so the best anticorrosive properties of the coatings to be achieved. The coating at 110 ^{o}C for 24 hours presented the best anticorrosive behavior. The morphology of the coating was examined via Scanning Electron Microscopy (SEM). Energy dispersive X-ray Analysis (EDX), Raman and Fourier Transform Infra Red (FT-IR) spectroscopy were used in order to the composition of the coatings to be examined. The behavior of the coating in aggressive environment (0,05M NaCl aqueous solution) was studied using Electrochemical Impedance Spectroscopy (EIS). The results showed improved anticorrosive properties; the total impedance values were increased about two **orders** of magnitude compare to the bare substrate after 500 hours. Coatings without nanoreservoirs and inhibitors also presented protection of the substrates but they were not as efficient as those that containing nanoreservoirs.

emekeridis@ims.demokritos.gr

Research on Corrosion Resistance of Electroless Plating Ni-W-P Coating

HUANG Yan-bin, **LU Ya-hui**, **SONG Gao-wei**, **MENG Zhao-fu**

Department of Equipment Remanufacturing,
Academy of Armored Forces Engineering, Beijing 100072
Address: Department of Equipment Remanufacturing ,
No. 21, dujiakan changxindian , Beijing, P.R.China, 100072
Fax: (+86)-10-66717102
E-mail：hyb1961@126.com

Abstract In order to enhance the corrosion and wear resistance of electroless plating Ni-W-P coating and broaden its application, in this paper an optimizing orthogonal test has been applied. The processing parameters have been optimized and some Ni-W-P coatings have been obtained with smooth and glittering appearance. The porosity of Ni-W-P coating (20μm) ranked class 9. The stability of solution was doubled, and the changing color time of the coating surface corrosion resistance is more than 2000 second with HNO3 dropping on. The hardness of layer is obviously improved by the Nano test 600 equipment. Furthermore the salt spray resistance of the layers can be up to 1000h with the thickness 30μm. By means of X-ray diffraction it can be proved that coatings' microstructure is amorphous phase. The surface appearance of deposition is typical lamerllar-like cells by SEM，which ranks close and neatly. The corrosion and wear resistance of optimized Ni-W-P coatings is better than Ni-P's. Due to its remarkable corrosion resistance and processing properties, the electroless Ni-W-P plating must be widely used in various fields.

Keywords: electroless plating; Ni-W-P; corrosion resistance; wear resistance

Effect of the parameters of low-temperature glow-discharge assisted nitriding on the properties of sintered austenitic steel

Agnieszka Brojanowska, Janusz Kamiński, Janusz Trojanowski, Tadeusz Wierzchoń
Warsaw University of Technology, Warsaw, Woloska 141 str. Poland

Abstract

The paper presents comparative results of examinations of microsturucture and properties of the nitrided layers produced on sintered 316L steel by low-temperature glow-discharge assisted nitriding with the samples placed on the cathode or in the plasma region (active screen glow-discharge nitriding). It has been shown that, in this process, a change of the polarization parameters affects essentially the thickness, surface topography, chemical composition, and phase composition of the nitrided layers produced on the sintered 316L steel samples, thereby affecting their corrosion resistance. The low-temperature glow discharge nitriding of sintered 316 steel samples, irrespective of whether placed on the cathode or in the plasma region, appeared to increase significantly the corrosion resistance and frictional wear resistance of this steel.

ALUMINIUM COATINGS FOR CORROSION PROTECTION APPLICATIONS

Sherif ZEIN EL ABEDIN[1,2], Nabil A. ABDEL GHANY [2], Amr S. ISMAIL[1] and Frank ENDRES[1]

[1]Institute of Particle Technology, Clausthal University of Technology, Robert-Koch-St. 42, 38678 Clausthal-Zellerfeld, Germany
E-mails: sherif.zein@tu-clausthal.de, aseis@tu-clausthal.de, frank.endres@tu-clausthal.de
[2]Electrochemistry and Corrosion Laboratory, National Research Centre, Dokki, Cairo, Egypt
E-mail: na_manakhly@yahoo.co.uk

In this paper we report on the electroplating of mild steel by adherent aluminium layers in ionic liquids. The increase of interest to use aluminium and its alloys in the car industry makes aluminium coating onto steel surface a hot topic of great importance. This is to avoid galvanic corrosion resulting from the direct connection between aluminium and steel. Moreover, coating of steel by thin layers of aluminium can improve its corrosion resistance. Due to their extremely large electrochemical windows, more than 5 volts, ionic liquids give access to the electrodeposition of metals, especially the elements that are only accessible from high temperature molten salts, such as Al, Ta and rare earth metals. Our results show that well adherent aluminium layers can be obtained after anodic oxidation of the substrate in the employed ionic liquids prior to bulk deposition of aluminium. The corrosion behaviour of mild steel without and with coating by adherent aluminium layers was investigated in 3.5 % NaCl solutions. Compared to the uncoated samples, the Al-coated mild steel exhibits higher corrosion stability indicating the improvement of the corrosion resistance by Al coating.

DETERMINATION OF THE ANTICORROSION PAINTS SUITABLE FOR THE MAINTENANCE OF DISTRICT HEATING PIPES

Tania GOTO[1], Yannick GOURBEYRE[1], Emmanuelle GAUDICHET[1], Bertrand GUILLEMOT[2]

[1] *Veolia Environnement, Anjou recherche, France, tania.goto@veolia.com*
[2] *Dalkia, Direction technique, France, bguillemot@dalkia.com*

Dalkia's district heating networks are made of steel pipes carrying hot or overheated water (from 110°C to 180°C). Those pipes are often isolated and buried in a concrete channel. The lack of accessibility of the pipes makes maintenance difficult. That's why this maintenance is mainly curative. Due to economic and safety reasons, Dalkia would like to optimize the curative maintenance the pipes.

To do so, 6 anticorrosion paints already used or in test on the field were qualified. This qualification consisted in the determination of the applicability of the paints at four temperatures (25°C, 70°C, 110°c and 180°C) and also in the determination of the durability of the eligible paints.

The results show that 2 paints are suitable for district heating pipes. The durability could be estimated.

Keywords: district heating; steel pipes; anticorrosion paints; applicability; durability

LIQUID-PHASE SILICONIZING METHOD FOR PREPARE SILICIDO-ALUMINIDE PROTECTIVE LAYERS RESISTANT TO HIGH TEMPERATURE OXIDATION

Tomas Kubatik, **Martina Jaglova, Eva Kalabisova, Vladimir Cihal**

SVUOM Ltd., Czech Republic, kubatik@svuom.cz

Titanium and titanium alloys have excellent combination ratio high strength versus low density. These properties are excellent for aerospace industry. A disadvantage of titanium and titanium alloys is only high oxidation rate at temperature 600 °C and above. Liquid-phase siliconizing by Al-Si alloys was studied as a simple nonexpensive method for preparation of protective layers on titanium alloy. This method is based on a great affinity of silicon to titanium and has been studied by several authors. The layers have great protective effect at higher temperatures. Layers were prepared by liquid siliconizing by Al-20wt%Si. Layer is composed from ternary phase 2 (Ti(AlxSi1-x)2). High temperature resistance of layers was evaluated during oxidation at high temperature. After high temperature oxidation changes in layer composition were observed by Scanning electron microscopy and Energy dispersive X-ray analysis (SEM/EDX). Liquid-phase siliconizing was presented as simple and effective method for preparing of protective layers on titanium alloys for high temperature application of component whichare not exposed to high stress application.

INFLUENCE OF $CeAlO_3$ NANO-POWDER ADDITION ON THE PERFORMANCES OF SILANE COATINGS FOR AZ31 ALLOY CORROSION PROTECTION.

Fabrizio Zucchi, Vincenzo Grassi, Federica Zanotto, Frignani Alessandro.
Corrosion Study Centre "A. Daccò", University of Ferrara, via G. Saragat 4a, 44122 Ferrara, Italy

Introduction

The formation of a silane conversion coating is currently proposed as an efficient way to protect from corrosion various metallic alloys. However, their barrier properties are impaired by the presence of a certain defectiveness, which allows an easy passage of the aggressive electrolytic solutions to the metallic substrate, and consequently the onset of the corrosion process. Therefore, an improvement in the protective characteristics of the silane layer should be reached by reducing its porosity. Since it has been found that nano-powders may improve the protective performances of silanic coatings, this paper intends to show the results obtained by protecting a Mg (AZ31) alloy by various silane coatings loaded with $CaAlO_3$ nano-particles.

Experimental

Square specimens of AZ31 magnesium alloy embedded in an epoxy resin were used. Their surfaces were prepared by emery papers up to 1000 grade, washed with distilled water, degreased with acetone and dried with hot air. These coupons were initially pretreated in a 10% HF solution for 60 sec, hot air dried and then immersed for 30 sec in the silane baths; after a hot air flux drying, they were finally cured for 1 hour at 100 °C. The treatment bath was a hydroalcoholic solution (90%/5%/5%, ethylic alcohol/water/silane) of various silanes: 3-Mercaptopropyl-Trimetoxysilane (PSH), 1,2-bis-triethoxysilylethane (BTSE), Vinyltrimethoxysilane (VS) and 3-trimethoxysilyl-propyl-methacrylate (PSMA). These baths were also modified with the addition of 250 ppm CeAlO3 nano-powders. The silane baths were regulated at pH 4, maintained under stirring condition for 12 hours and utilized for filming treatment after 48 hours from its preparation.

Electrochemical tests were performed in a 250 ml volume cell and the aggressive solution was 0.1M NaCl. The potentiodynamic polarization curves were recorded by applying a 0.2 mV sec^{-1} scanning rate and electrochemical impedance spectra were performed in the $10^5 \div 10^{-3}$ Hz frequency range, applying, at the corrosion potential, a 10 mV rms sinusoidal perturbation.

Conclusions

The addition of the $CeAlO_3$ nano-powder to the treatments baths increased either the inhibition efficiency of all the silanic coatings and the persistence of their protective action.

The best results of this nano-powder addition were experienced on PSH layer. In this case, after 168h immersion in 0.1 M NaCl solution, $CeAlO_3$ loaded PSH layer displayed an inhibiting efficiency over 99%.

Effect of titanium dioxide on corrosion properties of HA-TiO$_2$ nanocomposite coating fabricated by electrophoretic method

M. Amirnejad, Department of Materials Science and Engineering, Sharif University of Technology, Tehran, Iran
M. Mohammadi, Department of Materials Science and Engineering, Sharif University of Technology
A. Farzaneh, Yang Researchers Group, Shahid Bahonar University of Kerman, Iran
S. Velashjerdi Farahani, Razi Metallurgical Research Center, Tehran, Iran

ABSTARCT

Ceramic coatings on metallic substrates are used in many different applications. In Biomaterials science, Hydroxyapatite coating due to its similarity to the mineral part of bone structure is used for modification of implants surface. In order to improve the coating properties, composite coatings of Hydroxyapatite with ceramics, polymers and metals have been utilized. In this research, HA/TiO2 composite coatings with 5, 10, and 20 %wt. of TiO2 were fabricated on 316 stainless steel substrate by electrophoretic deposition. In order to study of the influence of TiO2 content in the coating, properties of coating such as morphology, structure, corrosion behavior in simulated body fluid, bond strength to the substrate and bioactivity of coatings, have been examined. SEM and XRD analyses were used to investigate the surface morphology and structure of coatings. Corrosion and bioactivity of HA/TiO2 coatings were studied by polarization and electrochemical impedance spectroscopy (EIS) methods. The results showed that increase in TiO2 content in coating led to increase in bond strength of coating to the substrate. Moreover, with increasing the amount of TiO2, corrosion current density of samples in the SBF was decreased. Investigation of bioactivity of coatings by EIS showed that TiO2 has a good effect on bioactivity of coatings.

Keyword: Hydroxyapatite, Titanium oxide, Composite, Electrophoretic, Corrosion; Bioactivity.

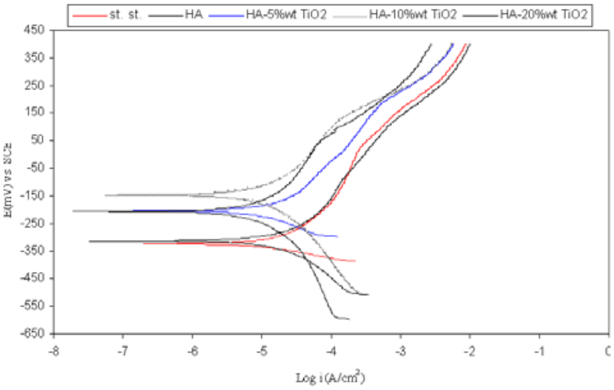


Fig.1. Polarization curves of different HA/TiO$_2$ in SBF solution

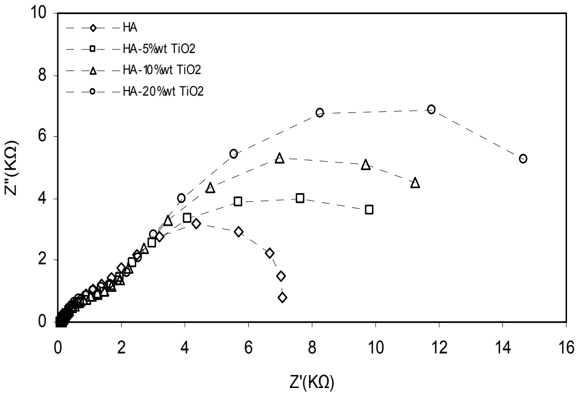


Fig.2. Nyquist plots of different HA/TiO$_2$ coatings after 48h immersion in SBF solution

PREPARATION AND CHARACTERIZATION OF AMORPHOUS PHOSPHATE COATINGS

L. Fachikov, Y. Tumbaleva, D. Ivanova
University of Chemical Technology and Metallurgy,
8 “Kl. Ohridski” Blvd., 1756, Sofia, Bulgaria, tel. / fax: (+ 359 2 868 11 20),
e-mail: fachikov@uctm.edu

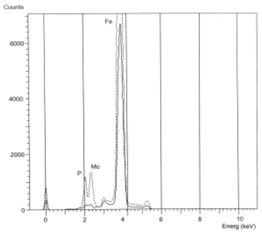
This study continues the investigation of preparation and characterization of amorphous phosphate coatings on carbon steels obtained in solutions of a new developed in UCTM-Sofia, product KAF-09OF.

Gravimetric, electrochemical and physical methods (XRF, TEM, XPS, AFM) have been used to determine the influence of pH (2÷6), temperature (20 ÷ 80°C) and agitation (0 ÷2000min^{-1}), over the mass/thickness, composition and structure of the coatings as well as passivation characteristics of the phosphating solutions with different pH, concentrations and temperatures.

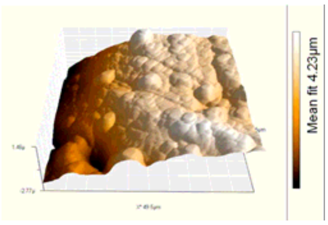
It has been established that the coatings are at greatest mass/thickness at pH 2.0 for all studied temperatures; the raising of the temperature from 20 up to 80°C leads to two - three times increased mass/thickness for all pH (2.0 – 6.0) of solutions.

The enhancement of pH and the agitation speed of the media lead to higher tendency to anode passivity of the steel.

The physical methods applied in the investigation have shown the composition, the probable compounds, the structure and roughness of the obtained phosphate coatings. The phosphate films are X-ray amorphous, with indefinite habit and very well expressive relief. The coatings contain basic elements such as oxygen, phosphorus, iron, molybdenum, calcium, which are probably combined as phosphate and oxide compounds.



XRF analysis of metal surface without coating (thick line) and after its obtaining (dotted line), 5 vol. %, pH 4.0, 60°C, 5 min.



Determining the roughness of the phosphate coating, 5 vol. %, pH 4.0, 60°C, 5 min.

The new phosphating product KAF-09OF has successfully employed in several Bulgarian firms for preliminary treatment in order to promote paint adhesion and thus corrosion resistance of painted articles.

Keywords: amorphous phosphating, iron phosphating, carbon steels.

CORROSION BEHAVIOUR OF DETONATION GUN SPRAYED Fe-Al TYPE INTERMETALLIC COATING

Cezary SENDEROWSKI[1], **Zbigniew BOJAR**[1]

[1]*Military University of Technology, Poland, csenderowski@wat.edu.pl*
[1]*Military University of Technology, Poland, zbojar@wat.edu.pl*

The detonation gun (D-gun) sprayed Fe-Al type coatings were investigated as an alternative for austenitic valve steel since they have been considered to possess good corrosion properties. Two different methods have been used to carry out the corrosion resistance of the Fe-Al type coatings. High temperature isothermal oxidation experiments, lasting 1 or 10 hours at 550, 750, 950 and 1100^{o}C under air atmosphere were completed. The microstructure, XRD and microhardnes analysis of the coatings after oxidation exposure were done. On the other hand, electrochemical corrosion resistance was evaluated by means of electrochemical measurements in 200 ppm Cl- (NaCl) and pH~14 (H_2SO_4) solution to simulate of the acid rain environment. A three-electrode electrochemical cell was used, with a calomel electrode as a reference electrode, a Pt-grid as a counter electrode and the sample with the coating as a working electrode.

It was found that D-gun sprayed Fe-Al type coatings show differences in the oxidation behaviour after 10 hours heating at those temperatures. The oxide layer ensures reasonable oxidation resistance even at 950 and 1100^{o}C heating temperature. Hematite, α-Al_2O_3 and metastable alumina phases were seen on the top surface of the coating, which preserves its initial thickness providing protection to the underlying substrate.

In general, only negligible changes of the phase composition of the coatings were noticed with simultaneous strengthening controlled in the micro-hardness measurements, even after 10 hours long heating at 1100^{o}C. It confirms high thermal stability of the Fe-Al type D-gun sprayed coatings structure.

The electrochemical corrosion tests reveal higher values of the breakdown potential for D-gun sprayed Fe-Al type coatings than the ones for the bulk Fe-Al type alloy and Cr21Mn9Ni4 austenitic valve steel. It enables these materials to the structural and multifunctional applications in aggressive environments including acids.

One can expect (on the basis of the experiments) the D-gun sprayed Fe-Al type coatings to be a very promising protection which can be employed to produce high quality elements exposed to corrosion conditions in aggressive environments and at high temperatures.

Study on the Technique and Properties of Electroless Plating of Ni-Cu-P Coating

BA-Jie, **HUANG Yan-bin, LIU De-gang**

Department of Equipment Remanufacturing,
Academy of Armored Forces Engineering, Beijing 100072
Address: Department of Equipment Remanufacturing ,
No. 21, dujiakan changxindian , Beijing, P.R.China, 100072
Fax: (+86)-10-66717102
E-mail：topbj1961@126.com

Abstract: In order to improve the corrosion resistance and the wear resistance of the coatings of electroless Ni-Cu-P plating and broaden its application, an optimized mathematical theory test has been applied in this research. According to the characteristic of application of engineering, the influence is researched between the quality of coating and the factors such as dissection of solution, pH value and temperature and so on. The parameters of technology have been optimized and some Ni-Cu-P coating have been obtained with smooth and glittering appearance. Through measuring the coating's thickness and testing the corrosion resistance and the porosity of the surface, the relationship between the influencing factors and the corrosion resistance as well as the best formulation is obtained. At the same time, the complex-agents can prevent copper from depositing first and obtain coatings with strong adhesion. The porosity results show that ferocxyl solution test showed that class 9 with the Ni-Cu-P coating layer (20μm). The changing color time of the surface coating is more than 800 second with HNO3 dropping. By the Nano model 600 test equipment it is shown that the average hardness of the optimal coating is 5.872GPa, and its average reduced modulus is 150.772 GPa. By XRD we can conclude that the coatings' structure is amorphous when the quantity of CuSO4·5H2O in the solution is less than 0.5g/L.The surface appearance of deposition were typical lamellar-like cells by SEM, which rank close and neatly. It is the processing parameters and bath composition, especially the complexants that we obtain the best formulation to possess high corrosion and wear resistance.

Keywords: Electroless plating; Ni-Cu-P; Properties; Depositing technique; Corrosion resistance

Engineering Application of various Electroless Plating coating in Vehicle Parts Remanufacturing

ZHOU De-long, Guo Ying, ZHAO Huo-ying, HUANG Yan-bin, XU Keke

Department of Equipment Remanufacturing,
Academy of Armored Forces Engineering, Beijing 100072
Address: Department of Equipment Remanufacturing ,
No. 21, dujiakan changxindian , Beijing, P.R.China, 100072
Fax: (+86)-10-66717102
E-mail zhdl1961@126.com

Abstract The vehicle parts remanufacturing can be obtained by some kinds of high and new surface engineering technology. Electroless plating technology is both a kind of advanced surface engineering and an unconventional machining technology. In this paper it is studied the application of dual, triplet and nano-composite electroless plating technology for abnormity and motive parts in vehicles, totally analyzed and solved the key points of technology on structure characteristics, solution choice of the plating , equipment , process of plating, surface quality, deposit properties and composite protective design in remanufacturing vehicle parts and gained the solution, equipment and optimized process which can be applied in the remanufacturing engineering. By this way it have improved the quality and scope of remanufacturing industrialization for parts and broadened the applied field of electroless plating. At last the application of electroless plating in vehicle parts remanufacturing was prospected.

Keywords: application; electroless plating; vehicle parts; remanufacturing;

SYNTHESIS OF ZIRCONIA NANO TUBES BY ELECTROCHEMICAL ANODISATION OF SPUTTERED ZIRCONIUM THIN FILMS

F. Vacandio, M. Eyraud, C. Chassigneux, T. Djenizian.
LCP - Laboratoire Chimie Provence (UMR 6264), Bâtiment Madirel, Université de Provence-Centre St Jérôme, 13397 Marseille Cedex 20.
Florence.vacandio@univ-provence.fr

Zirconia is a particularly interesting material showing good chemical and thermal stability, mechanical strength and good wear resistance. Moreover, zirconia is well known for its ionic conductivity properties: it is an electrical insulator which can become a pure ionic conductor when it is doped. So, the window of applications is wide including solid electrolyte fuel cell, oxygen sensor ... Hence, porous materials are very promising in various fields especially in energy. Indeed, these porous materials have the advantage of large specific surface and would thus reduce the size of electronic components and batteries for example.
Recent works have allowed the synthesis of nano zirconia tubes from electrochemical anodization of zirconium foils. The aim of this work is to develop electrochemical zirconia nanotubes from a thin layer of zirconium.

In a first step, thin films of zirconium were deposited on silicon by cathodic sputtering. These films were then electrochemically anodized in different (aqueous and organic) fluoride ions containing electrolytes. The films of zirconium (before and after anodization) were then characterized by X-ray Diffraction and Scanning Electron Microscope observations. The optimization of electrochemical parameters led to zirconia nanotubes of about 20 nm in diameter (Figure 1). Best results were obtained for 20 minutes of anodization at 20V, in an organic solution ($C_3H_8O_3$, NH_4F 0,35M, 2% H_2O).

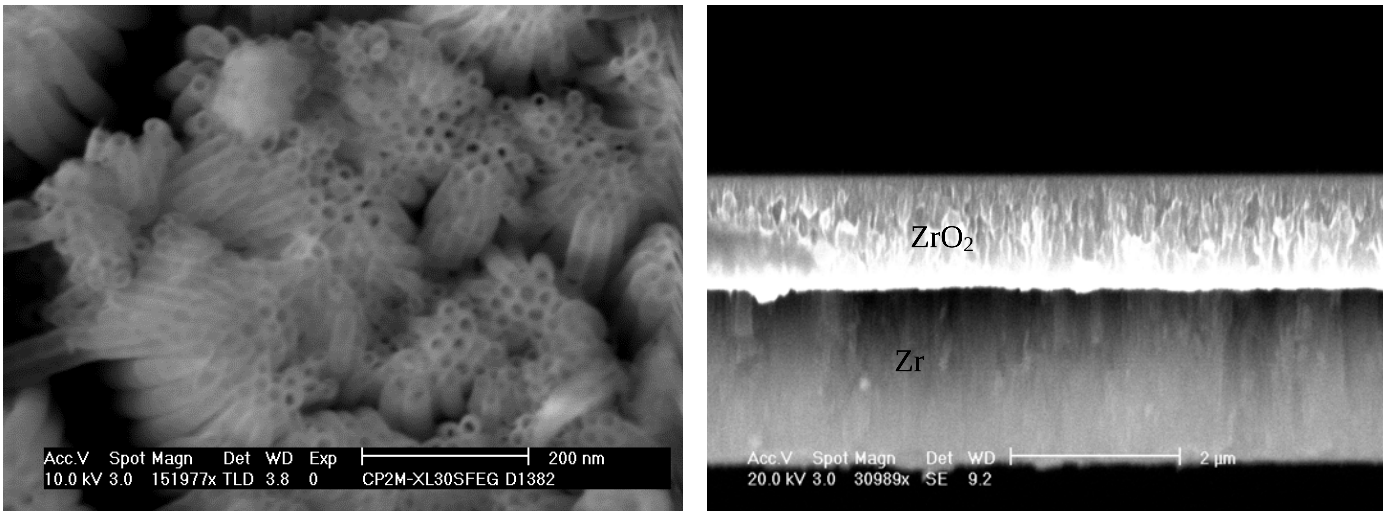


Figure 1 – Top View and Cross-sectional SEM images of Zirconia nanotubes.

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1-ethyl-3-methylimidazolium dicyanamid modified polypyrrole coating

Tunç TÜKEN, Mehmet ERBİL
The University of Çukurova, Science and Letters Faculty, Chemistry Department 01330
Adana-TURKEY

The hydrophilic nature and ionic mobility through the organic polymer coatings limits their use in anticorrosive applications. However, their oxidizing ability against various technical metals captured much attention, considering anodic protective behavior. The reversibly oxidation-reduction behavior of conducting polymer leads to storage and discharge of electrical charge and dopant anion, reversibly. This behaviour gives chance to design a primary coating which could deliver corrosion inhibiting species directly to defective area. It is already known that similar application was utilized in medicine technologies successfully; controlled dose releasing system. Along defective area, the metal oxidation occurs readily at metal/polymer interface and the polymer film (which is nobler to metal) is reduced. Since the driving force of the overall process is the metal oxidation (i.e. corrosion), the primary coating will release inhibitor molecules where it is exactly needed. Also the polymer film reduction will help metal surface passivation, by means of modifying corrosion products.

For this aim, 1-ethyl-3-methylimidazolium dicyanamid was used as inhibitory compound. The inhibitor molecules will be embedded through the polymer film during the synthesis. The synthesis mediums were aqueous and organic solutions while the electrochemical route was cyclic voltmammetry technique. Steel samples were coated with inhibitor doped polymer films and the corrosive behavior of coated material was investigated in 0.1 M HCl solution. For electrochemical analysis, EIS, potentiodynamic and chronoamperometric measurements were utilized. Also FT-IR analysis and AFM measurements were used for spectral analysis about the film structure and morphology. The inhibitory effect of 1-ethyl-3-methylimidazolium dicyanamid was also tested directly on bare steel, in the same corrosive test solution. It was shown that 1-ethyl-3-methylimidazolium dicyanamid could be successfully implanted in polypyrrole films. Also, it could show the inhibitory effect through the polymer film.

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Electrochemistry, morphology and degradability of polypyrrole on copper

Mehmet ERBİL , **Tunç TÜKEN**
The University of Çukurova, Science and Letters Faculty, Chemistry Department 01330
Adana-TURKEY

Polypyrrole films on copper are generally considered as simple physical barrier films on the surface, since the electrochemical synthesis involves considerably high anodic potentials. Then the product is generally found in poorly adhered and mostly degraded form. In this study, the electro polymerization parameters and quality of resulting film have been investigated by means of AFM, SEM, FT-IR, EIS, potentiodynamic and chronoamperometric measurements. In order to examine morphology, degradability and electrochemistry of polypyrrole films on copper, regarding the synthesis parameters. Since the film is highly sensitive to synthesis conditions, influence of those parameters are rationalized concerning the applicability of coating. The relation between electrochemical behaviour and morphology is discussed pertaining to possible applications of coated material.

The polymer films were realized on copper from aqueous oxalic acid solutions of pyrrole. The electrochemical route was cyclic voltammetry and the effects of scan rate, monomer concentration, and potential range were investigated, during multistep and single step synthesis methods. It was evidently shown that the polymer film quality could be improved strikingly, applying a prior passivation stage (in multistep method) and optimizing the potential range. The AFM and SEM results showed that the film properties (adherence, degradability, surface roughness and particle size etc.) could be controlled effectively. The electrochemically obtained data, especially fitted EIS results, were handled with assistance of microscopy results and the evaluations were rationalized. FT-IR and AFM results clearly showed that less degraded polymer films with lower permeability could be achieved. The stability under anodic over potentials was also found reasonably well that it can be used for various electrochemical purposes.

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Heat treatment of nanostructured ZrO_2 corrosion barrier coatings on 316L stainless steel

F. Samiee, K. Raeissi* and M.A. Golozar

Department of Materials Engineering, Isfahan University of Technology, Isfahan 84156-83111, Iran (*Corresponding Author, Fax: +98 311 391 2752, E-mail: k_raeissi@cc.iut.ac.ir)

Abstract

An electrolytic ZrO_2 has been coated on 316L stainless steel. The effects of heat treatment on morphology, structure and corrosion behavior of coatings were investigated. It has been observed that the coatings are dense and compact after heat treatment at 200 ^{o}C but FTIR analysis have shown that absorbed water is still exist at this temperature. Results showed that the suitable temperature for zirconia electrodeposition is 400 ^{o}C in which the coating is uniform and no residuals hydroxide exist either. In addition, an outstanding improvement in corrosion behavior was observed after heat treatment at 400 ^{o}C. It is also revealed that as temperature increased, the coating's cracks became more significant, especially after heat treatment at 600 ^{o}C. So the substrate became more susceptible to localize corrosion. In deed, the anticorrosive and adhesion properties were strongly affected by the temperature of the treatment.

Keywords: zirconia; coating; amorphous; nanocrystalline; heat treatment; corrosion resistance

Zinc electrodeposition in the presence of oxalic acid from sulphate bath

Sh. Khorsand, K. Raeissi* and M. A. Golozar

Department of Materials Engineering, Isfahan University of Technology, Isfahan 84156-83111, Iran

(*Corresponding Author, Fax: +98 311 391 2752, E-mail: k_raeissi@cc.iut.ac.ir)

Abstract

Zinc coatings were electrodeposited on mechanically polished low carbon steel substrate from an acidic sulfate bath. The effect of oxalic acid as a chelating agent on nucleation and growth mechanism, surface morphology, predominant texture and corrosion behavior of zinc electrodeposits was investigated. The results showed that the zinc deposits have mostly basal and low angle pyramidal planes parallel to the substrate surface in the absence of oxalate anions, whereas in the presence of oxalate anions, the prism and high angle pyramidal planes were dominant. Furthermore, the coating surface morphologies obtained at the presence or absence of oxalate anions was quite different. The zinc coating obtained in bath containing oxalic acid allowed easier hydrogen evolution. Correlation between nucleation modes of zinc electrodeposition in the presence and absence of oxalic acid showed that the instantaneous nucleation was predominant in both cases. Electrochemical impedance spectroscopy (EIS) revealed that in the bath containing oxalic acid, the growth of deposit was controlled by diffusion differ from that observed in the absence of oxalic acid, which was charge transfer controlled.

Keywords: Zinc electrodeposition; Nucleation; Growth; Oxalic acid; AC impedance; Morphology

A POLYPYRROLE/AL FLAKE PIGMENT FOR CORROSION INHIBITION

Christopher Alan VETTER[1], **Victoria Johnston GELLING**[1]

[1]*North Dakota State University, United States, v.j.gelling@ndsu.edu*

Currently, there are many problems associated with application of polypyrrole as a corrosion inhibitor. These problems stem from the inherent insolubility, brittleness, poor adhesion, and sometimes catastrophic failure of pure polypyrrole films. These problems make the application of polypyrrole as a coating difficult for both processing and performance considerations. In this study, polypyrrole was coated onto an aluminium flake pigment via an aqueous chemical oxidation reaction to produce a composite pigment. By incorporating this composite pigment into an epoxy primer, the mechanical properties of the epoxy binder and the corrosion inhibiting properties of the pigment can be combined. Phosphate, molybdate, or vanadate dopants were also incorporated into the composite pigment to investigate their effect on the performance of the pigment. The characterization of the pigment was performed via conductive atomic force microscopy (CAFM) measurements, a scanning electron microscope (SEM), and X-ray photoelectron spectroscopy measurements. The pigment's effectiveness as a corrosion inhibitor was evaluated on an aluminium alloy 2024 T3 substrate via potentiodynamic polarization measurements, coupling current measurements, scanning vibrating electrode technique (SVET) measurements, and ASTM B117 weathering. The results indicate that the polypyrrole is activating the aluminium flake to anodic activity causing it to act as a sacrificial anode when coupled with the aluminium 2024 substrate. When the pigment is doped with sulfate or phosphate, it does not significantly inhibit corrosion in defect areas. When the pigment is doped with molybdate or vanadate however, corrosion inhibition in defect areas is observed.

COMPARATIVE CORROSION STUDY OF A NEW TYPE OF “Ni-FREE” ALLOY FOR DECORATIVE APPLICATIONS

Stefano Caporali[1] and **Ugo Bardi**[2]

1 Chemistry Department, University of Florence and Consorzio Interuniversitario di Scienza e Tecnologia dei Materiali (INSTM), via della Lastruccia, 3 – 50019 Sesto Fiorentino (FI), Italy., stefano.caporali@unifi.it
2 Chemistry Department, University of Florence and Consorzio Interuniversitario di Scienza e Tecnologia dei Materiali (INSTM), via della Lastruccia, 3 – 50019 Sesto Fiorentino (FI), Italy., ugo.bardi@unifi.it

Nickel is the primary determinant of contact sensitization, therefore there is now a tendency to take nickel out of goods that could be in contact with human body. However this needs careful evaluation of the corrosion properties of nickel substitution especially in the fashion and jewellery industry where aesthetical defects are not acceptable. This paper analyse the corrosion behaviour of a recently patented Cu-Sn-Zn-In alloy, named “Quatro®”. The alloy is substantially nickel-free and can be obtained as thin coatings by electrodeposition from aqueous solutions. The obtained coatings show mechanical and aesthetical properties similar to the nickel ones constituting a potentially inexpensive alternative to this one.

In this paper the corrosion properties of Quatro® coatings, electrochemically deposited on brass substrates, were evaluated by free corrosion tests and analysis of electrochemical parameters such as open circuit potential, corrosion current, break-down potential and potentiodynamic polarization curves. In NaCl solution the corrosion properties of this alloy result to be similar to the traditional nickel coatings. In view of possible applications of this alloy as “Ni-free” solution for jewellery application, the corrosion properties in artificial sweat were also tested. In this environment, the investigations evidenced higher corrosion activity, assessing this solution not suitable for top finishing goods designed to be in contact with skin.

Keywords: Ni-free; Electroplating; Corrosion; Polarization Curves; Artificial sweat

Corrosion behaviour of plasma sprayed WC-Co/Al_2O_3 coatings in 3.5% NaCl solution

K. Hassan*, A.M. El-Aziz*, Y. Fouad*, M. el-Meniawy**

**German University in Cairo, Materials Engineering, 11835 New Cairo, Egypt*
***Zagazig University, Faculty of Engineering, Zagazig, Egypt*

A major challenge in technological development is to meet requirements for new materials in progressively more severe conditions. Mainly material's surfaces play an important role in determining its optimum performance to operating environment. Upon this basis developing of the coating is required. Plasma sprayed coatings are used in a wide range of industrial applications primarily for wear resistance, frequently in a corrosive environment. For this purpose, plasma sprayed WC-Co/Al_2O_3 ceramic coating by different deposition techniques and parameters have been subjected to corrosion test in order to investigate and evaluate their corrosion behavior and properties. Open circuit potential (OCP), potential cyclic voltammetry (PCV) and marine test (ASTM B-287-62) were performed to characterize and study the corrosion behavior. Optical microscopy (OM), scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) were used to analysis and investigate the microstructure of each sample after and before the corrosion test. It was observed that the parallel coating deposition parameters had a better corrosion resistance than the perpendicular coating deposition parameter; however pitting corrosion was observed in the parallel coated samples while in the perpendicular coated samples uniform corrosion was the predominate corrosion mechanism. It was also found that the grains size have a significant effect on the corrosion behavior. The samples coated by WC-Co coarse grains and then the second layer of Al_2O_3 fine grains had better corrosion resistance than the other grain combination of fine WC-Co and Coarse Al_2O_3 grains.

Corresponding author A.M. El-Aziz

STUDY ON THE ANTIFOULING ABILITY OF A SILICONE-BASED COATING WITH MICROHYDROGEL SURFACE

Cunguo LIN[1], Jinwei ZHANG, Li WANG, Jiyong ZHENG, Yanlei PENG

[1] *State Key Laboratory for Marine Corrosion and Protection, Luoyang Ship Material Research Institute, Qingdao 266071, China.*
lincg@sunrui.net

Biological fouling can bring about some unwanted and detrimental consequences to marine ship, such as increasing fractional drag and biocorrosion. Usually, the ship hull will be painted an antifouling coating to prevent biological fouling. The best performing coatings are those containing metal based compounds like copper or tributyltin, however which can lead to serious irreversible adverse influence to the marine ecological environment, such as imposex in oysters, and death of dolphins, porpoises as well as whales, so it is necessary to develop new eco-friendly antifouling alternatives to protect marine ecological environment.

It is well known that silicone-based coatings act essentially by means of a barrier layer with a combination of properties including ultra-smooth surface, low surface energy and low elastic modulus, which are necessary to minimize chemical and mechanical locking of fouling species, and this makes silicone become a very attractive candidate in developing new eco-friendly antifouling materials. Now, some antifouling coatings based on poly(dimethyl siloxane) (PDMS) have already been marketed as non-toxic marine coatings. However, it is also a matter of fact that some marine organisms still can adhere onto the silicone surface, especially diatoms, which can develop slime films and do not release from vessels operating at high speeds over 30 knots, and this can increase the fractional drag by as much as 5%-25%. Because silicone based materials is promising and important in developing new eco-friendly antifouling coatings, it is very significant and necessary to take some ways to further improve its antifouling ability against diatoms.

In this paper, a silicone-based coating with microhydrogel surface was designed and prepared. The preparation of the coating was introduced and characterized. When this coating was immersed in seawater, a microhydrophilic environment could appear at the interface between coating and water. Studies have shown that diatoms was very hard to adhere to hydrophilic surfaces, therefore the microhydrophilic environment was helpful to improve its antifouling ability against diatoms. Meanwhile, the continuous dissolvement of microhydrogels could make the surface dynamic, and this would effectively lower the bonding force between foulers and coating surface. Test results showed that, in comparison with control silicone coating, this coating could improve its antifouling ability against diatom Navicula sp. by 59%□and also had a very good inhibition efficiency for mussels settlement. Therefore, the microhydrogel surface could further enhance the antifouling ability of silicone-based coatings.

A comparative study of the corrosion protective properties of Cr(VI) free conversion treatments

C.R. Tomachuk[1], A.R. Di Sarli[2], C.I. Elsner[2], I. Costa[1],
[1] Instituto de Pesquisas Energéticas e Nucleares, IPEN/CCTM, São Paulo, SP, Brasil, tomazuk@gmail.com
[2] Centro de Investigacíon y Desarollo en Tecnologia de Pinturas – CIDEPINT, La Plata, Argentina – direccion@cidepint.gov.ar

Abstract

The corrosion resistance of pure zinc coatings can be improved through the application of suitable chemical passivation treatments. Hexavalent chromium compounds have widely been used to formulate conversion layers providing better anticorrosive protection as well as anchorage properties to painting systems. However, taking into account that they are produced using hazardous chemical ingredients, the development of alternative and "green" technologies with equivalent protective performance is a paramount purpose of many R&D laboratories working around the world [1]. In this work, the corrosion behavior of zinc coatings obtained from free-cyanide alkaline baths and latterly subjected to a trivalent chromium based passivation treatment, with and without a sealing treatment, was studied. The experimental work involved electrochemical impedance spectroscopy measurements in sulfate solution, surface microstructural and morphological characterization by electronic microscopy as well as chemical analysis by EDXS. The analysis and interpretation of all the data coming from these batteries of tests allowed inferring that both the trivalent chromium based conversion treatment + adequate sealer provided a good corrosion resistance and, therefore, together with an adequate painting system, they could be a less polluting and less toxic alternative to the traditional chromate coatings.

Keywords: zinc, conversion treatment, corrosion, impedance spectroscopy

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Corrosion resistance of Cr(III) conversion treatments applied on electrogalvanised steel and subject to chloride containing media
Materials Chemistry and Physics 119 (2010), pp. 19-29

Corrosion behavior of Electrostatic-sprayed polypropylene protective powder coatings for pipeline

G. Palumbo [1], P. Russo [1], S. Lyon [2], D. Acierno [1]

[1] Department of Materials and Production Engineering, University of Naples “Federico II”,
P.le Tecchio 80125 Naples, Italy
E-mail: gaetano.palumbo@unina.it
[2] Corrosion and Protection Centre, School of Materials, University of Manchester, UK
Sackville Street, Manchester M60 1QD, UK

The organic coatings play an important role in the protection of metals from aggressive environments, and is considered one of the most effective methods, especially in aggressive conditions [1,2,3].
The technology based on electrostatic-spray powder coatings is suited to meet the stringent environmental regulations curtailing the VOC emission.
Powder coatings provide environmental advantages over traditional coatings: they do not release volatile organic compounds (VOCs) and show a reduced solid waste profile when compared to traditional coatings [4].
Polypropylene is used in ordinary pipelines giving advantages compared with the standard coatings, e.g. fusion bonded epoxy resin because high mechanical properties (impact resistance, penetration resistance, etc.) and/or heat resistance are required [5].
In the present work, we have focused our research on the corrosion behavior of modified polypropylene powder coatings containing different pigments such as red iron oxide, titanium dioxide with different concentrations. These compositions were applied on grit blasted mild steel specimen by Electrostatic-spray technique and investigated by electrochemical impedance spectroscopy (EIS) and compared with traditional epoxy resin powder coating. The EIS study was carried out on samples after various exposure intervals in 3,5% NaCl solution.

Keywords**:** Epoxy Resin, Red Iron Oxide, Titanium Dioxide, Pigments, Electrochemical Impedance Spectroscopy, EIS, Coatings, Polypropylene

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Corrosion resistance of multilayer Ni-base coatings on AZ31 Mg alloy

M. Tafazoly, M. Monirvaghefi, M. Salehi, A. Saatchi, F. Tabatabaie, Isfahan University of Technology/IR

Abstract

Multilayer coating, consist of Ni-P and Ni layers on AZ31 magnesium alloy substrate were prepared by combining electrodeposition with electroless coating from a sulfate salt, aimed to decrease the porosity and increase the corrosion resistance of the coating. As comparison, electroless coating on the magnesium alloy with different thickness were also presented in the paper. The properties and structure of the plating coatings were investigated by means of scanning electron microscopy (SEM), X-ray diffraction and electrochemical polarization measurements. The electroless and electroplate Ni coating both had nanocrystalline structure. The electrochemical measurement showed that preparing thin layer electroplate Ni coating between electroless layers could make difference in the corrosion potential among layers plays a very important role in protecting the substrate from corrosion.

Corrosion in the Refinery Industry

INFLUENCE OF TEMPERATURE ON THE CORROSION OF FERROUS ALLOYS DUE TO NAPHTENIC ACIDS IN CRUDE OIL

University lecturer Dr. Lucian Georgescu, Universitatea "Gheorghe Barițiu Braşov, Centrul de Studii Ploieşti, România, Dr. chim. Dr. Ana Daniela Niculae, IPIP Ploiesti, Romania, Dr. Ovidiu Georgescu, S. C. GEXACOR COM SRL Ploiesti, Romania, Marius Moroşanu, Oil & Gas University, Ploiesti, Romania

Naphthenic acids are organic acids, with one or several saturated cyclic rings, alkylated in different positions, with a linear carboxylated chain. Due to their high boiling temperatures, they are present in the warmer zones of metallic equipment in the plants for the atmospheric distillation of crude (ADU) and vacuum distillation of naphtha (VDU) and cause intense corrosion processes in the tubes of the ovens, transfer lines, metallic equipment within the distillation columns etc.

The paper presents data concerning the influence of temperatures on steels in the presence of naphthenic acids in crude oil. This influence is more intense in zones where the flow of the fluid is bigger, while the temperature is between 200 and 410^{0}C. Corrosion processes above 410^{0}C are diminished due to the decay of naphthenic acids and formation of coke on the metal surface.

Based on studies carried out W1.0845 (19Mn5) test bars exposed in two plants which processing naphthenic crude oil with total acidity index numbers of 1.7 ... 2.0 mg KOH/g, respectively 3.2 ... 4.0 mg KOH/ g it results that the corrosion process becomes obvious beginning with 150^{0}C and it increases approximately linearly with the temperature up to 350^{0}C. At 200^{0}C the corrosion speeds have already consistent values. The values of the corrosion speeds of S235JR (SR EN 10027 – 2) carbon steel, of X6CrAl13 (SR EN 10088 – 2:1998) ferritic stainless steel and X5CrNi18 – 10 (SR EN 10216 – 5:2005) and X6CrNiMOTi17 – 12 – 2 (SR EN 10216 – 2:2005) austenitic stainless steels at temperatures of 100, 200, 300 and 380^{0}C, in heavy fuel oil, light and heavy vacuum distillate, after 40 days of testing are also presented. From the data obtained following these laboratory tests, it is found that for all the steels under study, the corrosion speed increases with the increase of temperature, the ascending rate of the curves being more pronounced above 200^{0}C.

To establish the influence of temperatures on the mechanical properties of steels, test bars made of the specified steel types have been tested in laboratory, being dipped for 40 days in light distillate and heavy vacuum distillate. Thus, the tensile strength of carbon steel dipped in light distillate decreased by 2 % 200^{0}C, by 4.3 % at 300^{0}C and by 5.7 % at 350^{0}C, while the flow limit decreased by 1.5 % at 200^{0}C, by 2.5 % at 300^{0}C and by 3 % at 350^{0}C. In the case of the other tested steels a similar behavior was found but at a lower level by ca. 1.5 %.

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EXPERIMENTAL STUDY ON THE IMPACT OF CORROSION OF THE CRUDE OIL WITH DIFFERENT TOTAL ACID NUMBER AND THE APPLICATION OF INHIBITORS AGAINST NAPHTHENIC ACIDS CORROSION

Mariyana K. Angelova,
University Prof. Assen Zlatarov,
8010 Bourgas, Bulgaria
E-mail: angelova_m@dir.bg

Nedyalka B. Petkova,
University Prof. Assen Zlatarov,
8010 Bourgas, Bulgaria
E-mail: nelco@dir.bg

Yordanka S. Tasheva
University Prof. Assen Zlatarov,
8010 Bourgas, Bulgaria
E-mail: jtasheva_2006@abv.bg

Pavlina G. Ivanova,
Lukoil Neftocim Bourgas,
8014 Bourgas, Bulgaria
E-mail: Ivanova.Pavlina.G@neftochim.bg

ABSTRACT

The purpose of the article was monitoring of the corrosive effect of Russian export blend toward carbon steel. The study was conducted using the set of model mixtures with different total acid number in the temperature range of Naphthenic acid corrosion. The experiment was carried out in laboratory conditions by eliminating the effects of salts from the oil samples. The corrosion rate was ascertaining in the all three phase conditions: liquid, vapor and vapor-liquid diphase by gravity method. Nine additives with inhibitivi effect towards naphthenic acids were testing. The additives were synthesized by sulphonation of heavy gas oil with 30% sulfuric acid solution and subsequent neutralization with bases and salts of alkali and alkaline earth metal.

Keywords: naphthenic acids, high temperature corrosion, inhibitors protection, laboratory test.

ISSUES ON CORROSION EQUIPMENT In INSTALLATIONS BY DISTRIBUTION DAV NAPHTHENIC ACIDS FROM CRUDE OIL

Prof. dr. eng. Nicolae Napoleon Antonescu, Oil & Gas University Ploieşti, Drd. Marius Moroşanu, Oil & Gas University, Prof. dr. eng. Marius G. Petrescu, Oil & Gas University, Dr. chem. Ana Daniela Niculae, IPIP Ploiesti, Dr. University Lecturer Lucian Georgescu, University " George Barițiu " Braşov, Dr.eng. Ovidiu Georgescu SC Gexacor SRL Ploieşti

Naphthenic acids from crude oil distillation presented to a large range of temperatures. The largest amount of naphthenic acids resulting in the temperature range PRF 350 ... 410 ^{0} C. Acids, distributed with oil that have the same boiling points, allow establishing a correlation between total acidity index (IAT) and aggressive action in the area of technological environments [1, 2].

This paper shows the distribution of total acidity in crude oil processing facility DAV total acidity 1,6 ... 2,1 mg KOH/ g. The low molecular weight naphthenic acids are more aggressive than high molecular weight acids. Naphthenic acids with short chain, the light fractions have high acidity, while the acid content is low. In contrast, large chain naphthenic acids from heavy fractions have low acidity and high in acid content. The more aggressive in terms of corrosion are acids contained in oil and diesel, which have high acidity and corrosion product of naphtenate iron dissolves easily in liquid petroleum fractions. The investigations made that speeds the corrosion of carbon steel S235JR (SR EN 10027 – 2) increases with increasing total acidity. In case of cancellation of acidity to IAT = 0 speeds much lower corrosion fits between the limits 0,00041 to 0,00055 g / m^{2}h, the petrol and diesel at ambient temperature.

The presence of sulfur compounds (H2S, mercaptans, etc.) intensifies the corrosion processes especially at high temperatures. Following this attack forms a layer of ferrous sulfide which, depending on technological conditions, may be adherent, continuous, and free of pore reducing the rate of naphthenic acid corrosion.

To determine the test specimens were carbon steel S235JR (SR EN 10027 – 2) and stainless steel X6CrAl13 (DIN EN 10028 – 2:1998) and X5CrNi18 – 10 (DIN EN 10216 – 5:2005) with and without coating sulfide in solutions of naphthenic acids with IAT 148 mg KOH/g for 30 days at a temperature of 100^{0}C. The data presented may notice that there is a compact layer of iron sulfide corrosion decelerates due naphthenic acids. The presence of large amounts of naphthenic acids in crude oil, with a high speed of technological flow, can damage film FeS allowing the initiation of localized corrosion forms. Laboratory tests conducted with specimens of carbon steel on the corrosive action of the diesel they were introduced sulfur compounds have shown the influence of the quantity and nature of these compounds on corrosion.

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CORROSION PROBLEMS OF MODERN PETROLEUM REFINERY

Vladislav V. BURLOV [1], Alla I. ALTSYBEEVA [2], Tatyana M. KUZINOVA [3],
Vladimir L. SOKOLOV [4]
[1-3]All-Russian Scientific Research Institute of Petrochemical Processes, Saint-Petersburg, Russia
[4] PA «Kirishinefteorgsyntez» PLC, Kirishi, Russia

The problem of local corrosion damage of oil refining units has recently become considerably aggravated that is connected both with increase in aggressiveness of oil being processed, and with long serviceable life of units (for the majority of refineries of Russia – more than 30 years). In all oil refining towers made with plating layers of 08X13 steel, while in service, to corrosion cracking fissuring of the welded seams, seam-side zones and metal of plating are subjected that is connected with the high propensity of the 08X13 steel to pitting corrosion. Occurrence of pittings leads to decrease in corrosion stability and mechanical properties of the equipment and frequently – to sudden destruction and emergencies. Operational experience of refineries testifies to necessity of essential adjustments of design specifications: propensity of metal to local kinds of corrosion should be the defining factor in comparison with the size of general corrosion. The proved choice of constructional metals and methods of the equipment manufacturing is one of the key moments of modern system of oil refining units' protection against corrosion.

Propensity of ferrite, martensitic, austenitic-ferrite, austenitic and carbonaceous steels to pitting corrosion in operating duty of all types oil refining units' operation and in laboratory conditions by chemical and electrochemical methods - in water solutions of the electrolytes, modelling steaming condensates during preparation of the equipment to repairs is investigated.

It is found, that the greatest propensity to pitting corrosion the 08X13steel, being the basic material of oil refining towers' plating layer, is possessing that is the main reason of corrosion cracking fissuring of the welded seams, seam-side zones and metal of plating. It is shown, that steels being the most resistant to pitting corrosion in all modes of units' operation, are the steels alloyed with molybdenum that defines the expediency of replacement of the 08X13 steel with the 015X18M2B steel for towers' plating and use of the 10X17H13M3T and 08X21H6M2T steels for manufacturing of the equipment instead of the 12X18H10T type steels. Inhibitors of general and pitting corrosion of the 08X13 steel for the equipment steaming process and the methodology of their pilot tests carrying out are proposed. It is established, that the basic parameters of the 08X13 steel's pitting resistance while adding the most efficient inhibitors to solutions of electrolytes are close to those of steels, being alloyed with molybdenum and containing greater concentration of chrome, without inhibitors' additives in corrosive medium. It is shown, that the degree of inhibiting action of the 08X13 steel pitting corrosion depends on the inhibiting anion's nucleophilic reactivity force.

Cathodic Protection

pH variation during laboratory immersion corrosion tests

Sérgio E. A. Filho[1], Zehbour Panossian[1], Vanessa Y. Nagayassu[1], Neusvaldo L. de Almeida[1], Diogo Lima e Silva[1]; Eduardo W. Laurino[2], Gutemberg de S. Pimenta[2]

Abstract

Before starting laboratory corrosion tests, it is common procedure to characterize both, the test solutions and the metallic coupons. During and after the end of these tests, the focus is directed mainly to the metallic coupons, giving little attention to the eventual modifications of the test solutions, especially to the pH changes. Additionally, it is assumed that the pH of the test solutions increases continuously due to the alkalinization provoked by the cathodic reactions responsible for the metal corrosion.

In this work, some corrosion tests are described, in which the pH variations were monitored. The obtained results showed that not always does the increase of the pH occur, but the pH changes are depending on the test conditions, such as test solution composition, the degree of aeration and the degree of confinement.

Keywords: corrosion test, pH changes

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[1] IPT – Instituto de Pesquisas Tecnológicas do Estado de São Paulo S.A. Institute for Technological Research – Brazil

[2] CENPES – Centro de Pesquisas e Desenvolvimento Leopoldo Américo Miguez de Mello. PETROBRAS Research Center– Brazil

Automotive Corrosion

Corrosion Fatigue Properties of Joined Materials for the Automotive Industry

Nicolas Lautrou, Nathalie LeBozec and Dominique Thierry
French Corrosion Institute, Brest, France

The automotive industry utilizes a wide range of joining processes, materials, coatings and designs to meet criteria such as performance, durability, safety, styling and cost. As a consequence, new materials need tailored assembling techniques and further investigations on the corrosion performances and the mechanical properties of these joined materials.

A prototype that allows fatigue corrosion to be performed on joined panels in cyclic corrosion tests has been developed. This prototype allows fatigue load to be applied on the specimens at a maximum tensile load of 3.5 kN and at maximum frequency of 0.5 Hz. Several single lap joints were tested with various materials (carbon steel, EG steel, HDG steel, magnesium and aluminium alloys) and assembling techniques (adhesive bonding, clinching, clinching together with adhesive bonding).

As shown in Figure 1, preliminary results were obtained after 2 weeks of exposure in a Renault corrosion test (ECC1) with and without simultaneous fatigue load and, compared to unexposed samples. From the tensile test results of clinched and adhesive bonded carbon steel / HDG steel assemblies in terms of resistance to failure, no difference could be observed before and after the cyclic corrosion tests when no fatigue load was simultaneously applied. In the case of fatigue load simultaneously applied during 2 weeks of exposure to ECC1, a clear reduction of resistance to failure was observed. Although these results are still preliminary as for instance the fatigue load was not optimized, this illustrates quite well the importance of simultaneous fatigue and corrosion exposure on the mechanical properties of the joints.

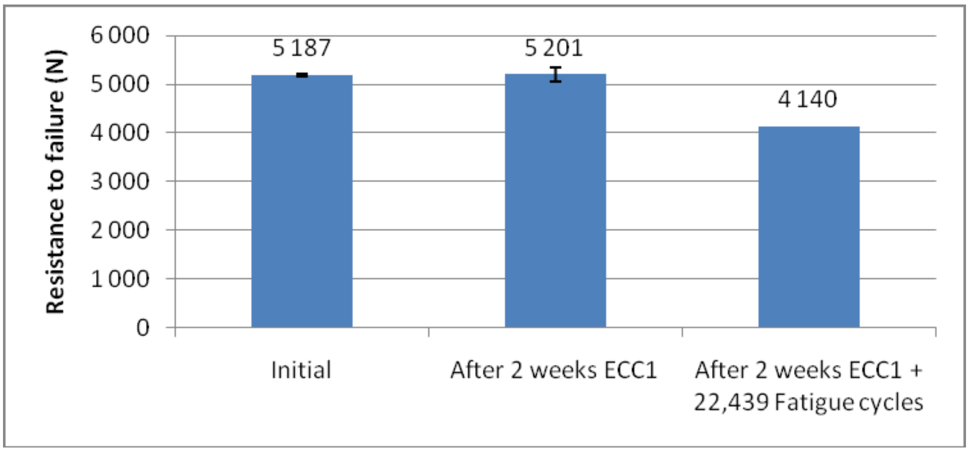


Figure 1: Example of the combined effects of fatigue and corrosion on the resistance to failure of carbon steel / HDG steel clinched and adhesive bonded samples.

CORROSION BEHAVIOR OF FERROUS AND NON-FERROUS METALS IN PALM BIODIESEL

M. A. Fazal[1], A. S. M. A. Haseeb[2], H. H. Masjuki[3]

[1]*University of Malaya, Malaysia, jewel_mme.buet@yahoo.com*
[2]*University of Malaya, Malaysia, haseeb@um.edu.my*
[3]*University of Malaya, Malaysia, masjuki@um.edu.my*

Recently, envrionmental awareness and concern over the rapid exhaustion of fossil fuel have led to an increased popularity of biodiesel as an alternative fuel for automobiles. However, corrosion of automotive materials in biodiesel is one of the concerns related to durability of engine life. This study aims to investigate the corrosion characteristics of copper, brass, aluminum and cast iron at room temperature. Static immersion tests in B0 (diesel), B100 (biodiesel) were carried out for six months. At the end of the test, corrosion characteristic was investigated by weight loss measurements and changes on the exposed metal surface. Fuels were analyzed by using TAN analyzer, GC-MS in order to investigate the acid concentration, changes in composition respectively. Surface morphology was examined by Optical microscope, Scanning electron microscope connected with Energy dispersive spectroscopy and XRD spectra. Results showed that the extent of corrosion was higher for copper, brass and cast iron while aluminium exhibited less corrosion.

EVALUATION OF THE CORROSION AND WEATHERING RESISTANCE OF AUTOMOTIVE COATINGS BY EIS TECHNIQUE

N. Tahmassebi
Islamic Azad University, Mahshahr branch, Color engineering group
Postal Code 63519, Bandar-e-Mahshahr, Khuzestan, Iran, n.tahmassebi@mahshahriau.ac.ir

The aim of the present study was to evaluate the corrosion and weathering resistance of automotive coatings by using of EIS (electrochemical impedance spectroscopy) technique. The EIS test was performed in a 3.5% solution of NaCl on weathered coatings. The EIS results were analyzed by fitting the data to an equivalent electrical circuit consisting of a CPE (constant phase element) in parallel with a coating resistance and both in series with the electrolyte resistance. The values of the CPE parameters, i.e. Y_0 (the CPE constant) and n (the CPE power) and coating resistance were subsequently correlated to the corrosion starting and the photo-oxidation of topcoat during weathering. Increases in the value of Y_0 together with decreases in the value of n were according to the onset of cracking in the topcoat. Additionally, sudden variations in are the values of Y_0, n and coating resistance were coincided with the topcoat peeling and the onset of corrosion.

Corrosion Behavior of Metals (Al, Fe, Zn) in Alternative Fuels using EIS method in Two Electrode Cell

Yon-Kyun Song[1], **Geunwoong Lim**[2] **and Heesan Kim**[2]
[1] POSCO Technical Research Laboratories
Gumho-dong, Gwangyang, Jeonnam 545-090, KOREA
[2] Hongik University
300, Sinanri, Yeonggigun, Chochiwoneup, Chungnam, 339-701, KOREA address
(Corresponding author e-mail; *petersong@posco.com*)

In order to overcome the limited deposits in fossil fuels, many kinds of alternative fuels such as biodiesel, ethanol, methanol, natural gas have been developed. As usage of these fuels as an automotive fuel, automotive makers are required to develop materials compatible to all fuels. Among these fuels, biodiesel and ethanol are selected because ethanol is reported to be relatively corrosive, and the auto-oxidation of biodiesel induces corrosive environments. The corrosion rates of metallic materials have been measured by immersion test or potentiodynamic test; however, low conductivity of these fuels makes immersion test employed despite of the time consuming test.

In this study, to overcome a shortcoming of electrochemical methods and to evaluate the corrosion rate of aluminum and its alloys, iron, and zinc, electrochemical impedance spectroscopy (EIS) was taken and a two-electrode cell was devised where the distance between tow electrodes is controllable at the rage 100 μm to 1 cm. Immersion test provides corrosion rate decreased in the order of zinc, iron, and aluminum. In addition, the corrosion rates of all the metals decreased with time imply that the corrosion rate is controlled by transport across electrolyte or corrosion products. The analysis of EIS with the cell devised for this study shows that the polarization resistance (Rp) increased in the order of zinc, iron, and aluminum, which is the same order as in the immersion test. On aluminum, showing the best corrosion resistance, the effect of magnesium as an alloying element was evaluated in ethanol containing acid and/or chloride and corrosion by EIS test. As the concentration of magnesium increased, the Rp of aluminum alloy increased in ethanol as well as biodiesel. However, the increase of Rp with the concentration of magnesium decreased. The optimum content of magnesium and the role of magnesium will be mentioned and discussed in details.

Tribocorrosion

Erosion of Compressor Impeller by Black Powder

M.Saremi and M.Kazemi
Faculty of Metallurgy& Materials Engineering, University of Tehran, Tehran, Iran.
saremi@ut.ac.ir

Wear of metals is a distractive phenomenon which causes failure of industrial rotating machineries and components. It comes as a result of the relative movement between the component and a moving metal, liquid or erosive particles or both in which the otherwise protective layer will be deteriorated. Many parameters and variables can affect the rate of wear including; particle shape, size and composition as well as the impact velocity of the moving parts, while the metal composition and physical properties are also effective on enhancing or reducing the effect. Therefore it is necessary to investigate the influence of such components on the stability of surface of specific machineries.

In the present work the failure of gas compressors in a gas transmission line is investigated. It was found that the impeller blades were eroded severely from the joint to the hub in such a way that a large gap of 1-2 centimetres were created on the joints and erosion lines were also observed on the nearby surface. The main cause of the failure was the impacting black powders found in the transmission line and especially in the filtration system.

In a series of simulated laboratory tests samples of the impeller metal 14CrMoV6-9 steel was erosion- wear tested in contact with black powder at different rotating speeds of 4000-6500 RPM. Some major components of black power such as hematite, water and organic hydrocarbon were systematically added to rank the major effective components in the wearing process. It was found that all of the above mentioned parameters are effective on enhancing the rate of wear of the blade alloy. But at a constant rotation speed, the most important parameter was water content that increased the rate of wear 5-6 times. The next effective component was the particle size of hematite in which macro hematite doubled the rate of wear Fig.1.

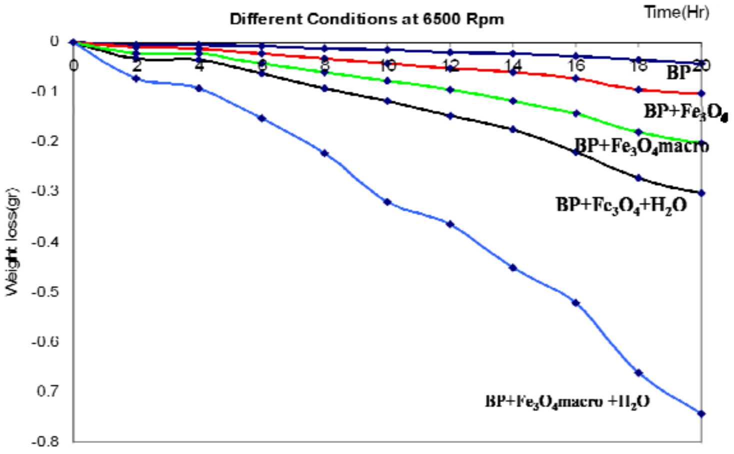


Figure 1. Weight changes at different conditions

That means erosion corrosion had a major role on enhancing the wear process. Of course rotation speed was also another major enhancing parameter. The hardness of the impeller metal was a decisive controlling factor to mitigate the wear. It was concluded that wear may be mitigated or even stopped by metallurgical improvements.

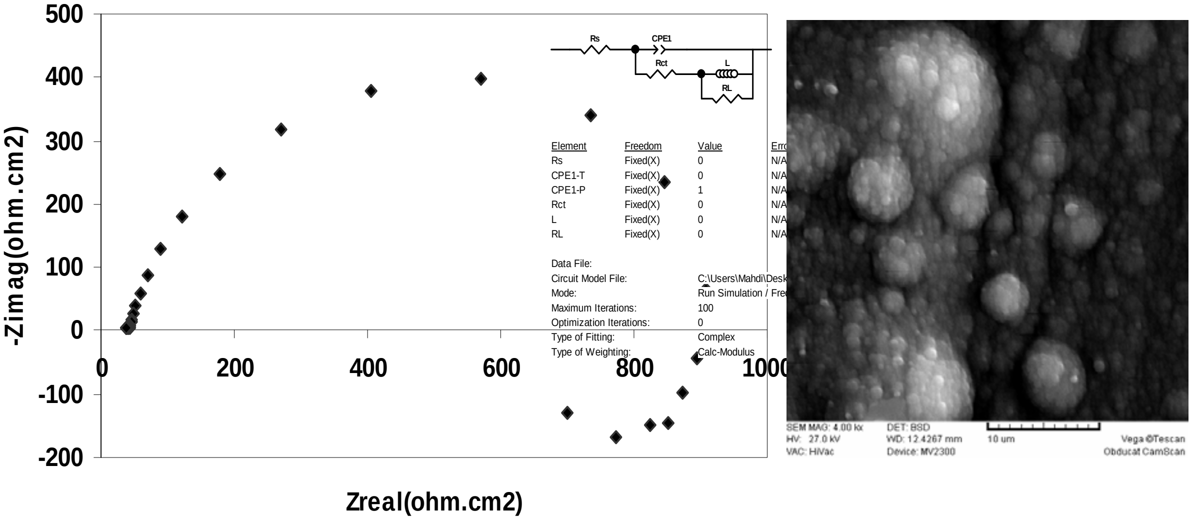
Corrosion of Polymer Materials

Application of Polypyrrole on Aluminum alloy 5052 and Investigating of its Corrosion Resistance

M. Saremi[1] and T. Tarani[2]
Department of Metallurgy& Materials, University of Tehran, Tehran, Iran

Aluminum alloys are used for their light weight, high conductivity and mechanical properties but they are sensitive to general and localized corrosion at some environments. While most of the organic coatings used for corrosion protection are non conductive, application of conductive polymer on Al can improve its corrosion resistance, retaining the conductivity and providing new applications. However application of polypyrrole on Al is not easy due to the formation of oxide layer during anodic polarization. The aim of this work is to deposit polypyrrole on Al alloy and to investigate its corrosion resistance.

Electrodeposition of polypyrrole on aluminum 5052 was successfully carried out by cyclic voltammetry from aqueous oxalic acid solution. Homogenous and adherent film was formed and its morphology was examined by SEM (figure1,right).The corrosion behavior was evaluated by using open circuit potential (OCP) variation test, polarization and electrochemical impedance spectroscopy (EIS) in 0.1 M NaCl solution. The presence of polypyrrole on aluminum surface resulted in the shift of OCP to more positive potentials and reduction in its corrosion rate. The nyquist plot of the films shows an inductive loop that is due to the occurrence of undoping process (figure1, left). It is concluded that the presence of polypyrrole can reduce the corrosion of Al5052 while retaining its conductivity.



Element	Freedom	Value	Erro
Rs	Fixed(X)	0	N/A
CPE1-T	Fixed(X)	0	N/A
CPE1-P	Fixed(X)	1	N/A
Rct	Fixed(X)	0	N/A
L	Fixed(X)	0	N/A
RL	Fixed(X)	0	N/A

Data File:
Circuit Model File: C:\Users\Mahdi\Desk
Mode: Run Simulation / Fre
Maximum Iterations: 100
Optimization Iterations: 0
Type of Fitting: Complex
Type of Weighting: Calc-Modulus

Figure 1-The SEM image of the synthesized polypyrrole (right) and the nyquist plot recorded in o.1 M NaCl including the corresponding equivalent circuit (left).

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[1]) saremi@ut.ac.ir
[2]) tinatarani@ut.ac.ir

EFFECT OF POLY(L-LACTIDE) BLOCK ON PHASE STRUCTURE AND DEGRADATION OF MULTIBLOCK COPOLYESTERS PREPARED FROM L-LACTIDE AND ε-CAPROLACTONE

Congshu HUANG[1], Zhangji YE[2], Jingjing WANG*[3], Zhipeng XIE[4]

[1] *Xiamen Branch of Luoyang Ship Material Institute, China, E-mail:hcs05@126.com*
[2] *Affiliation Xiamen Branch of Luoyang Ship Material Institute, State Key Laboratory for Marine Corrosion and Protection, China, E-mail: yezhangji725@163.com*
*[3] *Affiliation Xiamen Branch of Luoyang Ship Material Institute, State Key Laboratory for Marine Corrosion and Protection, China, E-mail: jingjing811014@163.com*
[4] *Affiliation Xiamen Branch of Luoyang Ship Material Institute, China, E-mail: zhipengxie1982@gmail.com*

Hydroxyl terminated multiblock copolyesters of L-lactide and ε-caprolactone (P(LA-co-CL)-OH) were synthesized by melt copolymerization of ε-caprolactone (ε-CL) and L-lactide (L-LA) with stannous octanoate (Sn(Oct)2) as the catalyst. Then diisocyanate terminated copolyesters (P(LA-co-CL)-NCO) were obtained via the reaction of P(LA-co-CL)-OH and hexamethylene diisocyanate (HDI), and then reacted with polyol resin to prepare biodegradable polyurethane. The copolyesters were characterized by FT-IR, 1H-NMR, GPC, DSC and XRD methods which confirmed the successful synthesis of multiblock copolyesters. PLA block created worse conditions for crystallization of copolyesters and effected on the degradation of coployesters were discussed. The hydrolysis in seawater of polyurethane containing copolyesters could be expected the potential use of P(LA-co-CL) in antifouling paints.

Corrosion and Corrosion Protection of Drinking Water Systems

Effect of a magnetic device on carbon steel corrosion – Preliminary field data

E. A. de Souza and J. A. C. P. Gomes
Federal University of Rio de Janeiro
Rio de Janeiro, Brazil

D. S. de Freitas
National Institute of Technology
Rio de Janeiro, Brazil

Abstract

As the process of corrosion deposits in industrial cooling systems is a real and growing problem due to use of non-potable water, the application of magnetic treatment on these systems in order to remove these impurities responsible for the process of scaling and deposit is the focus of this work The motivation is the recent study in laboratory in which the results obtained from the analysis of water and metallic coupons suggested a positive action of the magnetic treatment in relation corrosion protection. However, the preliminary results showed that magnetic effect in carbon steel probes cannot be directly attributed to an electrochemical mechanism. In the field analysis carried out in industrial cooling system, the electrochemical techniques like potential the open circuit (OCP) and linear polarization resistance (LPR) as well as weight loss and ultrasonic measurement have been applied with the objective to verify the corrosiveness of the water in the metallic surface. The physical-chemical parameters of the water also have been analyzed in order to evaluate the effect of the magnetic treatment in the ionic species of the water. The results obtained have shown high corrosion rates indicating a deterioration of metal surfaces, even if operating efficiently. A relevant aspect is the absence of deposits on the metal surface, possibly by the action of magnetic field in the metallic structure. Thus, the effect of the magnetic field in the cooling water remains unclear concerning electrochemical aspect.

Corrosion Related Problems with UNS S 31803 Duplex Steel Riser Pipe in Water Wells for the Great Man-Made River Project – Libya

Salah M. Elkoum

Great Man-Made River Authority
P.O. Box 9468
Benghazi-Libya
Telephone: 00218 61 22 39590
E-mail: Selkoum@yahoo.com

Hussain S.Boshalla

Great Man-Made River Authority
P.O. Box 641
Benghazi-Libya
Telephone: 00218 913709529
E-mail: hboshalla@yahoo.com

Abstract

The Great Man-Made River Project (GMRP) in Libya is the World's largest water supply project. The project is part of the infrastructure development of Libya. Aquifers are being developed in the mid-south of the country and the product water is taken by pipeline to the populated coastal regions for irrigation, domestic and industrial use. A contractual requirement of the project is for minimum maintenance and a 50 year design life.

Well pump Riser pipes have been supplied and installed in the wellfields. The major components of the well pump riser pipe assembly are: riser pipe, pipe couplings, gaskets and seals, fasteners, centralizers (casing guides), cable and sterilization pipe clamps or straps and riser pipe head piece.

The riser pipes used were 8in NB schedule 20 longitudinally single beam welded duplex stainless conforming to ASTM A790 UNS S 31803 with a PREN number greater than 34. Each piece of tubing has an overall length of 6metres. A corrosion problem of these riser pipes have occurred after a short period of operation. This paper will discuss these problems and explain the remedial action taken to put these pipes in service.

Effect of Hydrodynamic Conditions on Copper Release in Drinking Water Systems

Gustavo Jeria, Ignacio T. Vargas, Magdalena M. Walczak, Pablo A. Pastén,
Gonzalo E. Pizarro.
Pontificia Universidad Católica de Chile, Santiago/Chile

Copper is widely used in drinking water distribution systems due to its relatively low cost and favorable mechanical properties. However, copper corrosion may generate copper concentrations exceeding the thresholds prescribed by international drinking water standards. *In-situ* measurements performed in a real system found that the copper mass released under flowing water conditions (pipe flushing) was greater than the copper mass release estimated considering only the mass of copper in the pipe's bulk water before the tap is opened. This work presents *in-situ* and laboratory results of copper release into the water and its dependence on structure, solid-liquid interface properties, and the pipe flow regime (turbulent vs. transition flow).

Our results show that the solid-liquid interface plays an active role liberating copper corrosion by-product particles into the bulk liquid. Under flow conditions, interfaces with compact and smooth corrosion by-products induce lower mass of copper released compared to irregular and feature-rich pipe surfaces. Hydrodynamic effect on copper release was observed for both, laboratory and field systems. The mass of copper liberated during flushing experiments was about three (laboratory) to nine (field) times the mass of copper in the bulk water before the tap was opened. This difference is probably due to ageing, that plays an important role on feature-rich surfaces development.

The results of this work highlight the necessity to incorporate the hydrodynamic effects to the analysis of corrosion and corrosion by-products release into drinking water piping systems.

Corrosion of Acheaological and Heritage Artefacts

Protection of metallic industrial cultural heritage against atmospheric corrosion

Katerina Kreislova, Dagmar Knotkova, Tomas Kubatik, Hana Geiplova
SVUOM Ltd., Prague/Czech Republic

Abstract

With the progress of technical development many industrial objects become to be a part of cultural heritage. That is an increasing aim to preserve them. Long term atmospheric corrosion effects and deterioration of protective coatings on large historic steel structures and other metallic objects represent a specific task for the conservation and restoration specialists. It is lack of knowledge how to apply the modern technologies of corrosion protection with the respect requirements of the monumet care and take advantage of conservation approaches.

SVUOM specialists inspected some typical objects (structures and machines) in mines and technical scansens, evaluated long term deterioration effects and defects on protective coatings applied on old, not correctly prepared surfaces. In cooperation with the monument care specialists the differentiated approaches for the conservation had been proposed. Evaluation of the corrosivity of the exposure locations is necessary as the first step in the choice of optimal corrosion protection. Interdisciplinary problems and gaps in knowledge in corrosion protection of metallic technical cultural heritage have been formulated.

Workshop on Corrosion in Natural Environments

Influence of hydrogen absorbed by metal to active mild steel dissolution in near-neutral pH soil electrolyte

***Tatiana NENASHEVA*, Andrey MARSHAKOV**
A.N.Frumkin Institute of Physical Chemistry and Electrochemistry,
Russian Academy of Sciences, Moscow, Russia

Currently most of failures at main pipelines arise due to local corrosion processes. The major one of them is stress corrosion cracking in metal under delaminated isolation coating. By that reason the investigations of mild and low-alloyed steel corrosion behavior in undercoating electrolyte imitating media (i.e. solution in corrugated coating of underground pipeline) are being conducted in many countries.

The paper is devoted to researching of the influence of atomic hydrogen to active mild steel dissolution kinetics in near - neutral pH electrolytes.

The tests were carried out on steel specimen in deaerated NS-4 solution (undercoating electrolyte), borate buffer, and their mixtures (pH 5,0 ÷ 8,3) at room temperatures.

One of the most probable reasons of local corrosion nucleus development is electrical potential difference between two areas on metal surface. For instance it can be the difference between the tip of crack (or pitting bottom) and the rest of surface. In this connection the influence of hydrogen absorption into steel to open-circuit potential has been examined. It was shown that hydrogen absorption leads to slightly negative shift of open-circuit potential of steel in the solutions with pH more than 5. It can be related to both metal dissolution acceleration and cathodic reaction decrease.

The influence of absorbed hydrogen on iron dissolution rate has been tested by bipolar electrode method. It was shown that maximum accelerating effect of atomic hydrogen is increasing while solution pH and corrosion activators concentration (chloride and sulphate ions) are increasing. In media with pH 5,0 the anodic current is slowly decreasing in time. In electrolyte with pH 8,3 the current is sharply decreasing to the value of dissolution rate of non hydrogenated metal.

Properties and protective ability of patina layer on long-term exposed weathering steel constructions in the Czech Republic

Katerina Kreislova, Dagmar Knotkova, Tomas Kubatik, Alena Koukalova
SVUOM Ltd., Prague/Czech Republic;
Jiri Had, Petr Sajdl, ICT Prague/Czech Republic

Abstract

In the frame of research project the properties of corrosion layer – patina had been analysed on 14 constructions made from weathering steel (bridges, poles, etc.) exposed for 25 – 33 years at the Czech republic. The exposure conditions had been mostly industrial or urban. The surface of steel bridge construction had been affected by chloride only as a results of leakage of de-icing salts from highways.

The patina was evaluated by appearance, thickness measurement and by chemical and structural analysis. From these data the protective ability index (PAI) [1] was calculated for patina layers developed in various conditions of wetness and contamination of construction surface.

The non suitable corrosion effects shall occured in some cases:

- the limit of industrial pollution in given locality is higher than limit for protective patina forming,
- the local effect of specific pollution, mainly chloride from de-icing salts,
- the desing of structure affected the long-term wetness of surface,
- the non properly done maintenance of weathering steel structures and/or maintenance of secundary constructions.

Literature

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Semiconducting behavior of passive film formed on stainless steel in borate buffer solution containing sulfide

Hong-Hua Ge, Jing Shen, Guo-Ding Zhou, Fei Song, Li Zhao
Shanghai University of Electric Power, Shanghai Key Laboratory of Colleges and Universities for Corrosion Control in Electric Power System and Applied Electrochemistry, Shanghai Engineering Research Center of Energy-Saving in Heat Exchange Systems, Shanghai 200090, China

The semiconducting behavior of passive film formed on 316L stainless steel in borate buffer solution containing sulfide was studied by capacitance measurements (Mott-Schottky approach), electrochemical impedance spectroscopy and potentiodynamic polarization. The results reveal that the measured capacitance values of the stainless steel electrode have frequency dependence and hysteresis, showing the amorphous or highly doped semiconductor property of the passive film. The Mott-Schottky plots indicate p-type semiconducting behavior related to chromium oxide of the passive film at -1.12 ~ -0.78V and n-type semiconducting behavior to iron oxide at -0.47 ~ +0.35V, with an acceptor density 11.2×10^{20} cm^{-3} and a donor density 7.50×10^{20} cm^{-3} respectively. The existence of sulfide in the solution obviously increases the acceptor densities which reaches to 215.6×10^{20} cm^{-3} with the sulfide concentration of 12 $mg\cdot L^{-1}$, and therefore have a more conductive behavior. The presence of sulfide also decreases the impedance values and enlarges the passive current of the electrode. (figure 1)

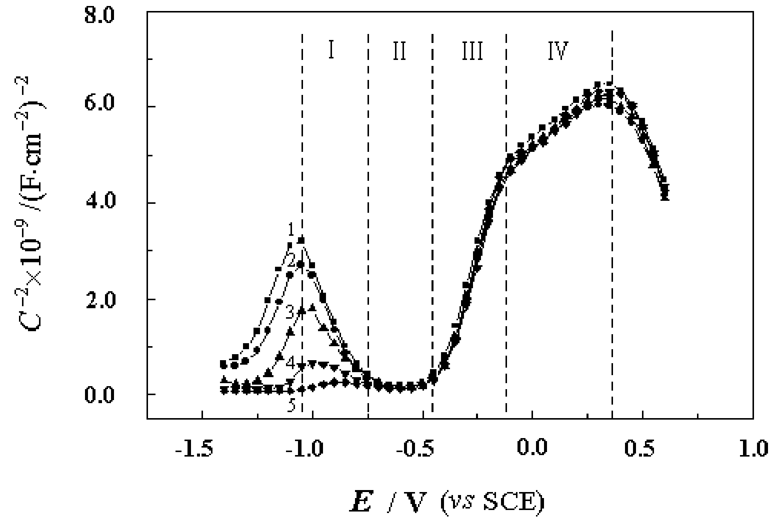

Fig.1 The Mott-Schottky plots for stainless steel electrode in borate buffer solution containing sulfide at various concentrations for 1 hour

Sulfide concentration: 1) 0 $mg\cdot L^{-1}$; 2) 3 $mg\cdot L^{-1}$; 3) 6 $mg\cdot L^{-1}$; 4) 9 $mg\cdot L^{-1}$; 5) 12 $mg\cdot L^{-1}$

Acknowledgements: Supports of this study by Science and Technology Commission of Shanghai (Project Numbers: 08DZ2210800, 08DZ2201400, 09DZ0500400, 10DZ0500300, 10DZ2210400) are gratefully acknowledged.

Characteristics Studies of Electropolished 316L Stainless Steel in Simulated Body Fluid for Biomedical Utilization

Nazly Hassan[1] **and Nabil Abdel Ghany**[2]

[1]*Composites and Nano Structured Dept., New materials and advanced Technology Institute, Mubarak City for Scientific Research and Technology Applications, New Borg Elarab, Alexandria*, Egypt, na_hassan12@yahoo.com
[2]*Electrochemistry and Corrosion Dept., National Research Center, Cairo*, Egypt, na_manakhly@yahoo.co.uk

The field of biomaterials has become a vital area, as these materials can enhance the quality and longevity of human life. Biomaterials are materials of natural or man-made origin that are used to direct, supplement or replace the functions of living tissues of the human body. It is well known that a good biomaterial should possess the fundamental properties such as better mechanical and biological compatibility and enhanced wear and corrosion resistance in biological environment. By means of electropolishing the influence of various parameters on the substrate features is highlighted. In this paper, we illustrated the effect of potential, bath temperature and composition and polishing time on the substrate morphology in order to enhance the properties of 316L stainless steel (316L SS) to be used in biomedical applications. Since the corrosion resistance of a metal depends strongly on the structure of the metal and the state of the surface, the proper electrochemical treatment of the metal surface may significantly improve its corrosion resistance. The corrosion behaviour of the electropolished samples were then investigated in simulated body fluid using electrochemical measurements, namely polarization and electrochemical impedance spectroscopy techniques. Different corrosion parameters were obtained and the results revealed that the electropolished 316L SS samples exhibit a higher corrosion resistance than that the unpolished ones. Furthermore, Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray analysis (EDAX) were carried out to characterize the surface morphology and also to understand the structure of the unmodified and modified SS substrates.

Key words:

Electropolishing, Simulated body fluid, 316L Stainless Steel, electrochemical measurements, corrosion resistance.

Workshop: Corrosion and Corrosion Protection in the Aerospace Industry

Phase composition and corrosion of magnesium alloys

Galina MOROZOVA
All-Russian Institute of Aviation Materials «VIAM», Moscow, Russia,

Magnesium alloys are one of the lightest construction materials with high specific strength (14 - 18.5 km) and very attractive technological and exploitation characteristics. Mg-alloys are more often used in the European Union countries for aviation construction. The main limitation for their industrial application is insufficient corrosion resistance in the ocean and sea conditions.

The method of physico-chemical phase analysis was used in this work. This method is based on electrochemical phases isolation followed X-ray and chemical analysis.

We have investigated the influence of different intermetallic compounds on the corrosion properties of industrial Mg-Al-Zn-Mn and Mg-Zn-Zr alloys in various technological conditions. Alloy composition phase quantity, their crystal structure are discussed in present work. We are investigated the role of Fe-form as harmful admixture which accelerates corrosion process with hydrogen depolarization and means of admixture neutralization are discussed.

It was determined the role of soluble hydrogen in the process of phase formation and corrosion. Ability to hydrogenation of Magnesium and its alloys in systems Mg-Al-Zn-Mn (ML5), Mg-Zn-Zr (ML12) was investigated in humid environment.

It was shown that hydrogen does not effect on phase composition of ML5 alloy. Heat-treatment defects and interfaces promote hydrogenation of the alloy. Hydrogen concentrates in alloy's surface layer and decreases corrosion rate in 3% NaCl solution.

Hydrides of zirconium were found in the Zr-doped alloys, that decreased plastic properties and corrosion resistance of above mentioned alloys.

Hydrogen concentrates in aggregates of Laves phase $ZrZn_2$ and thereby amplifies doped elements segregation in bulky foundry of ML12 alloy. Line inclusions of the Laves phase stimulate local corrosion and cracks spreading.

The method of physico-chemical phase analysis was used in this work. This method is based on electrochemical phases isolation followed X-ray and its chemical analysis.

Investigation of the alloying effect on corrosion resistance of Zn-7Al-3.7Cu solders

V.P. Zhylikov, A.D. Zhyrnov
All-Russian Institute of Aviation Materials (VIAM), Moscow, Russia

Soldering of thin-walled Al alloys components with Zn-based solders ensures minimal buckling because their melting temperature is lower than that of Al-based solders. Such Zn-based solders are widely used for soldering of Al wires of airborne equipment in aviation and in other industry branches. Zn-7Al-3.7Cu solders similar to the eutectic composition are most commonly used due to their lowered soldering temperature and satisfactory corrosion resistance. However, application of solders of the said composition results in dissolution of soldered alloy in the solder. It causes a decrease of service properties of the soldered joint.

It is recommended to add small quantities of Mg, Cd, Ce, Y, Bi and other metals (0.1-2.0%) in order to avoid this phenomenon.

At the same time, such additives may have an effect on corrosion resistance of solders. This work was focused on investigation of the effect of different alloying components on corrosion resistance of Zn-7Al-3.7Cu composition. The studies were carried out in salt chamber and in 3%NaCl solution with the subsequent analysis of corrosion products by alternating-current polarography to estimate the role of alloying elements in the course of corrosion process inside and out of the soldered joints with aluminium.

A negative effect of 1-2% Bi was found. Small quantities of Ni, Cr, Ti, Ce, Y (0.1-0.3%) and Ge (0.5-2.0%) additives have no practical effect on corrosion resistance of Zn-based solders.

A positive effect is provided due to a combined alloying with several additives: Cd+Mg+Cr+Ni or Cd+Bi+Mg+Cr. The above negative effect of Bi was not observed after such multi-component alloying.

Analysis of NaCl solutions (carried out after 7 days exposure of solders and soldered joints in these solutions) demonstrated that the content of Al, Bi, Cu, Co, Cr and Ni was out of the polarographical method sensitivity (10^{-7} mg/l).

Dissolution rate of the solder base (Zn) was similar inside the soldered joint and out of it. A predominantly selective dissolution of Mg and Cd was observed. However, corrosion losses of Mg and Cd are insignificant in the total balance because their content in solders is not higher than 1-2%. At the same time, they increase cathodic process overvoltage providing a reduction in corrosion rate of zinc.

Influence of laser treatments on the corrosion behaviour of titanium alloys.

J.M. Sánchez-Amaya[1], Z. Boukha[2], M. R. Amaya-Vazquez[2], L. González-Rovira[2],
F.J. Botana[2].

[1]Titania, Ensayos y Proyectos Industriales S.L. Puerto de Santa María, Cádiz.
[2]LABCYP. Departamento de Ciencia de los Materiales e Ingeniería Metalúrgica y Química Inorgánica. CASEM. Universidad de Cádiz.
Avda. República Saharaui s/n, Apdo. 40, Puerto Real, 11510. Cádiz. SPAIN.

Abstract.

Due to their high strength, low density and excellent resistance to corrosion and oxidation, titanium and titanium alloys are widely employed in different fields, such us medical, aerospace, automotive, petrochemical, nuclear and power generation industries. The heat treatments are known to modify the properties of these alloys. In the present contribution, the influence of different laser treatments on the properties of two titanium alloys (TiG2 and Ti6Al4V) is studied. The influence of experimental variables, as the laser power and the processing rate, on the microstructure and the corrosion behaviour of the samples was investigated. The laser treatments were performed with a High Power Diode Laser. Several parallel laser scans were made over the samples, with the objective of having enough affected area to perform the corrosion tests. Not treated samples were also studied for comparative purposes. The corrosion behaviour of the samples was analysed by means of linear polarisation tests, which allowed the estimation of the polarisation resistance parameter (R_p).

Keywords:
Corrosion, Titanium alloys, Laser treatment, High Power Diode Laser, Linear Polarisation tests.

Investigation of corrosion resistance of D16T alloy non-clad sheets at various distance from a sea (the Black Sea, Chakva settlement)

Semyonychev V.V., Zhirnov A.D.
All-Russian Institute of Aviation Materials, Moscow, Russia

Change of chlorides concentration depending on a distance from the sea and an influence of chlorine ions concentration on a level of corrosion damages of D16T alloy non-clad sheets was investigated.

Concentration of chlorides was defined by a method of “dry canvas”at the distances of 50,100, 200, 500, 2000m from the sea. Specimens of D16T alloy non-clad sheets of 5mm thickness were also exposed on the same bench. The time of corrosion tests was 30 months.

Relative humidity was recorded using hygrographs, mounted on benches at the distances of 50 and 2000m from the sea. In connection with the fact that a difference of readings of the hygrographs at various distances from the sea didn’t exceed instrument errors, but a concentration of sulfurous gas constituted not more, than $4 \cdot 10^{-3}$ mg/m^3, it was taken, that the level of corrosion damages of the specimens is determined by the concentration of chlorine ions and naturally by atmosphere humidity that was the same for the chosen distances from water’s edge and an average temperature was 16ºC. Initial mechanical characteristics of the specimens corresponded to the following values: σ_B = 490 MPa, $\sigma_{0,2}$ = 350 MPa.

By the results of investigation it was established, that the rate of deposition of chlorides is decreasing monotonously when growing the distance from the sea and is equal to 7.7 mg/m^2 per day (50m), 4.1 mg/m^2 per day (100m), 3.5 mg/m^2 per day (200m), 1.6 mg/m^2 per day (500m) and 0,7 mg/m^2 per day (2000m).

Thus, the concentration of chlorides in atmosphere changes by 10 times when growing the distance from the sea.

By corrosion tests of D16T alloy under the same conditions it was established, that the time till appearance of pittings, the rate of corrosion and its depth differs also by order. But mechanical characteristics of the alloy –ultimate strength and yield strength, determined after corrosion tests at the distances of 50m and 2000m differ by 15-20%.

Workshop on Nanotechnologies

Electrodeposition of Nano structured Zn-Ni-Al_2O_3 composite coatings from acidic and alkaline baths

M.A.Shoeib[1],A. A. Abdul Azim[1]and, H.Soliman[1*].

[1] Surface Treatment and Corrosion Control Department, Central Metallurgical Research and Development Institute, CMRDI, P.O. Box: 87, Helwan, Cairo, Egypt.

mshoeib@yahoo.com

Abstract

Many chemical and physical methods have been developed to prepare particle-metal-composites, but the most of them are expensive. Electrolytic codeposition of particles with metal matrix is a more low cost technique to prepare composite, furthermore electrodeposition methods is one of the most important techniques for producing nanocomposites and nanocrystal coatings.

Zn-Ni/nano Al_2O_3 composite coatings were prepared from acidic and alkaline electrolytes by electrodeposition technique. The microstructure of coatings was characterized by means of XRD, SEM and EDS, also the corrosion resistance was investigated. With addition of alumina to the acidic bath presented excellent corrosion resistance which mainly related to the uniform distribution of the nano alumina powder in the coatings. For alkaline bath, the high corrosion resistance of the deposited composite depended on high γ-phase intensity and surface compactness.

Keywords: Zn- Ni-nano Al_2O_3 composite; uniform distribution; γ-phase; compactness, corrosion resistance

Electrochemical corrosion performance of the electrodeposited nanocrystalline Ni-P-Cr films with and without dispersions of Al_2O_3 nanoparticles from trivalent chromium

[*]M.A.Shoeib, [**]O.El.Abdel - Salam and[**] A.M. Yousef
[*]Surface Treatment and Corrosion Control Department, Central Metallurgical Research and Development Institute, CMRDI, P.O. Box: 87, Helwan, Cairo, Egypt; [**]Faculty of engineering,Cairo University, Cairo, Egypt, mshoei8b@yahoo.com

Coating with nickel and nickel alloys offer deposits with better attractive properties which find wide applications. Nickel when alloyed with phosphorus ,to produce an amorphous structure, show excellent resistance to aqueous corrosion , also when introducing Cr which act as film forming element can significantly improve their corrosion resistance. The co-deposition of nanoscaled particles during an electroplating process has been shown to bring such an improvement in the properties of the coated layer obtained. This technique involve the deposition of a uniform film of alumina particles incorporated with Ni-P-Cr matrix of the coated brass substrate. The influences of bath composition on the trivalent chromium electrodeposition process and deposited coating properties were studied. The effects of plating parameters such as current density, bath pH and plating time on structure and morphology of deposited coatings were investigated in detail. XRD, SEM, EDAX and XPS techniques were used to characterize the NI-P-Cr deposited coatings. Results show that the composition, microstructure and surface morphology of the Ni-Cr-P coatings depend on bath composition and plating conditions including bath pH, current density, plating time, etc. Also the effect of adding Al_2O_3 nano –powder with different concentrations on the mechanical properties and on the corrosion resistance is studied. From the results we can conclude that the compromised conditions to obtain a recognizable % of Cr with reasonable % of Ni and P are:

pH = 3
Temperature = 25^0C
Current density = 30 A dm^{-2}

Also the optimum concentration of the Al_2O_3 nano –powder is 50g/lit which offer better mechanical properties compared to that obtained from the measurements of the properties of the coated Ni –P –Cr layer with the same chemical composition. Potentiodynamic polarization tests showed that increasing in the co-deposition content resulted in an enlarged passive region of the nc-Ni in 3.5% NaCl through reducing the corrosion potential and increasing the breakdown potential. The effect of heat treatment on the deposited layer is also observed on the improvement on the mechanical properties and the corrosion resistance on the coated layer with and without Al_2O_3 nano –powder.

Keywords: Electrodeposition; Electrochemical corrosion; Nanocrystalline ,Ni-P-Cr film; Al2O3 nanoparticles; X-ray photoelectron spectroscopy

Nano-Hydroxyapatite – Electroplated Titanium Alloy implant.

M.A.Shoeib[1], B. Wielage[2], S.Steinhäuser[2] and Th. Lampke[2],
[1]Surface Treatment & Corrosion Control Dept., Central Metallurgical Research & Development Institute (CMRDI), Helwan, Cairo, Egypt.

[2]Chemnitz University of Technology, Institute of Composite Materials and Surface Technology, 09107 Chemnitz, Germany

mshoeib@yahoo.com

Abstract.

Nanomaterials have wide-ranging implications in a variety of areas, including chemistry, physics, electronics, optics, materials science and biomedical sciences. HAp has attracted much attention primarily due to its participation in the biological calcification process of teeth and bone formationDue to its crystallographic similarity to various calcified tissues of vertebrates, HAp has been extensively used as a substitute material for damaged teeth or bone over the past three decades, and its compatibility with surrounding tissues has been experimentally proven. Hydroxyapatite (HAp) is commonly used to coat titanium alloys (Ti–6Al–4V) for orthopedic implants. However, their poor adhesion strength and insufficient long-term stability limit their application. Novel sol-gel ceramics possess excellent chemical stability and cytocompatibility. The aim of this study is to use the novel sol-gel and dip coatings technology as coatings for Ti–6Al–4V. The sol–gel method was used

to produce the coatings and phase composition, microstructure, thickness, surface roughness and adhesion. A hydrothermal post-treatment method has been developed to eliminate the crack defects in the coatings, and to improve the structure and property for the coatings. This study was designed to electrodeposite hydroxyapatite thin layer on the treated surface by sol gel technique. The coatings were analyzed by X-ray diffraction (XRD), scanning electron microscopy (SEM), atomic force microscopy (AFM) and scratch test, respectively. As proved by XRD , provided porous TiO_2 and SiO_2 matrices that are suitable for nucleation sites of hydroxyapatite crystals and prevented abrupt phase changes at the hydroxyapatite-coatings substrate interface. The results indicate that HAP coated onto treated Ti–6Al–4V by sol-gel possessed improved adhesion strength and chemical stability, compared to HAP-coated Ti–6Al–4V prepared without sol-gel treatment, suggesting their potential application as coatings for orthopedic implants.

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Keywords: Hydroxyapatite, Titanium alloy; sol-gel, morphology, AFM

Corrosion of bare and surface modified metallic nanoparticles in simulated body fluids

[1]*Maros Halama,* [2]*Dasa Halamova,* [2]*Vladimir Zelenak,* [1]*Barnabas Palincar*

[1]*Technical University of Kosice, Faculty of Metallurgy, Letna 9, 042 00 Kosice*
[2]*P.J.Safarik University, Faculty of Natural Science, Moyzesova 16, 040 01 Kosice*

Abstract:

The corrosion properties of superparamagnetic Fe nanoparticles (SPIONs) made by our own patent [1], commercially available ZnO NPs and surface treated NPs by 2% carboxymethylcellulose (CMC) as carrier liquid and of Fe NPs doped mesoporous materials were studied by using ultra-fast linear voltammetry which allow doing estimation of degradation properties under conditions of simulated bioenvironments, esp. physiological solution and simulated body fluids (SBFs) via measurements of polarization curves of NPs attached on the surface of carbon paste electrode (CPE).

The aim of study is to assess life-time of pure and surface treated nanoparticles and thus indirectly assess contribution of the part of drug delivery system or interaction with application environment on the degradation properties of NPs. This could be useful information before application of nanoparticles as potentially drug delivery carriers, as additives in cosmetic industry etc. Up-mentioned technique seems to be universal for comparison of corrosion characteristics such as corrosion potential - E_k, corrosion current density - J_k and polarization resistance - R_p for majority of bioenvironments. Developing new technique in this strong interdisciplinary topic (nanotechnology, chemistry & corrosion and medicine) could lead to achieve more precise information related to degradation of NPs, their life-time and interaction with chosen environment. This is important step to guarantee more safety in nanotechnology and thus prevent public health.

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Characterization of electrophoretically deposited nanocrystalline hydroxyapatite on Titanium for biomedical applications

A. M. Elbasiony(1), **N.A. Abdel Ghany** (1, *)

Hydroxyapatite coatings were directly prepared on cleaned surface of titanium by electrophoretic-deposition method in a sol-gel bath of freshly prepared hydroxyapatite. The morphology , structure , phase ,function groups of the electrophoretically deposited coating layer were investigated with scanning electron microscopy (SEM), X-ray diffraction analyzer (XRD) and Fourier transform infrared spectroscopy (FTIR) techniques. The results demonstrated that pure and homogeneous hydroxyapatite coating can be obtained with Calcium / Phosphorus molar ratio 1.67 which is similar to the human bone Ca/ P molar ratio. The resistivity against corrosion was also investigated for the coated titanium using electrochemical impedance technique which shows that the coated titanium has less corrosion resistance than the uncoated sample.

Keywords: **Hydroxyapatite, biomaterials, electrophoretic deposition, Titanium**

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* Corresponding author: E-mail: na_manakhly@yahoo.co.uk (Nabil Abdel Ghany)

PERMSNABSBYT

ZAO PPMTS Permsnabsbyt
614030, Russia,Perm,
ul. Karbysheva, 32
Phone +7 342 290-77-07,
+7 342 294-08-27
Fax +7 342 285-00-82
+7 342 285-03-87
http://www.pss.ru/
e-mail: pss@permonline.ru

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Yours sincerely,
A.G.Redekop,
Director General