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Abstracts / Extended Papers of Posters

Study of alkylphenol-formaldehyde oligomers modified with amines containing imidazoline fragments as corrosion inhibitors in the composition of preservation fluids

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Metal corrosion control is an important area of technical, economic and environmental activity. To protect metal structures from corrosion, there are many options, among which a special place is occupied by corrosion inhibitors. At the same time, the main attention is paid to the influence of the functional groups in their composition, the availability of a cheap raw material base, stability and manufacturability in use. In order to protect against corrosion of equipment subject to long-term transportation and storage, preservation fluids and lubricants are used, which in turn are obtained on a petroleum basis, and, as a rule, with the use of oil-soluble corrosion inhibitors. Among the wide variety of such compositions, in particular oligomers, the role of those created on the basis of phenol and its derivatives is very important, which is associated with the existence of a real raw material base - oil, gas, inexhaustible reserves of coal, the possibility of carrying out similar transformations and modifications, the availability of technological modes. The presence of phenolic hydroxyl and methylol groups, as well as aromatic nuclei with a delocalized six-electron cloud, has a positive effect on the adhesion properties on the metal surface, forming a protective layer, and therefore on the inhibitory characteristics of phenol-formaldehyde oligomers. From the point of view of obtaining highly effective corrosion inhibitors with a set of required properties, the development of methods for modifying the products of polycondensation of phenol and its alkyl-substituted derivatives with formaldehyde by nitrogen-containing organic compounds is of great importance. The advantage of the latter as modifiers mainly lies in the saturation with polar fragments, reactivity, high thermal stability, and also in providing environmentally less hazardous products.

The purpose of the scientific research is to develop a process for obtaining monoalkyl(C₈-C₁₂)phenol-formaldehyde oligomers (APhFO) modified with amines containing imidazoline fragments based on fatty acids obtained from various vegetable oils (sunflower, corn, cotton and palm) and polyamines (PA) (diethylenetriamine - DETA, triethylenetetraamine - TETA, polyethylenepolyamine - PEPA) and the use of these products as components of preservation fluids based on T-30 turbine oil in atmospheric environment, sea water and 0.001% aqueous solution of sulfuric acid.

Synthesis of imidazolines was carried out at a molar ratio of fatty acids isolated from various vegetable oils to DETA, TETA and PEPA 1-3:1, respectively, at a temperature of 230-240°C. When choosing molar ratios, special attention was paid to the amount of free amine fragments in the final products, which determines the

functionality of the latter. The modification process was carried out by the interaction of alkylphenols with formaldehyde at a molar ratio of 1:0.85 in an acidic medium at a temperature of 95-98°C and the continuation of the reaction, followed by the addition of imidazolines in an amount of 0.1 - 0.3 mol relative to 1 mol of alkylphenols at a low temperature (50°C) and an increase in temperature to 95 -98°C, at which the process was carried out until the resin was obtained.

The anticorrosion efficiency of preservation fluids based on T-30 turbine oil and APhFO modified with imidazolines based on fatty acids of various vegetable oils and PA on a steel surface was studied. The best results are shown in the table.

№	Composition of preservation fluids	Percentage in oil T-30	Climate chamber Corrosion box 1000E, (condensation regime), days	Seawater, days	0.001 % aq. sol. H ₂ SO ₄ , days
1	T-30 APhFO mod. by imidaz. FASO:TETA= 1:1 /0.1 mol to 1 mol APh/	10	485	324	372
2	T-30 APhFO mod.by imidaz. FACO:DETA = 1:1 /0.3 mol to 1 mol APh/	10	365	301	310
3	T-30 APhFO mod. by imidaz. FAPO:PEPA=1:1 /0.1 mol to 1 mol APh/	10	396	307	321
4	T-30 APhFO mod. imidaz. FACtO:PEPA= 2:1 /0.1 mol to 1 mol APh/	10	356	267	282

Thus, it can be said that the more C=C double bonds, polar amine fragments, and imidazoline cycles in the composition of oligomeric macromolecules, the higher the protective efficiency. The above structural elements lead to high adhesion and the formation of a dense protective layer on the surface of the metal. It should also be noted that the inhibitory properties of modified APhFOs depend on the length of the polyamine chain, on the number of moles of the nitrogen-containing modifier with respect to alkylphenols and on the quantitative content of oligomers in mineral oil.

Aluminium alloy corrosion inhibition by eco-friendly composition of natural polysaccharide and potassium sorbate

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Al-Cu-Mg alloys find extensive use in the aeronautical, automobile, railway, shipbuilding, and construction industries due to their low density and high strength. However, they are susceptible to local corrosion caused by differences in electrochemical properties of intermetallic inclusions and the aluminium matrix. Corrosion inhibitors are one of the most effective means of anti-corrosion protection of aluminium alloys. Traditional inhibitors are synthesized using expensive and toxic chemicals. They pollute the environment and are difficult to dispose of. Environmentally safe "green" corrosion inhibitors from raw plant materials, particularly natural polysaccharides, are a good alternative to synthetic inhibitors [1]. In particular, it was established that guar gum (GG), a natural water-soluble nonionic polysaccharide extracted from the seeds of the guar plant *Cyamopsis tetragonolobus*, effectively slows the corrosion of steel in acidic environments. However, as it was previously shown [2], the effectiveness of aluminium alloy corrosion inhibition by this biopolymer is insufficient in a neutral chloride environment. Therefore, in this work, an attempt was made to strengthen the protective effect of GG on an aluminium alloy, AA2024-T3, in a sodium chloride solution by combining it in one composition with the potassium salt of sorbic acid (PS).

Corrosion inhibition of AA2024-T3 aluminum alloy was studied in a 0.1% sodium chloride solution, to which GG and PS were added separately and in the form of their mixture. The methods of DC polarization, electrochemical impedance spectroscopy (EIS), scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX) were used.

It was established (Fig. 1) that the impedance module of an aluminium alloy at a current frequency of 0.1 Hz (Z_{01}) in a corrosion solution increased by 10–12 times under the influence of the GG+PS inhibitor mixture. Adding guar or potassium sorbate to the corrosion environment does not significantly increase the value of Z_{01} . The formation of two-time constants (Fig. 1) can be observed in the frequency dependences of the phase angle of the alloy, which can be attributed to the electrochemical processes of corrosion on the metal surface and the formation of an organic surface film. The shift of the maximum dependence

of phase angle to the range of higher frequencies of 100–1000 Hz and its increase after adding the mixture of inhibitors to the solution indicates the formation of an effective protective adsorption film on the metal. A two-time constant equivalent circuit was used to model the EIS spectra of the aluminium alloy in the chloride solution. A considerable increase in the metal charge transfer resistance R_{ct} and the surface film resistance R_f in the environment inhibited by the GG + PS mixture was established, which was maximal when the ratio of its components was equal. Based on the EIS results, the inhibitory efficiency of the studied composition on aluminium alloy in chloride solution is 94%.

SEM/EDX results confirm the formation of an organic protective layer on the surface of the alloy. The components of the inhibitor mixture are adsorbed on the surface of the aluminum alloy, sealing its natural oxide film. Presumably, the formation of poorly soluble complex compounds of biopolymer and sorbate with aluminum and copper cations also occurs. The increased anti-corrosion efficiency of the guar+sorbate inhibitor mixture on the freshly formed surface of the aluminum alloy using the wire guillotine method was also revealed in the corrosion environment.

Thus, an environmentally safe inhibiting composition based on equal amounts of guar gum and potassium sorbate has increased protective properties on an aluminium alloy in a neutral sodium chloride solution due to the formation of an adsorption protective film on the surface of the metal and the sealing of the oxide layer. The anti-corrosion efficiency of the composition exceeds 90%, which makes it promising for industrial use.

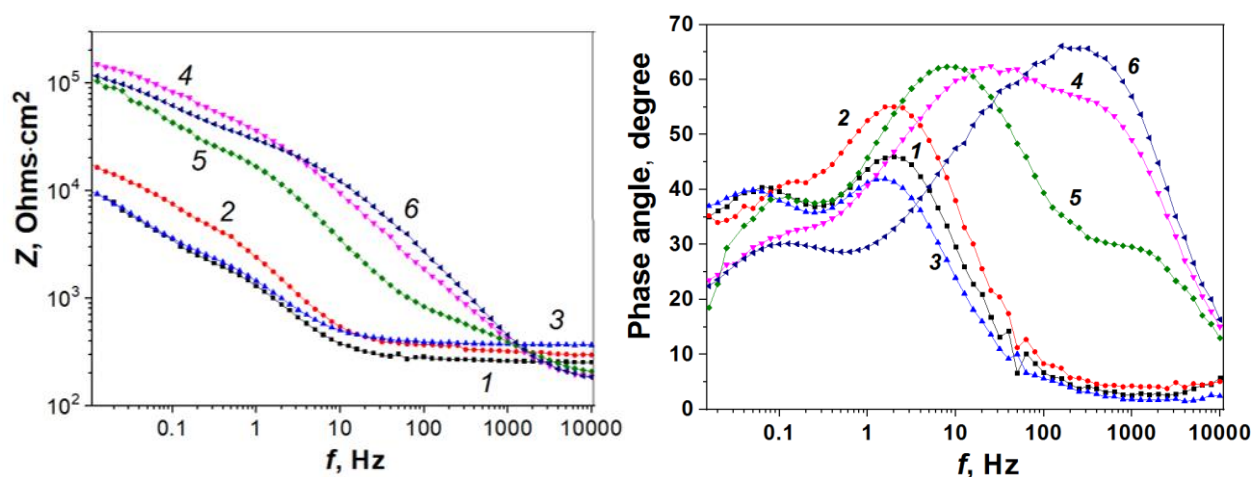


Fig.1. Bode plots of AA2024-T3 alloy in 0.1% NaCl solution (1) inhibited with 2 g/l of GG (2); 2 g/l of PS (3); 2 g/l of GG + PS (1:1 ratio) (4); 2 g/l of GG + PS (1:3 ratio) (5); 2 g/l of GG + PS (3:1 ratio) (6)

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Volatile corrosion inhibitor study in a thin film electrolyte and standard electrochemical cell

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This research aims to examine the applicability of two-electrode cell with thin film of electrolyte for study of volatile corrosion inhibitors (VCI). VCI protects the metal in such a way that forms an invisible protective film on the metal surface, thus not affecting the physical properties or functionalities of the metal. Studies on corrosion inhibition behavior of VCIs is usually conducted by visual methods (VIA test) or by electrochemical measurements in classical electrochemical cell. However, as VCI compounds are mainly used for atmospheric corrosion protection it is interesting to examine to study them under thin film electrolyte conditions.

This work examines the influence of two commercial volatile corrosion inhibitors on carbon steel corrosion by using the electrochemical impedance spectroscopy (EIS). Firstly, studies are conducted in a classical electrochemical cell with aqueous electrolyte (artificial acid rain pH = 6.5 or 1% NaCl solution).

In the second case, EIS studies are conducted on a specially designed disk plate¹ electrode consisting of two identical steel samples (1 cm x 1 cm). In some samples, the inhibitor was applied to the surface by evaporation, while in others as a thin film of the inhibitor solution of certain concentrations.

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Electrochemical evaluation of AFA alloys in carbonate molten salt as TES material applied to CSP plants

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Abstract

The use of carbonate molten salts for the new generation of concentrated solar power (CSP) plants has been proposed and analysed during the last years to improve the efficiency of the turbine block, increasing their thermal energy storage (TES) temperature above 600°C. However, due to the high corrosive impact in commercial alloys, it is necessary a better understanding and control of the corrosive species for a successful development of the new generation of concentrated solar power (CSP) plants [1]. In this study, two alumina forming austenitic (AFA) alloys corresponding to HR242 and HR233 grades, were exposed to the eutectic ternary $\text{Li}_2\text{CO}_3\text{--K}_2\text{CO}_3\text{--Na}_2\text{CO}_3$ (32.1–34.5–33.4 wt%) salt mixture at 650 °C during 500 hours.

A special setup was designed in order to integrate electrochemical electrodes in the corrosion reactor to carry out electrochemical impedance spectroscopy (EIS) tests and linear polarization resistance (LPR) during the isothermal immersion.

For a better selection and proposal of specific equivalent circuits to propose the corrosion mechanism in the AFA alloys, this work proposes a distributed relaxation times (DTR) methodology that uses EIS data from carbonate corrosion, representing the different polarization processes involved in the corrosion reactions [2]. The ECM models proposed, are more specific than those present in the literature, generally focus on molten salts [3], without specific information of the molten salt chemistry.

The evolution of the corrosion products during exposure time was studied by means of scanning electron microscopy (SEM) and X-Ray diffraction (XRD), obtaining the

formation of protective alumina scales and a better corrosion resistance in HR233 alloy with a corrosion rate of 0.177 mm/year.

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Effects of Temperature and Relative Humidity on Chloride-induced Stress Corrosion Cracking Behavior in Austenitic SS Welds

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Dry storage of spent nuclear fuel now gathers tremendous interest in worldwide due to the limited capacity for interim storage. Since the dry storage systems will be installed in sea-shore, chloride-induced stress corrosion cracking (CISCC) will be potential degradation phenomenon for the system. In this study, 304L-ER308L and 316L-ER316L weld plates are prepared and their CISCC behavior is tested in cyclic corrosion chamber with various temperature and relative humidity (RH). In our findings, 316L-ER316L is immune to CISCC while 304L-ER308L is susceptible to CISCC. However, CISCC is not observable for 304L-ER308L when RH is lower because deliquescence and penetration of chloride and oxygen is prohibited.

Monitoring the galvanic corrosion of copper-steel coupling in bentonite slurry - early exposure period

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Abstract

In the Scandinavian and Canadian nuclear waste disposal programs copper is proposed material for the absolute barrier preventing the release of radionuclides. For this reason, the corrosion of copper has been studied extensively in various environments and conditions. In the case of a two part container for spent nuclear fuel, consisting of an iron-based inner structure with copper coating, the copper coating may be damaged during the deposition process. If the coating is damaged, possible perforation of the copper may result in intensive galvanic corrosion between copper and steel. The present work focuses on the corrosion of steel galvanically coupled to copper and exposed to a slightly saline environment under oxic conditions. The study was performed in a bentonite, saturated with simulated saline groundwater (bentonite slurry) and in a simulated groundwater only, at open circuit potential and room temperature. Attention was given to evolution and intensity of the anodic activities on the steel electrode and the cathodic activities on the copper electrodes, in the early days of exposure to oxic environments. For this purpose, coupled multi-electrode arrays (CMEAs) were implemented and currents were monitored over various periods and conditions. After CMEAs measurements were carried out, different microscopic and spectroscopic investigations of surface modifications were employed. To verify the type and extent of the corroded damage, microCT scans of the electrodes were conducted as well.

Expected results

Galvanic corrosion currents between the carbon steel and pure copper will be monitored by the use of CMEA, which enable monitoring of anodic and cathodic currents on 25-coupled electrodes from copper, one being from steel. When is considered galvanic corrosion of steel in a steel-copper pair, the presence of

dissolved oxygen is very important. In the system with Aspö groundwater only, high anodic current density are expected while in the system with bentonite slurry, lower and decaying anodic current density are expected. The reduction in the anodic current in this environment will be studied and correlated to dissolved oxygen.

Corrosion of steel in contact with bentonite under conditions relevant for nuclear waste disposal

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Abstract

Carbon steel is considered by many countries as a potential canister material to encapsulate high-level nuclear waste (HLW) before final disposal in a deep geological repository. Depending on the repository concept, compacted bentonite may be used as backfill material. Groundwater will eventually migrate through the barriers and induce steel corrosion. Information on corrosion rates (i.e., service lifetime of the container) and corrosion mechanisms are of high importance for the Nuclear Disposal Safety Case.

A low-alloyed carbon steel and a spring steel of comparable composition, though with higher Si content, were selected in this study. The higher Si content of the spring steel is expected to reduce substantially the corrosion rate by forming of a layer of iron silicates better protecting the surface than for the carbon steel. This hypothesis was tested by performing corrosion experiments in closed vessels under anoxic and water saturated conditions at room temperature (RT) and at 50°C. Coupons were polished and the MX-80 bentonite was pre-equilibrated with synthetic Grimsel pore water prior to use. After 3 months of reaction time, and cooling down to RT where necessary, pH and redox potential (E_h) were measured in-situ and the composition of ultra-centrifuged pore water determined by ICP-OES and IC. Coupons were analyzed by various techniques and corrosion rates were determined from weight loss measurements.

Relatively comparable pH values were measured for the carbon steel (pH 8.40) and the spring steel (pH 8.14) at RT, and lower values were measured in experiments conducted at 50°C. E_h values were not much affected by temperature, but were significantly lower for the carbon steel (around -380 mV). The composition of the pore water in all experiments were relatively comparable. The corrosion rate for the spring steel was larger than for the carbon steel and values increased with temperature. No

presence of corrosion products on the surface of both steel coupons could be detected by XRD analysis. However, morphological changes could be seen at the surface of both coupons by SEM, and a change in chemical composition of the exposed surfaces was evidenced by SEM-EDX analysis. Elemental compositions point to the presence of a thin layer of Fe-silicate covering the coupons. Complementary information on elemental composition and oxidation state of the new-formed mineral was provided by surface sensitive XPS analysis.

Overall, the investigated spring steel is less corrosive than carbon steel under elevated temperature conditions while at room temperature the investigated carbon steel has more corrosion resistance compared to spring steel. The increase of corrosion rate with temperature agrees with reported studies and is expected to decrease with reaction time (e.g., doi.org/10.5006/1.3287691) owing to the development of a more compact alteration layer at the surface of coupons. This assumption is being investigated in experiments with longer reaction time and the comparison of results from both materials will enable to conclude whether Si present in the steel has a significant impact on the corrosion resistance.



Room Temperature (25°C)



Elevated Temperature (50°C)

KEYWORDS: Nuclear waste disposal, MX-80 bentonite, Metallic Corrosion, Anoxic, Carbon steel

Assessing the role of surface conditions in SCC susceptibility of Alloy 182 in simulated LWR environments

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Ni-base Alloy 182 is a widely used weld filler and attachment pad metal in dissimilar metal welds (DMWs) between low-alloy and stainless steel or Ni-base wrought alloy components in light water reactors (LWRs). It is highly susceptible to in-service stress corrosion cracking (SCC) under operating conditions. Several incidents of SCC in Alloy 182 DMWs during LWR service have not only seriously reduced plant availability, but also challenged integrity, safety and lifetime of LWRs. The mitigation of SCC is thus crucial for safe & efficient long-term operation (LTO) of LWRs.

The initiation and propagation of SCC cracks occur by the cyclical rupture and re-formation of the service-grown Cr-rich protective oxide film at the substrate-environment interface. Thus, the surface state of the component (topography, surface/subsurface microstructure, and residual stresses) plays an important role in both SCC initiation and mitigation. Peening (shot peening, cavitation peening, etc.) is a promising mitigation method that produces high compressive surface residual stresses (RS), which are claimed to prevent SCC initiation. To mitigate SCC, the compressive RS must be higher than the weld tensile RS and operating stresses, with the cumulative total stress being below the threshold stress for SCC. Peening also results in a surface affected layer with modified microstructure. A severely plastically deformed (SPD) surface layer is formed at the surface (having highly strained nano/ultrafine grains) followed by a strained subsurface layer with distinct grain structure. The dense network of dislocations and nanograin boundaries provide faster diffusion paths for Cr from bulk to oxide-substrate interface, potentially forming Cr-rich protective oxides that might help to suppress SCC. The higher hardness & strength of the surface layer, on the other hand, tends to increase its inherent SCC susceptibility.

In addition, there may be accelerated relaxation of the compressive stresses during LTO in high-temperature water (HTW). Thus, with time, the inhomogeneous plastic deformation in the surface affected layer and relaxation of compressive RS may lead to higher SCC susceptibility than unpeened surface. Long-term effect of peening on SCC is thus, highly complex and demands systematic investigation and quantification for industrial applicability.

The current work briefly summarizes the results of HTW oxidation and SCC initiation tests performed on Alloy 182 specimens with different surface finishes (peened, machined, electro polished, etc.). Tests were carried out in the temperature range of 220 to 350 °C in simulated boiling water reactor (BWR) environment as well as in primary pressurized water reactor (PWR) environment. The SCC initiation behavior of Alloy 182 weld metal was investigated by in-situ crack growth rate monitoring in HTW autoclaves using reverse direct current potential drop (DCPD) method. Oxidation coupons were characterized for their morphology and chemical compositions. The effect of surface conditions, surface and subsurface microstructure and nature of residual stresses on the protectiveness of the oxide film and SCC initiation susceptibilities of Alloy 182 in HTW are briefly discussed herein.

Understanding hydrogen-material interactions in additively manufactured Inconel 718

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Exposure to hydrogen is known to significantly degrade the ductility, toughness, and fatigue resistance of pure metals and structural alloys [1]. With the imminent development of a hydrogen infrastructure, which implies an increasing number of elements working in contact with hydrogen across countless industrial sectors, there is a need to understand hydrogen-material interactions and map regimes of safety operation in new metals resulting from additive manufacturing (AM) techniques. Due to its excellent mechanical properties, AM Inconel 718 holds great potential in sectors where tailored-made, high-reliability components are necessary: aerospace (jet engines), power generation (boilers and turbines), transport (fuel-cells) and oil&gas industries (valves, pipes, vessels...) [2]. Nevertheless, although many of these AM components are intended to be used in extreme hydrogen-rich environments, little is known about the interaction of hydrogen with AM Inconel 718. Therefore, the aim of this work is to understand the fundamental hydrogen-material interactions in AM Inconel 718 across different scales: from absorption, diffusion and trapping of hydrogen atoms in the AM microstructure, to the macroscopic effect of hydrogen on its mechanical properties.

The study was conducted using 40x20x20 mm³ blocks of AM Inconel 718 printed by means of laser-powder-bed fusion selective laser melting (LPBF-SLM). Wrought Inconel 718 was employed as a reference and different heat treatments were applied to the as-printed (AP) additively manufactured condition in order to gain more insights into the hydrogen-microstructure interplay. A comprehensive examination of the microstructures and porosity characterization was conducted by means of SEM and EBSD. 10x10x0.5 mm³ samples were EDM machined, ground, polished until 1 µm - to ensure good surface quality - and electrochemically charged with hydrogen in deaerated 3 wt. % NaCl solution at 90°C. A three-cell electrode system composed of a Pt counter electrode and a silver/silver chloride (Ag/AgCl) reference electrode was

employed, and hydrogen was generated by imposing a constant current density of 5 mA/cm². For all the conditions considered, the specimens were charged for 1, 2, 4, 7 and 14 days to assess the influence of charging time on hydrogen absorption. After charging, the samples were stored in liquid nitrogen to minimize hydrogen egress prior to testing. An ultra-high vacuum thermal desorption system with a regularly calibrated Hiden Analytical RC PIC quadrupole mass spectrometer (TDS) was used to (I) measure the hydrogen concentration in the samples after the electrochemical charging process and (II) perform isothermal TDS experiments [3]. The combination of both techniques with FE analysis is used to assess hydrogen trapping and determine the hydrogen diffusivity of all the studied Inconel 718 conditions. On the other hand, flat dog-bone 0.5 mm-thick tensile specimens, pre-charged with different hydrogen contents following the procedure described above, were tested in air at a strain rate of 10⁻⁶ s⁻¹ in order to assess the effects of dissolved hydrogen in the mechanical behaviour of AM Inconel 718. SEM and EBSD were employed to study the fracture surfaces and gain insight into the fundamental mechanisms responsible for hydrogen-induced degradation.

In general, it has been observed that the dense cellular dislocation structure developed in the as-printed AM condition increases considerably the hydrogen uptake and plays an important role in hydrogen trapping, diffusivity, and mechanical behaviour. The application of appropriate heat treatments can help annihilate structural defects and improve the mechanical performance of the alloy in presence of hydrogen [4]. This work aims to lay the foundations for the development of hydrogen-resistant AM alloys that facilitate the establishment of hydrogen as the energy source of the future.

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Study of deuterium evolution reaction and absorption into low alloy steel

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Electrochemical deuterium (D) charging provides a viable method to prepare metal-needle deuterium charged samples for Atom Probe Tomography (APT) analyses, allowing atomic-scale observations of hydrogen interactions with structural features. These analyses have the potential to provide a fundamental understanding of hydrogen trapping at various structural features, such as grain boundaries and carbides, supporting the design of alloys resistant to hydrogen embrittlement.

This study investigates the kinetics of D production and absorption into a low alloy steel. Firstly, potentiodynamic cathodic polarization curves in deuterium and similar acid and alkaline aqueous electrolytes are compared. Then, H and D charging is conducted by applying constant cathodic potential for times from 4 to 72 hours, followed by measurements of the absorbed concentrations by Thermal Desorption Spectroscopy (TDS). The results are afterwards used to establish an appropriate protocol for charging APT needles for atomic deuterium observation in the alloy structure.

Numerical Study: The mechano-electrochemical effect of X100 buried pipelines with pre-existing corrosion defect

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The new high-strength low alloy steel API X100 is a cost-effective steel grade and has the ability to withstand high operating conditions without the need for increasing pipe wall thickness. However, buried transmission pipelines suffer from external corrosion and cracking, the corrosion kinetics in near-neutral pH environments is not yet fully studied. Therefore, conducting research to contribute to a clearer understanding of the corrosion kinetics in near neutral pH soil environment will therefore have unique novelty when conducted on the modern HSLA steel grades such as API X100. Also, formulating and developing models to simulate the X100 steel pipeline corrosion in nn-pH soil environments is of great importance and benefit to the electrochemical science and assessing the pipeline integrity. This work presents and discusses the results of two numerical models conducted on X100 steel, contributing to a clearer understanding of the corrosion kinetics and crack propagation of corroded pipelines occurring in these environments. The results of this research can be used for assessing the integrity of buried oil and gas transmission pipelines, however they can also be extended for the use of other infrastructural and engineering applications such as steel reinforcements of buried structures. Two numerical models were conducted for the purpose of studying the corrosion kinetics and growth rate of a buried pipeline with a semi-elliptical corrosion defect and the crack propagation due to the stress concentration buildup on the defect center. The first model was formulated using Comsol Multiphysics v5.6 and the results showed that the electrolyte potential at the corrosion defect center is shown to be the highest when compared to the remaining geometry. Also, the anodic current density at the corrosion defect center was found to increase from its initial value of 12 A/cm^2 to a final value of 15 A/cm^2 . This is due to the effect of stress in promoting the defect growth with time by changing the potential in a more anodic direction making the material more susceptible to corrosion. In addition to that, the anodic current density at the defect sides are higher than that of the center of the defect because it is closest to the cathode making the transfer of current density from the anode to the cathode easier. The results from this model was taken as corrosion defect depths

and were used as inputs to the second model to evaluate the crack initiation and propagation using the XFEM approach. The results were divided into three parts, the initiation and propagation of the crack, the burst pressure of corroded pipelines and the von Mises stress distribution along the crack path.

Investigation of Corrosion Behaviour of Plastic Mould Steels under Oxygen Free and Oxygen Saturated Conditions

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Steels for plastic injection moulds are available in different alloy compositions. Mechanical properties, such as wear resistance and hardness, are the most important properties of these steels. Corrosion resistance of these steels is also an important property, which is why there are high-alloy steel compositions.

The cooling and temperature control systems for moulds have different types of fluid circuits. There are open and closed systems, which has a direct influence on the oxygen content in the fluid. There are also different types of water, such as hard and soft water, and different types of additives, for example biocides or corrosion inhibitors.

The aim of this work is to investigate the corrosion behaviour of various typical plastic mould steels under high and low oxygen conditions. With these results, a mould tempering device will be developed that controls the oxygen content in a closed water-based liquid system. If this is successful, chemical additives can be dispensed with and good corrosion behaviour can be achieved, even for low and unalloyed steels.

Steels with different chromium contents typical for this application were selected for the tests. Heat treatment was carried out in a typical way for these steels. Corrosion behaviour was measured by open circuit and potentiodynamic measurements in soft water at 50°C. Oxygen-free and oxygen-saturated conditions were investigated.

Comparison of chromium-free aluminium desquamation methods

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Abstract

Desquamation of metals consists in the selective dissolution of the oxides layers without damaging the underlying metal by immersion in bathes of well selected chemistries. The selectivity of a desquamation process can be defined by the ratio of the aluminium oxide dissolution rate to the metal corrosion rate. In the case of aluminium alloys, the objectives of the desquamation may be:

- To clean the surface to enable the determination of the depth of localized corrosion by microscopy
- To weight the oxides mass and metal loss since in neutral water chemistries aluminium corrosion tends to generate a mass gain
- To determine the oxides layer specific gravity If the oxides layer thickness is known
- To determine the oxides layer thickness if the oxides layer specific gravity is known

To achieve the selective dissolution of oxides without altering the metal, the chemistry of the dissolution bath should either contain a strong cathodic inhibitor or be able to replace the passive layer of the metal with a conversion layer which is not soluble in the desquamation bath. This last technique is historically used for aluminium for which the formation of a Cr(III) rich oxide from the reduction of Cr(VI) present in the desquamation bath is performed [1][2].

However due the carcinogenicity of hexavalent chromium containing reagents [3], an effort to replace chromium in desquamation baths chemistries is to be made. This paper presents a comparison of three chromium free aluminium desquamation techniques. Two methods from published standards and a new method using manganese oxides.

The comparison of the desquamation techniques is made on AA1100 samples. These samples were pre-oxidized either in deionized water at 35 °C to form a hydrothermal

oxide as studied by Hart [4] and Alwitt [5] or submitted to a sulfuric anodization followed by a water sealing in accordance with a state of the art practice [6].

The first method tested consists in the bathing in concentrated nitric acid as proposed by [1]. This method is found to be not selective towards tested oxide layers dissolution. However, its efficiency is shown to be improved by preliminary breaking the oxide by a heat treatment aiming at the oxides' dehydration and quench. Its use remains of interest for thin oxides layers of less than a micrometre for it is the less aggressive technique tested.

The second method, from [2], uses a phosphoric acid and sodium molybdate bath to dissolve the oxides. The third method is based on a bath of phosphoric acid and potassium permanganate. These two methods are found to be efficient and selective towards the oxides tested and both being far less harmful than the hexavalent chromium methods. The permanganate bathing colours the localized corrosion indications making any further visual examination easier.

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KEY WORDS: desquamation, gravimetry, aluminium, bayerite, anodizing

Influence of calcium on the thermal oxidation of CoO and cobalt

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Abstract

In the present study, it was found that the beneficial effect of a CaO coating on Co oxidation rates is due to the shift of the Co/CoO phase boundary to higher P_{O_2} , leading to a decrease of the driving force of diffusion.

Keywords : Oxidation – Coating – Diffusion - Calcium – Cobalt.

1-Introduction

This work is performed with CaO-coated Co polycrystals, in order to eliminate the influence of additive elements on the transport properties of the metal. The results have been analyzed taking into account a fundamental approach of transport processes under non-equilibrium conditions [1-4] and transport properties of pure and doped $Co_{1-x}O$ single crystals [5].

2. Basic equations

2.1- General equations

Oxidation process of $Co_{1-x}O$ is governed by cation exchanges with cationic vacancies α time ionized ($V^{\alpha'}$), whose concentration depends on both, temperature and oxygen partial pressure ($\frac{1}{2}O_2 \rightleftharpoons O_O + V^{\alpha'} + \alpha h^\circ$). According to the charge neutrality condition, one can show that [4,6]:

$$[h^\circ] = \alpha [V_{Co}^{\alpha'}] = AK_V^{1/(\alpha+1)} (P_{O_2})^{1/2(\alpha+1)} \quad (1)$$

where K_V is the equilibrium constant of formation of defects, O_O an oxygen ion on its normal site, h° an electron hole, $V_{Co}^{\alpha'}$ an α time negatively ionized cationic vacancy, $A = \alpha^{1/(\alpha+1)}$ and square brackets concentrations in mole fraction.

The thermodynamic and transport properties of undoped and Ca-doped $Co_{1-x}O$ single crystals were determined from electrical conductivity measurements [6]:

$$\sigma = e \mu p = \sigma_o (P_{O_2})^{1/2(\alpha+1)} \exp(-\Delta H_\sigma / RT) \quad (2)$$

where e is the electrical charge of electrons, p the hole concentration per cm^3 , μ the hole mobility, regarded generally as a thermally activated hopping process ($\mu = \mu_o \exp(-\Delta H_\mu / RT)$), ΔH_σ the enthalpy of conductivity with $\Delta H_\sigma = (\Delta H_\mu + \Delta H_V) / (1+\alpha)$, ΔH_V the enthalpy of formation of defects, ΔH_μ the hole enthalpy of mobility and α the mean electrical charge of point defects which can be determined from the slopes (Eqs.1,2):

$$(d \ln \sigma / d \ln P_{O_2})_T = 1/2(\alpha+1) \quad (3)$$

One can recall that these results show that calcium has a reducing behaviour in Co_{1-x}O , leading to the formation of singly ionized cobalt cations (Co^+) [6]. This reduction influence the concentration of intrinsic defects (Eq.1) through the electroneutrality condition:

$$\alpha[V_{\text{Co}}^{\alpha'}] + [e'] = [h^\circ] + [\text{Ca}_{\text{Co}}^\bullet] \quad (4)$$

2.2- Transport processes under non equilibrium conditions.

Under non equilibrium conditions, fluxes of cations (J_i) and cationic vacancies (J_v) appear in p-type semi conducting oxides, coupled through the condition [4,7]:

$$J_v + \sum J_i = 0 \quad (5)$$

Taking into account that no electrical current flows through the film ($I_t = FJ_h = 0$) and assuming a virtual local equilibrium between electrically charged species and neutral atoms ($A + \alpha h^\circ \rightleftharpoons A^{\alpha+}$), Wagner [1-3] has shown that the cationic fluxes in the “z” direction, with respect to the oxygen sublattice (or laboratory reference frame), may be written as:

$$J_i = -\frac{C_i}{RT} D_i \frac{d\eta_i^{\alpha+}}{dz} = -\frac{C_i}{RT} D_i \left(\frac{d\mu_i^{\alpha+}}{dz} + z_i F \frac{d\Phi}{dz} \right) = -\frac{C_i}{RT} D_i \frac{d\mu_i}{dz} \quad (6)$$

where $d\mu_i/dz = RT d \ln a_i$ is the chemical potential gradient of the neutral species, $d\eta_i^{\alpha+}/dz$ the electrochemical potential gradient of the charged species, related to their chemical potential gradient ($d\mu_i^{\alpha+}/dz$) by the relation:

$$\frac{d\eta_i^{\alpha+}}{dz} = \frac{d\mu_i^{\alpha+}}{dz} + z_i F \frac{d\Phi}{dz}, \quad (7)$$

F the Faraday constant, Φ the Nernst potential, $C_i = x_i C_M$ the cation concentration per unit volume (mol/cm^3), D_i the diffusion coefficient of cations i , z_i their valence and C_M the concentration of cationic sites in the lattice.

To express Eq.6 in a form including measurable parameters, it was assumed [3,5] that in the solid solution ($\text{AO}-\text{BO}\gamma$) the concentration of $\text{BO}\gamma$ ($x_{\text{BO}\gamma} = m$) is low enough ($x_{\text{AO}} \ll m$) that the Raoult law may be applied ($a_{\text{AO}} \approx x_{\text{AO}} = 1-m$). Therefore, taking into account the local equilibrium between the different species in each element of volume ($1/2\text{O}_2 + A \rightleftharpoons \text{AO}$, $\gamma/2\text{O} + B \rightleftharpoons \text{BO}\gamma$), it follows [4]:

$$J_A = -\frac{C_A}{RT} D_A \frac{d\mu_A}{dz} = C_M D_A \left[\frac{dm}{dz} + (1-m) d \ln a_O / dz \right] = C_M D_A \left[\frac{dm}{dz} (1-m) \mathcal{F} \right] \quad (8a)$$

$$J_B = -\frac{C_B}{RT} D_B \frac{d\mu_B}{dz} = -C_M D_B \left[\frac{dm}{dz} - m \gamma d \ln a_O / dz \right] = -C_M D_B \left[\frac{dm}{dz} - m \gamma \mathcal{F} \right] \quad (8b)$$

where $\mathcal{F}$ is the external driving force of diffusion, depending of the oxygen potential gradient ($d \ln a_O / dz$) across the oxide ($a_O = P_{\text{O}_2}^{1/2}$) which can be related to the cationic vacancy concentration gradient ($V^{\alpha'}$) (Eq.1) :

$$\mathcal{F} = d \ln a_O / dz = (1 + \alpha) d \ln [V^{\alpha'}] / dz \quad (9)$$

3. Experimental results

3.1- Kinetic demixing

Kinetic demixing processes occur in multicomponent oxides in presence of an external driving force. Consequently, a concentration gradient (dx_i/dz) sets up progressively in a multi-component oxide (A,B,O) if the diffusion coefficients of cations A and B are different (Eqs.8).

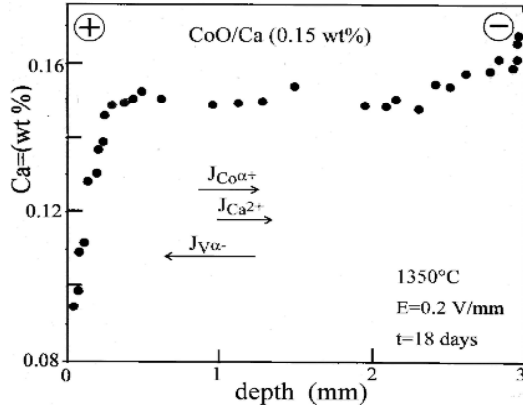


Figure 1- Kinetic demixing profile of calcium (0.15wt%)-doped Co_{1-x}O single crystal, maintained in air under 0.2V, for 18 days at 1350°C.

In Fig.1, we have reported the kinetic demixing results in a Ca (0.15 wt%)-doped Co_{1-x}O single crystal maintained under an applied electrical field (E) of 0.2 V/mm in flowing air, at 1350°C for 18 days. EPMA analysis shows an enrichment of calcium near the cathode. Therefore, it follows from Eqs.8 that:

$$D_{\text{Ca}} > D_{\text{Co}} \quad (10)$$

It should be noted that in undoped Co_{1-x}O $D_{\text{Ca}} < D_{\text{Co}}$ due to correlation effects [6].

3.2- Thermal oxidation of uncoated and CaO coated cobalt polycrystals

Oxidation experiments were performed in a Setaram thermobalance with square coupons (1cm² by 0.1cm thick), sintered from high purity powder Johnson Matthey powder (99.995 wt%) , isostatically pressed. Coupons were first oxidized at 1250°C. The oxide was removed on one main surface, which was then polished to a 1μm diamond finish. Coating deposition was achieved by sputtering a CaO target on this surface.

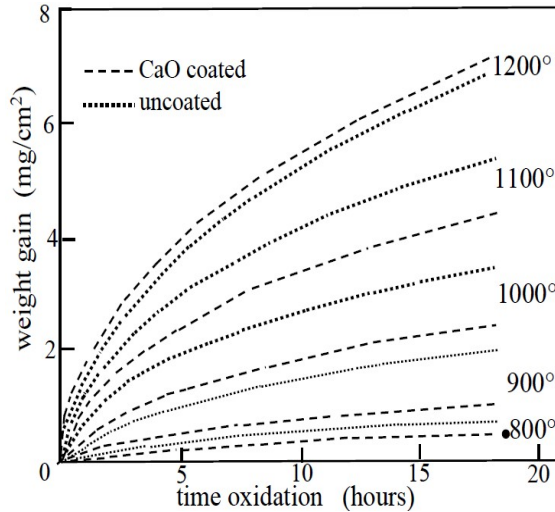


Figure 2- Weight gain versus time of uncoated and CaO coated cobalt polycrystals, under $P_{\text{O}_2}=0.21 \text{ atm}$.

In agreement with the Wagner theory [1], these results follow a parabolic law, and the weight gain per unit area ($\Delta m/s$) can be expressed by the following relation:

$$(\Delta m/s) = k_p \sqrt{t} + k_o \quad (11)$$

where k_p is the parabolic rate constant.

3.3- Composition of scales

The calcium profile through fracture sections of the oxidation layer developed on CaO-coated cobalt was determined by EPMA analyses. At 900°C, the profile presents a maximum in a localized zone, which coincides with the position of the initial cobalt surface. From either side of this maximum, the amount of calcium is low and increases in the outer layer, in agreement with the kinetic demixing of calcium in Ca-doped Co_{1-x}O single crystals (Fig.1). When the temperature increases, the calcium becomes progressively more diluted in the thicker layers. At 1100°C, it shows only a small increase close to the metal/oxide interface due to equilibrium segregation.

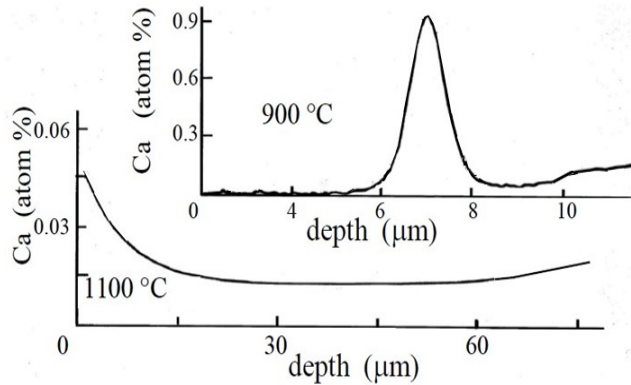


Figure 3- Calcium concentration –depth profiles in oxide films, after 18h of oxidation at 900°C and 1100°C. Metal/oxide interface taken as initial position of analysis

4. Discussion

The results (Fig.2) show that CaO coatings reduce the oxidation rates, at $T < 1200^\circ\text{C}$. They have been analyzed from the thermodynamic and transport properties of undoped and Ca-doped Co_{1-x}O single crystals [5] and the general expressions of the rate of oxidation ($v = -\Sigma J_i / C_M$).

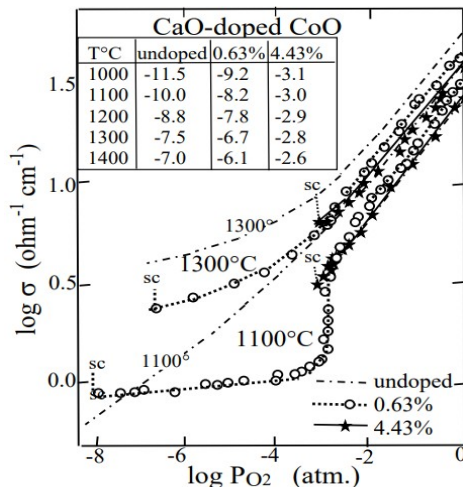


Figure 4- Influence of the calcium concentration on the electrical conductivity of undoped and Ca-doped Co_{1-x}O , at 1100° and 1300°C [6].

The dissociation pressure of Co_{1-x}O in undoped and doped single crystals is reported in the Table, between 1000° and 1400°C. It is also indicated (sc) on the σ plots

Taking into account that the calcium concentration is low in the oxidation layers developed on CaO-coated cobalt (Fig.3), its rate of growth can be described by the relations [5,7]:

$$\text{CaO-coated cobalt: } v_{\text{oxid}} \approx D_{\text{Co}} [-(dx_{\text{Co}}/dz) - \mathcal{F}_{(\text{Ca-doped CoO})}] \approx - D_{\text{Co}} \mathcal{F}_{(\text{Ca-doped CoO})} \quad (12)$$

$$\text{uncoated cobalt polycrystals: } v_{\text{oxid}} = - C_M D_{\text{Co}} \mathcal{F}_{(\text{CoO})} \quad (13)$$

with $\mathcal{F} = d \ln a_O / dz = \frac{1}{2} d \log (P_{\text{O}_2}) / dz$.

The oxidation rate of coated cobalt polycrystals is controlled by a competitive effect of the diffusion coefficient of cobalt (D_{Co}) and of the driving force of diffusion ($\mathfrak{F}$). The presence of a maximum calcium amount (Fig.3), which coincides approximately with the position of the initial cobalt surface at $T=900^{\circ}\text{C}$, indicates that the concentration of solute calcium cations is higher in the inner layer, leading to a decrease of P_{O_2} near the phase boundary Co/CoO. Consequently, the decrease of the oxidation kinetics of the coated polycrystal (Fig.6) is due to a decrease of $\mathfrak{F}$ (Eq.13). When the temperature increases, the calcium concentration decreases progressively due to both the thickening of the layer and the outward diffusion of calcium in the layer (Fig.3). At $T=1100^{\circ}\text{C}$, it shows only a small increase close to the metal/oxide interface due to equilibrium segregation. Consequently, at higher temperatures the oxidation is controlled in uncoated and CaO-coated cobalt by D_{Co} .

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A New Method for Deriving Metastable Pourbaix Diagrams of Stainless Steels Using Density Functional Theory Calculations

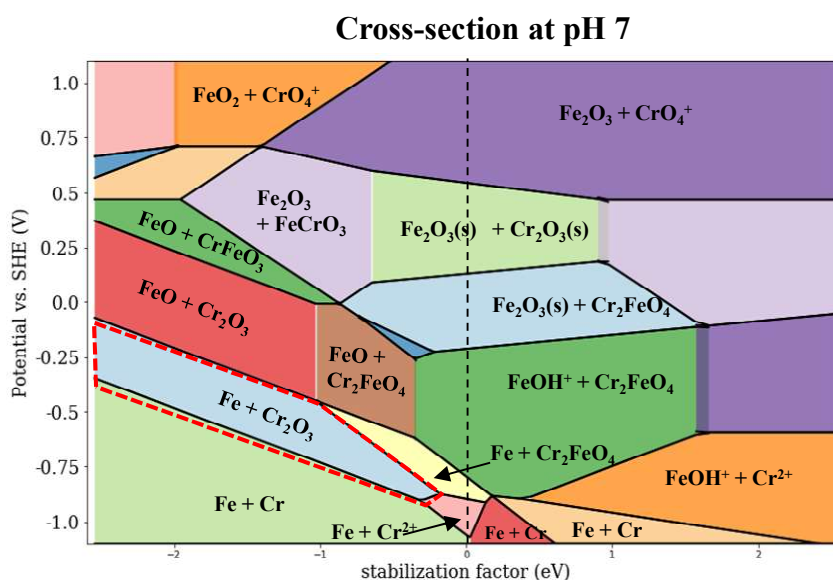
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This paper proposes a new method of deriving metastable Pourbaix diagrams of stainless steels (SS) using Density Functional Theory (DFT) calculations. The goal is to investigate the thermodynamic equilibrium of the passive film in relation to the metallurgical conditions and the chemistry of the environment. By using advanced numerical search and optimization algorithms from the Materials Project database (MPD), a new approach has been developed to identify the intricate chemical equilibria that exist in passive films by incorporating nonequilibrium effects as a correction factor. It was demonstrated that parameters such as the nucleation conditions of the Cr_2O_3 oxide are likely to stabilize the inner layer of the passive film.



Metastable Pourbaix diagram of the Fe17Cr/H₂O system at 25 °C and pH 7 generated by applying a perturbation round the equilibrium position.

Modelling of Anodic Delamination of Coated Stainless Steels Using Finite Elements

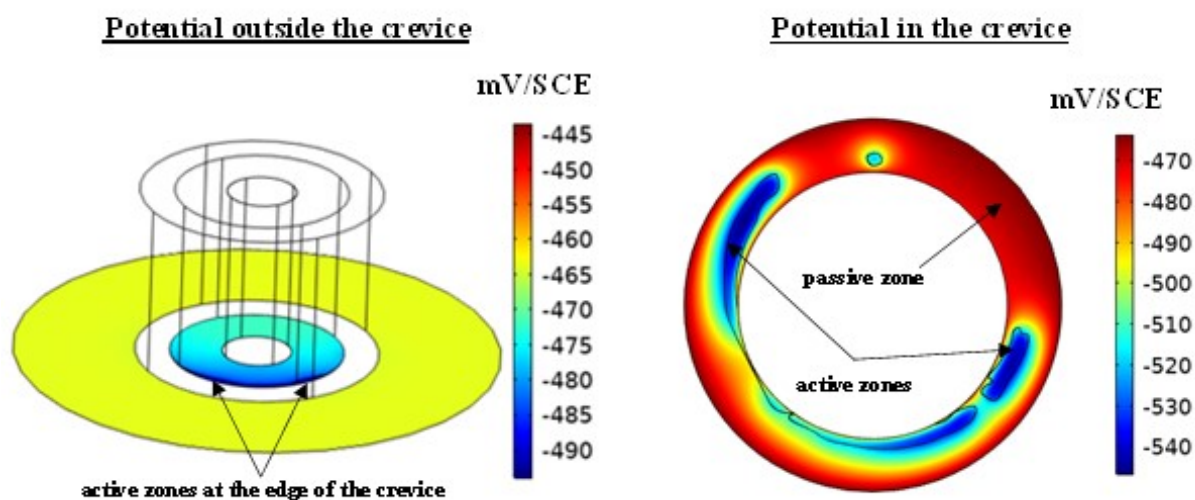
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This paper presents the results of a numerical study on the anodic delamination of coated stainless steels (SS) for automotive applications. The finite element modelling framework (FEM) was used to estimate the local pH in the confined zone under a paint layer. The FEM analysis of the reactive system included a description of the galvanic coupling between a cathodic zone located on a scratch and an anodic zone confined under a paint layer, and a mass balance of the dissolved species. The results showed that, in the absence of matter exchange with the external environment, the entire anodic current was located near the cathode/anode interface, leading to all the corrosion damage being located near this interface. However, when an exchange with the external environment was allowed, a gradual repassivation near the interface was observed, resulting in the transfer of all the anodic activities to the bottom of the confined zone, which accelerated the delamination rate.



Calculated potential distribution inside and around the crevice

The influence of LPSO structures on corrosion of Mg in acidic solutions

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Magnesium (Mg) alloys are promising materials utilized in many branches of industry including aviation and biomedicine. The use of Mg alloys can significantly reduce the weight of the elements. The limitation of the application of these alloys is their low corrosion resistance, the associated intense hydrogen evolution, and thus the uncontrolled degradation of the material. The corrosion rate of Mg alloys depends on their chemical and phase composition as well as microstructural factors.

This study aimed to investigate the effect of the LPSO structures on the corrosion resistance of Mg alloys depending on the manufacturing method and chemical composition. It was verified whether a deformation and chemical composition improve corrosion resistance. The materials studied were MgZnYAl alloys prepared via ingot metallurgy (reference material) and using extrusion of powders to Cu molds. The corrosion resistance of these materials was also compared with the corrosion behavior of MgZnCaMnY alloy produced via powders compaction during extrusion. Electrochemical tests and corrosion rate measurements were carried out to determine the corrosive properties. The next stage of the research was the characterization of the corroded surface. The methods used to describe surface changes in the materials studied were scanning electron microscopy (SEM) and optical profilometry.

The results of this work show that the manufacturing method has a significant influence on the corrosion resistance of Mg-LPSO alloys. The chemical composition of the alloys determines the micro-galvanic coupling between the matrix and LPSO phases which is the main reason for various corrosion responses of the materials in acidic solutions.

This research is realized under the project “Development of Advanced Magnesium Alloys for Multifunctional Applications in Extreme Environments” No. V4-JAPAN/2/15/MagMAX/2022 financed by the National Centre for Research and Development in Poland in the framework of Visegrad Group (V4)-Japan Joint Research Program—Advanced Materials.

An experimental study of corrosion during latent heat storage

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The lack of fossil fuels and their negative impact on the environment has led to the search of alternative energy sources in recent years. Several research groups are engaged in the development of technology and equipment for the efficient thermal energy storage in the form of latent heat obtained from the phase-change materials (PCMs). The PCMs ability to accumulate heat is significantly higher than that of substances utilising sensible heat. Moreover, they accept or deliver heat at a constant temperature. In the past decades, an extensive research has been carried out in the identification of various PCMs. Inorganic salt hydrates are the most important group of PCMs due to their high latent heat of fusion and thermal conductivity. To apply these materials in the latent heat storage systems, it is necessary to know their corrosion effect on the construction materials.

In this work, corrosion behavior of selected metals used in heat exchangers (stainless steel, carbon steel, aluminium and copper) was studied in two assumed PCMs: a mixture of magnesium nitrate hexahydrate and calcium nitrate tetrahydrate (1:1) and nickel nitrate hexahydrate. Corrosion sensitivity of selected metals was assessed through electrochemical measurements and gravimetric analysis.

Acknowledgements

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Structures and dynamics of corrosion inhibitors near electrified interfaces

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In the automotive industry, steel has been an important material for body construction over several decades. Challenged by the regulatory demands for safer, cleaner, and more fuel-efficient vehicles, numerous steels of different composition and mechanical properties are used, predisposing resulting multi-substrate assemblies to localised corrosion. Zn-based coatings are applied via galvanisation processes for corrosion protection. However, additional organic corrosion inhibitors are required to provide active protection over a longer lifetime. With increasing awareness of sustainability issues, the development of organic and environmentally friendly corrosion inhibitors is in high demand.

The search for new environmentally friendly corrosion inhibitors entails the electrode-electrolyte interface. Here, two inhibitory processes can be distinguished in general:

- a) the competitive adsorption of a corrosive species or the inhibitor at the inner Helmholtz plane (IHP), and
- b) the mechanical blocking film at the outer-Helmholtz plane (OHP) preventing corrosive species to reach the surface of a substrate.

So far, the modelling of (b) and its inhibitor-inhibitor and inhibitor-electrolyte interactions has mostly been neglected. Instead, most computational studies focus on process (a) and model the inhibitor-surface interactions ignoring the impacts of the aqueous environment like pH and salinity. Corrosion inhibition efficiency is often exclusively correlated with the electronic properties of a molecule.

Here, we present the computational modelling of the OHP for various inhibitor candidates in an aqueous NaCl electrolyte. By using classical molecular dynamics and a constant-charge model approach the electrolyte structure and dynamics near the electrified interface is simulated to give mechanistic insights in protective films in the early stages of their formation.

Influence of rainfall on corrosion behavior of carbon steel under atmospheric environment

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A combined cyclic corrosion test including the rainfall conditions was conducted to investigate the effect of rainfall on the atmospheric corrosion behavior of carbon steel. The developed atmospheric corrosion sensors were used as the electrodes, and the corrosion rate was monitored during the corrosion test by an electrochemical impedance method. The monitoring of corrosion rate was conducted by continuously measuring the impedances at low frequency (10 mHz) and high frequency (10 kHz) at 5-minute intervals.

The corrosion rate showed a high value in the salt spraying process of the combined cyclic corrosion test, and gradually decreased in the drying process. The surface got wet due to the absorption of salt in the wetting process, which led to an increase of the corrosion rate again. The corrosion rate during the wetting process was higher than that during the salt spraying process. This result is attributed to the large influence of the oxygen reduction reaction as the reduction reaction in the early stage of corrosion. In the corrosion test including a rainfall process, the corrosion sensor showed a sharp increase in corrosion rate immediately after the rainfall process. In the early stage of corrosion, the shorter the rainfall time, the higher the corrosion rate. However, the corrosion rate in the rainfall process was almost the same value after the formation of corrosion products regardless of the rainfall time. Regarding the effect of rainfall on corrosion, it is well known that there are the corrosion suppression effect by washing away deposited salt and the corrosion acceleration effect by giving water, and the latter effect was larger under the corrosion test with the conditions of this study.

Optimizing design and fabrication of anodized tunneling surface for aluminium foils

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ABSTRACT: Electrochemical etching method has been used to construct anode aluminium foils with large surface area for electrolytic capacitor application. The applied current concentrated on surface defects would cause excessive corrosion of aluminium substrate and accelerate the initiation of merged tunnels. The addition of low-concentration corrosion inhibitor solutions effectively improved the anodized tunnel and electric current distribution. Various organic molecules as 8HQ, BTA, MBT, Citric Acid and Oleic Acid were analyzed using DFT and MD simulations. Relationship of physicochemical parameter and experimental tunnel density was established. Self-assembly treatment with sodium oleate presents considerable improvement on optimization of size and structure of etched tunnels. Experimentally, aluminium foils with high etched tunnel density nearly $1.5027 \times 10^7 \text{ cm}^{-2}$ could be prepared after 0.10 mmol L^{-1} sodium oleate treatment. Theoretically, molecular dynamic and quantum chemistry calculations reveal the self-assembly process of sodium oleate in forms of oleic acid on Al (100) facet. The results indicate that the oleic acid monolayer will form at molecular density nearly 0.855, 0.847 and $0.844 \text{ mol. nm}^{-2}$ as electric field E equal 0, $0.10 \text{ V \AA}^{-1}$ and $1.00 \text{ V \AA}^{-1}$, respectively. From calculations of surface coverage in electric field conditions, experimental adsorption isotherm has been corrected to determine the optimal concentration of self-assembly composition. Based on results of anodized tunneling, the subsequent demonstration application will be combined with the finite element method for numerical simulation and process optimization of field experiments.

Keywords: aluminium foils; corrosion; electrochemical etching; modeling.

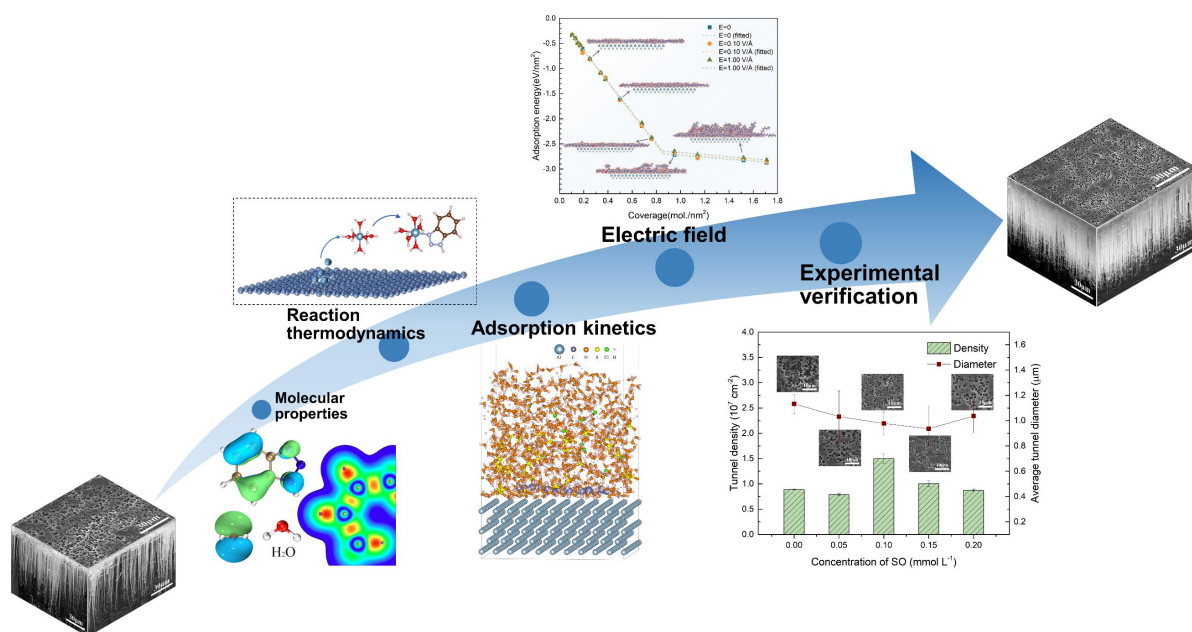


Figure 1. Optimizing design and fabrication of anodized tunneling surface for aluminium foils

Evaluating the effect of tin additions on the corrosion performance of Fe-Cr-xSn alloys in different environments

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Abstract

Stainless steel and Ni base alloys are widely used in different industrial applications due to their excellent corrosion resistance and mechanical properties. The observed kinetic stability of stainless-steel alloys is due to the formation of a “passive” reaction product film on the surface that effectively isolates the reactive metal from the corrosive environment. Different alloying additions in stainless steel alloys affect the structure and composition of their thin oxide film differently, so understanding the role of individual alloying elements on the passive film composition and localized corrosion is very important, in order to design and develop new corrosion resistant alloys for the industry. In this study, the independent effect of Sn on the localized corrosion resistance and its contribution towards passivity in Fe-Cr alloys was investigated in detail. Fe-16Cr-xSn cast austenitic alloys were developed. The results of electrochemical investigations using Potentiodynamic polarization (PDP) and Electrochemical impedance technique showed that the alloy with 0.2% Sn showed the highest localised corrosion resistance when the experiments were performed in 3.5% NaCl and 0.5M H₂SO₄ solution at room temp.

Keywords: Stainless steel; repassivation rate; EIS; Localised corrosion; Passivity;

Introduction

The phenomenon of passivity in metals and alloys contributed significantly to make metals-based civilization possible [1]. It is the passivity, due to which reactive metals behave in a passive manner when in contact with oxidizing aqueous environments, even though thermodynamically there is a large driving force for the reaction of the metal with oxygen. When a passive film is formed on the metal surface, underlying metal is not able to react further with the corrosive environment [2]. It is generally agreed that the quality of the “passive” film (its structure, defect density, chemistry) is the one responsible for increased corrosion resistance of the metal and alloy [3]. The metals, which exhibit passive behavior undergo localized corrosion problem due to localized defects/failures in the film and such defects account for almost 30% of industrial corrosion failure. 300 series austenitic stainless steels (8-12 wt. %Ni) are widely used as structural materials in corrosive environments due to their excellent corrosion resistance and mechanical and physical properties and ease of fabrication. Unfortunately because of their high price (due to high Ni content), these steels are not used in many application, where otherwise, they would be an ideal choice. So therefore, there is an trend to replace these expensive high Ni austenitic stainless steels with more economical alloys such as high Mn-N stainless steels (200 series). Mn (γ -stabilizer) which is 7 to 8 times cheaper per ton than Ni, varies from (6 ~11 wt. %) in these 200 series stainless steel alloys. But the Mn

alone is not as effective γ -stabilizer as Ni and this problem can be solved by using a combination of Mn and N in these new stainless steel alloys. Nitrogen in addition of functioning as an austenite stabilizer also improves corrosion properties and has several other benefits such as increased strengthening and retardation of sensitization. The addition of new alloying elements to develop new materials can influence both the corrosion resistance and the microstructure of alloys, which in turn will affect the mechanical and fabrication properties. Pitting Resistance Equivalent Number ($PREN = \%Cr + 3.3 \times \%Mo + 16 \times \%N$) can be used to estimate the corrosion resistance of stainless steels. It is a valuable equation, however it serves only as a guide to evaluate different stainless steel alloys. It is not recommended to use this as an actual corrosion resistance prediction tool for a specific corrosive environment. It is also worth mentioning that there are other alloying elements, which also affects the corrosion resistance properties significantly. There have been studies on the corrosion behavior of Mn and N in high Mn-N stainless steel alloys. It has been found that Mn usually decreases the corrosion resistance of stainless steels. Therefore, the addition of other elements such as Cu, Si and Sn may improve the corrosion resistance properties of such alloys. From corrosion point of view, some researchers reported the use of Sn in ferritic and austenitic stainless steels with conflicting results. The most probable reason for such conflicting results is that the researchers studied the effect of Sn in commercial alloys with many alloying additions and so there can be synergistic effects, which can be misleading.

Data shows that austenitic Fe-Cr-Mn-Ni-N (AISI 200 Series) SSs have corrosion resistance similar to those AISI 300 series SSs during atmospheric exposure and under oxidizing conditions [4]. The Fe-Cr-Mn and Fe-Cr-Mn-N steels are, however, inferior to 300 series with respect to general corrosion resistance especially under reducing conditions [5]. The reason for this is that chromium and nickel have beneficial effects on the corrosion resistance of steels, while manganese is generally considered to have a detrimental effect on the general corrosion resistance of stainless steels. The effect of Mn on the pitting resistance of Fe-Cr-Mn alloys is rather controversial with various effects being observed. Lunarska et al. [6] believe that this controversy is mainly due to the fact these steels are extremely sensitive to the presence of micro constituents such as carbon, nitrogen, sulphur and phosphorus [7,8]. Toor et al. [9-13] while investigating the independent effects of Cu and Si in such alloys, reported an improvement of corrosion resistance properties of these alloys. Si reported to increase the corrosion resistance of these alloys both in anodic and in chloride media by stabilizing the passive film with its enrichment. It is reported by several researchers that the addition of Sn improves the corrosion resistance properties of austenitic stainless steels in acidic environments [14-16]. The beneficial effect of increasing tin content on the corrosion resistance was related to Sn containing passive film. Nam et al. [14] investigated the synergism of Sn with other elements and reported that Sn can improve the passive film stability in the presence of Sb and Cu. Pardo et al. [17, 18] investigated the synergistic effect of Sn and Cu in AISI 304 and AISI 316 in acidic environment and reported the tin addition improved the corrosion resistance of these alloys. They found that the synergistic effect was much more than the independent effect of Sn or Cu in the alloys. However in another work, Pardo et al. [18], reported the maximum useful content of tin up to 0.1 wt. %. They have found that higher Sn contents, though can inhibit the pit nucleation and pit propagation rate was increased. This propagation was linked with severe acidification during the hydrolysis in Sn containing alloys. Other researchers such as Osozawa [19] and Takizawa et al. [20] also reported a positive effect of Sn and Cu together in austenitic stainless steels. *In this work, the independent effect of Sn on the corrosion performance in chloride and acidic chloride solution using potentiodynamic polarization and impedance spectroscopy etc. The results showed an improvement in overall corrosion performance of the alloys.*

Experimental methods

Fe–16Cr–xSn (x = 0, 0.15, 0.2 wt.%) alloy buttons were prepared using vacuum arc melting. The cast alloys were homogenized for around 90 min at 1150 °C and then hot rolled into 5 mm thick plates. The hot rolled plates were cold rolled to about 3mm thick sheets, and then solution annealed for 30 min at 1050 °C, followed by water quenching. Chemical composition of the alloys is given in Table 1. Prior to all the corrosion analyses, the SS alloy specimen ($1 \times 1 \times 10 \text{ mm}^3$) are positioned on the epoxy mounting with an electrically connected wire. After mounting, the surface of samples was mechanically ground with the emery sheets of different grit size and cleaned with distilled water and rinsed with ethanol.

Results and discussion

Corrosion Performance of the alloys in NaCl solution

Fig. 1 shows the potentiodynamic polarization of the designed alloys 3.5 wt.% NaCl solution at room temperature. It is clear that among the designed alloys, 0.15% wt.% Sn alloy exhibited the best corrosion performance when measured in terms of pitting potential (E_{pit}), corrosion potential (E_{corr}) and passive current density (i_{pass}). The lowest performance was shown by Alloy with 0% Sn and alloy with 0.2 % Sn showed good performance and pitting potential was almost similar like that of 0.15% Sn alloy, however its i_{pass} was higher. It seems that an increase in Sn content supports to the passivation in NaCl solution and that is quite evident based on electrochemical impedance spectroscopy results.

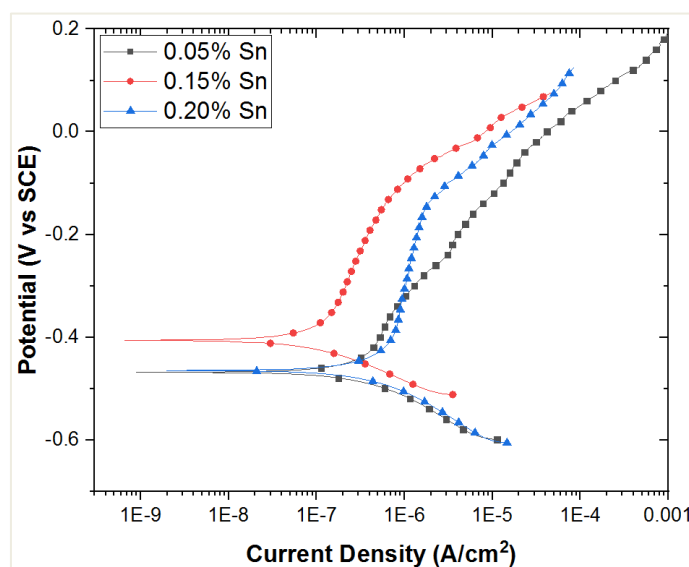


Fig.1. Potentiodynamic polarization of the alloys in 3.5 % NaCl solution.

The electrochemical impedance spectroscopy (EIS) is an important tool for examination of passive layers and pitting corrosion. Mansfeld et al. [20-22] have demonstrated that pitting corrosion of aluminum alloys can be detected by characteristic changes of impedance spectra. y showed the best performance. The phase angle occurred to be a very sensitive indicator of the initiation of pitting corrosion. An estimation of pit growth rate has been made by Mansfeld et al. [23,24]. The obtained relationships were similar to those of Hounkeler and Boehni [25] being pits growth rates as a function of exposure time. The paper of Scully et al. [26] indicates that impedance spectroscopy can be used to investigate the passivity of aluminum as well as its pitting behavior. EIS method has been employed to detect and monitor pitting corrosion of other materials than aluminum and its alloys [27]. Oltra and Keddam [28, 29] have compared impedance results with the theoretical model of pitting corrosion. Wenger et al. [30] have

shown that the characteristic features of the impedance spectra of stainless steel do not only depend on electrochemical state of the pits and of the remaining part of electrode surface, but also on the geometrical changes related to the development of pits. The change of roughness effect induced by the development of pits on steel was very seldom considered [31]. According to the opinion of Wenger et al. [30] the application of constant phase element instead of capacity should not be explained a priori by the influence of diffusion and possible porosity effect. However, Park and Pyun [32] elucidate the occurrence of constant phase element by roughening of the electrode surface resulting from the formation and growth of pits. Recently Darowicki et al. [33, 34] derived a new impedance method, which allows obtaining the changes of impedance spectra as a function of time. This method was successfully applied to investigation of stress corrosion cracking process, measurement of electrode surface changes and impedance investigation of kinetics and mechanism of electrode reaction during linear changes of potential. The application of this new method to investigation of pits initiation process on stainless steel is very interesting due to existence of some controversial opinions about the mechanism of this stage of pitting corrosion. The penetration mechanism has been discussed by Hoar et al. [35] and various others [36, 37]. Fig. 2 (a,b) shows the electrochemical impedance spectroscopy of the designed alloys in NaCl solution both the Nyquist and Bode plots respectively. Polarization resistance (R_p), an important property which is directly linked with the corrosion resistance of the materials, is derived from Nyquist plot. As the polarization resistance (R_p) is increased, the corrosion rate is decreased, so based on Fig. 2(a) it is clear that alloys exhibited one time constant and 0.15 % Sn alloy exhibited the highest corrosion resistance. All the alloys exhibited capacitive behaviour as one time constant is evident in Fig. 2(a). Bode plot of Fig. 2(b) shows the total impedance $|Z|$ and phase angle as a function of frequency respectively. It is quite obvious from Fig. 2(b) that alloys exhibited sort of constant total impedance along with low phase angle at higher frequencies. Both the total impedance ($|Z|$) and phase angle values were high at low frequencies and at intermediate frequencies a uniform slope of -1, was observed, which represents the capacitive performance.

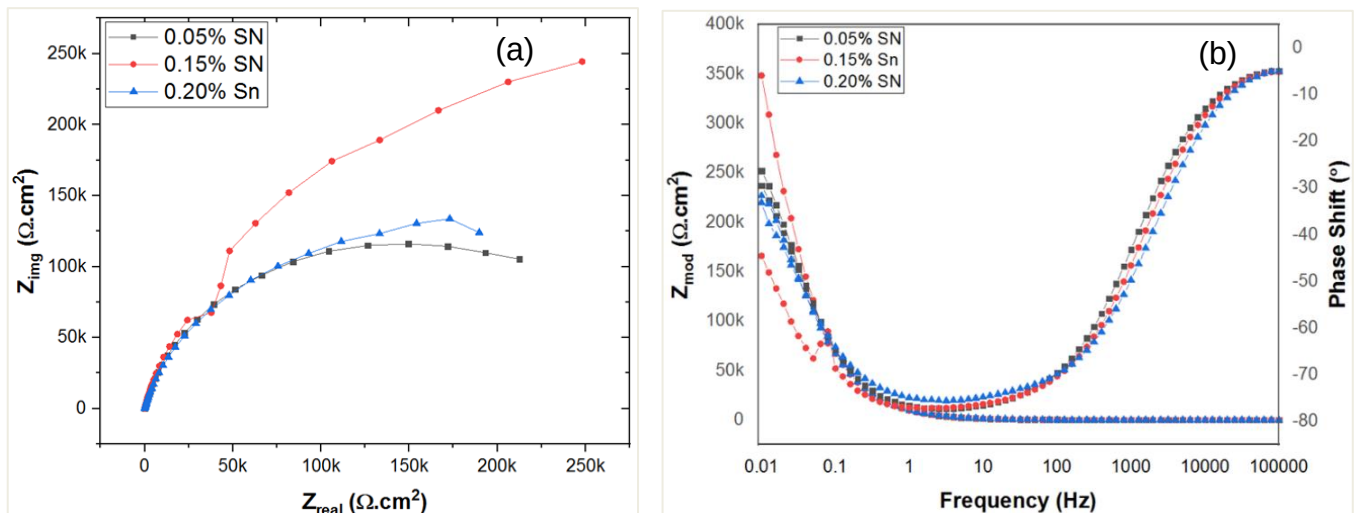


Fig.2. Electrochemical impedance spectroscopy of the designed alloys in chloride solution (3.5 % NaCl)

Corrosion Performance of the alloys in H₂SO₄ solution

Fig. 3 shows the potentiodynamic polarization of the designed alloys in 0.5 M H₂SO₄ solution at room temperature. It is clear that among the designed alloys, 0.2 wt.% Sn alloy exhibited the best corrosion performance among the developed alloys, when measured in terms of pitting

potential (E_{pit}), critical anodic current density (i_{crit}) and passive current density (i_{pass}). The lowest performance was shown by Alloy with 0% Sn, as it exhibited highest i_{crit} and lowest E_{pit} . Alloy with 0.2 % Sn showed the highest E_{pit} , lowest i_{crit} and i_{pass} values. It seems that an increase in Sn content supports to the passivation in acidic solution and that is quite evident based on electrochemical impedance spectroscopy results.

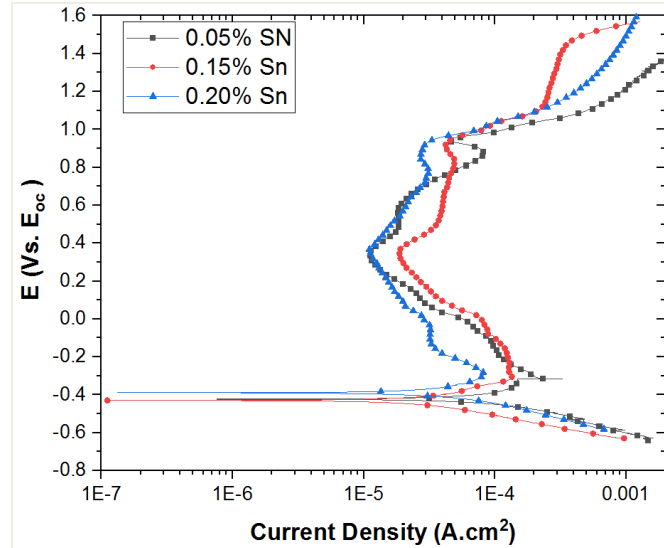


Fig.3. Potentiodynamic polarization of the alloys in 0.5M H₂SO₄ solution.

Fig. 4 (a, b) shows the electrochemical impedance spectroscopy of the designed alloys in acidic solution and it is clear from Fig. 4(a) that alloys exhibited one time constant and 0.2 % Sn alloy showed the best performance. Bode plot of the alloys confirmed the highest total impedance for alloy 0.2 % Sn. When the experiments were performed in 3.5 w.% NaCl + 0.5 M H₂SO₄ solution at room temperature, a similar trend was observed in which alloy with 0.2 wt.% showed the best corrosion performance among the developed alloys. Randles model was used for curve fitting and Table 1 shows the detailed EIS data after curve fitting.

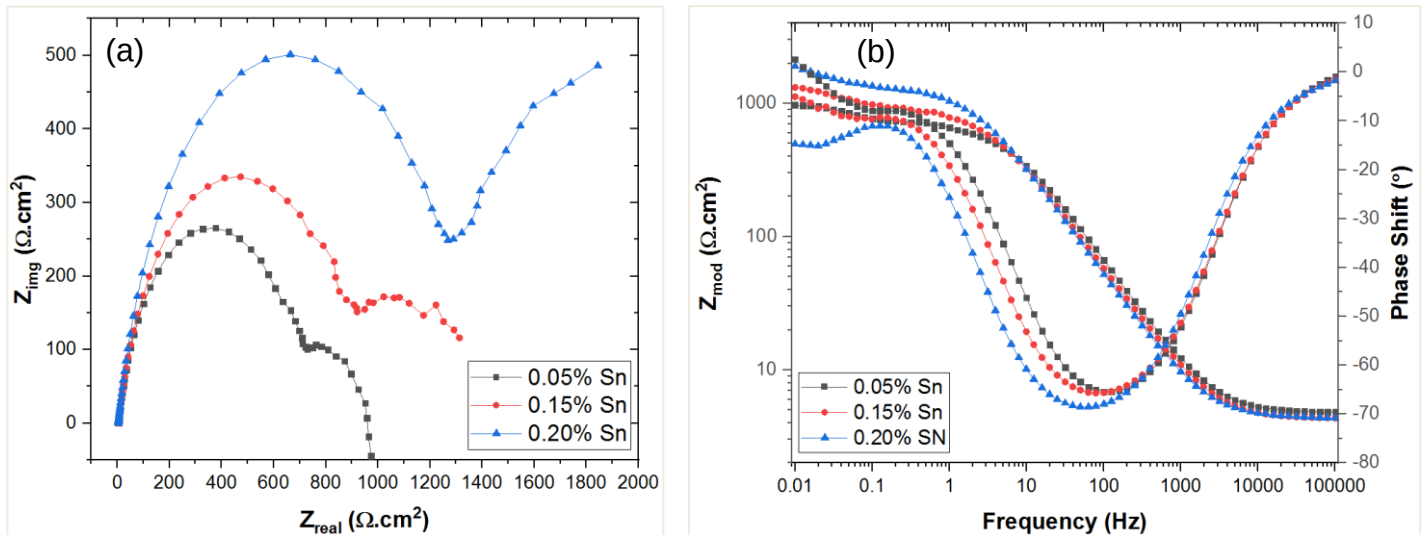


Fig.4. EIS of the designed alloys in 0.5M H₂SO₄ solution

Table 1. EIS data of the alloy after curve fitting using Randles model.

% Sn	Test Sol.	R _s	R _{ct}	R _f	C _{ct}	a-ct	C _{cf}	a-f	L
0.05	NaCl	5.6	2.08x10 ⁵	2.86x10 ⁴	1.48x10 ⁻⁵	7.76x10 ⁻¹	2.06x10 ⁻⁵	3.52x10 ⁻¹	-
	H ₂ SO ₄	4.7	2.10x10 ²	7.18x10 ²	9.47x10 ⁻³	9.46x10 ⁻¹	7.55x10 ⁻⁵	8.22x10 ⁻¹	1.255
	NaCl+H ₂ SO ₄	9.5	1.28x10 ³	7.59x10 ²	1x10 ⁻⁵	9.06x10 ⁻¹	5.40x10 ⁻⁵	7.85x10 ⁻¹	-
0.15	NaCl	4.9	2.90x10 ⁵	6.14x10 ⁴	2.68x10 ⁻⁵	8.96x10 ⁻¹	2.89x10 ⁻⁵	8.54x10 ⁻¹	-
	H ₂ SO ₄	4.2	9.20x10 ²	4.08x10 ²	9.15x10 ⁻³	8.14x10 ⁻¹	8.57x10 ⁻⁵	8.50x10 ⁻¹	-
	NaCl+H ₂ SO ₄	7.3	6.02x10 ²	2.39x10 ³	3.25x10 ⁻³	8.94x10 ⁻¹	5.96x10 ⁻⁵	8.03x10 ⁻¹	-
0.2	NaCl	6.5	2.10x10 ⁵	3.28x10 ⁴	2.05x10 ⁻⁵	8.63x10 ⁻¹	2.14x10 ⁻⁵	8.39x10 ⁻¹	-
	H ₂ SO ₄	4.3	1.34x10 ³	1.11x10 ³	8.25x10 ⁻³	7.93x10 ⁻¹	9.15x10 ⁻⁵	8.31x10 ⁻¹	-
	NaCl+H ₂ SO ₄	7.8	1.40x10 ³	3.43x10 ³	8.78x10 ⁻³	8.64x10 ⁻¹	7.0x10 ⁻⁵	8.64x10 ⁻¹	-

4. Conclusions

The results obtained based on different electrochemical experiments can be summarized as below;

- 1) The results of potentiodynamic polarization experiments in chloride solution showed that both the alloys with 0.15% and 0.2% Sn exhibited almost similar corrosion resistance.
- 2) Based on potentiodynamic polarization experiments in acidic chloride and acidic solution, it can be concluded that alloy with 0.2 wt.% Sn exhibited the highest corrosion resistance.
- 3) Alloy with 0.2% Sn showed highest pitting potential (E_{pit}), lowest passive current density (i_{pass}) and critical anodic current density (i_{crit}) respectively.
- 4) Electrochemical impedance spectroscopy results exhibited the highest semicircle (Nyquist plot) for alloy with 0.2 wt.% Sn, which means this alloy has the highest polarization resistance and lowest corrosion rate.

Acknowledgements

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Modelling of the Physical and Electronic Properties of Hematite (α -Fe₂O₃) with Density Functional Theory

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Steel is one of the most utilised materials in the industry. Steel corrodes when it is exposed to air and moisture in the atmosphere. The corrosion of steel is one of the main issues in many industries. Understanding the electrochemical reactions involved in the corrosion process would help corrosion engineers detect corrosion issues in an early stage and take preventive measures. The underlying mechanisms have been investigated experimentally by researchers with various techniques. However, there's still a lack of understanding of molecular-level mechanisms, which involve charge transfer processes, the formation and breakup of chemical bonding at a complicated metal-oxide-liquid interface. To model this highly complicated physical-chemical process involved in the corrosion process a multi time and length scale approach is needed that is founded in predictive, accurate and highly efficient computational methods. As a first step we have utilised first principles calculations based on density functional theory (DFT) to compute the electronic structure of the metal-oxide bulk and surfaces.

One of the most common products from iron corrosion is hematite (α -Fe₂O₃). This work studied bulk hematite's (α -Fe₂O₃) physical and electronic properties, including the equilibrium lattice constant, bond length, band structure, and density of state (DOS). Simulations with different treatments of electronic exchange and correlation (PBE0, GGA+U, GGA-PBE) were compared to establish the best compromise of computational efficiency and accuracy. Particular care is taken to describe correctly the nature of the band gap and the magnetic coupling which emerge as key factors in the thermodynamics and kinetics of interface interactions.

This contribution will provide some ideas about the underlying mechanisms of undercoating corrosion using atomistic simulations. We utilised a combination of first principle techniques, the density functional theory-based molecular dynamics (DFT-MD) simulations, to obtain the energies of surface protonation and the chemical reactions of adsorbates. The widely used code CRYSTAL is found to be highly efficient for hybrid exchange density functional theory calculations which are required for

strongly correlated metal oxides, and CP2K implements first principles molecular dynamics of complex interfaces.

Evaluation of local corrosion in AlZn10Si8Mg aluminum cast alloy

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Intermetallic precipitates in aluminum alloys play an important role in the corrosion resistance and durability of the aluminum products. In this paper, we will investigate the relation between microstructure and local corrosion on AlZn10Si8Mg aluminum cast alloy.

Light optical microscopy (LOM), SEM/EDX and SKPFM will be used to characterize the electrochemical behavior of precipitates like Mg_2Si or AlFe versus the aluminum matrix.

Figure 1 shows a typical microstructure of AlZn10Si8Mg obtained by Light optical microscopy. Mg_2Si and AlFe precipitates have been identified using SEM/EDX analysis.

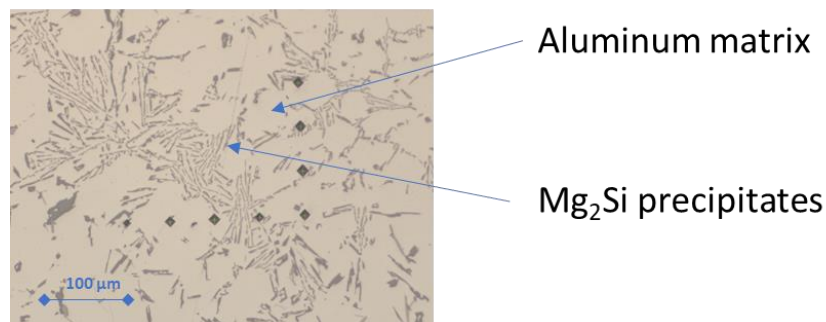


Figure 1 : microstructure of AlZn10Si8Mg

Using an indent network it will be easy to perform correlative imaging between SEM/EDX and SKPFM measurement and attribute a Volta potential to a specific phase (precipitates, matrix).

In figure 2, AFM and SKPFM maps show the topography and the Volta potential repartition obtained on AlZn10Si8Mg polished sample. Mg_2Si precipitates protrude slightly from the surface because of their greater hardness than the matrix and have a lower potential than the matrix corresponding to a nobler element.

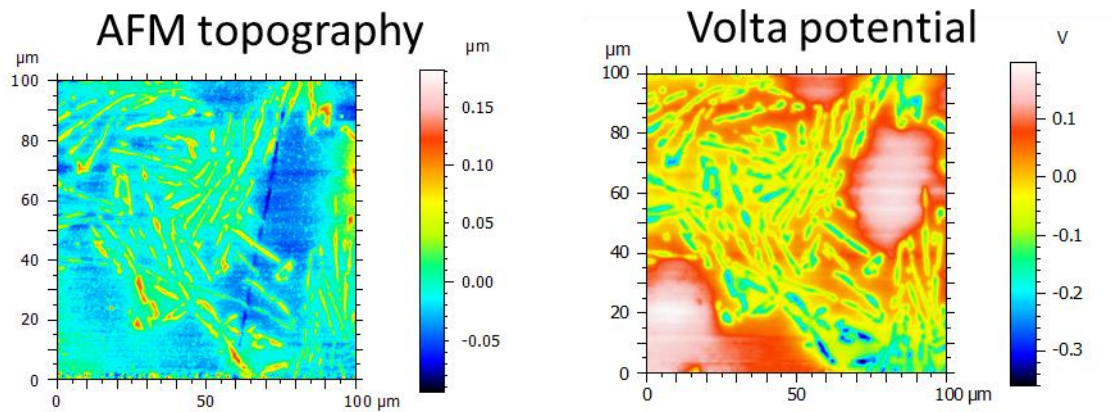


Figure 2: AFM (topography) and SKPFM observations on AlZn10Si8Mg area

Conclusions:

Identification of intermetallic precipitates on AlZn10Si8Mg have been done by coupling LOM and SEM/EDX analysis.

Coupling SEM/EDX and SKPFM analysis in the same location allow us to determine the volta potential of the Mg_2Si phase and the matrix. Using this data it will be possible to estimation the mechanism of local corrosion in such aluminium alloy.

Corrosion modeling of welded joints of wind power facilities

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Corrosion problems in offshore wind power facilities are a significant contributor to operation and maintenance (O&M) costs, typically around 15–30 percent of the total life cycle costs. Corrosion can degrade the structural material, contribute to fatigue cracking, brittle failure, and unstable failure [1], and the integrity of the entire structure can be significantly compromised. In the literature, there are many numerical simulations of the growth of pits and cracks in seawater under the influence of mechanical loads [2]. The main drawback of these studies is that they do not take into account the difference in the equilibrium potential of the structural parts of the welded joint, which leads to the formation of a multi-electrode electrochemical interaction.

This work aims to develop a methodology for numerical modeling of corrosion processes in the zone of the welded joint, as well as the electrochemical interaction of metal surfaces in places of insulation defects.

It is proposed to develop the model in 2 stages:

1. Corrosion modeling of a welded joint considering the different electrochemical activity of its sections (Fig. 1, a). This step allows to determine the value of corrosion currents and calculate the corrosion rate based on these data.
2. Similar to step 1, with modeling of the anti-corrosion coating (Fig. 1, b, c).

COMSOL corrosion simulations require the following input parameters for each material: cathodic and anodic exchange current density, local current density, Tafel slopes for anodic and cathodic reactions, and equilibrium potential. Most of the electrochemical input data for the simulations are taken from the COMSOL material library for "High Strength Low Alloy Steel". The base metal (BM), heat affected zone (HAZ) and weld metal zone (HSM) differed only in the value of the equilibrium potential taken from [3].

The preliminary results of the simulation of the distribution of the corrosion current show its greatest value at the BM-HAZ boundary. At the next stage, a partial repair of the anti-corrosion paint was simulated (one of the paint defects was eliminated). In this case, both an increase to 60% and a decrease to 20% of the corrosion current were recorded. The results indicate the complexity of electrochemical

interactions in multi-electrode systems and confirm the possibility of simulating the electrochemical interaction in COMSOL for more than 2 defects. The resulting distribution of corrosion currents on the surface helps to identify areas with a high risk of corrosion.

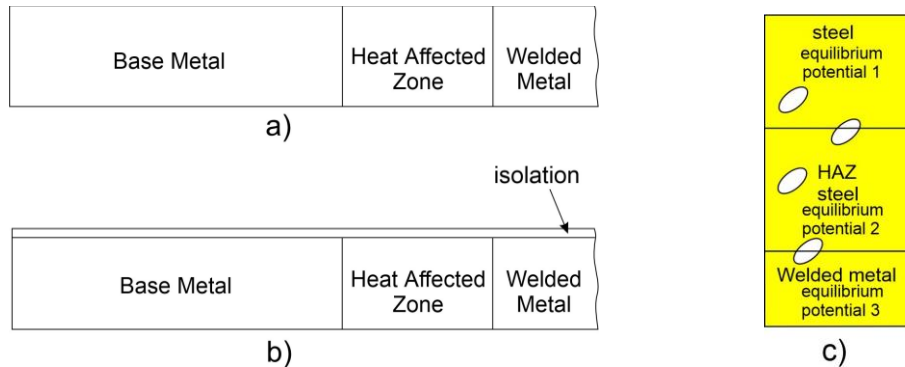


Fig. 1. Scheme of construction of the geometry of the sample for modeling: welded joint (WJ) (a), WJ with isolation (b), WJ with isolation defects (c)

Conclusions:

Computer modeling allows to quickly assess the course of corrosion processes, however, most software packages have limitations when building models. To study the corrosion processes of wind power facilities, it is suggested to use modeling in COMSOL Multiphysics followed by its correction using experimentally measured electrochemical parameters in order to quickly assess the impact of changes in environmental parameters on the speed of corrosion processes and to identify areas of the structure that require additional protection and regular monitoring. It is necessary to widely combine natural and experimental studies with computer modeling of corrosion processes.

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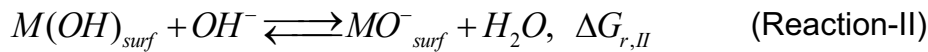
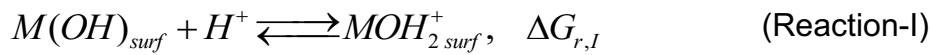
Correlation between pitting susceptibility and surface acidity, point of zero charge of passive film on aluminum

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The dependence of point of zero charge (PZC) on intrinsic surface acidity of passive film (Al_2O_3) on aluminum are investigated using density functional theory (DFT) calculations. The modifications of Zn, Al, Cr, Nb, Si, Mo and Sc alloying elements on NH_3 adsorption, NaCl adsorption, pH_{pzc} of Al_2O_3 and pitting resistance of aluminum are discussed. The exact correlation between pitting susceptibility and surface acidity, pH_{pzc} of passive film is proposed. The efficiency of above elements on pitting resistance of aluminum gives the ratios that Si: Zn: Cr: Mo: Nb: Sc = 3.0: -0.5: 1: 3.3: 2.2: 0.1. The influences of Sc on pitting potential and pH_{pzc} of aluminum are predicted based on the results and confirmed by experiments.

DFT-Calculated pH_{pzc}

The oxides or the passive-film-covered metals exposed to aqueous solutions show terminating surfaces with an outermost layer of hydroxyl groups due to their interaction with water molecules. The hydroxyl groups on surface will interact with H^+ and OH^- from solution following the Reaction-I and Reaction-II, which makes the surface site positive-charged or negative-charged.



where $\Delta G_{r,I}$ ($\Delta G_{r,II}$) represents the Gibbs free energy of Reaction-I (Reaction-II) respectively. The pH_{pzc} of the oxides surface is calculated by DFT based on the thermodynamic. And the effect of alloying elements oxidizing into the passive film on the pH_{pzc} of oxides is studied.

Correlations between surface acidity and pH_{pzc} , pitting susceptibility

The surface acidity of Al_2O_3 is investigated using the probe NH_3 molecule to be adsorbed on surface, and the adsorption of NaCl is also considered. In order to reveal the relevance between pitting susceptibility and surface acidity as well as pH_{pzc} , the adsorption energy of NaCl , the calculated pH_{pzc} of $\text{X-Al}_2\text{O}_3$ and the pitting potential of the binary alloys of aluminum are plotted as a function of the adsorption energy of NH_3 .

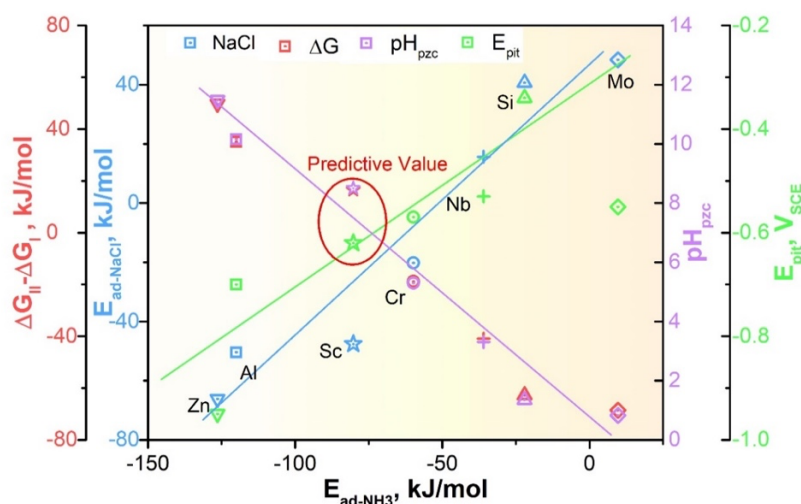


Fig. 1 The correlations between susceptibility to Cl^- , pH_{pzc} , pitting potential and surface acidity on $\text{X-Al}_2\text{O}_3$ surface.

In this work, the bridges between surface acidity and pH_{pzc} , pitting susceptibility are established by DFT calculations. Based on the model, the efficiency of above elements on pitting resistance of aluminum is evaluated, which gives the ratios that $\text{Si: Zn: Cr: Mo: Nb: Sc} = 3.0: -0.5: 1: 3.3: 2.2: 0.1$. Furthermore, the pitting potential of $\text{Al-1.5\% Sc}$ is predicted according to the calculated results and confirmed by experiments.

Characterization of aluminum alloys for its application as end plate material in fuel cells

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Abstract In this study, the electrochemical corrosion behavior of aluminum alloys AlMg3 and AlSi10Mg(Fe) – used as the potential end plate material in a fuel cell – was analyzed in the low-conductive coolant Glycantin. The focus was on the comparison between the initial state and the anodized (ELOXAL-coated) surface state. For analysis of the corrosion sensitivity, the electrochemical impedance spectroscopy and potentiodynamic polarization were carried out. The experiments were conducted at 80 °C and at room temperature, analyzing the corrosion characteristics of the aluminum alloy at operating conditions and at non-operating conditions of the fuel cell. Subsequently, electron microscopic investigations were performed, identifying the damage evolution characteristics of the corroded surface states. The results showed that with increase in temperature, the uncoated Al alloys are more prone to corrosion. The ELOXAL-coated surface showed higher corrosion resistance in the coolant, both at room temperature and at 80 °C.

Keywords Aluminum alloy; coolant; end plate; fuel cell; electrochemical characterization



Vergabe und Projektbegleitung durch:



Introduction

End plates are one of the components of a Proton Exchange Membrane Fuel Cell (PEMFC) stack. They provide structural support to the entire stack and have an inlet and outlet for the reactant gases and the coolant. Thus, the end plate material should have good mechanical and electrochemical stability. Aluminum alloy is the most commonly used material as end plate in a fuel cell. It has low density, high strength, low-cost production and is easy to manufacture [1]. The corrosion resistance of aluminum alloys depends highly on the pH of electrolyte medium and the naturally formed oxide layer helps to inhibit the corrosion attack. In acidic medium, the natural oxide layer is not stable and can be destroyed locally. In neutral solutions, they have high tendency to passivate and thus exhibits good corrosion resistance [2]. To improve corrosion resistance, anodization or ELOXAL coating is done. It is an electrolytic oxidation process where an aluminum oxide layer is grown on and bound to the natural oxide layer on the surface of aluminum alloy. This ELOXAL layer is amorphous, and up to few micrometers thick. It protects the surface of the alloy by acting as a barrier to the corrosion attack [3].

The main aim of this study was to understand the corrosion behavior of uncoated and ELOXAL-coated aluminum alloys in low conductive fuel cell coolant under the working fuel cell conditions. For this purpose, fuel cell coolant Glycantin FC G20-00/50 was used. It is an ethylene glycol based inhibited coolant with low electrical conductivity. Since the operating temperature of PEMFC is 80 °C, the electrochemical investigations were carried out at room temperature and at 80 °C. These electrochemical studies were done with electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization techniques. The surface changes due to the corrosion were then investigated by scanning electron microscope (SEM).

Materials and Methods

Materials

In this study, two aluminum alloys: AlMg3 and AlSi10Mg(Fe) with the chemical composition given in Table 1 were used. AlMg3 alloy was manufactured by casting process followed by milling whereas AlSi10Mg(Fe) alloy was manufactured by die-casting process. AlSi10Mg(Fe) alloy was obtained from Handtmann Leichtmetallgießerei Annaberg GmbH. The samples for electrochemical analysis were cut from automotive parts and were measured without any surface preparation to analyze the corrosion behavior of the aluminum alloys in as-received state.

Table 1 Chemical composition of AlMg3 and AlSi10Mg(Fe) (wt.-%)

	Si	Fe	Cu	Mn	Mg	Ni	Zn	Ti	Al
AlMg3	0.4	0.4	0.1	0.5	2.6 - 3.6		0.2	0.15	Rest
AlSi10Mg(Fe)	9 - 11	0.45 - 0.9	0.08	0.55	0.25 - 0.5	0.15	0.15	0.15	Rest

Methods

The electrochemical studies were performed on as-received uncoated and ELOXAL-coated alloys. ELOXAL layer was applied on both aluminum alloys. Before the ELOXAL process, the AlMg3 alloy was cleaned with ethanol and water. To remove surface contaminations and the passive oxide layer, the sample was pickled in 10 % NaOH at 55 °C for 1 min. This was followed by neutralization in 33 % HNO₃ at room temperature for 1 min. After pickling and neutralization, the samples were washed with distilled water for 2 min. The process of pickling

and neutralization was not done for AlSi10Mg(Fe) alloy. Instead, the samples were rinsed with acetic acid to degrease the surface. Anodization was done in 17 % H₂SO₄ at room temperature for 45 min at constant current of 1 A/dm² for AlMg3 alloy and at constant voltage of 20 V for AlSi10Mg(Fe) alloy. After the anodization, the samples of both alloys were sealed cooked in water for 45 min at ~100 °C.

The electrochemical studies of the as-received uncoated and ELOXAL-coated alloys were performed using a Gamry Instruments Interface 1010 B potentiostat. A three-electrode cell setup was used with aluminum alloy as working electrode, Pt mesh as counter electrode and a saturated Ag/AgCl electrode as reference electrode. Ethylene glycol-based coolant Glyscant FC G 20-00/50 was used as electrolyte. The measurements were performed at room temperature (RT) and at 80 °C. The electrolyte temperature was kept at 80 °C using a thermostat. Before and after the measurements, the samples were rinsed with ethanol and distilled water. To reach an equilibrium state, the system was kept steady for 30 mins before starting the electrochemical measurement. Potentiodynamic polarization was performed at a scan rate of 0.1 mV/s from $-0.2 \text{ V} \leq E_{\text{corr}} \leq -0.1 \text{ V}$ for uncoated samples and from $-0.2 \text{ V} \leq E_{\text{corr}} \leq 0.3 \text{ V}$ for ELOXAL-coated samples. Electrochemical Impedance Spectroscopy (EIS) was carried out at frequency range of 20 kHz to 0.01 Hz with a potential amplitude of 10 mV for uncoated samples and 50 mV for ELOXAL-coated samples. The obtained impedance data was fitted to an equivalent circuit using the Gamry Echem Analyst program (Fig. 1). Scanning electron microscope (SEM - TESCAN, MIRA 3 XMU) with accelerating voltage of 20 kV for uncoated samples and 10 kV for ELOXAL-coated samples was used to study the surface morphology before and after the electrochemical measurements.

Results

Electrochemical impedance plots obtained for uncoated and ELOXAL-coated Al alloys at RT and at 80 °C are shown in Fig. 2 (A-D) in the form of Nyquist plots. The plots for uncoated Al alloys (Fig. 2A-B) are characterized by one semicircle and an inductive loop at the low frequency region for AlMg3 alloy at 80 °C and AlSi10Mg(Fe) alloy at RT and 80 °C. The exception is AlMg3 alloy at RT exhibiting only one semicircle. This impedance plots were modeled by equivalent circuit as shown in Fig. 1A. Here R_s is solution resistance, R_p is polarization resistance, CPE is constant phase element and the inductive elements are R_L and L . The corrosion resistance of the material can be understood from the diameter of the semicircle representing the polarization resistance. With increase in polarization resistance, the corrosion sensitivity is decreased indicating the material is corrosion resistant. The diameter of uncoated AlMg3 alloy at RT is almost $6 \times 10^6 \text{ ohm cm}^2$ while at 80 °C is $1.25 \times 10^5 \text{ ohm cm}^2$. Whereas, for AlSi10Mg(Fe), the polarization resistance is up to $5 \times 10^5 \text{ ohm cm}^2$ at RT and $4 \times 10^4 \text{ ohm cm}^2$ at 80 °C. This indicates that with increase in temperature, the polarization resistance is decreased and as a result, the material is more prone to corrosion. Also, the presence of inductive loop at low frequency region suggests that there is an increase in corrosion sensitivity.

In case of ELOXAL-coated Al alloys (Fig. 2C-D), a highly depressed semicircle at high frequency range followed by initiation of another semicircle curve is observed. The equivalent circuit is represented by three resistors and two constant phase elements (CPE) in Fig. 1B. The inner semicircle corresponds to the resistance (R_1) of passive oxide layer and the outer semicircle represents the resistance (R_2) due to porous and inhomogeneous ELOXAL coating. The polarization resistance of all the ELOXAL-coated Al alloys is higher than uncoated Al alloys. Furthermore, no inductive loop at low frequency region is observed here. This shows the effectiveness of this ELOXAL layer against corrosion.

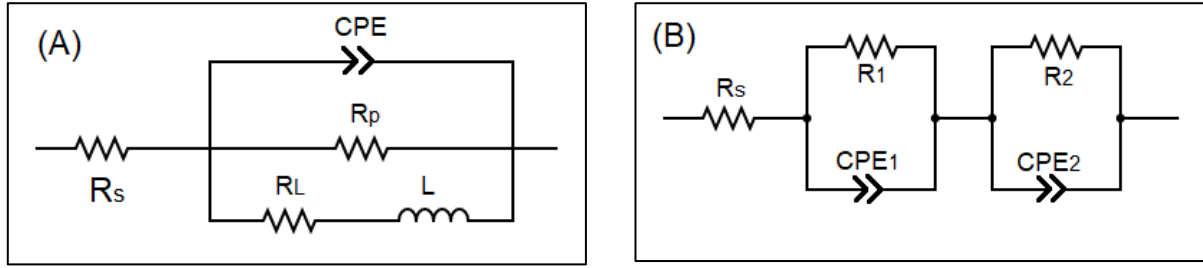


Fig. 1 The equivalent circuit used for (A) uncoated and (B) ELOXAL-coated Al alloys

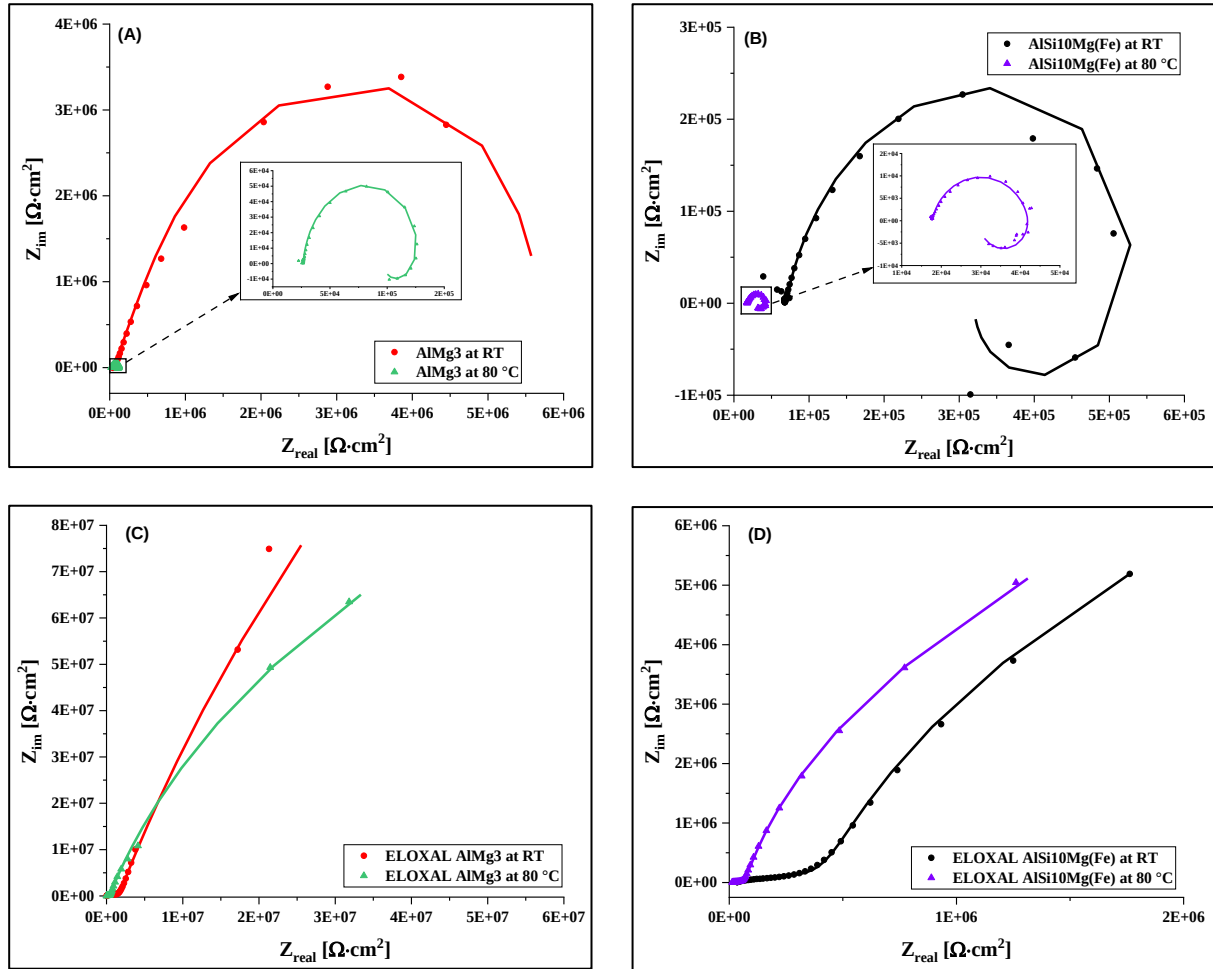


Fig. 2 Nyquist plots for (A) uncoated AlMg3 alloy at RT and 80 °C; (B) uncoated AlSi10Mg(Fe) alloy at RT and 80 °C ; (C) ELOXAL-coated AlMg3 alloy at RT and 80 °C ; (D) ELOXAL-coated AlSi10Mg(Fe) alloy at RT and 80 °C in coolant.

Fig. 3 shows the potentiodynamic polarization curves of uncoated and ELOXAL-coated AlMg3 and AlSi10(Mg)Fe alloys in coolant at RT and 80 °C. For both uncoated Al alloys (Fig. 3A), it can be observed that at 80 °C, there is a decrease in corrosion potential and an increase in current density. The corrosion potential (E_{corr}) value is shifted from -0.51 V to -0.55 V and -0.46 V to -0.48 V for uncoated AlMg3 and AlSi10Mg(Fe) alloys, respectively. This indicates that when the temperature is increased, the material is less resistant to corrosion. The anodic current density of AlMg3 alloy sees no significant change at RT implying that the material shows passivation behavior and is protecting the surface against corrosion. However, at 80 °C, there is a slight peak increase at around -0.2 V. This could possibly be due to local breakdown of passive oxide layer. The micrographs obtained by SEM after the polarization of AlMg3 alloy

at RT showed no changes in the surface. But at 80 °C (Fig. 4A), it was observed that for AlMg3 alloy, at certain weak points on the surface, there is an initiation of corrosion attack and also flaking of the surface material. This flaking of the surface is generally caused as a result of stress between the grains. In case of AlSi10Mg(Fe) alloy, there is an increase in the anodic current density both at RT and 80 °C. At RT, the surface analysis showed no changes but at 80 °C (Fig. 4B), a local passive oxide breakdown was observed. With increase in temperature, the passive oxide layer is not protective enough and as a result, the material is prone to undergo corrosion. This behavior agrees with results observed in EIS plots. On comparing the two uncoated Al alloys, it is evident that AlMg3 alloy is more corrosion resistant than AlSi10Mg(Fe) alloy irrespective of the temperature change.

For both of the ELOXAL-coated alloys (Fig. 3B), the corrosion potentials at RT and 80 °C remains almost similar. But there is slight increase in the current densities at 80 °C. The anodic current density shows passive behavior generally associated with ELOXAL-coated material. No visible signs of corrosion was found for ELOXAL-coated AlSi10Mg(Fe) alloy at RT and 80 °C and the surface morphology remains nearly unaffected. For ELOXAL-coated AlMg3 alloy (Fig. 4C), presence of voids and microcracks were observed in the ELOXAL layer. With an increase in temperature (Fig. 4D), the initiation of corrosion attack from these voids and microcracks were observed at very few sites. But overall, the surface of the samples was remaining unaffected indicating the high corrosion resistance of ELOXAL coating.

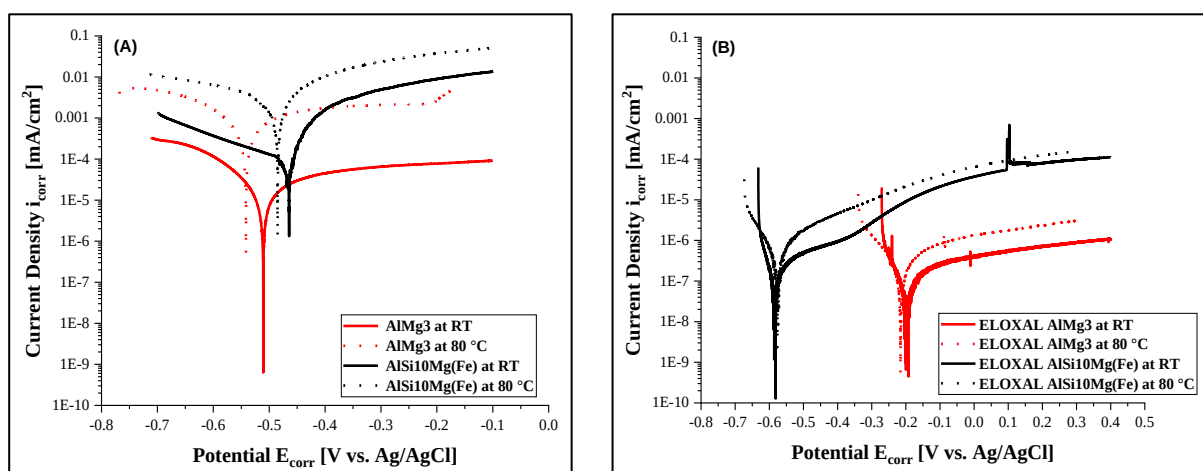


Fig. 3 Potentiodynamic polarization curves of (A) uncoated and (B) ELOXAL-coated AlMg3 and AlSi10Mg(Fe) alloys in coolant at RT and 80 °C

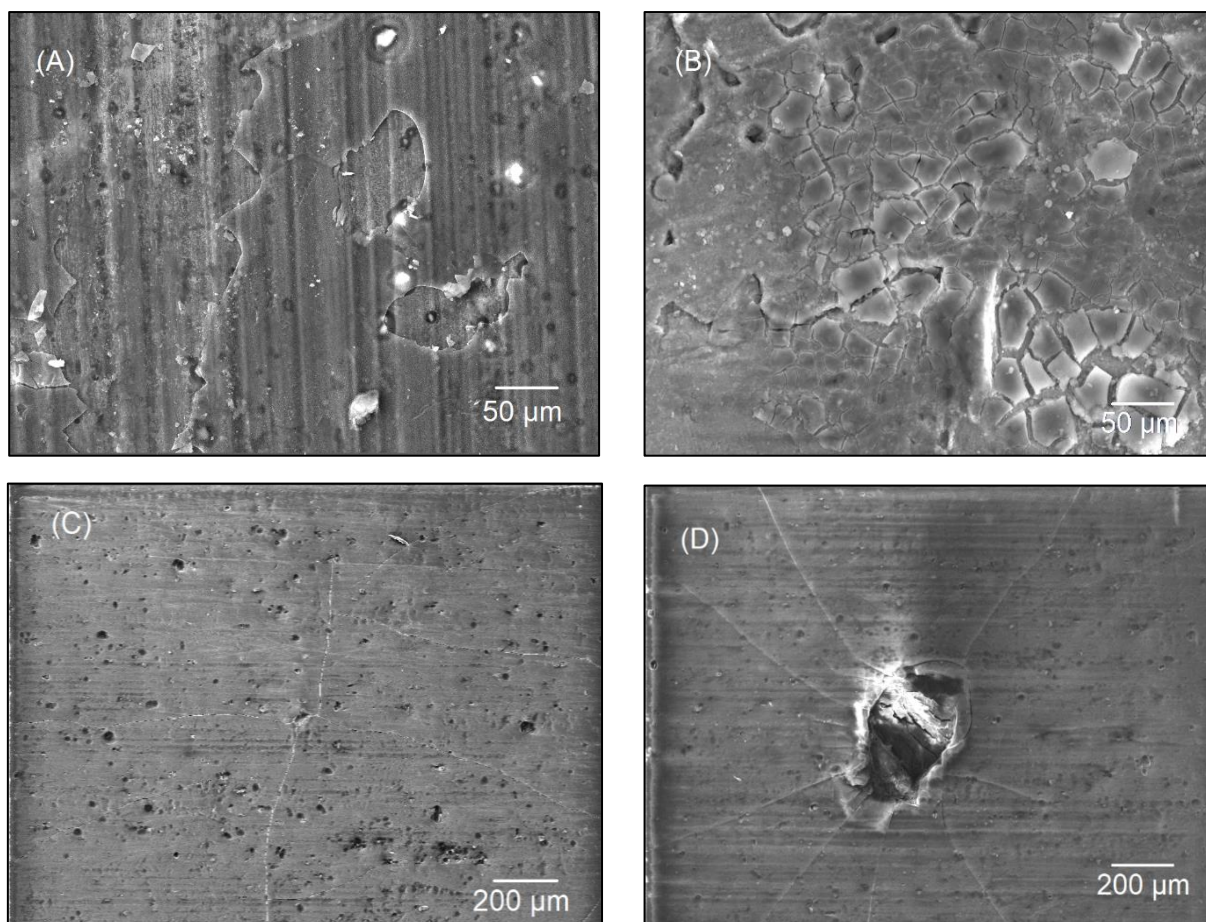


Fig. 4 SEM images of (A) uncoated AlMg3 alloy after polarization at 80 °C; (B) uncoated AlSi10Mg(Fe) after polarization at 80 °C; (C) ELOXAL-coated AlMg3 alloy before polarization at 80 °C; (D) ELOXAL-coated AlMg3 alloy after polarization at 80 °C

Conclusion

In this work, the electrochemical corrosion behavior of uncoated and anodized (ELOXAL-coated) AlMg3 and AlSi10Mg(Fe) alloys in coolant at room temperature and 80 °C was analyzed by electrochemical impedance spectroscopy and potentiodynamic polarization techniques.

From EIS spectra, the increase in corrosion sensitivity of the Al alloys was observed with increase in temperature. Also, ELOXAL-coated Al alloys exhibited higher corrosion resistance of the material in the coolant at both temperatures. Similar results were also obtained by polarization curves indicating that the EIS spectra are in good agreement with the polarization curves.

The overall surface morphology of both uncoated Al-alloys after the electrochemical analysis at room temperature remains unaffected implying the protective behavior of passive oxide film. But at 80 °C, corrosion attack was initiated at certain weak points on the surface leading to flaking off the material for uncoated AlMg3 alloy and breakdown of passive oxide layer for uncoated AlSi10Mg(Fe) alloy. The presence of voids and microcracks in the ELOXAL layer of AlMg3 alloys became the target site for the corrosion. But such sites were very few and showed the protective behavior of ELOXAL-coated Al alloy against corrosion. Consequently, the ELOXAL-coated Al alloy surfaces indicate a significant increase in corrosion durability and finally contribute to an increase in long-term performance of the fuel cell.

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Electrochemical noise analysis using statistical analysis, frequency domain analysis and frequency-time domain analysis

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In contrast to established corrosion monitoring methods, e.g., Tafel analysis (figure 1) and electrochemical impedance spectroscopy (figure 2), electrochemical noise analysis (ENA) has great potential for identifying the corrosion type. For this, voltage and current are recorded without electrical perturbation (figure 3), which makes it non-destructive and widely applicable [1]. This is particularly relevant for limited power supply applications such as corrosion protection in offshore asset management. The focus of this work is to investigate and enhance both the corrosion rate determination and corrosion type determination with three different approaches.

Electrochemical Noise Analysis

All experiments presented (p. 2) were done with carbon steel (C110S 1.1274) WEs, Ag/AgCl RE (3 M KCl) and 0.1 M K₂SO₄ electrolyte connected in zero-resistance-amperemeter (ZRA) mode. The simplest approach, statistical analysis (figure 4), yields a noise resistance $R_n(t)$ as the quotient of standard deviations of voltage and current. Under strict conditions, $R_n(t)$ can be assumed equal to the polarization resistance from Tafel analysis to calculate the corrosion rate. The frequency domain analysis (figure 5) consists of power spectral density computations of EPN and ECN. The division generates a squared spectral noise impedance $R_{sn}(f)$, which can be related to corrosion rate and type. [1]

The latest and most promising approach is the frequency-time domain analysis done via wavelet transform (figure 6). The signal is decomposed into several frequency ranges to determine on which time scale the corrosion process takes place. Short time scale crystals (D2, D3) indicate metastable pitting, whereas medium time scale crystals (D4 – D6) and long time crystals (D7-D8) show the presence of localized and general corrosion, respectively. The dominating corrosion type is evaluated in an energy distribution plot (EDP) (figure 7). [2]

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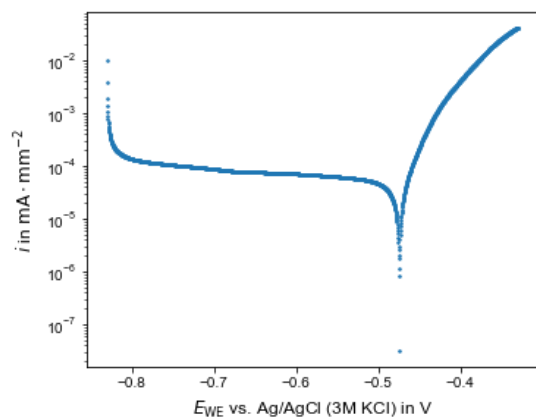


Figure 1: Tafel plot; scan rate 0.1 mV/s, voltage range $E_{\text{corr}} \pm 250$ mV.

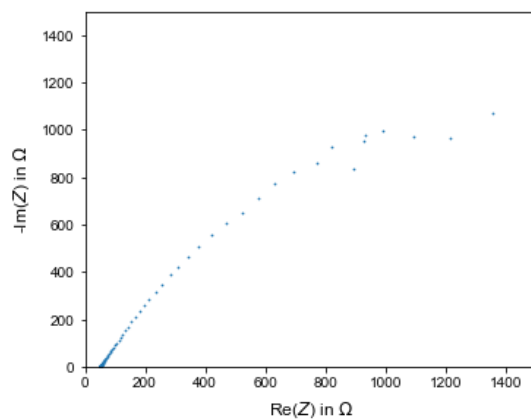


Figure 2: Nyquist plot; frequency range 100 mHz – 100 kHz, voltage amplitude 10 mV.

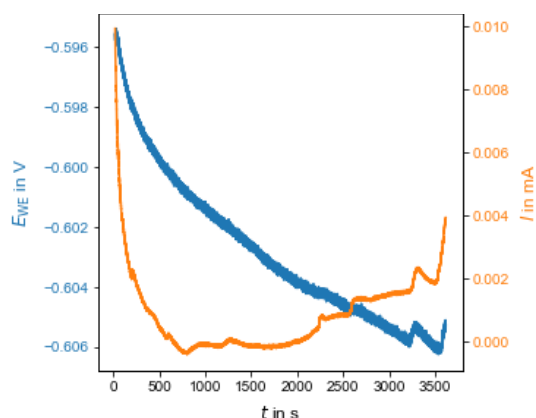


Figure 3: Electrochemical potential noise (EPN) and electrochemical current noise (ECN).

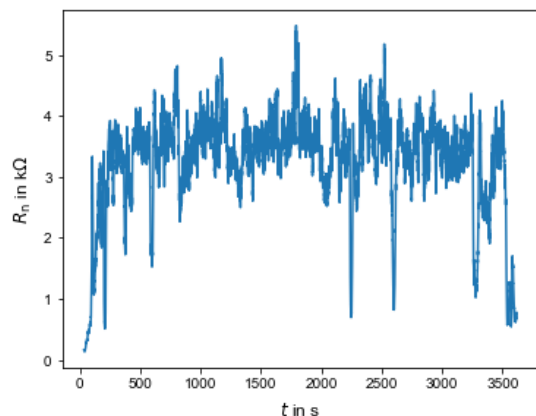


Figure 4: Noise resistance $R_n(t)$ via statistical analysis as quotient of standard deviations of EPN and ECN.

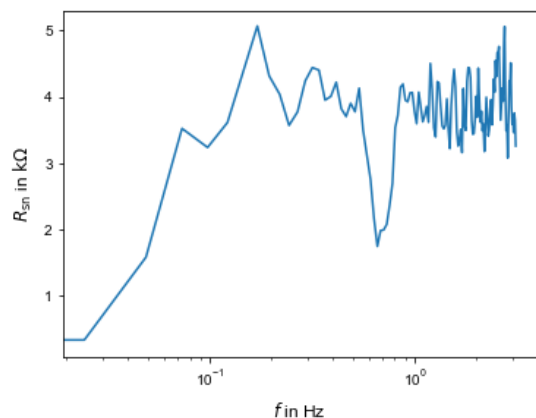


Figure 5: Spectral noise impedance $R_{\text{sn}}(f)$ calculated with power spectrum densities of EPN and ECN via FFT.

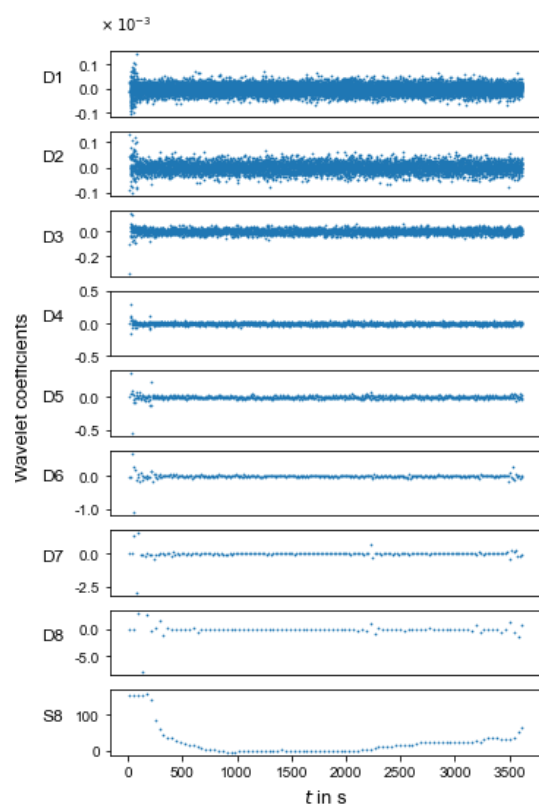


Figure 6: Decomposition of ECN in smooth crystal (S8) and detail crystals (D1-D8) via wavelet transform (db4 wavelet).

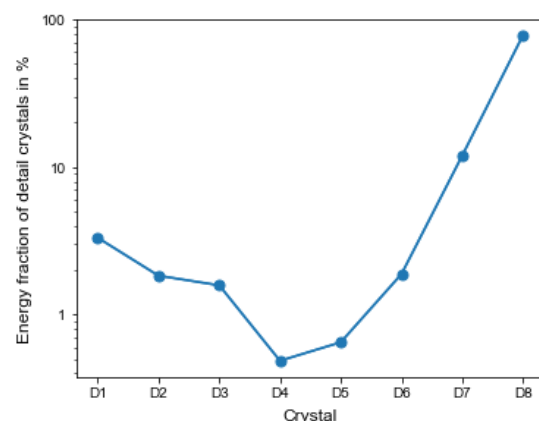


Figure 7: Energy distribution plot of D1-D8 calculated from decomposed signal.

Novel Approaches to Corrosion Analysis through Data-Driven Computer Vision and Reflective Microscopy

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Stainless steel and other metals have been vital to human progress, forming a protective film on their surfaces that lowers corrosion rates. However, localized corrosion remains a risk, particularly when aggressive species like chloride ions attack the surface film. Recent advances in optical microscopy have enabled in-situ investigation of localized corrosion, generating vast amounts of data that require new data analysis and computer vision techniques. This study discusses such techniques and their application in analyzing the generated data.

We studied the electrochemical corrosion of stainless steel 316L in a 0.01 M NaCl solution using an opto-electrochemical approach. Linear sweep voltammetry was used over a potential range of -0.5 V to +1.4 V (vs 3.4 M Ag/AgCl) at a scan rate of 0.01 V/s and ca. 1-40 Hz acquisition rates. Results revealed pitting corrosion kinetics, oxygen bubble formation initiation, and surface film dissolution/formation as a function of potential and local phase composition. Machine vision algorithms were used for data analysis, and statistical tools were used to assess spatial and temporal randomness of reactivity patterns. This study demonstrates the potential of modern data analysis methods to provide insights into corrosion processes.

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Revisiting the effect of nickel on the corrosion resistance of Fe-Cr alloys

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Nickel is widely used, being found in stainless steels, high-temperature corrosion resistant alloys and recently high-entropy alloys (HEAs) or multi-principal element alloys (MPEAs). This versatile alloying element with a unique combination of properties of high strength, ductility and corrosion resistance exhibits its broad applications in the aerospace and automotive engine components and exhaust system, nuclear power and petrochemical industry, as well as food processing and marine science.

However, the effect of Ni on corrosion resistance, especially on the pitting resistance has yielded some ambiguous findings. For example, Azuma et al.^[1] when investigating 25 wt.% Cr, 3 wt.% Mo stainless steels found that the addition of 4 wt.% Ni in better pitting resistance, but most of this improvement was lost when the Ni content was increased to 30 wt.% Ni as the microstructure was converted from ferritic to austenitic. However, other workers have shown that alloying with Ni promotes passive behavior and resistance to pitting,^[2] but also causes preferential dissolution of ferrite in the duplex stainless steels.^[3] Furthermore, Ni itself is not presented as a component in the equation to rank the pitting resistance equivalent numbers (PRENs), yet it is well accepted that Ni is resistant to corrosion, especially for stress corrosion and high temperature corrosion due to the formation of a thin layer of nickel oxide. So far, there have been more studies are focused on Ni effect on the phase compositions and microstructures or mechanical properties rather than its influence on the Fe-Cr passive films.

In this paper, the effect of varying nickel content on the pitting corrosion resistance of a series of Fe-Cr alloys produced by arc melting is presented. For conventional Fe-Cr binary alloys, it is well known that a critical concentration of Cr content of about 12 wt.% is required to form a complete passive film.^[4] For alloys with Cr content above this 12 wt.% Cr limit, cyclic potentiodynamic polarization tests in 3.5 wt.% NaCl revealed that as little as 3 wt.% Ni to Fe-Cr alloys can significantly improve pitting resistance. However, the impact of Ni content on alloys with less than 12 wt.% Cr was even more remarkable. For example, while it is not surprising that we found a Fe₉₀Cr₁₀ alloy exhibited no passivity, but the addition of 20 wt.% Ni conferred this alloy with spontaneous passivation, displaying a pitting potential of 0.11 V vs. SCE. To get further understanding of the role of Ni plays in passive film stability, the effect of varying amounts of Ni on incomplete passive films, i.e. alloys with < 12 wt.% Cr, was further investigated and the results will be presented in the paper. Overall, this work provides a more comprehensive elucidation of the effect of Ni on the corrosion resistance of Fe-Cr alloys, which may help to the optimize the alloy composition in developing new corrosion resistant HEAs and MPEAs.

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Application of cryo-atom probe tomography to study early-stage corrosion mechanism at liquid-solid interfaces at near atomic scale

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Abstract

In the last decades, atom probe tomography (APT) has become a key technique for studying the chemical structure of materials down to the subnanometre length scale with a mass sensitivity in the range of ppms. In contrast to other analytical methods, APT has the same detection sensitivity for all atoms even for light elements such as Li, B, H, O, which makes it particularly unique.

APT measurements require a needle-shaped specimen with an end radius in the range of below 100 nm to realize high fields to field evaporate atoms - layer by layer - and reconstruct a 3D map of the evaporated ions using dedicated reconstruction algorithms.

Using cryo-atom probe tomography, in-situ corrosion tests were performed in an environmentally controlled glovebox, with pure water as a test medium on a selected Mg-based (MgCa) alloy for implants. After a defined time, the corrosion state was frozen by plunging the sample into liquid nitrogen. Using a newly developed cryo lift-out method, a lamella containing water, oxide, and metal was extracted and finally successfully shaped into an APT specimen. Cryo-APT of a corroding Mg alloy has revealed an inward growing magnesium hydroxide and intermediate corrosion products, namely hydroxides of different compositions, as well as the partitioning of alloying elements between the metal, hydroxide, and oxide. This new trove of information has been facilitated by the unique capabilities of APT to prepare metal-liquid interfaces and to observe and quantify hydrogen. This has not previously been possible and has hindered the development of a truly representative model of the aqueous corrosion of Mg alloys.

New developments in the determination of the rate of electrochemical corrosion

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The determination of corrosion rate in aqueous solutions is generally based on electrochemical methods. The most typical way of corrosion rate assessment is the extrapolation of the Tafel slopes to the corrosion potential applying the Butler-Volmer (BV) equation to the corrosion system.

The BV equation is frequently linearized in the range of higher polarization and this is the standard way of assessment of the corrosion current. However, this linear extrapolation is not possible, or, at least, not reliable under certain conditions, especially in industrial corrosion rate monitoring. A viable alternative can be the assessment of the polarization resistance.

The determination of the polarization resistance can take place by DC or AC (EIS) measurements. The latter one is capable of separating the solution resistance, but it can have severe errors if the low frequency data are biased by any distortion of the 'depressed semicircle', which occurs frequently in corrosion measurements. Our proposed solution was developed for the determination of the polarization resistance from the higher frequency range of the spectrum, involving only the measurement data obtained at frequencies higher than the critical frequency ($f_{\text{crit}} > (2\pi RC)^{-1}$). The following functions were proposed and tested successfully for the assessment of the reciprocal of the polarization resistance [1]:

$Y'_C = Y_{\text{PR}} + \sum_{n=1}^N P_n \omega^n.$	(1)
$\frac{Y'_C}{\omega} = \frac{Y_{\text{PR}}}{\omega} + K_1.$	(2)
$\frac{Y'_C}{Y''_C} = \frac{Y_{\text{PR}}}{Y''_C} + K_2.$	(3)

where Y'_C and Y''_C are the real and imaginary parts of the ohmically compensated admittance, Y_{PR} is the principal admittance, which is the reciprocal of the polarization resistance, ω is the angular frequency and P_n , K_1 and K_2 are constants.

The accurate assessment of the corrosion current also requires the values of the Tafel slopes. In order to avoid the polarization in a wider range which may cause distortion of data or is practically impossible in industrial corrosion monitoring (LPR) systems, we proposed the following quadratic and linear approximations of the BV equation [2,3]:

$\ln\left(\frac{J}{\eta}R_p\right) \approx A\eta + \frac{S^2}{3!}\eta^2$	(4)
$\ln\left(\frac{J}{\eta}R_p\right)/\eta^2 \approx \frac{A}{\eta} + \frac{S^2}{3!}$	(5)

where J is the current density, η is the polarization, R_p is the polarization resistance, A is the asymmetric and S is the symmetric parameter of the transformed BV equation.

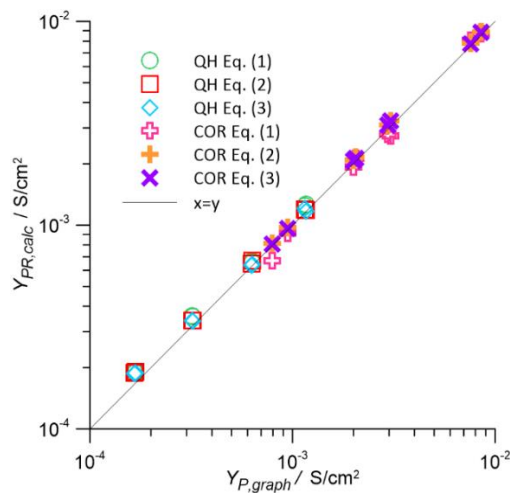


Figure 1. Dependence of the principal admittance, obtained with Equations (1-3), on the graphical polarization admittance. QH: quinhydrone redox system COR: a series of corrosion systems.

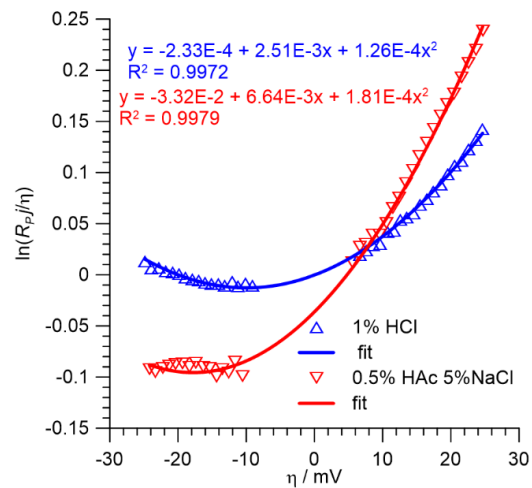


Figure 2. Measured steel polarization data and fittings according to Equation (4).

The models were also tested in industrial systems and the feasibility of corrosion monitoring was verified.

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Effect of dissolved O₂/CO₂ mixture on SCC of API 5L X70 pipeline steel in simulated environments

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For decades pipelines have been installed and operated around the globe to transport oil and gas and are considered a safe and economic means of transportation. One of the major concerns in their operation is corrosion. One of these is stress corrosion cracking (SCC), which is caused by the combined action of stresses (induced by internal fluid flow or other external forces) and a corrosive environment. The presence of trace gases, in particular CO₂, O₂, and H₂S or their combination, can cause an increase in corrosion and can lead to premature failure.

This research work investigated the stress corrosion behaviour of API 5L X70 pipeline carbon steel in 4 tests in simulated saltwater solution (3.5% NaCl). Tests were at either 5 °C or 25 °C and had gas introduced by bubbling (either N₂ or 20%O₂/80%CO₂). The introduction of N₂ acted to reduce any dissolved air or oxygen with the aim of reducing the corrosion rates. C-ring specimens were stressed to 80% and 95% yield strength. The change in corrosion rates and potentials over time were monitored by linear polarization resistance (LPR). Dimensional metrology based on optical microscopy was used to study the corrosion extent (measure the cumulative probability of metal loss exceedance), followed by scanning electron microscopy (SEM) to examine the microstructure.

Results obtained from the exposed samples in solution with N₂ (control experiment) show correlations between corrosion rates and both temperature and stress conditions. At 5 °C, the change in metal was observed to increase with applied stress, while at 25 °C, higher applied stresses lowered the cumulative probability of metal loss. Surface roughness was observed to increase with increasing exposure temperature from 5 °C to 25 °C. In contrast, results with the O₂/CO₂ mixture showed more rapid corrosion rates and metal change, with much higher increases in roughness of the specimens' surfaces. An undercutting corrosion morphology was observed, which increases in depth from 5 °C to 25 °C. Discontinuous microcracks were observed in the specimens exposed in solution with O₂/CO₂.

Estimating a century of corrosion: the toxic ammunition at the Paardenmarkt

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At the end of World War I, mainly German toxic munition was dumped on the “Paardenmarkt”, a silt bank 1 km off the Belgian coast. Over the years, the munition sank away and got buried. Lately, sampling campaigns detected extremely small traces of TNT and other components in the water column above the Paardenmarkt in 2019. Within the framework of the DISARM project, we aim to assess the physicochemical state of the ammunition to back possible solutions for this dumpsite. Because it is forbidden to disturb the ammunition, accumulated corrosion losses will be estimated on an experimental basis combined with advanced modelling. The experimental set-up is based on Petersen et al. (2019). Small different metal samples (60x60x3mm) (steel, messing and zamak) are set up in three different configurations in small goblets (Figure 1), which are submersed in continuously refreshed water (seawater, fresh water and brackish water). The soil in the test containers is a mixture of silt and sand, approximating the conditions of the Paardenmarkt soil, based on granulometry results for location K16 (Francken, 2005).

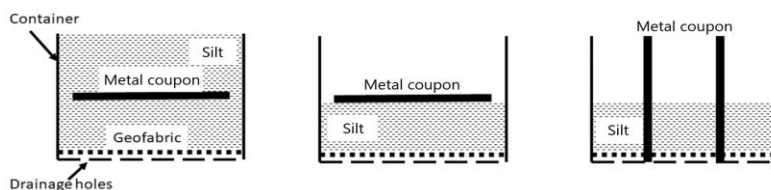


Figure 1 The configurations in which the metals are put in the test goblets

The metals selected represent a grenade. Brass is commonly used to construct the cartridge containing the propellant. Steel is always used to construct the shell. Brass samples represent the cartridge, steel samples represent the shell and the galvanic effect is simulated by connecting a brass plate to a steel coupon. To determine which metal to be used to represent the fuse, we analyzed how frequently different fuse types and materials were utilized on WW I grenades (Figure 2, based on General Staff (1918) and on data provided by DOVO, Poelkapelle). Steel was the most

common material used for a fuse when considering all types of grenades. When only toxic grenades are considered, steel and zamak are equally used, both 60%. Chemically, zamak will sacrifice itself to protect the steel shell. Lastly, leakage most frequently occurs at the thread between the zamak fuses and the steel shells. Consequently, zamak is chosen to represent the fuse in the experimental setup, both as a single component as well as coupled to steel.

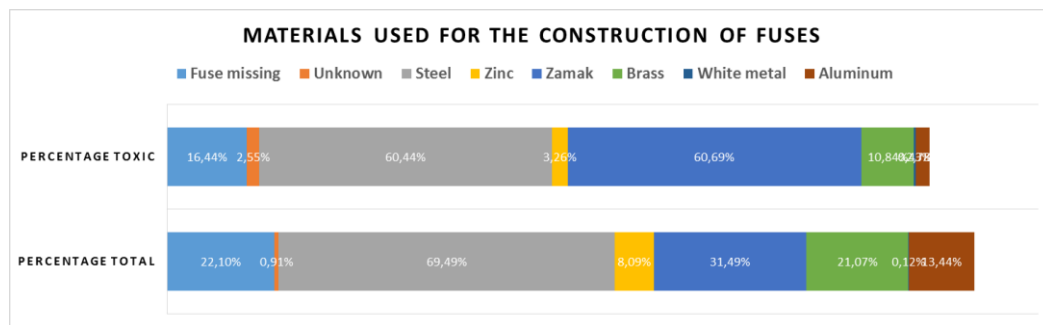


Figure 2 Materials used for the construction of fuses

The samples will be taken out after 2 years of submersion. Weight loss measurements will be performed as well as XRF measurements before and after the removal of the corrosion layer. The influence of the salinity of the water and the configuration of the metal on the corrosion rate of steel will be determined. The corrosion rates found will be compared with predictions based on a bimodal corrosion model (Melchers, 2003; De Baere, et al., 2020).

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Effect of microstructure on the electrochemical behaviour of 42CrMo4 QT steel

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This work focuses on the electrochemical behaviour of 42CrMo4 QT steel, which is employed for manufacturing components strengthened by quenching and tempering for application in mechanical components, such as those in marine engines. This leads to a heterogeneous tempered bainite microstructure consisting of acicular ferrite and cementite. Moreover, segregation of alloying elements might take place during the steel manufacturing process.

The electrochemical behaviour of the steel was investigated by large scale potentiodynamic polarization in different electrolytes (sodium sulphate with and without addition of chlorides with neutral and acid pH). A detailed characterization of the microstructure of the steel was performed by field emission scanning electron microscopy and energy dispersive x-ray spectroscopy in order to evaluate the morphology and chemical composition of the inclusions. The initiation of pitting corrosion at the inclusion sites was investigated with a localized approach combining topographic and surface potential maps obtained by means of the scanning Kelvin probe force microscopy technique and the morphology of inclusion sites after the immersion in an aggressive electrolyte. The effect of different inclusion types is discussed considering their galvanic coupling with the surrounding steel matrix and the existence of gaps at the periphery of the inclusions promoting the formation of an occluded cell.

Silicon Effect on Corrosion Behavior of Al-Mg Alloys in Marine Environment

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Aluminum-based alloys have been increasingly used to replace traditional alloys, e.g. steels, because of its intrinsic features such as better corrosion resistance and lower specific weight. Nowadays, this class of alloys is being used for a variety of engineering applications, mainly in the aerospace, automotive and offshore industries. Al-Mg-Si alloys can be used in the manufacture of metallic equipment and components, and as a coating to protect tanks, risers and pipelines exposed to marine environments. This work proposes a detailed analysis of the influence of Si content on the morphology of microstructure, and on the corrosion behavior of an Al-3wt.%Mg-X (X = 1 and 3 wt.%Si) alloy. A solidification apparatus promoting growth under unsteady-state heat flow conditions was used to obtain samples associated with a wide spectrum of cooling rates, thus permitting an extensive range of microstructures to be examined. Experimental results including microstructural characterization, nature and distribution of intermetallics associated electrochemical impedance spectroscopy (EIS) plots, potentiodynamic polarization curves, and equivalent circuits are used to evaluate the corrosion response. The solidification evolves from high cooling rate cells, followed by a transition from cells to dendrites that occurs at a cooling rate of about 1.0 K/s. In the two analyzed alloys, the best corrosion resistance was observed to be related to the refined cellular morphology.

Key-words: Al-Mg-Si alloys, Solidification, Marine Environment, Electrochemical Behavior

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Development of environmentally friendly anti-fouling corrosion protection systems for marine application

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This work targets the development of environmentally friendly anti-fouling paints for corrosion protection of hulls or propellers, stern drives, shafts and other underwater metallic parts in marine applications. Several commercial anti-fouling systems are based on the chemical release of biocides to reduce the adhesion of micro-organisms on submerged surfaces. These are potentially harmful substances for the marine ecosystem and their use could be strongly limited in the future. Another approach in the development of anti-fouling paints is the use of fouling-resistant and fouling-release coatings, which promote a weak interfacial bond between micro-organisms and the paint favoring their removal during navigation or mechanical cleaning. The most effective systems are mainly silicone-based, which are chemically stable in marine environments and environmentally friendly. Nevertheless, this silicone-based paints often display poor mechanical properties and often require the application of a primer to improve their adhesion.

This work presents a preliminary investigation of the corrosion protection properties of eco-friendly anti-fouling systems. In particular, different primers for copper and aluminum surfaces are investigated in order to evaluate their corrosion protection in combination with commercially available anti-fouling paints. This was assessed by electrochemical methods (electrochemical impedance spectroscopy) and salt spray testing. Besides, the anti-fouling properties were evaluated by immersion tests in marine environment. Moreover, the efficiency of different biocides and fouling-release coatings is considered in this work.

Effect of microstructure partitioning on intergranular corrosion of duplex stainless steel

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Abstract

Duplex stainless steel (DSS), which possess good mechanical properties and excellent corrosion resistance, is widely used in chemical and Marine engineering fields. However, in harsh service environment, DSS is still facing the threat of local corrosion. The crystal structure and element content of ferritic and austenitic phases are different, causing a significant impact on the local corrosion behavior of DSS. Therefore, it is of great significance to study the effect of two phases on its local corrosion behavior.

Intergranular corrosion is one of the most typical corrosion types of stainless steel. In this paper, solid solution treatment was used to carry out microstructure partition of 2002 (C 0.019, Si 0.48, Mn 4.52, Cr 20.21, Ni 2.04, Mo 0.01, Cu 0.19, Fe Bal.), and three samples with different proportions of two phases were obtained (Table 1). The double loop electrochemical potentiokinetic reactivation (DL-EPR), combined with microstructure characterization and analysis techniques were employed to investigated the effect of microstructure partition on the sensitivity and mechanism of intergranular corrosion. Corroded grain boundary density - the length of corroded grain boundaries in α phase per unit area ($\mu\text{m}/\mu\text{m}^2$) was proposed to characterize the sensitivity of intergranular corrosion.

Results show that, after aging treatment, Cr-rich phase was precipitated at α -phase grain boundary in DSS 2002 (Figure 1). Preferential dissolution occurred in the region around the grain boundary of Cr-rich phase, leading to intergranular corrosion and following the Cr-depletion mechanism. With the increase of solution temperature, the proportion of α phase increases and the tendency of intergranular corrosion increases (Figure 2). At the same time, the proportion of Cr in α phase decreased, which reduced the precipitation of Cr-rich phase at grain boundaries and decreased the tendency of intergranular corrosion. The combined effect of these two factors reduced the overall intergranular corrosion sensitivity of DSS 2002.

Table 1 The proportion and main element distribution of α and γ phases

Sample	Phase	Volume fraction (%)	Element content (wt.%)	
			Cr	Mo
1#	α	53.3	22.00 $\pm$ 0.79	0.35 $\pm$ 0.06
	γ	46.7	18.86 $\pm$ 0.75	0.21 $\pm$ 0.07
2#	α	57.4	21.87 $\pm$ 0.68	0.32 $\pm$ 0.10
	γ	42.6	19.13 $\pm$ 0.69	0.31 $\pm$ 0.08
3#	α	68.4	21.60 $\pm$ 0.74	0.29 $\pm$ 0.06
	γ	31.6	19.73 $\pm$ 0.69	0.35 $\pm$ 0.06

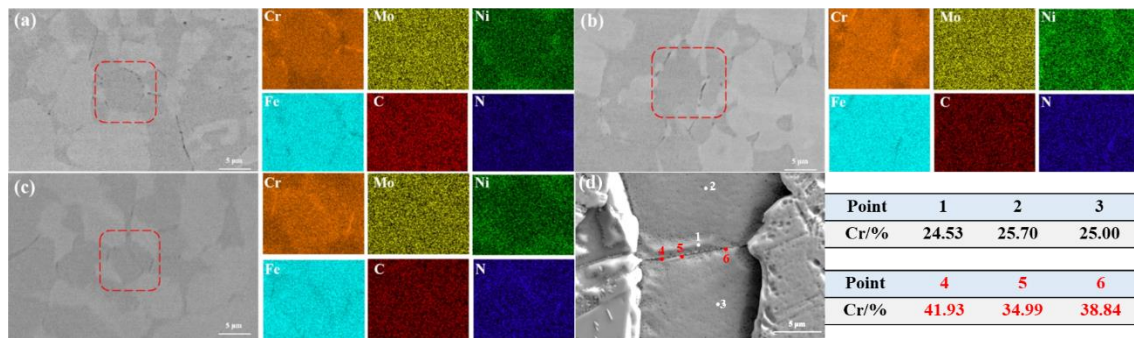


Figure 1 Microstructure morphology and element distribution of three samples after sensitization: (a)1#, (b)2#, (c)3# and the corrosion morphology and EDS analysis of 3# after DL-EPR test

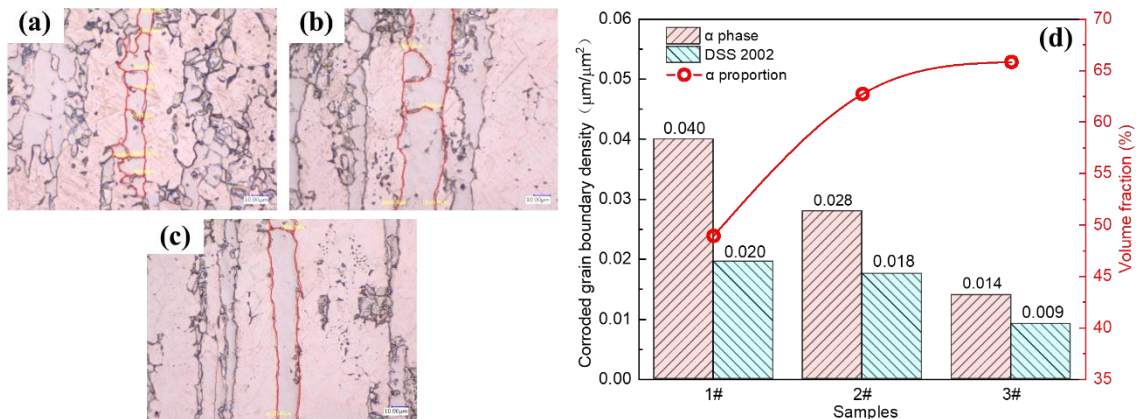


Figure 2 The observation of corroded grain boundary density of three samples after DL-EPR test: (a)1#, (b)2#, (c)3# and (d) the statistical result

The Mechanism of Passivation Breakdown of Multi Principal Element Alloys in Aqueous NaCl Electrolytes at Different pH

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Owing to their favorable mechanical and anti-corrosion properties, Multi Principal Element Alloys (MPEAs) experience high academic and industrial interest as novel materials for engineering applications. Several MPEAs have been studied for their general corrosion behavior but studies of their dissolution at high anodic (transpassive) potentials and local corrosion behavior remain scarce.

In order to understand the passivation breakdown behavior which fundamentally leads to a material's deterioration by corrosion and the mechanisms of transpassive dissolution of CrMnFeCoNi and CrCoNi, different investigation techniques were employed. On the nanoscale, the analysis of the corrosion morphology of the surface before, during and after passivation breakdown was carried out by means of in-situ atomic force microscopy (AFM). Scanning electrochemical microscopy (SECM), as a microscale scanning probe technique, was applied in the interrogative substrate generation-tip collection mode for the detection of evolving metal species and oxygen. As the oxygen evolution reaction (OER) may contribute a large percentile to the observed currents at high anodic potentials, SECM measurements were employed to analyze the onset of the OER. Potentiodynamic and potentiostatic techniques as well as different electrolytes were used to induce precisely controlled corrosion loads during the SECM experiments and for the ICP-MS analysis. By means of ICP-MS analysis, dissolved metal species were quantified to provide a fundamental understanding on the transpassive dissolution. Macroscopic corrosion properties of the alloys, i.e., electrical and chemical characteristics of the passive films were studied by means of potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and X-Ray Photoelectron Spectroscopy (XPS), respectively. The presentation will summarize our results on the corrosion and transpassive dissolution mechanisms of the studied Multi Principal Element Alloys.

Single-cell level investigation of microbiologically induced degradation of passive film of stainless steel combining multi-mode AFM

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Abstract

Atomic force microscopy (AFM) was employed for a single-cell level investigation of the effect of *Shewanella algae* on the passive film of a stainless steel at the initial stage of microbiologically influenced corrosion (MIC). *S. algae* is a facultative anaerobic and Gram-negative iron-reducing bacterium that belongs to the *Shewanella* species. AFM in dynamic mode, nano manipulation mode and peak force tapping-frequency modulation mode were performed to obtain the surface 3D topography and the corresponding potential distribution at the cell colonization site, respectively. The results provide new nanoscale evidence for MIC of stainless steels and permit a better understanding of bacteria/passive film interactions.

Corrosion enhanced by hydrogenotrophic methanogens differently enriched on copper and steel alloys

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The microbiological corrosion induced by methanogens is mainly studied on steel alloys, these being widely used in the Oil&Gas sector, where the most significant phenomena have been found. Most studies show that the effect of CO₂-rich environments, pH and flow conditions could modify the interaction of methanogens with the substrate as for the use of hydrogenase and the catalyzation of protective corrosion products, such as Siderite or Vivianite. In this work, the enrichment of a different pool of hydrogenotrophic methanogens and bacteria on the surface of two copper alloys (pure Cu and 60:40 brass), a duplex stainless steel (2205, with 22 wt. % of Cr) and very low carbon steel (C > 0.02 wt.%) was documented, starting from the same microbial pool. The corrosion induced by methanogens enriched media, in comparison with sterilized media, were documented during replicated two-week tests. Electrochemical investigations were performed using a three-electrode cell consisting of a working electrode (test alloy), a reference electrode (saturated Ag/AgCl electrode) and a counter electrode (titanium mesh). Investigations included open circuit potential (OCP) monitoring, electrochemical impedance spectroscopy (EIS), and potentiodynamic measurements. Chemical characterizations of the corrosion products and post-experiment observations were performed by SEM and micro-Raman spectroscopy (μ RS). Molecular analysis by next generation sequencing (NGS) of 16S RNA was performed by swabbing the surface of the material and identifying the microorganisms constituting the microbial communities for each case. Results evidenced a different enrichment of microorganisms depending on the material, and an increase of corrosion for both copper and iron alloys.

Subtopic: Microbial corrosion – Microorganisms and mechanisms

New multiparametric probe to monitor microbial corrosion in soil

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A new integrated multiparametric probe for the online monitoring of physico-chemical parameters and microbial corrosion in the soil is presented. The work deals with the application of electrochemical techniques already successfully used to monitor biofilm growth, corrosion, and other environmental/hydrochemical parameters in natural water systems. A BIOX probe, measuring aerobic microbial activities [1], is integrated into a three-electrode set-up to perform corrosion rate, soil conductivity, and redox potential measurements. The probe includes a zinc reference electrode, a large surface titanium counter electrode and replaceable working electrode, which can be suitably changed to perform tests with different materials. A thermometric probe is also incorporated into the sensor bundle. Signals are collected and stored by a data acquisition system. The multiparametric probe can be associated with a potentiostat allowing by it to carry out direct or alternated polarization curves on the working electrode. A compact set-up of the probes was designed and manufactured by AMEL S.r.l. company, optimized to be used at 20-50 cm of depth.

Tests with the multiparametric probe in sterilized and unsterilized soils, and at different soil humidity, have been carried out on different metal alloys (stainless steel, zinc, copper, and copper alloys) buried in garden soil. The results suggest that electrochemical techniques can be suitably applied by this simple probe configuration to monitor the early stage of biofilm growth and corrosion of metals in soil. A key role of soil humidity in the development of a stable biofilm is confirmed. Similarly, the soil humidity level is the limiting factor for corrosion phenomena. Electrochemical data concerning corrosion of different materials exposed, under different humidity levels (between 0 - 0.57 m³/m³), achieved by the multiparametric probe are here presented and discussed.

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Subtopic: Microbial corrosion – Monitoring

Taxonomic and proteomic characterization of corrosive biofilms on steel under differential metabolic conditions in freshwater media

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Objective and Methodology

Damage caused by microbially influenced corrosion (MIC) impedes the operability of marine metallic structures and has therefore been researched extensively. Likewise, biocorrosion effects were also observed in hydraulic installations across freshwater systems in Germany (1). In order to apply mitigation strategies, it would be imperative to elucidate the underlying metabolic processes that play a role in biocorrosion. The objective of our study was to characterize the microbial processes involved under sulphate-reducing conditions by identifying enzymatic and taxonomic patterns with Fe^0 or H_2 as electron donor and in the presence or absence of an organic carbon source. Corrosion scales sampled from an afflicted ship lock (in the Mittelland Canal, Lower Saxony) were incubated with or without metal coupons in microcosm systems. Three biotic treatments and the corresponding abiotic controls were set up in freshwater media with sulphate and the following substrates to enrich different corrosive microbial groups: [i] Fe^0 and CO_2 ; [ii] Fe^0 and CO_2 /acetate; [iii] H_2 and CO_2 . The treatments were incubated for 6 weeks under strict anaerobic conditions, while both gas and fluid phases were regularly sampled. Measurement of temporal changes of parameters such as Fe(II) , H_2 , sulphide, sulphate, acetate, protein concentration and pH were conducted in order to elucidate the MIC mechanisms stoichiometrically. 16S-rRNA amplicon sequencing and metaproteomics analyses were applied to gain a deeper understanding on the corresponding cellular processes.

Key results

Upon evaluation of the time course determined parameters, treatment [iii] showed a maximum sulphate consumption of 8.39 ± 0.75 mM accompanied by complete H_2 (electron donor) consumption after 13 days of incubation. Acetate concentration of

5.45±0.31 mM was detected and a higher dominance of the taxon *Acetobacterium* was observed. CO₂ fixation coupled with H₂ consumption is carried out in the Wood-Ljungdahl pathway among acetogens. Proteomic results indicated the expression of the enzymes CODH/ACS, methyl-THF red/hyd catalysing CO₂ reduction to acetyl CoA and finally acetate. Interestingly, the enzyme acetate kinase, which is synthesized specifically by the species *A.woodi*, plays a key role in ATP production during acetogenesis (2) and it was found to be overexpressed. On the contrary, in treatments [i] and [ii] a lower sulphate consumption (1.76±0.34mM, 3.39±0.93 mM) was observed since Fe⁰ as a solid substrate is complex to be utilized as an electron source. Acetate consumption of 0.43±0.15 mM was detected in treatment [ii]. Concomitantly higher corrosion was observed with an average coupon weight loss of 8.25±2.79 mM Fe⁰ compared to treatment [i] (4.98±0.83mM Fe⁰). The sulphate reducing family *Desulfocapsaceae* which can survive under chemolithoautotrophic conditions, was detected in treatment [i]. Whereas, higher abundance of the genus *Desulfovibrio* was observed in treatment [ii]. Enzymes such as dsrA, dsrB catalyzing the dissimilatory sulphate reduction/anaerobic respiration were identified. Additionally, CytC3 and 4Fe-4S ferredoxin were detected as membrane transporters potentially involved in electron transport from Fe⁰ into the cell (3). In conclusion, we identified a dominance of potentially corrosive sulphate-reducing and acetogenic bacteria along with proteins potentially involved in direct electron transfer from metal. Further exploration of the overexpressed proteins would help us to identify marker proteins involved in biocorrosion and metabolic pathway mapping of the identified enzymes to obtain an overview of the various cellular processes.

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Novel Metal Bionanohybrids against MIC Consortia

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Every metallic surface exposed to seawater is subjected to general corrosion, pitting corrosion but also to microbiologically influenced corrosion (MIC). MIC is a very complex process and is of great importance for metal structures exposed to marine environment. Often sulfate-reducing bacteria (SRB) and acid-forming bacteria (APB) are involved next to other corrosion relevant micro-organisms.

Different strategies have been developed to avoid MIC, including the use of compounds that inhibit the formation of biofilms, which adhere to the metal surface, or the use of antimicrobial agents in paints or coatings. For these purposes, biocides, polymers or species that generate acids can be used. However, this may involve aggressive or very expensive treatments. In search of new materials that can efficiently, safely, economically and sustainably combat biofilms, this work presents new bionanomaterials with antimicrobial properties which are based on the use of a protein as a scaffold for different metals, including copper or silver. The use of a protein as a scaffold allows the synthesis of stable, monodisperse nanoparticles (NPs) with controlled size and shape, in water at room temperature. In addition, the protein can act as *in situ* reducing agent. All this makes this process much more sustainable than the traditional NP synthesis.

Several types of these nanobiohybrids were tested against MIC related microorganisms (in solution) such as SRB and APB consortia directly isolated from corroded material exposed to industrial process water. Initial results illustrated antimicrobial efficiency against SRB, with APB remaining unaffected. Another group that we tested, the so-called slime-forming bacteria, were also impacted significantly by the tested nanobiohybrids. Following these experiments, biofilm formation of SRB

on steel coupons in the presence of the nanobiohybrids was also tested, and the results illustrated up to 50% reduction in biofilm formation for some of the concentrations. Therefore, we believe that these nanobiohybrids may have a promising future in MIC prevention. Discovering new compounds that can tackle MIC efficiently and sustainably is a major target in numerous sectors where MIC is a considerable risk.

Corrosion of Container Material for High-Level Nuclear Waste in the Presence of Bentonite or the SRB *Desulfosporosinus burensis*

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Ductile cast iron is investigated as a potential container material for the disposal of high-level nuclear waste in deep geological repositories (DGR) in claystone bedrock. The dynamic corrosion process depends on the conditions present in the DGR which are influenced and/or controlled by geochemical parameters (e.g., redox potential, pH, the ionic composition of the pore-water), physical parameters (e.g., pressure), and the influence of metabolically active microorganisms. Corrosion of cast iron will occur at the interface of the container surface and the bentonite backfill material, which contains natural microbial populations. In the investigated worst-case scenario, water would reach the container and introduce microorganisms inherent in the bedrock, such as sulfate-reducing bacteria (SRB).

The conditions in a DGR were simulated in microcosm experiments to investigate the impact of microbiologically influenced corrosion (MIC) on a potential container material. The anaerobic microcosms contained artificial Opalinus Clay pore water, N₂ atmosphere, cast iron coupons, as well as a Wyoming bentonite or the SRB *Desulfosporosinus burensis* (DSM 24089) (isolated at the Andra Underground Research Laboratory in Buré, France).

After incubation at 25°C for 50 days, the microcosms were analysed for bio- and geochemical parameters, i.e., pH, Fe(II):Fe(III), changes in their microbial populations, as well as SEM-EDX and Raman spectroscopy to identify secondary iron phases and corrosion products.

The coupon showed mild to severe pitting corrosion and various mineral phases on their surfaces. Additionally, the coupons from the *D. burensis* microcosms showed an increased concentration of carbon on their surface, i.e., an indication of a biofilm. Furthermore, the interaction of technetium-99 with the corroded coupons was investigated to assess the immobilisation of Tc by exposed and corroded cast iron.

Antifouling nano-designed composite as a mitigation strategy

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The pillars of the growth of a greener and healthier society are based on the sustainability of resources and materials, being themselves the basis of all social infrastructures. But the rising industrial activity in many different sectors, including water and wastewater management systems, marine operations, renewable energy platforms, and climate change, raise one of the biggest global threats: corrosion and biofouling on surfaces. The main underlying problem common to all these systems is the attachment and growth of microorganisms on surfaces in contact with aqueous streams, forming biofilms, promoters of Microbially Influenced Corrosion (MIC), which is estimated to affect up to 20% of corrosion in aqueous systems, costing billions of dollars only for rehabilitation costs [1]. Hitherto, the most effective anti-biofilm strategies have relied on toxic and persistent chemical agents (e.g., biocides) release, but these will eventually end up in the environment, which has a limited life cycle and brings ecological issues and urging the search for long-lasting and eco-friendly mitigation alternatives.

This work aims to contribute to overcoming these mitigation challenges by providing a novel approach that involves prior know-how on bioactive agents grafting [2, 3] for the immobilization of biocidal agents on the surface of metal oxide nanoparticles (NPs) (e.g., Ti and Si-based), allowing their bioactivity to be amplified or generated and improve their capacity against MIC, without leaching agents into aquatic media, extending their potential application. XRD and DRIFT spectra (Fig. 1c) confirmed the biocidal agent grafting on the NPs' surface and the maintenance of their characteristic crystalline structure. Morphological properties assessment of the bioactive nanocomposites by scanning electron microscopy (SEM-EDS) evidenced nanoparticles with a spherical geometry with a higher agglomeration supported by an organic/polymer matrix (Fig. 1b).

The antimicrobial susceptibility of nanocomposites against major waterborne microorganisms, including gram-positive and gram-negative, revealed promising inhibition effects. Figure 1a shows a representative antimicrobial action against the Methicillin-resistant *Staphylococcus aureus* (MRSA) obtained with a TiO₂-based developed nanocomposite. MIC-related enrichment cultures isolated from industrial environments for laboratory-based experiments are in progress to evaluate the capacity against MIC. The ultimate goal of this work is to use the nanocomposites as additives for coating formulations following prior developed methodologies [3].

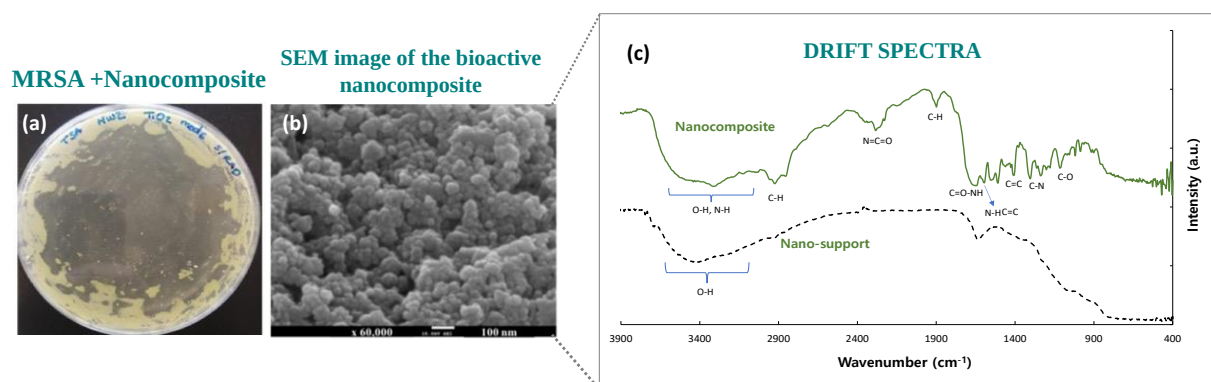


Figure 1. Antimicrobial action against the Methicillin-resistant *Staphylococcus aureus* (MRSA) of a bioactive TiO₂-based nanocomposite (a), together with its morphological details through an SEM image (b); and Fourier transform infrared diffuse reflectance (DRIFT) spectrum in comparison with the pristine nano-support.

Acknowledgments:

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Microbially induced corrosion and the environmental parameters influencing local microbial communities in waterways and estuaries

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Surface water are the subject of complex environmental and industrial processes, steering the water chemistry and having important ecological implications. For instance, the salinity gradient or ion composition may shift the abundance of bacterial species. Genera of iron-oxidizing and sulfur-reducing species can partake in microbially induced corrosion (MIC). Such genetic evidence has been found among communities active in overcoming kinetic barriers that lead to corrosion rates beyond normal levels (> 100 MPY).

For the Dutch-Belgian canal between Ghent and Terneuzen, steel coupons were placed as indicator to monitor MIC by metagenomic amplicon sequencing of the biofilm grown onto. The pitting index varied strongly among different locations, even in close vicinity, pointing towards highly local conditions. The first period of 3 months exhibited the largest differences in pitting corrosion, ranging from 5 near the *Moervaart* to 21 in *Heide*, corresponding to an average depth loss of $13.9\ \mu\text{m}$ and $37.7\ \mu\text{m}$, respectively.

Spots with elevated pitting index were characterized by the presence of *Gallionella* and *Rhodobacter*, known iron-oxidizing genera, and *Sulfurimonas*, *Desulfovibrio* and *Desulfomicrobiae*, recognized as sulfur-reducing genera. The biofilms on steel coupons with such elevated corrosion rates, presumed associated to the bacterial activity, did not differ significantly ($p = 0.35$) from other biofilms in alpha diversity, as expressed by inverse Simpson index. It implies genera of these bacteria outnumber others, which is yet to be confirmed by follow-up studies during the very early phase of microbial colonization and steel abrasion.

Finite Element Modelling of Microbiologically Influenced Corrosion

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Microbiologically Influenced Corrosion (MIC) is thought to responsible for 20% of all corrosion failures, with attack associated with anaerobe sulphate reducing bacteria (SRB) being financially the most destructive [1]. For microbial corrosion, the existence of a biofilm on the metal surface impacts corrosive species' production and transportation, which is yet understood poorly. Therefore, present corrosion models are risk-based and meant for ranking potential threats to the industrial assets, rather than trying to quantify those threats. Nevertheless, MIC usually leads to localized attack that is akin to pitting and crevice corrosion, the present model aims to develop a finite element mechanistic model for abiotic localized corrosion and then build on this features that are relevant to MIC. The model will eventually concurrently include mass transport phenomena, chemical, biochemical, and electrochemical reactions to account for the shortcomings of the previously developed MIC models. In addition, biofilms are known to be growing over the substrate continually and are heterogeneously stratified by depth in terms of pore size, diffusivity, living/dead biocells, etc. Typically, the outer layers contain aerobes that consume oxygen, which combined with sluggish diffusion of oxygen can create an anoxic environment at the biofilm / metal interface, especially for biofilms thicker than 100 μm . This anoxic environment allows destructive SRB to thrive, which via the reduction of sulphate can create alternative cathodic reactions to support the corrosion. Furthermore, biofilms are known to periodically fracture and partially detach from the substrate, which can allow dissolved oxygen to reach the previously anoxic regions with a subsequent on corrosion rates. Therefore, such characteristics are considered in the modelled biofilm. COMSOL Multiphysics, has been used for simulations with input parameters taken from literature and experiments. We are aware that there is a long way to achieve a complete model for MIC, but our developed multi-reaction moving boundary model is promising start for this journey.

Acknowledgment

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Effect of 5 Methyl-1H-benzotriazole as corrosion inhibitor on microbiologically influenced corrosion on mild steel in red sea water

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Microbial-influenced corrosion (MIC) has been widely recognized as a significant economic and environmental problem. 5 Methyl-1H-benzotriazole (MHB) was investigated as an inhibitor for the corrosion of mild steel in red sea water in comparison with the simulated sea water. Results from linear polarization (LPR) and potentiodynamic polarization confirm that MHB effectively inhibits corrosion in both solutions. However, in the presence of microorganisms in the red sea water, MHB's inhibition efficiency reduced noticeably. Weight loss and pit observation analysis are supporting the electrochemical data. This preliminary electrochemical results are to be followed by biofilm examination under confocal laser scanning microscopy and scanning electron microscopy. Even with the naked eye, the pitting corrosion is more prominent in the presence of the microorganisms when compared with simulated sea water.

Conductive nanowires accelerated corrosion of C1020 carbon steel by *Desulfovibrio vulgaris*

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Abstract

Microbiologically influenced corrosion (MIC) has been widely recognized as a significant economic and environmental problem in the oil and gas industry and many other industries. MIC caused by anaerobic biofilms can be classified into two main types based on the mechanisms: the extracellular electron transfer MIC (EET-MIC) and the metabolite MIC (M-MIC). The first includes microbes that can use extracellular electrons for respiration via cross-cell membrane EET, while the latter covers microbes that secrete corrosive metabolites. Sulfate-reducing bacteria (SRB) are believed to cause EET-MIC in carbon steel, which is a widely used metal in the oil and gas industry. In previous electroactive bacteria studies, proteinaceous nanowires have been shown to facilitate EET by acting as electron conductors. This study investigates the use of conductive magnetite nanowires as electron mediators to accelerate EET-MIC of C1020 by *Desulfovibrio vulgaris*. The addition of 40 ppm (w/w) nanowires resulted in 45% higher weight loss and 57% deeper pits after 7-day incubation. Furthermore, linear polarization resistance and potentiodynamic polarization results corroborated weight loss data trend. These findings suggest that the nanowires can be used to accelerate EET-MIC in lab tests or in identifying EET-MIC.

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The effect of copper tailings addition on the mechanical and electrochemical properties of mortars

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Abstract

Ordinary Portland cement is one of the busiest conglomerates manufacturing concretes, representing 5-8% of anthropogenic emissions [1]. Some industrial wastes have been investigated as supplementary cementitious materials (SCM), allowing the partial replacement of cement. This work studied the effect of copper tailings as sieved and milled as SCM, producing 540 Mton every year in Chile [2]. Physical and microstructural characterization of the copper tailings was carried out through scanning electron microscopy and X-ray diffraction. The replacement percentages varied between 5-15 wt.%, using a 0.5 water-cement ratio. Compression and flexion analysis were performed using mortar samples, according to ASTM-C109/C109M, and electrochemical measurements were done using a bar embedded in the mortar. Both analyses were carried out after 7, 28, and 90 days. XRD revealed amorphous phases mainly in the sieved samples than in the milled samples. After 90 days, using 10 wt.% cement replacement, for milled samples, the compression and flexion tests showed a variation of -15% and +4% for compressive and flexion resistance. For the sieved

samples, the variation was +10% in compression and +29% in flexion resistance. The open circuit potential showed a shift to more positive values with lower replacement percentages, suggesting the passivation of carbon steel. The electrochemical impedance spectroscopy revealed an increase in the electrolyte resistance and the impedance modulus over time, which was more significant for sieved samples, suggesting the best replacement for cement for samples with 5 wt.% of sieved tailings. The surface analysis revealed similar steel surfaces using 5 wt.% as a replacement for both treatments, with lower surface cracks than the control sample. Therefore, the sieved treatment showed better behavior in the mechanical and electrochemical proprieties than the milled treatment, favoring the evolution of the pozzolanic reaction, being a better treatment as a supplementary cementitious material.

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Numerical Insights into the Ability of Indirect Galvanostatic Pulse in Wenner Configuration to Locate Corroding Areas in Macrocell Corrosion of Steel in Concrete

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Abstract

The non-destructive monitoring of the corrosion of steel in concrete using indirect electrical techniques is gaining interest as it does not require any connection to the rebar. Here, we provide insights into the ability of the indirect galvanostatic pulse (GP) method, using four-electrode configuration placed on concrete surface, to locate corroding areas in macrocell corrosion in the Wenner configuration, in which C_1 and C_2 inject a direct current and P_1 and P_2 measure the resulting potential difference (Figure 1a). This technique differs from the conventional one in three-electrode configuration with a connection to the rebar, as the current that polarizes the rebar is not constant but decreases over time. Consequently, the temporal evolution of the potential difference measured between P_1 and P_2 can be explained by the increase of the potential difference related to concrete resistance and the decrease of the potential difference related to the rebar (Figure 1b, c).

Using numerical simulations considering macrocell corrosion, it was shown that the presence of an anodic area disturbs the current distribution in the material, which is explained by the different capability of anodic and cathodic areas to consume the impressed current. Consequently, the evolution of the transient potential is slowed down as compared to uniform corrosion (Figure 2). This effect is notably dependent on the position of the anode with respect to the current probes, with a higher sensitivity when the corroding areas are below or in their vicinity. Hence, the interpretation of spatial measurements of transient potentials made over the length of the rebar can provide insights in the localization of the anodic areas (Figure 3). For the estimation of their length, which is one of the main current problematic issue when performing any measurement on reinforced concrete (RC) structures, adjusting the probe spacing during the spatial measurement appears interesting to modulate the sensitivity of the technique to macrocell corrosion [1].

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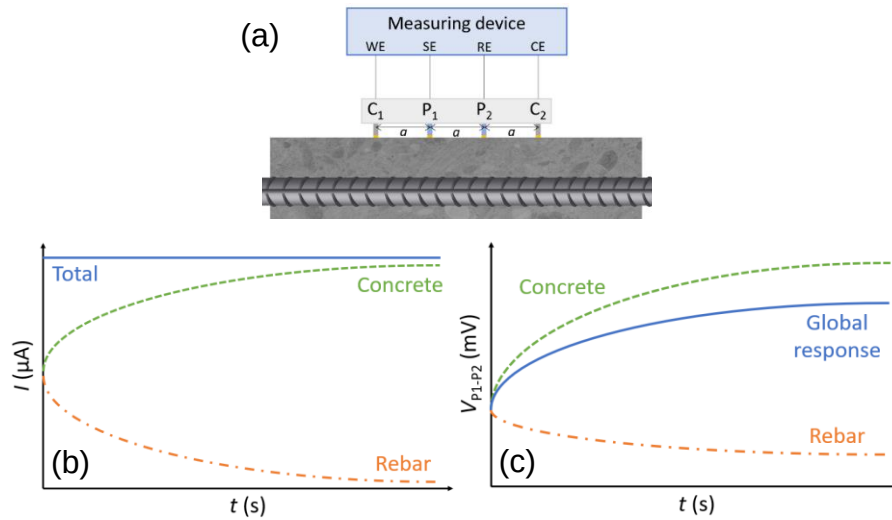


Figure 1. (a) Schematic representation of the indirect GP technique in Wenner configuration. (b) Evolution of the distribution of the current in the concrete and in the rebar; (c) evolution of the potential difference attributed to concrete resistance, the rebar, and the global response.

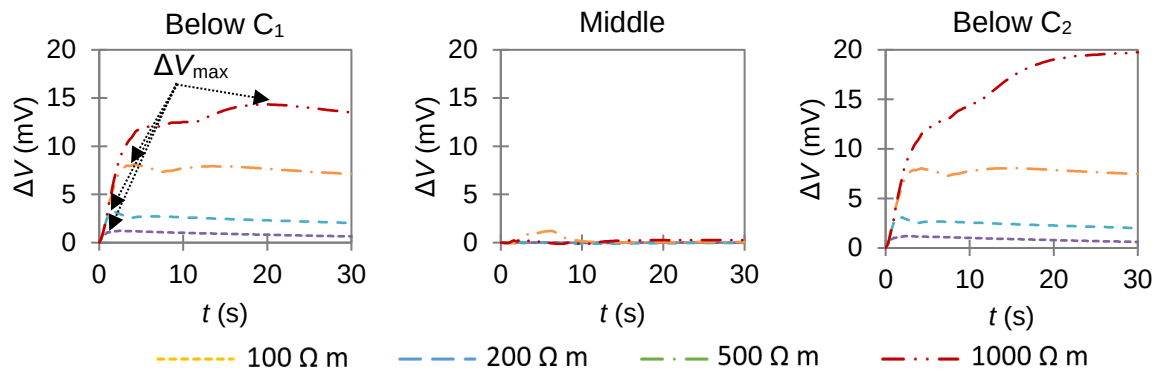


Figure 2. Example of the temporal evolution ΔV – which represents the comparison of V_{P1-P2} for macrocell corrosion with V_{P1-P2} for the reference passive corrosion, calculated as $\Delta V(t) = V_{P1-P2}(t)$ for passive corrosion - $V_{P1-P2}(t)$ for macrocell corrosion – in the presence of a highly corroding area at different positions relative to the monitoring device for specific input parameters (four different concrete resistivities).

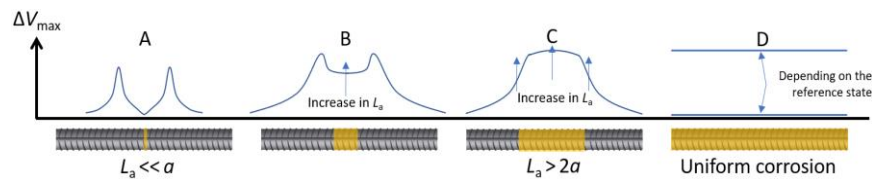


Figure 3. Schematic representation of the main scenarios expected when monitoring a rebar with one highly corroding area. The figure shows the evolution of ΔV_{max} values as a function of the measurement position, illustrating the potential interest of the method for estimating the position and length of anodic areas.

Effect of current passage on the protective properties of concrete

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Direct electrical current is used in several ways for its healing effect in reinforced concrete structures. In long-term application, it is used for cathodic protection, both in preventive and remedial mode. In the latter case, higher current densities are introduced from an external power source. In both of these cases, the DC current induces the migration of chloride ions from the cathodic reinforcement to the surface anode. DC current applied for a short time is used for electrochemical extraction of chlorides. The principle based on chloride migration is the same, except that higher current densities are applied. The passage of current through an ionic conductor, such as wet concrete, induces the transport not only of chloride but also of other ions such as hydroxides or calcium and sodium ions. This can cause local concentration changes, dissolution and changes in the microstructure of the cement binder and affect its sorption properties towards chlorides. Thus, concrete after chloride extraction may be less resistant to future chloride penetration. The paper summarizes latest results of research on the influence of DC current on the microstructure of cement binder and its sorption and transport properties towards chlorides. Concrete and mortar samples based on Portland cement (OPC) and samples containing supplementary materials (fly ash, microsilica) were loaded with different levels of DC current. The change in microstructure was evaluated by mercury intrusion porosimetry. Electrochemical impedance spectroscopy was also successfully applied to characterize the pore system. By determining chloride concentration profiles, it was confirmed that the passage of DC current limits the penetration resistance of concrete and facilitates chloride transport by diffusion. The cause is probably the opening of transport pathways in the concrete microstructure and the limitation of the sorption properties of the cementitious cement.

Permanent corrosion monitoring of steel in concrete – Long-term performance

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Steel corrosion is one of the primary causes of degradation in reinforced concrete. To establish long-term maintenance planning, it is essential to know the condition of a structure and its degradation over time. Therefore, monitoring is required to guarantee the performance of structures throughout their lifespan. Maintenance and inspection plans rely on these systems, which periodically or continuously collect information using electrochemical, optical, and sound sensors, among others. However, the reliability of these sensors depends on environmental factors, materials' durability, and even power outages. These factors may damage the monitoring system, and the information acquisition can be temporarily or permanently interrupted.

This paper discusses the results of 21 years of monitoring a reinforced concrete structure in a marine environment, daily recorded with different sensors. Sets composed of a corrosion potential sensor, a galvanic current sensor, a concrete resistivity sensor and a temperature probe were embedded in the structure in seven areas in different exposure conditions. Concrete electrical resistivity sensor uses two-graphite electrodes installed in concrete at different cover depths (15 and 30 mm). Corrosion potential has been measured with a MnO_2 reference electrode. Galvanic current sensors include carbon and stainless steel electrodes installed in concrete at 15 and 30-mm cover depths. The temperature has been measured using an RTD platinum sensor. Data has been acquired with Datataker DT80 Universal Input Data Loggers. Chloride contamination and carbonation depth were also periodically measured.

The recorded monitoring data, which noticed changes due to the penetration of corrosive agents in the concrete, provided relevant information for the decision-making on maintenance of the structure with suitable paints to delay corrosion onset. The full potential of the analysis of the long-term monitoring results is displayed.

The maintenance procedure of the corrosion monitoring system during the 21 years and the main difficulties to warrant its suitable performance are also discussed in the paper.

Parametric Study of Top of Line Corrosion in Highly Sour Environments

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Top-of-line corrosion (TLC) can be categorized as sweet or sour depending on whether the environment is CO₂ or H₂S dominated, respectively. Contrary to its sweet counterpart, sour TLC is much less investigated. Very few studies have been published on it and considerable uncertainties remain on the influence of different environmental parameters. This work presents a systematic study of the effects of temperature and H₂S partial pressure on TLC of carbon steel. Special emphasis is given to the corrosion product layers formed under these conditions. A series of experiments, each of 7 days duration, were conducted at 20 bar total pressure in a CO₂/H₂S environment. The H₂S partial pressure was varied from 1 to 5 bar at two different gas temperatures (40°C and 80°C). The steel temperature was controlled to yield high condensation rates of the same magnitude scales (10⁻¹ mL/m²/s). Weight loss measurements and surface characterization reveal that the temperature was the controlling parameter which affected the morphology and protectiveness of the FeS scale formed.

Keywords: sour, top of line corrosion, H₂S, temperature, condensation rate, partial pressure

Effect of micro-alloying on corrosion behaviors of steels in CO₂ saturated brine solutions with different pH

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The influences of several alloying elements (C, Cr, Cu, and V) in minute quantities on the corrosion behaviors of low C steel in CO₂-saturated brine solutions were examined by a combination of electrochemical polarization, weight loss measurement, and metallographic observations of the corrosion morphology. The role of alloying elements in imparting anti-corrosion performance in aqueous CO₂ environments was interpreted based primarily on the properties of the corrosion scale formed on the steel surface. The results showed that the corrosion resistance of the tested microalloyed steel samples depends greatly on the pH of the CO₂ saturated solution. Based on the derived corrosion mechanism, this study presents effective alloy design strategies for the development of low C steel with superior corrosion resistance in aqueous CO₂ environment.

Synergistic effect of oleic acid imidazoline and CeCl_3 on carbon steel corrosion in CO_2 saturated chloride-carbonate solution

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The effect of CeCl_3 , oleic acid imidazoline and their mixture as corrosion inhibitors of AISI 1018 carbon steel corrosion in simulated brine solution saturated with CO_2 at 60 °C and pH = 3.3 was examined by means of weight-loss testing, electrochemical measurements, and surface analyses. All test methods showed a synergistic effect of compounds and a higher degree of corrosion protection compared to the action of individual compounds. The surface film, created by the adsorption of imidazoline oleic acid forms voids, while the cerium cation tends to fill these voids by creating a belayer film. In this way, a denser and thicker surface film is formed, which effectively protects carbon steel from corrosion in the tested conditions and proves the synergistic effect of oleic acid imidazoline and CeCl_3 .

Keywords: CO_2 corrosion, carbon steel, oleic acid imidazoline, CeCl_3 , synergistic effect

Tribocorrosion Behavior of of Ti–4Al–2.5V–1.2Fe alloy drill pipe after anodic oxidation treatment for oil & gas application

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The surface of a new Ti–4Al–2.5V–1.2Fe alloy used for titanium alloy drill pipe was processed by anodic oxidation treatment to overcome the poor tribological properties, and the tribo-electrochemical performance of Ti–4Al–2.5V–1.2Fe alloy before and after surface treatments were investigated under reciprocating sliding conditions at high contact loads and three electrochemical conditions (–0.5 V, OCP and +0.5 V), the effect of different drilling fluid and electrochemical conditions on the synergistic interaction between wear and corrosion of Ti–4Al–2.5V–1.2Fe alloy after anodic oxidation treatment were studied and compared with the untreated alloy by wear tests and surface analysis. The results revealed that after anodic oxidation treatment, the surface of the anodized alloy exhibited the smooth and Non-porous surface characteristics, the cross-sectional of anodized layer was fine porous, multilayer ceramic structure and were mainly composed of Al₂TiO₅, TiO₂, Al₂O₃ and amorphous substances. The current densities of Ti–4Al–2.5V–1.2Fe alloy after anodic oxidation treatment were significantly decreased due to the higher passivation film resistance than that of substrate both in water–based drill fluid and oil–based drill fluid. Tribocorrosion tests results disclosed that the coefficient of friction (COF) of Ti–5.5Al–4.5V–2Zr–1Mo alloy was significantly decreased after anodic oxidation treatment in both two drill fluids. In the water–based drill fluid, the potential of the surface was slightly increased when anodized layer slid against SiC at open circuit potential, and the coefficient of friction and mass losses were both significantly reduced when tribocorrosion test conducted at an anodic potential of +0.5V, which was contributed to the better stability, lower friction coefficient and thicker thickness

of repassivation oxide film on the surface of anodized alloy. While in the oil-based drill fluid, the potential of the surface after anodic oxidation treatment remained the same and the mass losses became smaller at open circuit potential, the corrosion and wear behavior of anodized layer sliding was independently of the electrochemical conditions applied, which was caused by the surface of the anodized layer was depassivated and replaced by loose and porous metastable oxide due to the lack of dissolution and oxidation environment in the oil-based drill fluid, when anodized layer is subjected to the synergistic interaction between wear and corrosion, this thin anodized layer are much easier worn out, and there were deeper and wider grooves, as well as a large number of delaminations and debris, formed during the reciprocating sliding, exhibiting the weaker wear resistance. These differences were also verified in the wear scar morphology observation.

This work will provides an important technical reference for prolonging the service life and reducing the failure accidents of Ti-4Al-2.5V-1.2Fe alloy alloy drill pipe in ultra-deep well drilling conditions.

Subtopic –Tribocorrosion

Simulation of localized corrosion propagation in inhibited media via potentiostatic test

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Limited research has been conducted on the propagation of localized corrosion in inhibited environments due to galvanic coupling between an inhibited surface and an active pit. Simulating this phenomenon is complex, which may explain the scarcity of research on this mechanism. The potentiostatic technique offers an interesting approach to simulate this corrosion mechanism, as it is driven by the potential difference between the surfaces. In this study, the potentiostatic technique was employed to investigate the performance of a primarily imidazolinium-based corrosion inhibitor under produced water conditions (5 wt.% NaCl, pH 4.5, CO₂) at temperatures of 55 and 80°C. Baseline tests using linear polarization resistance (LPR) and potentiodynamic polarization were conducted to characterize the inhibitor's performance. Anodic potentiodynamic sweeps at baseline revealed that the inhibitor fully desorbs from the surface at certain potential/current conditions. Four fixed potentials were defined and applied to simulate different scenarios for pit propagation. The potentiostatic tests showed that, at certain potentials, the injection of inhibitor did not decrease the measured current as expected from the baseline potentiodynamic sweeps. Additional inhibitor was found to be necessary under certain conditions to significantly decrease the current. However, at high current levels, further injections were ineffective, suggesting that substrate dissolution may undermine the adsorption of the inhibitor.

Keywords: Corrosion inhibition, Localized corrosion propagation, Inhibition efficiency, Imidazoline, High temperature, Potentiostatic.

Internal Corrosion Rupture of a 6-in Gas Line Pipe

F. Jewilli · A. Elhoud · K. Abouswa · O. Rageai

Abstract

A sudden leak of a 6-inch gas line pipe after being in service for one year was observed. The pipe had been designed to transport dry gas. The failure had taken place in 6 o'clock position at the stage discharge of the flow process. Laboratory investigations were conducted to find out the cause of the pipe rupture. Visual and metallographic observations confirmed that the pipe split was due to a crack initiated in circumferential and then turned into longitudinal direction. Severe wall thickness reduction was noticed on the internal pipe surface. Scanning electron microscopy observations at the fracture surface revealed features of ductile fracture mode. Corrosion product analysis showed the traces of iron carbonate and iron sulphate. The concluded remarks of the laboratory analysis confirmed that the pipe failed due to the effect of wet fluid (condensate) caused severe wall thickness dissolution resulted in pipe could not stand the continuation at in-service working condition.

Keywords Gas line pipe · Wall thickness · Ductile fracture

1 Introduction

Carbon steel parts in oil field application are often susceptible to suffer corrosion damage because of the presence of internal fluids such as natural gas and recovered water [1, 2]. A failure of component is affected by number of factors such as the fluid contents, metal chemical composition, microstructure, manufacturing, and service defects. However, improper fluid treatment or service in harsh condition can decrease a component age. The presence of water and gases (CO₂ and H₂S) are responsible for various degree of degradation [3, 4]. In the present case, detailed laboratory study was undertaken on the pipe ruptured section to establish the main cause of failure. At the end of the study, number of suggestions and recommendations to mitigate reoccurrence of similar failure were provided to the end-user.

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2 Failure analysis protocol

2.1 Visual Observations

Figure 1 shows the schematic of plant process and failed pipe location. General view of the failed pipe is shown in Fig. 2. The service temperature of the carbon steel pipe was 100 °C on average. The symbols of P_s and P_d represent the suction and discharge pressure of the flow process, respectively.

Figure 2a illustrates the external crack on the ruptured area. Figure 2b shows the internal view of the two halves of the pipe sample: the first half (left image) was the top part at 12 o'clock position and the second half (right image) was the bottom part of the pipe at 6 o'clock position. It can be seen from images that both halves have localized corrosion; the bottom part confirmed the longitudinal crack as indicated by the black arrow in Fig. 2b.

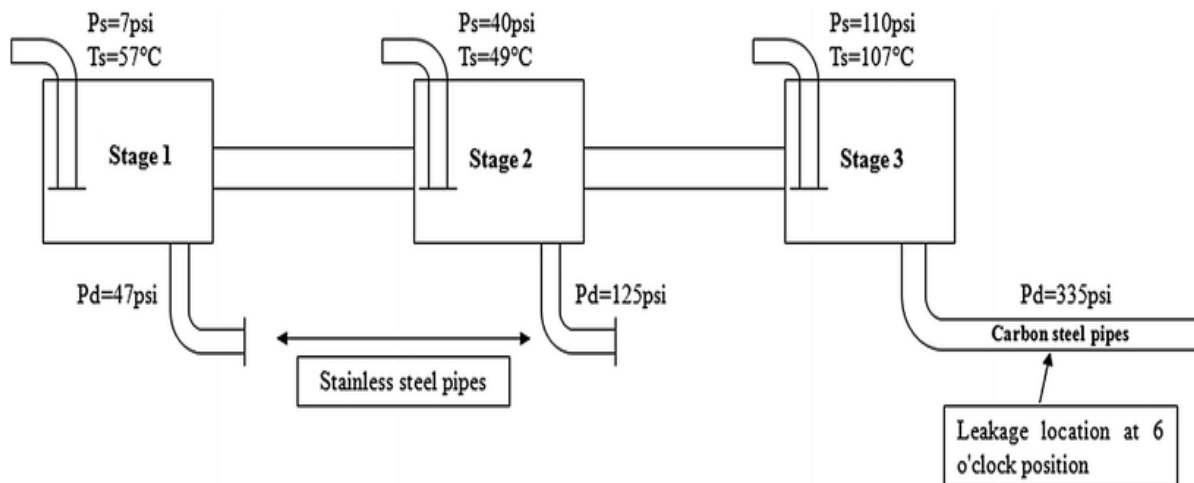
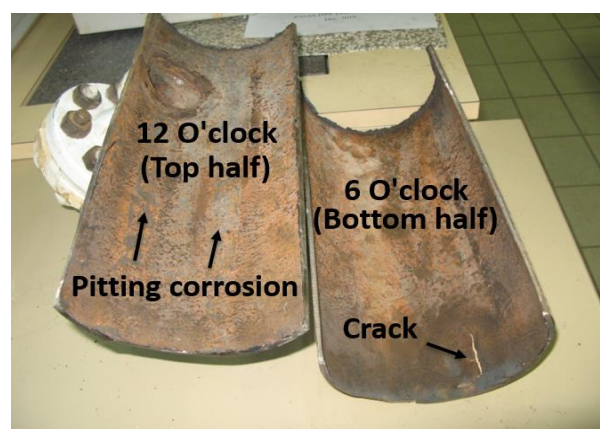


Figure 1 Schematic view of process diagram and the rupture location at the third stage



(a)



(b)

Figure 2 General view of the failed gas pipe; **a** external surface and **b** internal surfaces

3 Metallographic Observations

3.1 External Surface

Figure 3 illustrates the macroscopic observation of the ruptured area on the pipe external surface. The image shows the bulge of the pipe from the internal surface towards the external surface (denoted by black arrow caused by the rupture).

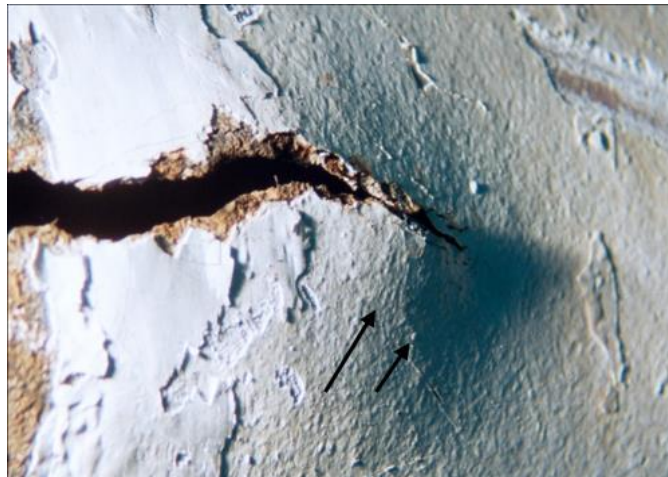


Figure 3 Macroscopic observation on the external pipe surface (magnification of 50x)

3.2 Internal Surface

Macroscopic investigation on the internal surface of the pipe was carried out to verify the wall internal condition. Localized pitting corrosion was also observed on the pipe wall as shown in Figure 4. Image in Figure. 5 will present a crack initiated at the pipe circumferential direction denoted by symbol I and then turned to the longitudinal direction as shown in the images which denoted by symbol II. The crack deflection angle from circumferential to longitudinal crack is clearly observed in the same image indicated by black arrows.



Figure 4 Macroscopic observation on the internal pipe surface shows pitting corrosion (magnification of 50x)

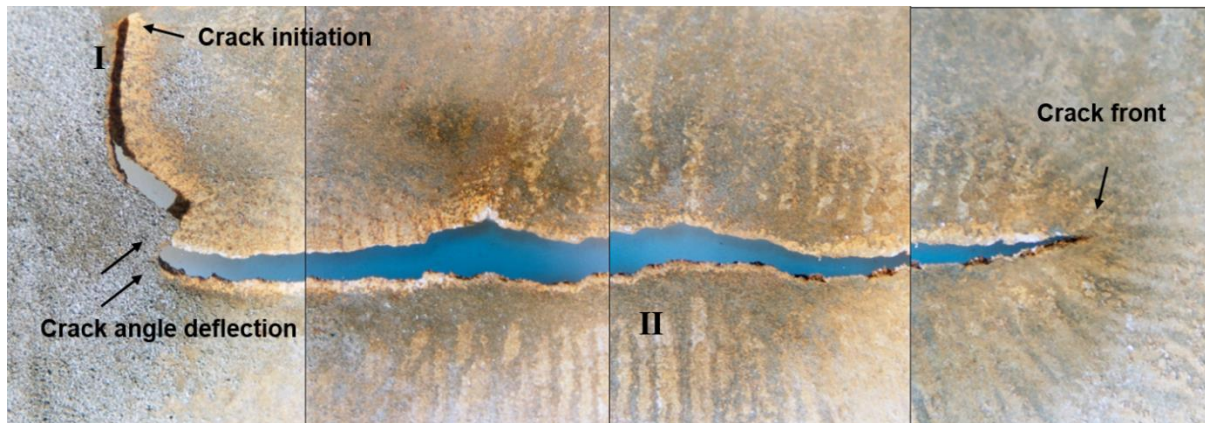


Figure 5 General view of the crack on the internal surface of pipe (magnification of 100x)

Macroscopic cross-sectional investigation between thickness of area away from the severely corroded and the thickness of the ruptured areas is shown in Figure 6. The thickness of slightly corroded area is denoted by symbol I where the remaining thickness at the ruptured area is denoted by symbol II. The variation in thickness can be noticed on area II.

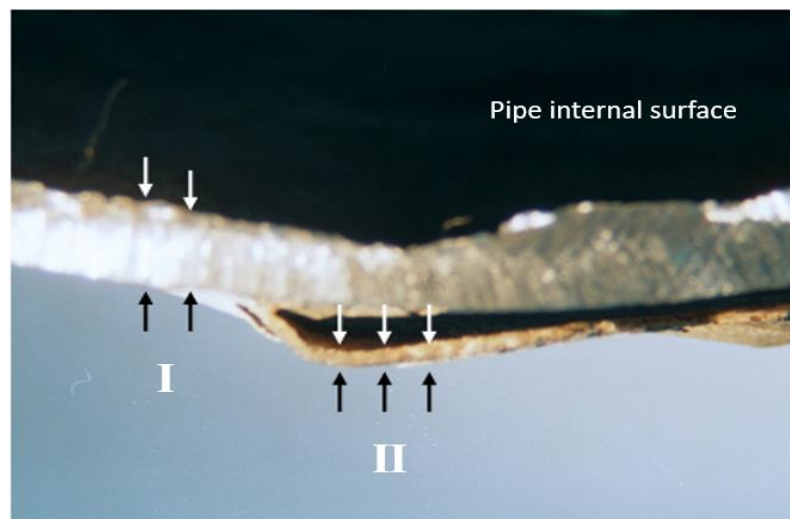


Figure 6 Thickness difference between slightly corroded and ruptured area (magnification of 150x)

3.3 SEM Examinations

The fracture surface morphology of the failed pipe was examined using SEM. The results of SEM analysis had taken on the crack initiation zone (I), as shown in Figure 7. The concluded remarks from the rupture features indicate the agreement in results which obtained by the SEM analysis and macroscopic observations. Both confirm the outcome that the presence of bulge on the external surface of pipe is a sign of ductile fracture mode. The fracture morphology on the crack surface consists of dimples and voids features.

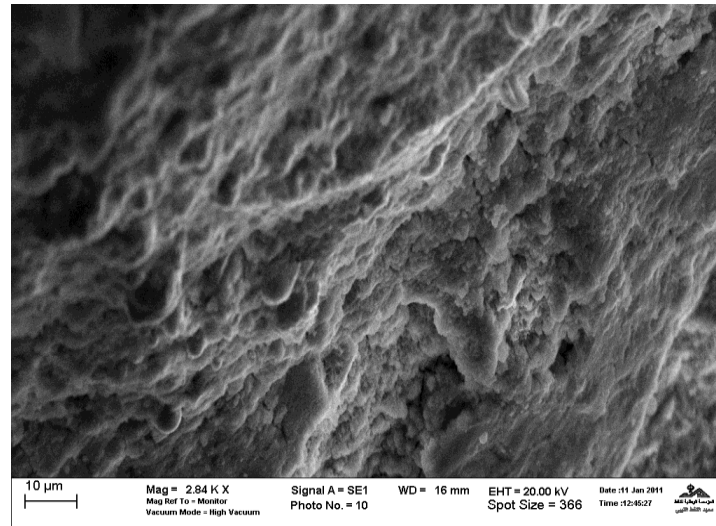


Figure 7 SEM image on the fracture surface

4 Chemical Analysis

The metal analyser detected the pipe chemical composition contains elements in wt% of 0.17C, 0.206Si, 1.02Mn, 0.095Cr, 0.034Ni, 0.028Mo, 0.015P, 0.036Al, rest is Fe. Samples of the corrosion product were collected from the failed pipe section and subjected to x-ray diffraction. The results of analysis are shown in Figure 8. The collected samples were primarily iron sulphide and iron carbonate. These two corrosion products are often the result of the chemical reaction between the iron and wet of H_2S and CO_2 .

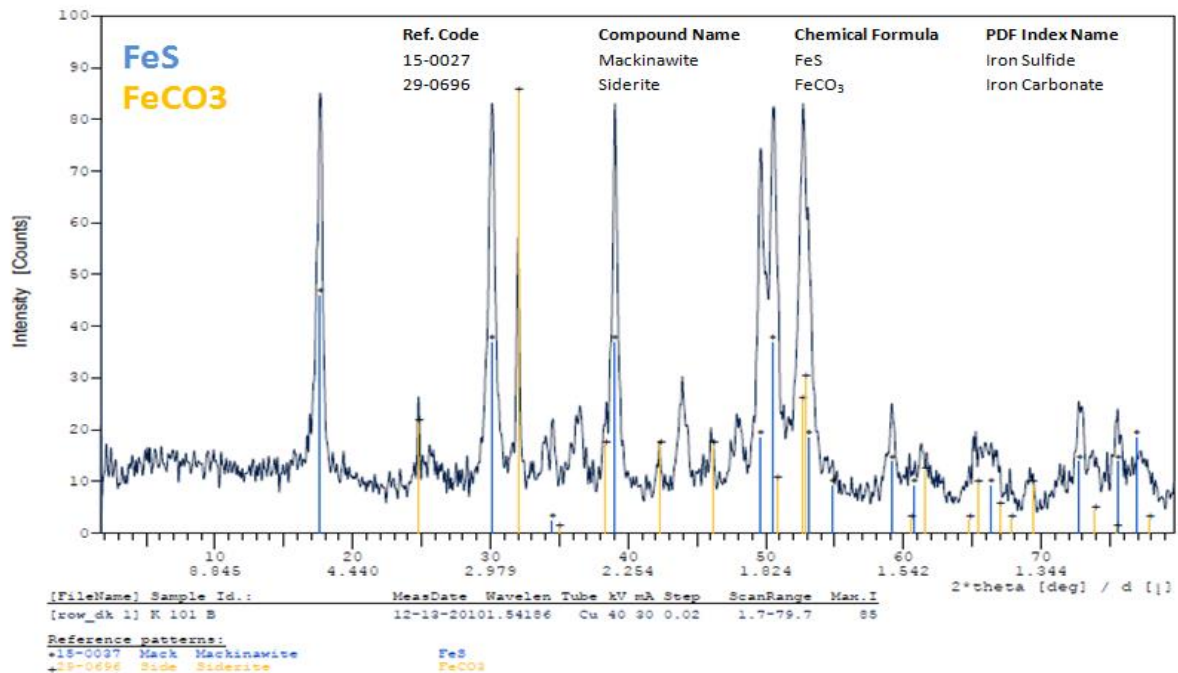


Figure 8 XRD analysis of corrosion product

5 Corrosion Rate

CASSANDRA software and the API 570 formula of long period corrosion rate were applied in the pipe estimated corrosion rate. The considered parameters in corrosion rate calculations and results are presented in Table 1. In CASSANDRA calculation, the parameters were inserted in the software and corrosion rate was calculated. Original pipe thickness and the remaining thickness at the damaged area used in measuring the corrosion rate by API 570 formula [5].

Table 1 Calculation of the corrosion rate parameters with Cassandra and API 570 formula

Parameter	Value	Parameter	Value
Partial pressure	335 PSI	Nominal thickness	6 mm
Temperature	225 F°	Actual thickness at the damage	0.9 mm
CO2 percentage	7.44 ppm	Period of service	1 year
H2S percentage	0.01 ppm	Calculated corrosion rate	CASS. API 570 4.6 mm/y 5.1 mm/y

6 Discussion

The gas has three stages of process as shown in the schematic diagram, Fig. 1. At the stage one and two, the gas still proposes to be wet and the selected pipe materials are stainless steel. Stainless steel pipes showed no sign of corrosion. Pipe at stage three is carbon steel considering that there was not sort of wet at this section. The corrosion process and the rupture mechanism of the pipe are discussed in three situations.

6.1 Fluid Became Corrosive

The presence of hydrogen sulphide, carbon dioxide, condensate and other corrosive species caused internal pipe wall corrosion. Dissolution of hydrogen sulphide caused the reduction in pH and produced sulphuric acid; this weak acid can cause pitting and acid attack.

In these medium, the iron Fe attack was found by acids leading to the formation of the FeS and FeCO₃; this chemical component has come from the activation of the iron in the solution. These interpretations were confirmed by the experimental results in Refs. [6, 7]. The absence of

internal chemical treatment or internal coating offered direct contact between the fluid and the pipe wall, resulting in pitting and general corrosion of the internal surface. The impact of fluid corrosivity on the pipe is indicated in laboratory metallographic observations and the corrosion product analysis.

6.2 Metal Wall Reduction

Degradation in forms of wall reduction as well as pitting corrosion of the internal pipe surface is clearly observed in the visual and the macroscopic analysis. Carbonic acid (H_2CO_3) and sulphuric acid (H_2SO_4) caused the corrosion reactions. Tendency to pitting corrosion of low-alloy steel in CO_2 increased in the temperature range of 70–110 °C [3]. The corrosive acid creates electrochemical corrosion cells on the pipe surface resulted in metal thickness reduction at the anodic area. High rate of metal loss indicated in the 6 o'clock position of the pipe. This is the location where the leakage was noticed during the pipe service. Pit density is observed on the pipe surface and away from the severely corroded area. The cluster of pits caused zones of corrosion where the preferable path for crack propagation.

6.3 Final Rupture

The history of the pipe demonstrated that the same working condition such as gas pressure, temperature and other factors remained the same till the time failure occurred. The reduction in the pipe thickness due to corrosion did not fit the working condition, and hence, the failure happened. This interpretation is in agreement with the observations displayed in Figs. 2, 3, 4, and 5 obtained by visual and macroscopic analysis. Crack observed in the macroscopic observation shows the crack and the final burst. The strength of the pipe wall is different depending on the wall thickness. The severe corrosion and the high reduction in metal thickness can impact the strength. The reduction in thickness could accelerate the rupture, and the crack initiated at the thinner area of the pipe metal thickness. After initiation, the crack turned to the longitudinal direction due to the shear stress which exceeds the shear strength, Fig. 5, area I. The crack propagated perpendicular to the internal hoop stress caused by the internal pressure. After initiation, the crack propagated faster due to the less metal strength at the corroded area. The bulge is an indication that the pipe failed in ductile manner. As the crack propagated, the pipe bulged out and split. The observed ductile fracture morphology supports the interpretation of the visual and the macroscopic findings. The metal tearing at the fracture surface is in ductile mode as described in Ref. [8, 9]. The presence of ductile voids is clearly observed in the SEM results.

7 Conclusions

- The gas pipe failure was due to the wall thinning caused by severe internal corrosion.
- The presence of traces of hydrogen sulphide and carbon dioxide in wet condition was responsible for the corrosiveness of the fluid.
- Dissolved hydrogen sulphide and carbon dioxide in wet condition formed corrosive acids and reduced the pH.
- Calculated corrosion rate revealed the fact that the pipe exceeded the corrosion allowance and the minimum required thickness in time less than the designed.

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A comparison of borides formed on 30NiCrMo16 and X10CrNiTi 18-09 steels

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Abstract

In this study, polarization resistance and electrochemical impedance spectroscopy (EIS) techniques were used to determine the corrosion resistances of 30NiCrMo16 and X10CrNiTi 18-09 (AISI 321) borided and non-borided steels. The powder-pack method was employed to boride the steel samples for 1, 2, and 8 hours at 1223 K. A compact layer of FeB/Fe₂B was developed on the surface of the AISI 321 steel, whereas structural tests of the borided steel surfaces revealed the presence of a Fe₂B layer with isolated FeB teeth on the 30NiCrMo16 steel. In a corrosive solution of 1M HCl (pH=0.13), polarization resistance and EIS of the borided and unborided steel surfaces were tested. After being exposed to the acid solution for 56 days, the EIS data were examined. Equivalent electrical circuits were used to obtain the impedance curves of borided and non-borided steels. The results of both electrochemical techniques showed that the samples are successfully shielded from the corrosive effects of HCl by boride layers that have grown at the steel surfaces.

Keywords: Fe-B system, Boriding, Iron borides, EIS technique.

Introduction

When boron diffuses into and mixes with a substrate material to generate a single or double-phase metal-boride layer on the surface, the process is known as boriding. Contrary to many other surface treatments, boron diffusion allows hard boride layers to form on the majority of alloys and metals. When ferrous materials are bored, either a single (Fe₂B) or double (FeB/Fe₂B) layer with a clearly defined composition is created. Each layer's thickness influences the mechanical and chemical behaviour of borided steels and is influenced by the boriding temperature, the treatment time, the steel's chemical composition, and the quantity of boron around the sample surface [1].

Corrosion resistance is one of the most significant qualities enhanced by boriding. The corrosion resistance of borided steels has been the subject of various research over the past several years that have attempted to quantify it using methods other than continuous and cyclic immersion corrosion testing [2,3].

To assess the corrosion resistance of materials with surface coatings nowadays, electrochemical methods are usually used. Tavakoli and Mousavi Khoie [4] used a 3% NaCl solution to calculate the corrosion resistance of several grades of borided steels. It was determined by an electrochemical test using the impedance spectroscopy technique that the presence of boride layers increased corrosion rate during the course of 1, 4, and 2–4 days of exposure. Additionally, Jiang et al. [5] proposed the use of the polarization method and electrochemical impedance spectroscopy (EIS) technique to assess the corrosion behaviour of low carbon borided steels submerged in a 3.5 weight percent sodium chloride solution (although the duration of the borided steels' exposure to the acid solution was not specified in this study). Results of electrochemical experiments signified that the presence of Fe₂B on the surface of

low-carbon borided steel improved its corrosion resistance in comparison with non borided steels. Analogous results were obtained for the AISI 316L SS borided by the powder-pack method [3]. Electrochemical tests (Tafel and polarization techniques) were performed in 1 mol/dm³ HCl, 1 mol/dm³ NaOH, and 0.9% NaCl during 1 and 168 h at 310 K for each solution. The presence of FeB/Fe₂B layers decreased the assessed corrosion resistance for the HCL solution. Nevertheless, in the case of NaOH and NaCl solutions, the corrosion resistance of the borided stainless steel decreased. It has been found that the corrosion resistance of the borided samples tend to be improved for longer periods of immersion in all solutions.

For the polarization resistance technique, a minor potential perturbation was applied to the working metal electrode and the subsequent current response was recorded. The linear polarization resistance (LPR) is the ratio between the applied potential and the resulting current response and it is inversely proportional to the corrosion current [6].

Electrical impedance spectroscopy (EIS) is a powerful electrochemical technique extensively used in corrosion field. The analysis of impedance measurements are commonly conducted using the equivalent electrical circuits, including passive elements, i.e. resistors, capacitors, inductors, and constant phase element. This permit EIS data to be used to determine the electrochemical system properties. In this work, polarization resistance and electrochemical impedance spectroscopy (EIS) techniques were used to determine the corrosion resistances of two borided and non-borided steels.

Experimental procedure

Powder-Pack Boriding Process

The powder-pack boriding process was applied on square commercial samples of 30NiCrMo16 and X10CrNiTi18-09 (AISI 321). Chemical compositions of these steels are: 0.27wt.%C, 0.5wt.%Mn, 0.28 wt.% Si, 1.2 wt.%Cr, 2.26 wt.% Ni, 0.16 wt.% Cu (30NiCrMo16), and 0.086 wt.%C, 1.52 wt.% Mn, 0.297 wt.% Si, 17.71 wt.% Cr, 10.82 wt.% Ni, 0.16 wt.% V, 0.51 wt.% Ti, 0.171 wt.% Cu (X10CrNiTi18-09 / AISI 321). Before boriding, the specimens were polished, cleaned at room temperature with an alcohol solution and deionized for 15 min. Then, they were dried and stored in clean-room conditions. Specimens were inserted in a closed cylindrical container inclosing 5% B₄C, 5% NaBF₄ and 90% SiC at 1223 K during 1h, 2h and 8h. When the treatment was finished, the container was removed from the furnace and gradually cooled at room temperature.

The borided samples were prepared using ground from 240 to 4000 grit SiC sand paper. The microstructures of the boride layers were observed in a Scanning Electron microscope (SEM) instrument.

The microstructure of the boride layers formed on the surface of the 30NiCrMo16 and X10CrNiTi18-09 (AISI 321) steels was also investigated by X-ray diffraction (XRD) applying regular 2 Θ - ω scan procedure. An XPERT PRO instrument was utilized with Cu K α radiation at $k = 0.154$ nm.

Electrochemical corrosion evaluation

The electrochemical corrosion assessment of borided and non-borided steels immersed in 1M HCl was separated into two procedures: the first procedure consist at studying the behaviour of the open circuit potential (EOCP) as a function of time, while the second one interested in the EIS technique using an electrochemical work station (PARSTAT 4000 instruments) provided with VersaStudio Software.

All the experimental tests were conducted at room temperature and open circuit potential (EOCP) in a classical three-electrode cell with an Platinum cylindrical pole as counter electrode and an Ag/AgCl mini-electrode as a reference electrode. The test sample (working electrode) was taken horizontally at the bottom of the cell and attached to an acrylic cylinder. The steel samples were initially immersed in an electrolyte solution for about 30 min at room temperature to stabilize the open circuit potential (EOCP).

EIS measurements were recorded over 56 days of immersion in acid solution, applying a sinusoidal input signal $E_0 \sin(xt)$. x is the frequency and it ranges from 1 to 10 MHz using a sinusoidal potential perturbation with a 10 mV amplitude. Electrochemical parameters were determined by fitting a suitable equivalent electrical circuits (EECs) to the experimental data.

Results and discussions

Microstructure of Borided Steels

Cross-section microstructures of the 30NiCrMo16 and X10CrNiTi 18-9 borided steels are depicted in Fig.1. The boride layer formed on the surface of the 30NiCrMo16 steel exhibited a saw-tooth morphology with Fe_2B layers with isolated FeB teeth. This was confirmed by the XRD pattern shown in (Figure 2b). The depth of Fe_2B layer was about $111 \pm 6 \mu m$. The saw-tooth morphology of the boride layers can be justified by the presence of improved diffusion paths within the Fe_2B crystal lattice [7]. Structural analysis of the surface of borided steel X10CrNiTi 18-09 revealed the presence of FeB/Fe_2B layers with a total thickness of $29 \pm 3 \mu m$. The substitution mechanism found that chromium was concentrated at the top of the boride pillars, suggesting that chromium inhibits the growth of the boride layer. Boron flux is reduced in high chromium zones. Therefore, the columnar shape of growth is reduced compared to 30NiCrMo16 boride steel [8,9]. X-ray diffraction (Fig. 2a) conducted on the surface of the borided X10CrNiTi 18-09 samples showed the presence of $FeB-Fe_2B$ layers. Furthermore, chromium reacts with boron to form interstitial compounds such as Cr_2B . Nickel diffuses into the boride layer and under the surface layer he precipitates as NiB [10].

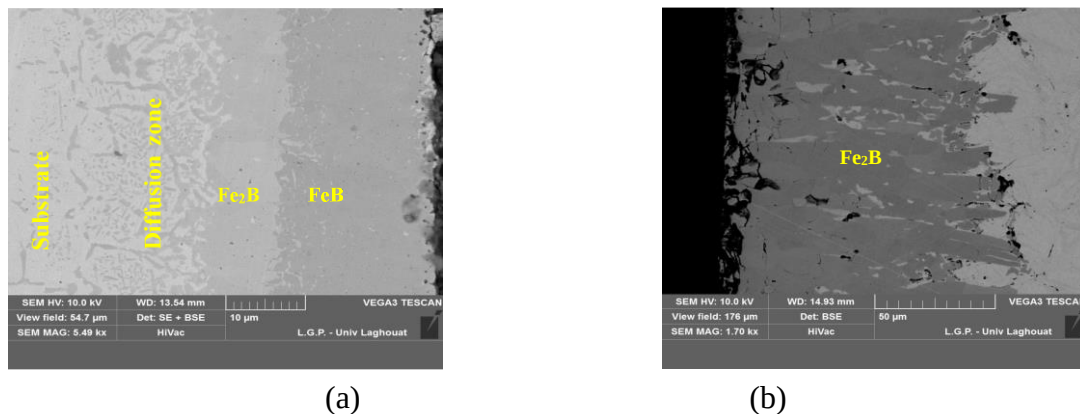


Fig. 1. Cross-section microstructures of borided steels at 8h of treatment (a) X10CrNiTi18-09, (b) 30NiCrMo16

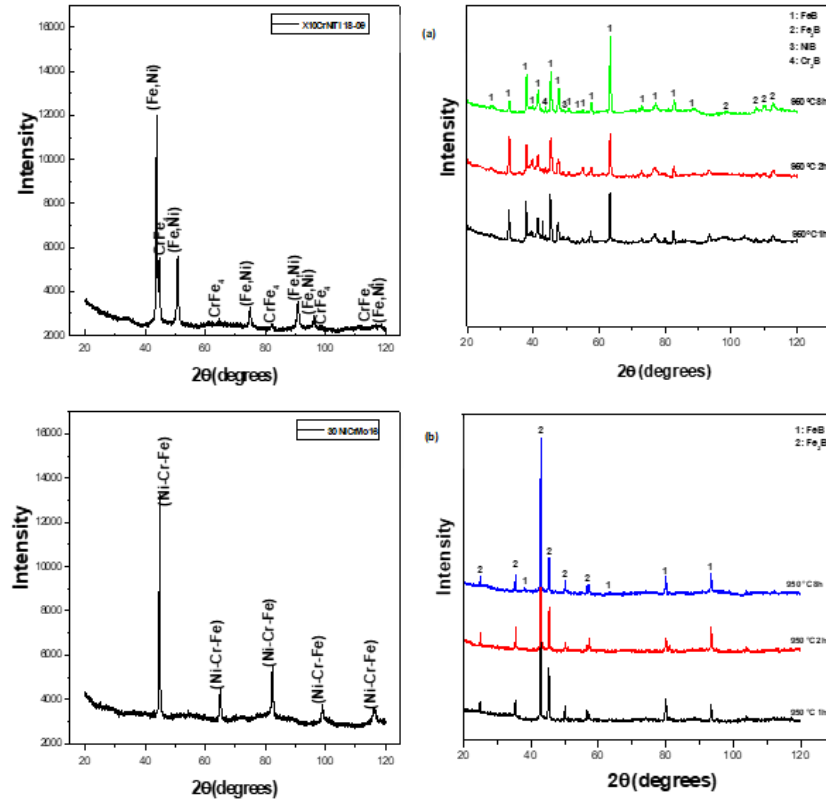


Fig.2. X-ray diffraction patterns obtained on the surface of: (a) X10CrNiTi 18-09 non-borided and borided steel, (b) 30NiCrMo16 non-borided and borided steel.

Fig.3 presents the Nyquist plots obtained for the X10CrNiTi 18-09 borided and non-borided steels. The obtained results are summarized in Table 1. The corrosion resistance of X10CrNiTi 18-09 borided steel attained its maximum value of $2534.8 \Omega \text{ cm}^2$ for 08 hours of treatment and 56 days of immersion in HCL solution. The corrosion resistance drop to about $354 \Omega \text{ cm}^2$ for non borided X10CrNiTi 18-09 steel.

For the 30NiCrMo16 borided steel, the corrosion resistance of Fe_2B layer (R_c) showed a maximum value of around $226 \Omega \text{ cm}^2$ after 08 hours of treatment and decreased to a corrosion resistance of about $76.263 \Omega \text{ cm}^2$ after 56 days of immersion of non borided steel (Fig.4). The electrical parameters of the borided and non borided 30NiCrMo16 steel are illustrated in Table 2.

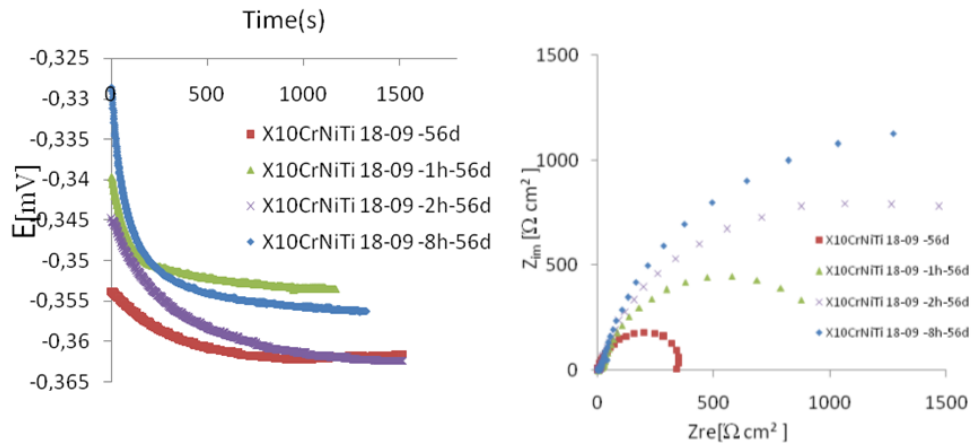


Fig.3. Behaviour of the open circuit potential, Eocp and experimental impedance plots (Nyquist format) for X10CrNiTi 18-09 non-Borided and borided steels recorded during 56 days of immersion in 1M HCl

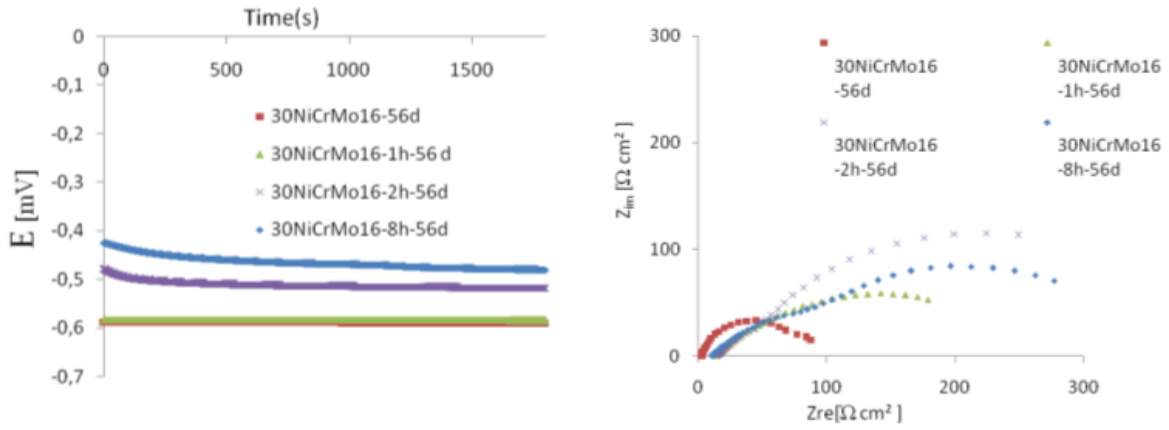


Fig.4. Behaviour of the open circuit potential, EOCP and experimental impedance plots (Nyquist format) for 30NiCrMo16 non-Borided and borided steel recorded during 56 days of immersion in 1M HCl

The electrochemical parameters were estimated by fitting an appropriate equivalent electrical circuits (EECs) to the experimental data (Fig. 5).

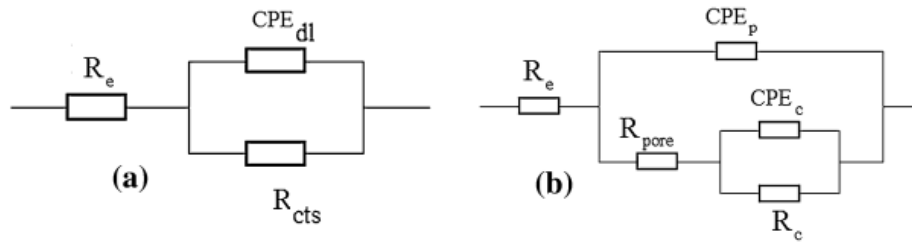


Fig. 5. EECs used for numerical fitting of impedance data: (a) non-borided and (b) borided steels

- R_e [$\Omega \cdot \text{cm}^2$]: Electrolyte resistance ;
- R_{cts} [$\Omega \cdot \text{cm}^2$]: Resistance of the electron charge transfer of the substrate;
- R_{pore} [$\Omega \cdot \text{cm}^2$]: Resistance of the pore;
- R_c [$\Omega \cdot \text{cm}^2$]: Resistance of the boride layer;
- C_p [$\mu\text{F}/\text{cm}^{-2}$]: Capacitance of the pore;
- C_{dl} [$\mu\text{F}/\text{cm}^{-2}$]: Electrochemical double layer of the substrate;
- C_c [$\mu\text{F}/\text{cm}^2$]: Capacitance of the boride layer.

Table 1. Analysis of Nyquist for non borided and borided X10CrNiTi 18-09 utilizing EECs over 56 days of corrosive immersion.

Non-borided steels	R_e [$\Omega \cdot \text{cm}^2$]	R_{cts} [$\Omega \cdot \text{cm}^2$]	C_{dl} [$\mu\text{F}/\text{cm}^2$]	N_{cts}			
X10CrNiTi 18-09	15.649	354.61	89.08	0.81			
Borided steel	R_e [$\Omega \cdot \text{cm}^2$]	R_{pore} [$\Omega \cdot \text{cm}^2$]	C_p [$\mu\text{F}/\text{cm}^2$]	N_p	R_c [$\Omega \cdot \text{cm}^2$]	C_c [$\mu\text{F}/\text{cm}^2$]	N_c
X10CrNiTi 18-09 -1h	11.707	164.96	103.8	0.83	802.63	59.2	0.73
X10CrNiTi 18-09 -2h	8.394	281.2	60.5	0.84	1673.9	27.32	0.74
X10CrNiTi 18-09 -8h	5.07	2534.8	43.1	0.87	281.5	11.7	0.78

Table 2. Analysis of Nyquist for non borided and borided 30NiCrMo16 utilizing EECs over 56 days of corrosive immersion.

Non-borided steels (a)	$R_e / [\Omega \cdot cm^2]$	$R_{cts} / [\Omega \cdot cm^2]$	$C_{dl} [\mu F/cm^2]$	N_{cts}			
30NiCrMo16	4.96	76.263	432.6	0.7			
Borided steel (b)	$R_e / [\Omega \cdot cm^2]$	$R_{pore} / [\Omega \cdot cm^2]$	$C_p [\mu F/cm^2]$	N_p	$R_e / [\Omega \cdot cm^2]$	$C_e [\mu F/cm^2]$	N_e
30NiCrMo16-1h	3.69	49.21	288.4	0.82	131.12	143.2	0.74
30NiCrMo16-2h	7.01	58.7	149.9	0.85	168.1	67.4	0.74
30NiCrMo16-8h	10.76	78.1	103.6	0.93	226.04	27.5	0.79

Conclusion

From examinations of the obtained results from polarization resistance and EIS electrochemical tests, borided steels displayed better corrosion resistance than non-borided steels. The X10CrNiTi 18-09 (AISI 321) borided steel appeared higher corrosion resistance than the 30NiCrMo16 borided steel due to contrasts in chemical compositions of the substrates and the impact of the microstructure of the boride layer. Fundamentally, alloying components such as chromium and nickel are included within the anodic response and improve the corrosion potential on the surface of X10CrNiTi 18-09 (AISI 321) borided steel. The corrosion resistances of borided and non-borided steels are specifically relative to the treatment exposure time.

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Characterization of Nano-structured graded multi-layered coating

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Keywords: Characterization, Nano-structured, Wear, cermet, graded.

This paper investigates the characterization techniques of Nano-structured cermet graded multi-layered coating. Nano-sized agglomerated powders were used to enhance the mechanical behaviour, wear, and corrosion protection (Hardness, corrosion, erosion-corrosion) of the coatings. The coating was applied onto selected carbon steel substrates (API-5L, Schedule-40, Grade-B) to simulate the material application used in oil and gas components that subject to corrosion and corrosion-erosion phenomena. The coating was deposited using three layers of coatings with various combinations of sprayed powders to create graded multi-layered coating. The surface morphology and the elemental composition of the coatings were examined using SEM and EDS techniques.

Design of Experiment for Advanced Nanostructured Coating: Dry Solid Particle Erosion Tests

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Keywords: Wear, Biomodal, Software, Nanostructure, Erosion.

One of the economical and fast solutions for failure against erosive wear in oil and gas industries is the deposition of cermets using HVOF thermal spray. Recently, especially with the new development of bimodal feedstock powders, the composition percentages of the mixed powders have played a key factor in the final coating performance. In the present study, a design of experiment (DOE) software was implemented to study the influence of different powder percentages on the coating performance. The coating mechanical properties and its performance were investigated via dry solid particle erosion tests, hardness measurement and SEM respectively. The results showed that both the hardness and erosion resistance of the coating increases as the composition percentage of the nanostructured WC-12Co increased due to the strong adhesion of WC nano size grains at the substrate/coating interface as a result of improved mechanical interlocking

Synthesis and properties of the Ni-Mo-B electrochemical composite anticorrosion coatings

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The purpose of this research is to develop nickel-based composite coatings doped with Molybdenum (for increasing corrosion resistance) and Boron (for increasing wear resistance); to establish optimal heat treatment regimes (for improvement the physical and chemical properties of the coatings) and to investigate electrochemical properties of coatings in corrosive environments.

The composition of the electrolyte-suspension with amorphous Boron and the electrolysis regimes were offered to obtain non-porous Ni-Mo-B composite coating with increased thickness (30...50 μm) and hardness (13.5...14.2 GPa). An effective electrolyte for the coating deposition was established: citrate with an ammonia buffer (mol/l): 0.200 NiSO_4 ; 0.004 Na_2MoO_4 ; 0.300 $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$; 23.100 B, current density $J_k=3 \text{ A/dm}^2$, temperature 60 $^\circ\text{C}$, pH9.5.

The regimes of heat treatment of the coating were proposed. After annealing at 850 $^\circ\text{C}$ for 2 h hardness of coating was increased to 13.5...14.2 GPa due to the boride phases formation. The high corrosion resistance of Ni-Mo-B coatings was established. Comparatively to the nickel coating, its corrosion rate in 3% NaCl solution was 3.5 times smaller (0.0002 mA/cm²) and it doubled in 5% HCl solution, but its value was negligible.

The developed Ni-Mo-B coatings are promising for applying to parts of pumps in the utility industry, pistons of gas compressor stations, flanges and fittings in the chemical industry and other small parts, that work at tribo-corrosion conditions.

An Investigation of Phase Impact on Corrosion Properties of Electrodeposited Zn-Ni Coatings

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Zinc plating has seen extensive application in general engineering industries, including some use as a replacement for cadmium. For decades, electroplated zinc has been used to provide an economical and highly corrosion resistant coating, but conventional zinc electroplates are being replaced by zinc alloys, since the alloys have a better overall performance. In summary of most literature, zinc–nickel coatings which have been claimed for Zn coatings alloyed with 9–17 wt.% Ni (γ -phase) have attracted much attention because they possess higher corrosion resistance and better mechanical characteristics in comparison with zinc and other zinc alloy coatings. However, compared with different literature, people normally would have different conclusions of either γ -Ni₅Zn₂₁, δ -phase or η -Zn phase has the dominant effect of the corrosion resistance of Zn-Ni coatings.

Investigation of Different Phases Effect on Corrosion Properties of Zn-Ni Coatings

Different phases have been proved to have the dominant influence on the good corrosion resistance of Zn-Ni coatings. Experiments were carried out under acid baths. The surface morphologies, phase composition and microstructure and phase structure of the coatings were examined and analysed by SEM, XRD and TEM, respectively. According to the dominant phases of Zn-Ni coatings summarized by different papers, we decided to investigate how the phases effect the corrosion properties by figuring out the main phase by XRD and TEM first and followed by polarization measurements and corrosion tests using salt spray tests.

From the gained results, when the composition of the phase in the coatings is single γ -Ni₅Zn₂₁ phase, it would show excellent corrosion resistance as compared with conventional Zn-Ni coatings with the combination of γ -phase and η -Zn phase. The results showed how different phase impact Zn-Ni coatings as when we want to present coatings with best corrosion properties, we would try from different parameters and conditions to make single γ -phase Zn-Ni coatings as its best performance when resisting corrosion.

Corrosion performance of cold spray coated stainless steel in nitric acid environment

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Stainless steels (SS) are corrosion-resistant in nitric acid environment. However, in more severe conditions (at high temperatures and in the presence of oxidizing ions), SS presents a high dissolution rate and, in most cases, the presence of intergranular corrosion due to the passage in the transpassive domain has been observed (1, 2). The use of coatings seems to be a promising way to improve the anti-corrosion properties of SS under such severe conditions. Specifically, coatings of valve metals such as Zr (3) and Ta (4) are interesting candidates.

Interestingly, cold spray process allows realizing deposits without melting the material, that is, without any phase transformation. The particles collide with the substrate at very high speed and low temperature, resulting in a stack of plastically deformed particles, forming a dense and highly adhesive deposit. This process has the advantage to be simple because it can work without a controlled atmosphere and without prior preparation or masking of the substrate. In addition, this technology allows the realization of coating, repair of parts or additive manufacturing (5, 6), but only few studies have been carried out on the behavior of such coatings (Ta or Zr) in nitric environments. Therefore, this study investigates the corrosion resistance of cold spray coatings under severe conditions (nitric medium containing oxidizing species).

Coatings were first characterized by optical and scanning electron microscopy on cross sections. They exhibit a good adhesion on the SS substrate and poor porosity.

Energy dispersive x-ray spectrometry and gun discharge mass spectrometry analyses show a good chemical homogeneity of the coatings. The surface roughness was also characterized with an interferometric profilometer.

Coating performances were studied by immersion and electrochemical tests (linear polarization and electrochemical impedance spectroscopy) in concentrated nitric acid solution.

During immersion tests, the dissolution rate was estimated by measuring the mass loss as the function of time and the evolution of surface morphology was followed by microscopy and interferometry. Additionally, the passive layer was characterized (chemical composition and thickness) by X-ray photoelectron spectroscopy. It was shown that the dissolution rate is significantly decreased due to the presence of the coatings.

The electrochemical measurements show that the corrosion of the SS is limited by the presence of the coating: the passive current strongly decreases and the passive-transpassive transition disappears or is shifted towards higher potentials.

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Corrosion resistance of Galvanised Zn-Al Steel Sheets Produced in a Hot Dip Process Simulator (HDPS)

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New demands for corrosion resistant coated steel for longer service life are growing as a result of the increased concern on protection of the environment. To avoid significant corrosion degradation in aggressive atmospheres, steel has to be coated by a protective coating.

It is already well known that the application of galvanized steel has been carried out successfully for more than 130 years and that even so it presents certain limitations. From the point of view of coating whose main mission is to protect against corrosion, it is known that in severe industrial or marine environments, the greatest the limitation it presents is related to high zinc dissolution rates. In addition, and as if this were not enough, recently, ecological restrictions have also been imposed. In the galvanizing industry, in order to conserve natural Zn resources and reduce production costs, great attention has been paid to further improvement of the corrosion resistance and workability of Zn or Zn alloy coated steel products to extend the coating lifetime with less material. That is why the search for new coatings and even new industrial galvanizing processes continues.

Aluminum coatings are considered an excellent alternative to zinc coatings. Coatings of Zn-Al alloys on steel sheet give a high corrosion resistance due to the corrosion prevention by zinc and the passivation by Al. Al is probably the most important element added to the HD galvanizing bath, with different concentrations to produce different properties of the bath and to control the microstructure of the layers in the coating, plus their effect on the reactions in or on the steel substrate: e.g. it produces ductile coatings by suppressing the growth of brittle Fe–Zn intermetallic phases. During the last decades, many research activities have been carried out to improve the corrosion resistance of HD galvanized steel products. Thus, the Zn-Al coatings Galfan and Galvalume have been developed. Although Galvalume or Galfan are successfully applied, especially in the construction industry, there is however, a growing interest in

the development of other ZnAl-based coatings, so big part of their R&D effort is focused on these advance.

In order to get so, many important industrial processing steps require a reliable procedure for process verification. Verification on production or pilot lines is neither economical nor efficient. It is in this context of complexity and industrial challenge where the objective of this work is located. The simulator for the HDP (Hot Dip Process) called DIPCA@SIM (Figure 1) located at IDONIAL is a unique research equipment which allows laboratory scale simulations of the (hot dip) coating and of the consequent annealing processes occurring in industrial production lines, serving for process and product improvement and development.

To improve and further develop the production and the final coating properties, hot dipping experiments were performed in a DIPCA@SIM simulator using steel sheet substrates, different bath compositions (Zn0.2Al, Zn5Al and Zn10Al) and various hot dipping parameters (such as bath temperature, entry and cooling speed and immersion times) to produce coated sheet steel samples with different coating thickness and microstructures. The **results** (in terms of surface appearance, corrosion resistance (SST) and microstructure) obtained by these simulations **show to be** excellent and **absolutely transferable to the production process of real continuous galvanizing lines**.

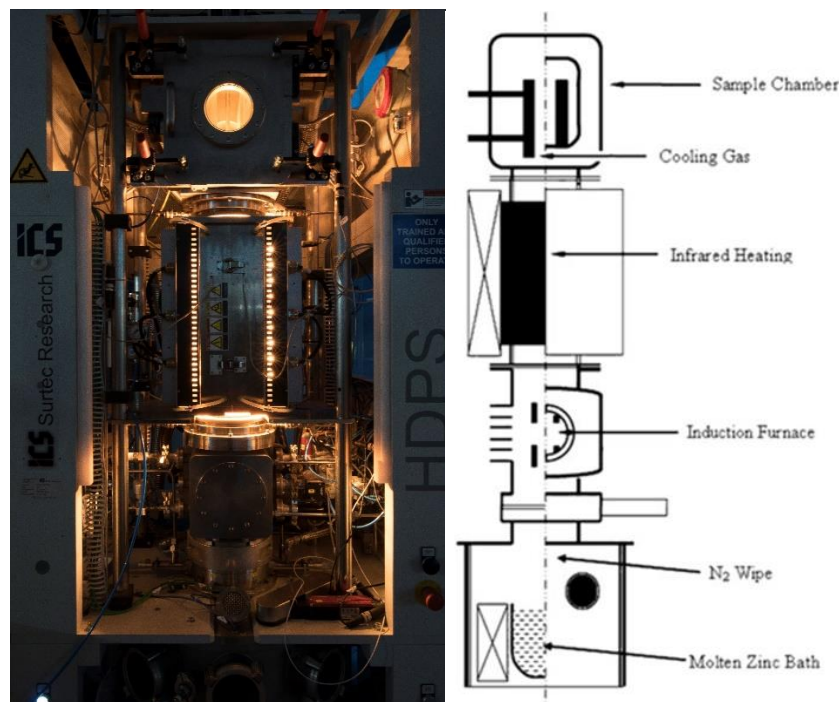


Figure 1. HDPS DIPCA@SIM

Corrosion control of ruthenium oxy-hydroxide coating for the development of robust pH sensors: observation and monitoring of the near field of a nuclear waste disposal site

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In Europe, nuclear waste repositories are being or will be installed in deep excavated rock formations, to isolate radioactive waste from human environment. In France, Callovo-Oxfordian formation (COx) has been identified as a deep geological formation to manage high and long-lived middle activity nuclear waste, under the supervision of ANDRA, the French national radioactive waste management agency.

In order to monitor the evolution of the nearby field around radioactive waste, the implementation of robust sensors turns out to be essential for safety reasons and reversibility of storage. pH is one of the most important parameters characterizing physical, chemical, and electrochemical transformations to be monitored.

Based on reversible interfacial redox processes that involve protons, metal oxy-hydroxides (MOx) potentiometric electrodes have been regarded as the most promising technologies for pH measurements due to their intrinsic mechanical stability regarding temperature, pressure, and aggressive environments.

This work reports the redox control of ruthenium oxy-hydroxide (RuOx)-based coatings for the development of promising and innovative robust pH sensors. Understanding the electrochemical behavior of such coatings is the key point of our research, as provides the basis for constructing the abacuses needed for developing robust and reliable field pH sensors.

The robust probe is a RuOx-coated ruthenium electrode. For a better insight into the coating, RuOx-based screen-printed electrodes (SPEs) were also used as tools for rapidly generating data sets. The electrodeposition of RuO_x was performed using cyclic voltammetry (CV) at different scan rates, from a solution containing dissolved RuCl₃·3H₂O at pH 2.

The electrochemical behavior of the RuO_x-coated electrodes was determined by cyclic voltammetry and electrochemical impedance spectroscopy. The use of the electrodes for pH sensing was then evaluated by potentiometric measurements by means of pH buffers solutions, at 25°C, under both oxidic (at atmospheric pressure) and anoxic conditions (in a glove box, pN₂ = 1 atm; pO₂ = 10⁻⁶ atm). These were done to the anticipated decrease in the redox potential in the CO_x pore water caused by the decrease in the O₂ concentration. Only the pH range that includes previously encountered or anticipated pH values in the CO_x during its evolution as a radioactive waste repository (pH 4 to 13) were studied.

The general convergence of the stabilization potential revealed the occurrence of an equilibrium state under the experimental conditions. RuO_x-coated electrodes responded rapidly to changes in pH (≤ 5 min) regarding the relative standard deviation (RSD) based on repeatability (RSD ≤ 3%).

RuO_x electrodes showed a high sensitivity (in the range from -63 to -67 mV/pH) under oxidic conditions (Fig. 1A) and, furthermore, the absence of oxygen (GB) causes a slight sensitivity expansion (Fig. 1B). The experimental standard potential is in agreement with Ru^{IV}/Ru^{III} redox couples which depends on both the material on which the deposit is made and the coating hydration, without affecting sensitivity.

Work is in progress to demonstrate the robustness of the RuO_x-coated ruthenium electrode into CO_x pore water solution over a long period.

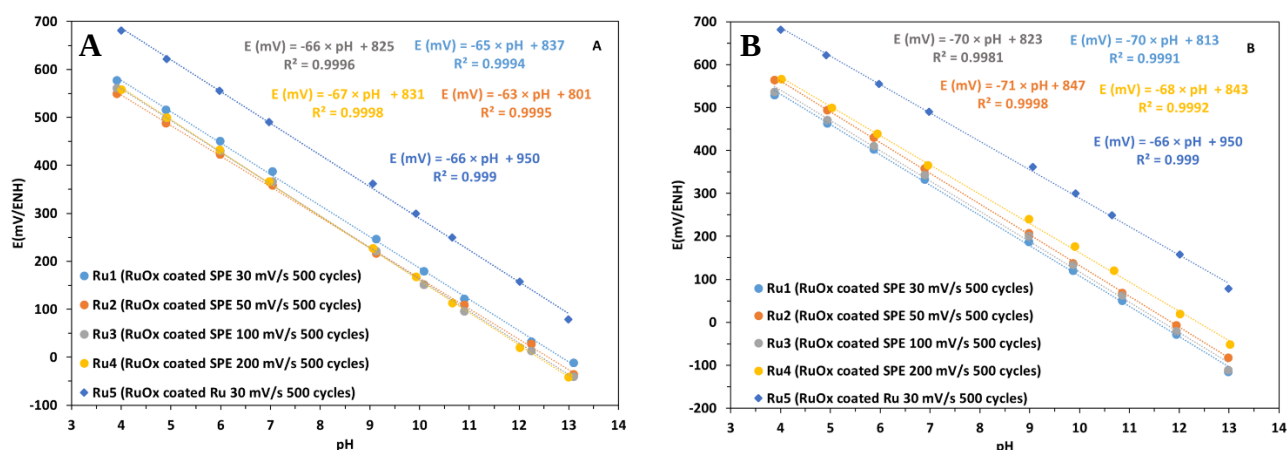


Figure 1: Open circuit potential of RuO_x electrodes as a function of pH under oxidic conditions (A) and anoxic conditions (B).

Advancing Geothermal Heat Exchanger Efficiency: Investigating Coating Solutions for Enhanced Heat Transfer and Reduced Corrosion in Heat Exchangers

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Abstract

The geothermal energy sector is one of the key solutions to reducing greenhouse gas emissions and achieving a low-carbon economy. According to the International Renewable Energy Agency (IRENA), geothermal energy now delivers around 15.96 gigawatts electric (GWe) in 2021, with this figure anticipated to rise to 18.3 GWe by 2025. Moreover, geothermal energy may be used to heat and cool buildings which account for more than 50% of worldwide energy consumption. When compared to standard heating and cooling systems, the usage of geothermal heating and cooling systems in buildings can result in up to an 85% reduction in carbon emissions. Additionally, geothermal energy has huge potential, with estimates indicating that it may fulfil up to 18% of world electricity demand and satisfy the electricity requirements of approximately 17% of the global population. It is anticipated that geothermal as renewable energy will progressively play larger roles in the energy sector. The figures demonstrate how important geothermal energy may be for achieving sustainable energy.

The purpose of this experimental study was to explore the influence of coatings in geothermal heat transfer systems. Corrosion mitigation was an important requirement of the coatings. The study was carried out in a laboratory-scale experimental setting, utilising a be-spoke geothermal heat exchanger. The study concentrated on the use of coatings on the heat transfer surfaces. These studies examined coatings that were

believed to increase heat transfer coefficient without compromising corrosion resistance. These were benchmarked against uncoated substrates.

The results of this study revealed that the coatings developed can sustain dropwise condensation over the duration of the tests. No increase in heat transfer performance was seen if the Organic Rankine cycle (ORC) fluid cannot escape from the plate, even in dropwise condensation mode, with a significant increase when this was allowed. Some coatings improved the system's corrosion performance, which is crucial in geothermal heat exchangers. Preliminary results suggest that thermal spray coatings, improved heat transfer efficiency. These coatings were also largely effective in mitigating corrosion in the short-term exposure tests.

In conclusion, our study shown that the use of coatings may enhance the heat transfer efficiency of geothermal heat transfer systems greatly. Some of the coatings were shown to improve system performance largely with an improvement in the corrosion performance. The findings of this study have substantial implications for the design and operation of geothermal heat transfer systems; however, more research is needed to improve coating selection and application in geothermal systems.

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Effect of heat treatment on the corrosion and mechanical properties of Nickel Tungsten alloy electrodeposits

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Binary Ni-W coatings display good mechanical, tribological and anti-corrosion properties, but are not able to reach the hard chromium coatings performances. Heat treatment processes were performed and evaluated in order to improve the Ni-W properties.

Ni-W alloy coatings were produced with different compositions and microstructures depending on the composition of the plating bath and the deposition parameters. After the electrodeposition, samples followed four different annealing heat treatment cycles.

The microstructure of the deposits was studied using X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM), while composition analysis of the coatings was performed by Energy-dispersive X-ray spectroscopy (EDS). The corrosion protection efficiency was evaluated by electrochemical characterisation and ageing tests. Sliding and Knoop hardness tests were performed to determine the friction coefficient and the hardness and to analyse the wear behavior of the coatings.

The results showed that heat treatment induced microstructural evolution and that the heat treated NiW coating at 500°C exhibited improved corrosion resistance compared to NiW as deposited with mechanical properties very similar to hard chromium coating.

Characterization of the corrosion behavior of Zn-Al-Mg coated steel under São Paulo acidic rain by Scanning Vibrating Electrode Technique

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Smart coatings tailored to enhance the corrosion protection of steel substrates are the target of the automotive industry, as they ensure the reliability and long-term performance of coated parts. In this field, galvanized steel progresses through the last decades entail the development of more durable, reliable, and sustainable anti-corrosive coatings, reducing the need for additional corrosion protection on coated components, while also lowering costs and fuel consumption in automobiles. The addition of aluminum and magnesium to the zinc bath leads to the formation of different metallurgical products in the galvanized layer, as well as more compact and stable corrosion products, increasing the service life of the steel. Also, the addition of those elements contributes to a self-repairing effect on scratches and at the cut edges, a crucial region under corrosive agents. In this study, electrochemical techniques were used to understand the corrosive process that occurs in Zn-3.5%Al-3%Mg alloy coated steel (ZM), when exposed to aggressive aqueous electrolytes, and the differences in its corrosion behavior with respect to conventional galvanized steels (GI). Besides the conventional polarization analysis, samples of ZM and GI were investigated by Scanning Vibrating Electrode Technique (SVET), a local probe technique outstanding in providing information about the corrosive process *in situ*, on the micrometer scale. Through SVET, it is possible to visualize the corrosion progress in terms of identifying anodic and cathodic regions with estimation of the respective currents and their evolution in space and time. The tests were performed synthetic acid rain, reproducing the conditions found in the city of São Paulo. The

study was complemented by Scanning Electron Microscope (SEM), Energy Dispersive X-Ray Analysis (EDX) and Glow-discharge optical emission spectroscopy (GDOES) analysis, for the identification corrosion products formed after exposure to the corrosive electrolyte. The superiority of ZM corrosion resistance over GI has been proven and attributed to the different corrosion products formed by the alloying elements added to the coating, therefore not observed in the conventional galvanized steel.

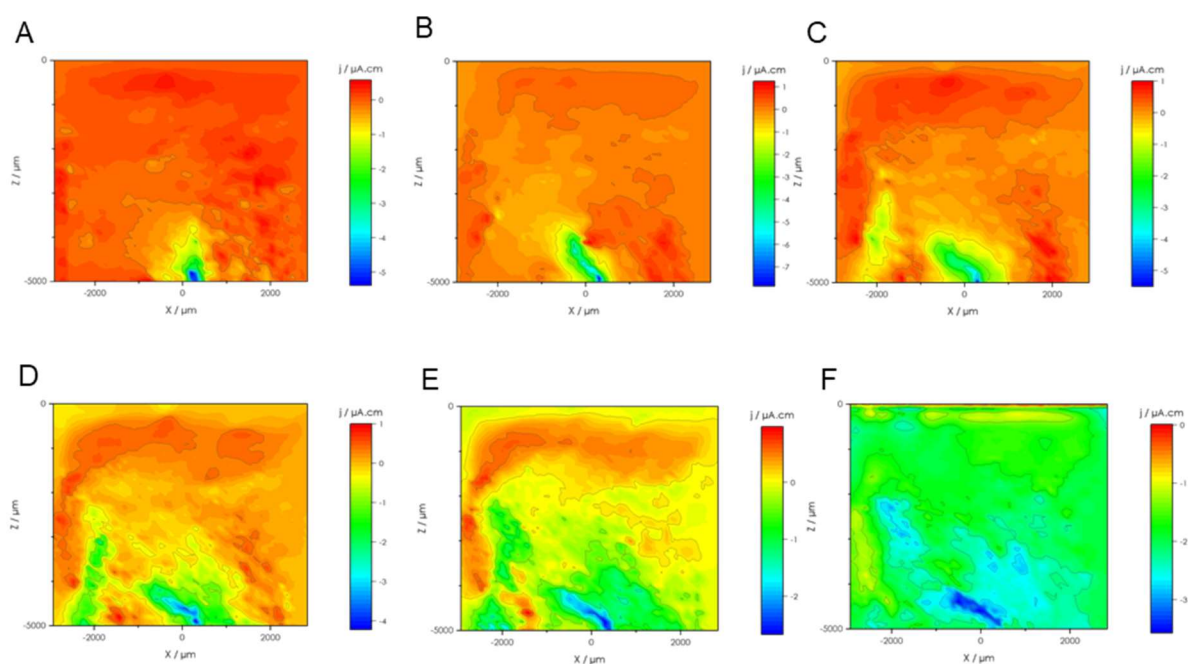


Figure 1 - SVET analysis of Zn-Al-Mg coated steel surface under synthetic São Paulo acid rain after 0h (A), 4h (B), 8h (C), 12h (D) 16h (E) and 20h (F) of exposition.

Corrosion behavior of anodic titanium oxide modified in-situ by vanadium incorporation

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Abstract

Corrosion protection is very important from both, a scientific and industry points of view. A coating system are usually involved in corrosion protection for aerospace and automotive applications. In this study the coating system consisted of anodic oxide layer was introduced on the top of two titanium alloys (industrial purity titanium and Ti64) to decrease the corrosion rate. The anodic layer was produced by classic anodization in ethylene glycol-based electrolyte containing of fluoride ions and water addition. Besides, the modified electrolyte with addition of NaVO₃ was used to anodizing low purity titanium, to incorporate of vanadium in-situ into anodic layer. The corrosion behavior of titanium covered by oxide layer with incorporation of vanadium into on was analyzed in detail. Moreover, the change in the anodic oxide morphology depending on anodizing conditions was also analyzed. It was found that electrolyte composition affected the morphology as well as corrosion protection of anodic oxide layer made on titanium.

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Corrosion resistance of micro-arc oxidation coating on AZ91-Ti MMC

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Abstract: Magnesium matrix composites with both high strength and ductility have been achieved by introducing metallic Ti particles. However, their poor corrosion resistance still needs to be compensated by protective coatings, such as micro-arc oxidation (MAO). In this work, AZ91-Ti metal matrix composites (MMC) were treated with MAO in silicate-based and phosphate-based electrolytes to reveal the effect of Ti reinforcement phase on the corrosion behavior of the coatings. The morphology and phase composition of the MAO coating on AZ91-Ti MMC changed compared to that of the pure AZ91 alloy. The Ti reinforcement phase discharges more intensely and forms discharge channels through the coating. The Ti particles are gradually oxidized to titanium dioxide, forming a composite MAO coating in situ. In addition, the thickness of coating on AZ91-Ti MMC was reduced due to the voltage leakage at the Ti-reinforcement phase. After 15 min treatment in the silicate electrolyte, the coating thicknesses of AZ91 and AZ91-Ti MMC were 26.9 μm and 23.8 μm , respectively. After the same time treatment in phosphate electrolyte, the coating thicknesses were 36.1 μm and 24.0 μm for AZ91 and AZ91-Ti MMC, respectively. The MAO coating provided effective corrosion protection for AZ91-Ti MMC. The self-corrosion current density of the coated AZ91-Ti MMC was reduced by about three orders of magnitude. Finally, the failure mechanism of the coating is proposed. The formation of discharge channels through the coating at the Ti reinforcement phase weakens the protective effect of the dense inner layer.

Corrosion and anodizing behavior of dissimilar AA2050-T84 and AA7050-T7451 alloys joined by Friction Stir Welding

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Abstract

Enormous efforts have been made to reduce fossil fuel consumption and greenhouse gas emissions in several sectors, such as the transport and agricultural sectors. Weight reduction is an efficient way to reduce fuel consumption. In this context, Aluminum alloys are excellent choices due to their properties of lightweight and high strength. However, corrosion is a major concern when using dissimilar alloys joined by welding. This might result in galvanic corrosion. Also, thermal effects during welding might affect the microstructure and the material corrosion resistance. Consequently, the study of dissimilar materials joined by Friction Stir Welding (FSW) is of great importance. In order to decrease corrosion susceptibility, surface protection of aluminum alloys against corrosion is a core issue in these applications. In this work, the corrosion resistance of the AA2050-T84 and AA7050-T7451 alloys welded by FSW, with or without TSA anodizing, was investigated. The corrosion resistance was evaluated by immersion tests in sodium chloride solution and monitored by electrochemical impedance spectroscopy (EIS). The anodic layers formed by TSA anodizing were analyzed and characterized by Scanning Electron Microscopy with Energy-Dispersive Spectroscopy (SEM-EDS). The results present the correlation between corrosion resistance, microstructure and surface film characteristics.

Keywords: Anodizing, Corrosion, Dissimilar Friction Stir welded alloys, AA2050-T84 and AA7050-T7541 alloy.

Plasma electrolytic oxidation pre-treatments as a way to affect the properties of oxide coatings grown on aluminum and magnesium alloys

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Aluminium and magnesium alloys represent one of the most important construction materials in many branches of transportation industries due to their high strength-to-weight ratio. This combination of properties can lead to lower power consumption and CO₂ emissions if they are applied in transport. However, these materials have one major drawback – they are susceptible to destruction through the process of corrosion. Many surface modification techniques have been developed to increase the lifespan of such materials. In the past, the most used techniques were based on the use of chromium (VI) which is harmful to humans and the environment. To reduce the negative impact on our lives and environment industries started to search for alternatives.

Plasma electrolytic oxidation (PEO) is a modern and environmentally safe method of protecting light metal alloys surfaces against corrosion. The workpiece is subjected to anodic polarization at a high voltage enabling dielectric breakdown of the grown oxide. This results in appearance of so called “micro-discharges” which are responsible for the formation of plasma and local melting of the metal at the surface. The surrounding electrolyte rapidly cools the surfaces, solidifying the obtained oxide from the expanding plasma bubbles. This process allows to obtain thick, compact, and microporous layers with very good mechanical properties and satisfactory corrosion resistance. The advantage of the PEO process is the possibility of conducting the treatment in baths containing compounds that are harmless to the environment such as solutions of silicates or phosphates.

In this research we focused on improving PEO coating properties on AW-6061 aluminium alloy and AZ91 magnesium alloy by obtaining pre-coats in a pre-treatment processes. For that purpose, we utilized methods of producing thin conversion coating

(CC) on the surface in Cr-free baths (with e.g., NaVO_3) and classical anodization methods. The presence of a pre-coat before PEO allowed for the instantaneous ignition of 'micro-discharges' without the need for the inefficient electrochemical formation of the oxide in the first seconds of the process. Then it was observed that the application of the pre-coat significantly lowered the time needed for the initiation of the so-called 'soft-sparking' which is a special type of regime in the PEO processing occurring at lower voltages making a more promising alternative for commercial implementation. In the research, the authors utilized techniques like SEM, EDS, XRD, Raman and EIS corrosion investigations to determine the effect of the PEO processing with the pre-treatment on the properties of the oxide coatings.

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Microstructure, mechanical properties and oxidation resistance of Zr-Hf-N coatings by magnetron co-sputtering

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This work aims to improve the mechanical properties and oxidation resistance of the Zr-based nitride hard coatings used for high speed, yet dry machining. The ionic radius of doped reactive elements dominates on the cell parameters of the Zr-based nitride hard coatings. Additionally, the charge valence of the dopants illustrates impacts on the phase structure, oxygen vacancy concentration and ionic diffusion rate of the oxide scales of the coatings. Incorporating a moderate amount of reactive elements improves both the mechanical properties and the oxidation resistance of the coatings. The influences of varying hafnium addition content on microstructure, mechanical properties and oxidation resistance of ZrN coatings were investigated in this study.

Zr-Hf-N coatings were fabricated by magnetron co-sputtering using pure Zr and Hf targets. Compared with magnetron sputtering Zr-Hf alloy target directly, the use of magnetron co-sputtering from two targets is less expensive and especially allows better control over the content of Hf. The atomic percent Hf/(Hf+Zr) increases from 0 to 8.5 % with Hf target power increasing from 0 to 150 W while Zr target power fixed at 250 W. Electron probe microanalysis (EPMA) and X-ray diffraction (XRD) results indicate that Hf atoms substituted Zr atoms in Zr-N lattice forming the solid solution Zr-Hf-N coatings. The surface and cross-sectional morphologies of the Zr-Hf-N coatings exhibit granular grains and columnar structure respectively, moreover the granular grains sizes increase with increasing Hf content. All the Zr-Hf-N coatings illustrate the preferred orientation of (200), showing independent of Hf addition. The indentation hardness of the Zr-Hf-N coatings first increases from 23.5 GPa to 28.6 GPa with increasing Hf content and is followed by a decrease to 25.5 GPa with a further improving in Hf addition content. The hardness improvement can be attributed to the solid solution strengthening effect and the decrease is due to the surface granular grain coarsening. Scratch tests also reveal the adhesion of the Zr-Hf-N coatings first increases with increasing Hf content and is followed by a decrease with over Hf doping content.

After thermal treatment for 2 h at 600°C in air, GIXRD and Raman scattering studies indicate the oxidation products are mainly the monoclinic-ZrO₂. The oxidation resistance of the Zr-Hf-N coatings was characterized by method of measuring thickness of the oxide scales using scanning electron microscope (SEM) cross-section observation. The results demonstrate that ternary Zr-Hf-N coating with 1.0 ~ 8.5 at. % hafnium has superior oxidation resistance than binary ZrN coating as a result of improved oxide scale adhesion and its spalling resistance. The high-temperature oxidation kinetics of the ZrN coatings are dominated by oxygen inward diffusion and metallic ions outward diffusion, respectively. The incorporation of Y³⁺ improves the phase stability of the t-ZrO₂. The reduction of oxygen vacancy concentration and improved stability of the t-ZrO₂ result in the increase of the oxidation resistance of the ZrN coating. Both the preferential outward diffusion of the reactive elements and the solute drag effect inhibit the fast growth of the oxide scale, resulting in the promoted oxidation resistance.

Performance of novel Polymer Derived Ceramic (PDC) coatings developed for refinery piping systems and in-situ corrosion monitoring by EIS-based sensor

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Novel protective *Polymer Derived Ceramic* (PDC) coatings with improved corrosion resistance was developed in the context of the European project ACHIEF. This project is aiming to introduce innovative materials to improve the energy performance of Energy Intensive Industries (EIs) and reduce CO₂ emissions in the industrial processes.

A specific use case was identified in refinery pipes carrying corrosive fluids aiming for a reduction of the corrosion and/or erosion damage by 40%. Novel coatings with increased durability could increase service life of equipment and components, leading to a reduction of O&M operations (by 20%) and improving the overall performance and efficiency of the plant.

In this scenario, a novel PDC coating, containing polymer derived ceramic and ceramic charges, was developed to protect the inside of a stainless steel pipe (AISI 321) against corrosion in acidic environment (HCl 2mol/L at 60°C). PDC are organic/inorganic materials formed by the pyrolysis of silicon containing polymer precursor (preceramic polymer precursor). Their properties (chemical composition, density) can be tailored at the molecular scale using suitable precursor and applying adequate thermal treatments. The processability techniques (spray, dip coating, brush etc.) lead to a relatively low cost and easy approach to produce ceramic coatings, which provide excellent corrosion protection in high temperature and/or harsh environment.

In order to find the optimal composition for this particular case, analysis of the thermal conversion of suitable preceramic precursors and the addition of ceramic charges were assessed together with the integrity and morphology of coatings (by SEM) and the adhesion of the coating on substrates. Electrochemical Impedance Spectroscopy (EIS) was applied to select the best corrosion performance composition in the defined acidic conditions. Results encourage the development of these coatings for the next steps of the project.

Advances on upscaling the selected coating for pilot testing in industry will be showed. Besides, a novel corrosion probe was also integrated in the refinery piping installation for in-situ and on-line monitoring using electrochemical techniques. The novel corrosion probe relies on the utilization of EIS method to determine the corrosion performance of the coated pipe. EIS is introduced as a useful tool not only at lab-scale but also for in-situ and real time estimation of the service life of components, corrosion resistance of novel coatings and prediction of failures in critical units, by correlating the process events to corrosion evolution.

The new EIS-based sensor system will facilitate the decision making and contribute to optimize the operation conditions, the coating/material selection and the maintenance costs of the plant.

Influence of the composition of the electrolyte and parameters of the synthesis of the plasma-electrolyte oxidized layer on alloy 1160 on its corrosion resistance in 3% NaCl solution

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Introduction. Plasma electrolytic oxidation (PEO) is a relatively new method of surface treatment of valve metals (Al, Ti, Mg, Zr, Ta), which is actively used to form wear-resistant and corrosion-resistant coatings on their surface. The versatility of such coatings allows their use in various industries. The formed PEO coatings are chemically inert in relation to most aggressive environments. However, the discharge channels leave pores in them, which can either be melted or reach the base metal. As a result of the penetration of corrosive media through the through pores, the metal base – aluminum alloy is subject to corrosive destruction, which is especially relevant for the Al–Cu system. In order to avoid penetration of an active corrosive environment through the through-pores of the PEO coating to the surface of the aluminum alloy itself, it is necessary to obtain a coating with minimal porosity. Therefore, research was conducted that allowed us to establish the effect of changing the modes of plasma-electrolyte oxidation and the composition of the electrolyte on the electrochemical behavior of the obtained oxide-ceramic coatings in a neutral aqueous environment – a 3% NaCl solution.

Research materials and methods. Oxidoceramic coatings were formed on samples of aluminum alloy 1160 in a silicate-alkaline electrolyte for 1 h. The regulated technological parameter of the process was the ratio of the cathodic and anodic components of the current j_c/j_a (15/10 A/dm²; 10/15 A/dm²; 10/10 A/dm²). In order to reduce the porosity of the synthesized coatings, 3...7 g/l H₂O₂ was added to the base electrolyte (3 g/l KOH + 2 g/l nNa₂O·mSiO₂). The characteristics of corrosion processes were studied in the potentiodynamic mode during the potential sweep at a speed of 1 mV/s. Exposure of samples with covers in the environment lasted 3 h...14 days.

Research results. The addition of H₂O₂ hydrogen peroxide to the basic electrolyte significantly increases the thickness of the oxide layer, especially for the ratio $j_c/j_a = 10/10$ (100

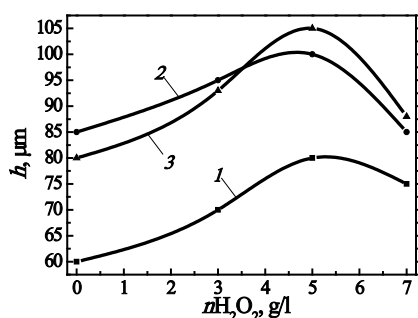


Fig. 1. The influence of the H₂O₂ content in the basic electrolyte on the thickness of the PEO layer depending on the ratio j_c/j_a :

1 – 15/10; 2 – 10/10; 3 – 10/15.

μm) and 10/15 (105 μm) (fig. 1). The thickness of the oxide layer reaches its maximum value at a H₂O₂ content in the electrolyte of 5 g/l, which is 80% greater than the thickness of the coating synthesized in the base electrolyte. When the content of H₂O₂ in the electrolyte increases above 5 g/l, the thickness of the oxide layer decreases, which is caused by a significant increase in the content of OH in the electrolyte. It was established that the maximum number of defects is formed at the ratio of current densities $j_c/j_a = 15/10$ A/dm², and the minimum is 10/15 A/dm². Although the maximum pore area was formed at $j_c/j_a = 10/10$ A/dm², the largest average pore

area was at densities of 10/15 A/dm². This indirectly indicates the largest size of d

effects in coatings synthesized under this regime.

It is shown that the rate of corrosion in coatings obtained by different regimes is different, and in some of them the corrosion process slows down over time, or even stops completely (fig. 2, curve 1, 2).

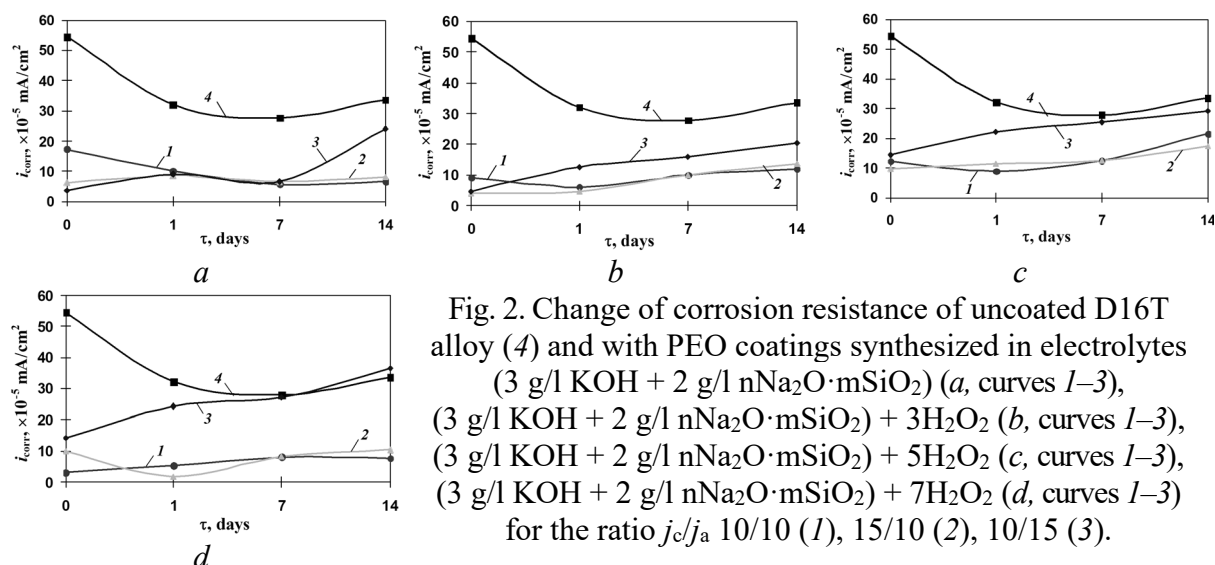


Fig. 2. Change of corrosion resistance of uncoated D16T alloy (4) and with PEO coatings synthesized in electrolytes (3 g/l KOH + 2 g/l nNa₂O·mSiO₂) (a, curves 1–3), (3 g/l KOH + 2 g/l nNa₂O·mSiO₂) + 3H₂O₂ (b, curves 1–3), (3 g/l KOH + 2 g/l nNa₂O·mSiO₂) + 5H₂O₂ (c, curves 1–3), (3 g/l KOH + 2 g/l nNa₂O·mSiO₂) + 7H₂O₂ (d, curves 1–3) for the ratio j_c/j_a 10/10 (1), 15/10 (2), 10/15 (3).

This is possibly due to the formation of PEO coatings with a minimal number and size of structural defects (pores and cracks), as well as the formation of poorly soluble secondary corrosion products that prevent the interaction of areas of aluminum exposed to corrosion with the corrosive environment. Only in some pores can corrosion develop deep into aluminum and

along its grain boundaries, turning into intercrystalline corrosion. Long-term exposure to a corrosive environment causes an increase in the number of through pores and an increase in corrosion currents. To prevent such phenomena, the obtained coatings should be compacted.

Conclusions. It was found that increasing the anodic current density in relation to the cathodic current from j_c/j_a 15/10 to 10/15 increases the thickness of the oxide layer by 30% – from 60 to 85 μm . Based on the analysis of potentiodynamic studies of oxide-ceramic coatings synthesized at different j_c/j_a ratios, it was established that they reduce corrosion currents by an order of magnitude compared to the original material. It was found that with an increase in the content of H_2O_2 in the electrolyte, the corrosion currents increase, which is caused by an increase in the size of the through pores in PEO coatings. Long-term exposure to a corrosive environment causes an increase in corrosion currents due to an increase in the number of through pores. To prevent such phenomena, the resulting coatings should be compacted.

Multifunctional nanocomposites epoxy coating with enhanced mechanical, anticorrosion and bactericidal properties

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Abstract

In this work, aluminium nanoparticles (Al NP) as fillers were homogenized with epoxy matrix to form multifunctional Al NP-epoxy nanocomposites on plates of gray cast iron. The samples were analyzed with SEM observation and EDX to evaluate and characterize the uniform distribution of Al NP in the nanocomposites. The effect of corrosion protection performance of nanocomposite was analyzed using scanning electrochemical microscopy (SECM) and electrochemical impedance spectroscopy (EIS). This analysis confirms improvement of the corrosion resistance of nanocomposite in comparison with epoxy matrix without nanoparticles. The introduction of Al NP into epoxy matrix the mechanical properties has been slightly increase. Furthermore, the antimicrobial test indicated that the nanocomposites had bactericidal activity against *Pseudomonas aeruginosa* and *Bacillus subtilis* bacteria. The small size of the aluminium particles and their rapid oxidation enable this nanocomposite to possess dual properties. Nanocomposites improve mechanical, anticorrosive and antimicrobial properties which means that they provide the better resistance to external mechanical influences and effectively prevent corrosion and bacterial growth.

Keywords: aluminium nanoparticles, epoxy matrix, corrosion, antibacterial properties, SECM

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Corrosion Properties and Thermal Stability of Polyurethane Coatings

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Polyurethane (PUR) is a type of polymer in which organic units are joined by carbamate (urethane) links. Because of its durability, PUR is often used in protective coating systems as a topcoat, where it protects substrates from various types of defects such as corrosion, abrasion and deteriorating process. Polyurethane coatings are also known for their ability to adhere well to a wide variety of substrates in a broad range of temperatures. Some types of PUR coatings can also be applied as a one coat “direct to metal” system.

The aim of this paper is to determine corrosion properties and thermal stability of polyurethane coatings. Solvent-borne PUR coatings dried under atmospheric conditions and by infrared radiation were examined. Corrosion properties of the coatings were characterized using a salt spray chamber. In order to determine physical properties of tested coatings, pull-off adhesion and pencil tests were performed before and after the exposure to salt spray chamber. To assess thermal properties of PUR coatings, thermo-gravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed. It was found that IR dried PUR coatings exhibit better physical and thermal properties.

Keywords: corrosion, PUR coatings, infrared drying, salt spray chamber, thermal stability

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High temperature resistant coatings for wood stoves

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Abstract

Protective coatings for corrosion protection covers the most important role in the industry, especially in metal structures where corrosion is more common due to external environmental influences. Heat resistant coatings are uniform and thin, durable to high temperatures and different corrosion loads, providing a wide range of desired appearances and properties. In the experimental part of the work, corrosion resistance tests and physical properties of the coatings were carried out before and after exposure to accelerated laboratory tests and cyclically elevated temperatures that corresponds to the conditions in exploitation. Surface roughness tests were performed, as well as chloride tests on samples without coating. Accordingly, hardness test, pull-off and cross-cut adhesion tests, salt and humid chamber tests were performed. The results show that the tested coatings have weaker protective properties in a salty atmosphere compared to warm-humid conditions, which is more in line with the real conditions of application of wood- burning stoves. The purpose of this paper was to show the properties of different heat resistance coatings which are used in the production of wood-burning stoves. Based on the obtained results of the experiment, an assessment of the quality and protection offered by the used coatings was given.

Keywords: corrosion, coatings, wood stoves protection

This study is part of the project “Development of an energy-efficient heating system for solid fuels from renewable energy sources using innovative technological procedures” (reference code: KK.01.2.1.02.0226.) which is co-financed by the European Union from the European Regional Development Fund. The contents of this publication are the sole responsibility of the Faculty of Mechanical Engineering and Naval Architecture, University of Zagreb.

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Application of Biochar Nanoparticles in Zinc Epoxy Coatings

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Woody biomass-derived biochar nanoparticles were successfully produced and incorporated into zinc epoxy coating formulations with zinc loading in the range of 10 vol.% to 30 vol.%. The anticorrosive performance of modified coatings was evaluated and compared to the unmodified coatings.

Barrier protection was enhanced by the modification, especially on formulations with lower zinc content (10 vol.% and 22 vol.%). Galvanic protection was remarkably extended on coatings modified by partly gasified biochar nanoparticles with 30 vol.% zinc loading, and the efficient galvanic protection period was increased from around 100 h to more than 600 h when being immersed in 3.5 wt.% solutions. The post-exposure characterizations revealed that the zinc utilization rate was upgraded.

The improvement was attributed to the filling of micropores and the extra electrical connections provided by biochar nanoparticles. This study imparts a sustainable solution for enhancing the anticorrosive performance of zinc epoxy coatings.

The Effect of Carbon-Based Surfaces on the Development and Structure of Marine Cyanobacterial Biofilms

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Marine biofouling is a process by which natural and artificial submerged structures are colonized by marine organisms, leading to serious economic, energetic, environmental, and ecological consequences. Since biofilm formation is one of the first steps of this natural process, a potential strategy to delay marine biofouling is to develop novel and environmentally friendly antifouling strategies, such as the manufacture of innovative nanocomposite coatings. Carbon nanotubes (CNTs) have been widely used for several applications due to their outstanding properties, including their mechanical strength, structural stability, and antimicrobial and anti-adhesive activities. However, since there are few studies evaluating the performance of CNTs on marine biofilm formation in long-term assays, furthering knowledge in this field may allow the development of new methodologies to control marine biofouling.

This work aimed to produce and characterize CNT-based surfaces and evaluate their performance against marine cyanobacterial biofilms. For this purpose, 3% (w/v) CNTs were incorporated into a commercially available epoxy resin, and the resulting composite was used to coat glass surfaces. Both CNT-based and control (glass and glass coated with epoxy resin) surfaces were analyzed by Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM). The effect of CNT-based

surfaces on the development and structure of *Nodosilinea* cf. *nodulosa* LEGE 10377 biofilms was monitored for 7 weeks under conditions that mimic the hydrodynamics of relevant marine environments. Biofilms were analyzed by Optical Coherence Tomography and SEM.

SEM and AFM showed that, while glass and epoxy resin (controls) were the most homogeneous and smooth surfaces, CNT-based surfaces were the roughest surfaces, presenting agglomerates of CNTs. Biofilm assay results demonstrated that over the 7 weeks, CNT-based surfaces delayed the development of cyanobacterial biofilms compared to control surfaces. Although there were no differences between the surfaces in the initial stage of biofilm formation, significant reductions in the wet weight, thickness, and biovolume of biofilms developed on the CNT-based surfaces compared to controls were observed in the maturation stage. Furthermore, the biofilms formed on the CNT surfaces were smoother and less porous than those formed on glass and epoxy resin surfaces. The higher antifouling activity of the produced carbon surfaces in the maturation stage may be related to the presence of CNT agglomerates that have a piercing effect on the cells' membrane of the initial biofilm layers. Overall, the incorporation of carbon nanotubes into polymeric matrices showed to be a promising approach to delaying cyanobacterial biofilm development under the marine environmental conditions mimicked in this work.

Romeu, M.J., et al., *The Use of 3D Optical Coherence Tomography to Analyze the Architecture of Cyanobacterial Biofilms Formed on a Carbon Nanotube Composite*. Polymers (Basel), 2022. **14**(20).

ANTICORROSION PERFORMANCE OF AN EPOXY COATING APPLIED ON THE CARBON STEEL PRE-TREATED WITH SILANES CONTAINING A NATURAL CORROSION INHIBITOR

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This work aims to evaluate a coating system containing an epoxy coating and a silane – VS + GPTMS - pre-treatment loaded with natural garlic peel corrosion inhibitor (*Allium sativum. L.*), applied on the carbon steel ASTM 1008. The samples were characterized using Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy (SEM), coupled with X-ray energy dispersion spectroscopy (EDS). The corrosion evaluation was performed using the electrochemical impedance spectroscopy (EIE) technique in a 3.5% NaCl solution.

The FTIR analysis revealed the presence of sulfur and nitrogen compounds in the inhibitor samples, which improves the adsorption of organic molecules in carbon steel substrates, increasing the inhibiting properties. The SEM images showed that the peel garlic extract minimizes the corrosion attack on the carbon steel surface. In addition, the EDS analysis also identified sulfur and nitrogen presence, confirming these inhibiting species in the sample surface after immersion tests.

The results showed that the silane film loaded with garlic peel inhibitor has a higher corrosion resistance than the other conditions, showing its applicability. In addition, the system with inhibitor presented a rougher surface, which benefits the anchoring of the paint that was applied, a statement that results in the better anti-corrosion performance of this system.

Evaluation of adhesion properties of coating film on Zn-Mg-Al galvanized steel sheets

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Iron is corroded by various factors such as moisture, salt and air exposure, causing problems in the building's exterior and structure. To solve this problem, studies have been continued about rust-resistant iron. The Zn-Mg-Al galvanized Steel in many industry is one of the most used material surface protection, because it has good chemical and corrosion resistance properties. Furthermore, Magnesium-added Zn-Al-Mg coated steel sheet is excellent for corrosion resistance of cut surfaces. In this study, adhesion was analysis using Scanning Kelvin Probe(SKP) and corrosion resistance of coated steel sheet was evaluated by Salt spray test and Electrochemical Impedance Spectroscopy(EIS) analysis.

A novel strategy to enhance the anti-corrosion of epoxy coating based on fluorinated graphene coupled with MOFs

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Epoxy resin (EP) coatings have been widely applied in the protection of metal substrates from aggressive media due to their excellent mechanical strengths, good adhesion and low cost. However, it is a still challenge for EP coatings to achieve ideal long-term corrosion resistances due to the crack formed during the preparation and the application which gives poor barrier properties to corrosive species. The addition of fillers to organic coatings has been regarded as a very effective approach toward the improvement of the properties of the coatings.

In this work, novel fillers were designed via fluorinated graphene (FG) and metal-organic frameworks (MOFs). Figure 1(a) shows the XRD of the powder which verifies the successful fabrication of FG@MOF fillers. Figure 2(a) and (b) shows the low-frequency impedance and wear rate of the coatings, the results suggest that the FG and FG@MOF fillers enhanced the anti-corrosive and wear properties of the coating dramatically. Especially, the FG@Triton@MOF filler which may be attributed to the treatment of FG by Triton to accelerate the growth of MOF on the surface of FG.

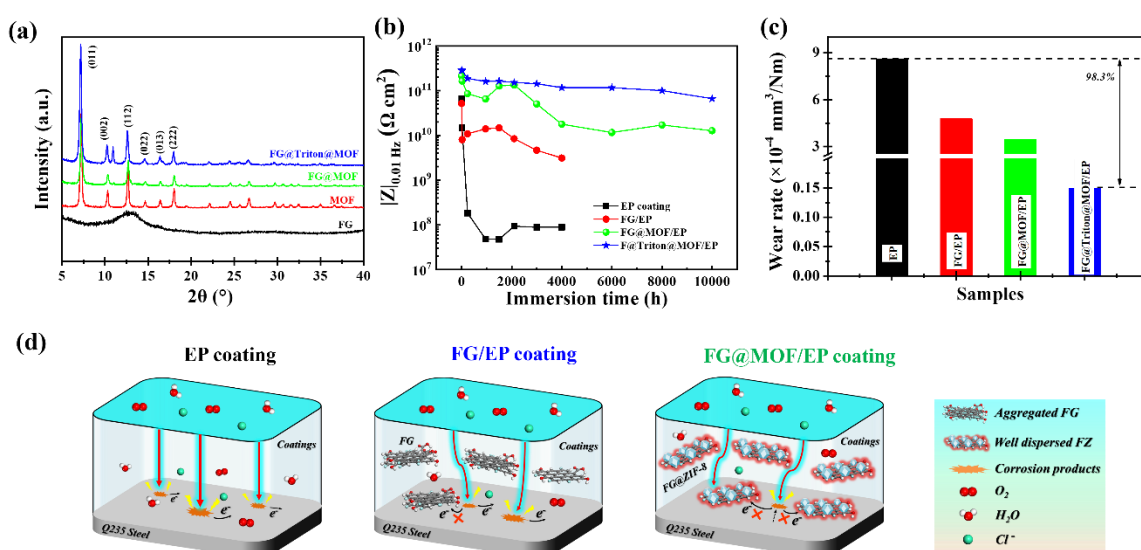


Fig. 1. (a) XRD of the fillers, (b) Low impedance modulus, (c) Wear properties of fillers modified EP coating, and the corrosion mechanism of different coatings (d).

Possibilities of Robotic Application of High-Temperature Coatings for Protection of Fireplaces

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Fireplaces are a popular heating solution in many households, but they require proper maintenance and protection to ensure their longevity. High-temperature coatings can provide adequate protection for fireplace surfaces exposed to high temperatures and corrosive elements. Robotic coating offers many benefits over traditional manual coating, including efficiency, accuracy, and safety. This paper explores the possibilities of robotic application of high-temperature coatings for protecting fireplaces. Using a developed simulation, the study examines the effectiveness of high-temperature coatings and compares the results of robotic and manual coating methods. The findings suggest that robotic coating can significantly improve the quality and consistency of coating applications and provide better protection for fireplace surfaces. The results of this study can be useful for fireplace manufacturers, and coating applicators interested in adopting robotic coating methods for protecting fireplaces.

Subtopic – Organic coatings

A durable and photothermal superhydrophobic coating with entwined CNTs-SiO₂ hybrids for anti-icing applications

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In this work, carbon nanotubes (CNTs) were grafted by silica nanoparticles to prepare CNTs-SiO₂ hybrids, which were then incorporated into epoxy matrix to construct a superhydrophobic coating by a facile one-step spraying method. The surface morphology, roughness and wettability of CNTs-SiO₂/epoxy coatings were tailored by changing the ratios of CNTs to SiO₂. The best hydrophobicity was achieved when the ratio of CNTs to SiO₂ was 1:3, showing a WCA of 159.3°. The introduction of entwined CNTs-SiO₂ hybrids could not only create a micronano hierarchical structure to increase the water repellency, but also offer good mechanical durability of the coating surface against repeated peeling and friction damages, as well as excellent chemical stability under various harsh conditions. Benefiting from the superhydrophobicity of the coating surface and the prominent photothermal conversion capability of CNTs, the CNTs-SiO₂/epoxy coating could significantly delay the water freezing time, and efficiently melt the ice layer within seconds under laser irradiation.

1 Surface properties of CNTs-SiO₂/epoxy coatings

Superhydrophobic coatings should possess high chemical stability and mechanical durability for practical applications in harsh outdoor environments. The properties of coating are shown in Fig.1 and Fig.2.

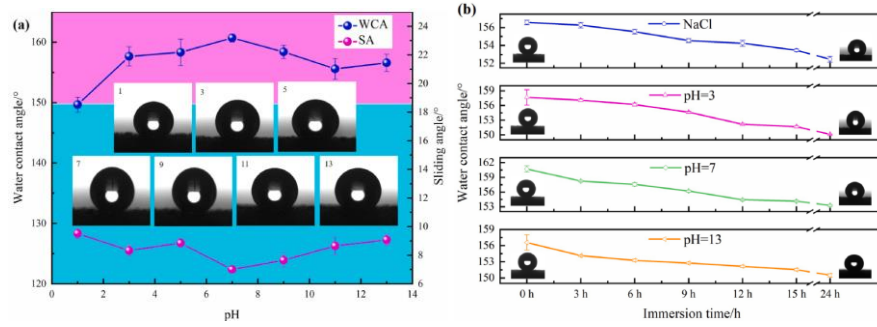


Fig. 1. (a) Effect of pH values on the WCAs and SAs of the CNTs-3SiO₂/epoxy coating; insets are the corresponding optical images of static water droplets of different pH values (6 μ L); (b) the variation of WCAs of the CNTs-3SiO₂/epoxy coating after being immersed in different solutions for different time.

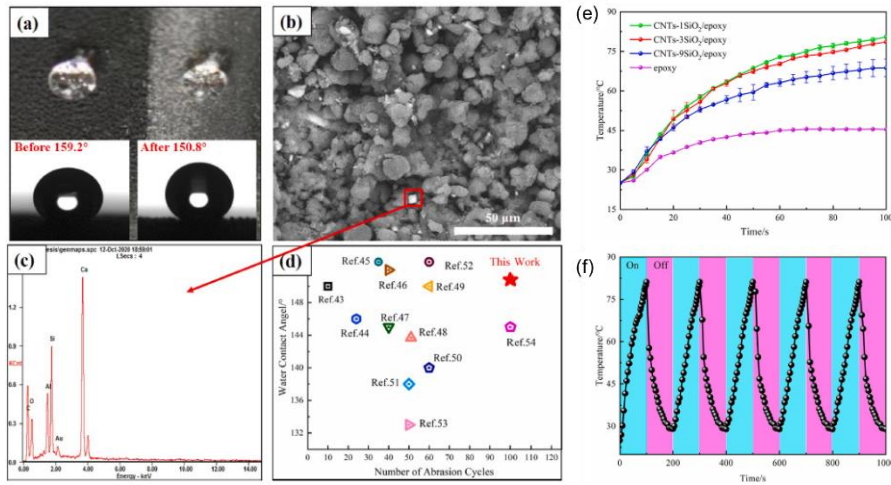


Fig.2. CNTs-3SiO₂/epoxy coating surface: (a) WCAs of before and after friction, (b) SEM image after friction, (c) EDS results, (d) abrasion cycles and WCAs reported in this work and reference, (e) The surface temperature changes of CNTs-1SiO₂/epoxy, CNTs-3SiO₂/epoxy, CNTs-9SiO₂/epoxy and blank epoxy coating during NIR irradiation; (f) the surface temperature of CNTs-3SiO₂/epoxy coating upon laser on/off cycles

2 Conclusion

In this work, the surface morphology and roughness of CNTs-SiO₂/epoxy coatings can be tailored by changing the ratios of CNTs to SiO₂, and the best hydrophobicity was achieved on the CNTs-3SiO₂/epoxy coating with a WCA of 159.3°. Furthermore, the superhydrophobic CNTs-SiO₂/epoxy coating showed a prominent photothermal conversion ability which could delay the water freezing time by 11 times compared with the blank epoxy coating, and significantly improve the deicing efficiency under NIR irradiation. Such multifunctional superhydrophobic surface holds great prospects in various industry fields such as for anti-icing and anti-fogging applications.

Tuning the colour of topcoats

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Keywords:

colour of topcoats, colour stability, aging tests

Abstract

The primary function of coatings is to protect the coated material against corrosion. However, aesthetic properties, mainly colour and gloss, are also a very important issue for users.

All new coatings are tested against the effects of various factors. To ensure colour stability, various types of aging tests are most often performed, based on a combination of changes in three basic parameters: temperature, humidity and UV radiation. The project, with the acronym ColourTune, aims to investigate which of the listed parameters has the largest share in the loss of colour stability, and then to answer the question of how to modify the composition of paints to obtain an optimal formulation.

In the first step of the project, samples were prepared in three colours: blue, red and yellow. Additionally, each colour was formulated with three different pigments. Before the aging tests, the coatings were characterized by many methods (e.g. colour and gloss measurements, 3D profilometry, SEM, WUR, stressmeter, etc.).

Currently, selected aging stages considering various parameter changes are in progress.

The research results presented in this paper are carried out as part of a project funded by the National Center for Research and Development under the Cornet Initiative.

Waterbased zinc primers with reduced zinc content

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Keywords:

waterbased zinc-pigmented primers, ecological paint, primers with reduced zinc content

Abstract

Zinc-rich primers are one of the best primers dedicated to long-term corrosion protection of steel structures.

Taking into account the environmental aspects and sustainable development, it is important to develop new products – more environmentally friendly and with a good anti-corrosion properties, such as waterbased zinc-pigmented primers with reduced zinc content.

The research results presented in this paper were carried out as part of a project funded by the National Center for Research and Development under the Cornet Initiative.

The effect of increasing the concentration of Zr-based conversion coating on the topography of the steel surface

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The effect of increasing the concentration of Zr-based conversion coating on the topography of the steel surface. Conversion coating based on zirconium is a novel eco-friendly pre-treatment process used to prolong corrosion durability in many applications. The chemically modified surface can simplify the production of metal products of high requirements for anti-corrosion. In this paper, an examination of the influence of the change in the concentration of the conversion coating medium on the morphological and corrosion properties of the substrate was made. The surface formed by the zirconium-based conversion coating varies systematically by changing the concentration parameter. In addition to the influence of concentration, the influence of the duration of contact between the metal surface and the medium was determined. The study was conducted on epoxy-polyester coated steel surfaces, with 3 different medium concentrations of Zr-based conversion coating. Surface characterization was determined using AFM, SEM and EDS mapping techniques, EIS and humidity chamber test. The results confirmed the hypothesis about the influence of the change in Zr-concentration on the morphological and corrosion properties of the steel substrate.

Keywords:

corrosion, steel, zirconium conversion coating, powder coating

The phosphonic acid inhibition of corrosion under the waterborne coating investigated by EIS

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Waterborne coatings are of great interest in many fields today due to new environmental legislative which restrict the emissions of volatile, harmful solvents from organic coatings. Unfortunately, they usually exhibit lower level of corrosion protection compared to the solvent based coatings, which can be correlated with corrosion of the metal substrate.

In our previous studies it was found that long-chain phosphonic acids can be used as bronze¹ and copper/nickel alloy² corrosion inhibitors. Self-assembled monolayer of phosphonic acids formed on a metal substrate represents a barrier to the attack of aggressive corrosive compounds which can penetrate into the protective coating. Acids consist of long-chains with two functional groups, where one of them reacts with the metal substrate, and the other with the environment, which in this study represents waterborne acrylic coating.

This study examines if pre-treatment by two phosphonic acids can improve the corrosion protection of bronze by waterborne acrylic coating. The influence of phosphonic acid structure as well as the influence of its application technique (dip-coating, brushing) are investigated.

The electrochemical impedance spectroscopy is conducted in terms of continuous immersion in simulated acid rain (pH 5). Additionally, the adhesion of the prepared protective systems is investigated by 'pull-off' test.

Acknowledgment: This work was fully supported and funded by the Croatian Science Foundation under the project IP-2019-04-5030.

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Influence of pre-treatment on the corrosion and adhesion properties of Al-anode coatings

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Aluminum is often used as a sacrificial anode for corrosion protection of steel. An example being the usage of hull anodes for the cathodic corrosion protection of boats. This is not suitable for aerospace application. There it is more common to use sacrificial anode coatings or varnish for corrosion protection. One of the biggest advantages when using aluminum sacrificial anodes instead of coatings containing chrome or cadmium is less impact on the environment and aluminum is not carcinogenic. When used as coating, it is important to ensure sufficient adhesion between the surface and the coating. Therefore, a certain surface roughness of the steel is desirable, while at the same time, the substrate must be as clean as possible of remains from the abrasive.

The goal is to find the ideal combination of pretreatment steps of the steel surface to ensure the best corrosion performance with a commercial aluminum anode material that is sputtered on top of the steel. At the same time, the aim is to get the maximum adhesion of the coating to the substrate, so that any delamination can be avoided, that would limit the protection performance of the coating.

Steel substrates are pretreated with three different types of commercial abrasives (glas pearls, aluminum oxide particles, and Nastra ®) at different pressures. To clean the surfaces after the abrasive pretreatment 37%-hydrochloric acid at 50°C is used. The final step is immersion into an ethanol bath and drying of the sample. In order to determine, which pretreatment step has the highest impact, samples with only etching or only ethanol bath are used as reference.

For evaluation of the surface morphology after the pretreatment, SEX/EDX-analysis is used, while at the same time, the surface roughness is measured using a laser scanning microscope. The treated samples are then coated using a magnetron sputter system.

Using SEM-analysis again, the surface properties and roughness are analyzed. Corrosion properties of the coatings are evaluated via electrochemical polarization and the corrosion products and effects are compared with EDX-analysis. For the analysis of the adhesion, pull-of tests and cross sectional analysis of the coatings are employed. These methods lead to the conclusion that the higher the pressure used for the abrasive, the rougher the substrate surface gets and shows more impurities of the remainders of the abrasive. At the same time, the rougher surface is easier to clean of the abrasive using etching, which can be explained by the bigger surface area exposed to the hydrochloric acid. On the other hand, it can be seen, that the pretreatment has significantly less impact on the corrosion performance than expected. Corrosion currents and potentials differ only by small margins. Meanwhile, there is an effect on the adhesion of the coating. With stronger pretreatment of the surface results demonstrate a better bonding between substrate and coating.

The results are of relevance for any industrial coating application, where the goal is to have the optimal adhesion between aluminum sacrificial coating and steel substrates.

One step pre-treatment that ensures corrosion protection, paint adhesion and cleaning properties (combining the worlds of chemical and mechanical pre-treatment)

Title – Arial 14 pt., bold, centered, 1.5-line space

Roland van Meer, AD Chemicals, Heijningen/Netherlands

MM31 is an innovative chemical pretreatment from AD Chemicals. The product combines the worlds of mechanical and chemical pretreatment. In the field of pre-treatment methods, mechanical pre-treatment (such as blasting or sanding) followed by a coating system is common practice. What would be the result if a mechanical pre-treatment could be combined with the added value of a chemical pre-treatment? This question has been the starting point for the development of MM31 which was a development trajectory of more than 7 years. For a regular chemical pretreatment, the generic process consists of degreasing, pickling and applying a conversion coating (a layer that provides added value through additional corrosion protection and paint adhesion properties). The degreasing and pickling step is in practical sense identical to the degreasing and mechanical pretreatment step in the “mechanical procedure”. However, after a mechanical pre-treatment, there is no added value to the metal in comparison with a chemical pre-treatment. By applying MM31 directly after a mechanical pre-treatment, the two worlds come together. This results in a clean, ready to coat surface and a quality improvement of the coated substrate on both corrosion protection and paint adhesion properties. This is the result of forming of a conversion layer. The product also offers protection against flash rust and undercreep corrosion (flash rust resistance on steel products, white rust protection on zinc, improved bare metal corrosion resistance on aluminum). This enables an extended storage time of up to 48 hours prior to coating. MM31 creates a chromium-3 based protective conversion layer, which is formed on the metal by a chemical reaction with MM31, whereby the metal itself contributes to the formation of the layer. This layer provides a more uniform metal surface.

Hence it is full chemical pretreatment applied in one easy process step by, for example, a lint-free cloth, manual spray gun with top cup or fully automatic paint system. MM31 replaces therefore a pre-treatment line with a simple process without the need for heated baths and the use of heavy chemicals. Another advantage of the technology is that it can replace solvents in the business process with a user-friendly and non-aggressive chemical. Making this switch protects employees against exposure to harmful substances.

The product is multi-metal and can be applied on steel, galvanized steel, aluminum, magnesium and stainless steel, amongst others.

Test results MM31

Over the course of the development trajectory MM31 has been tested very thoroughly by extensive salt spray testing, CASS test and performing a wide range of additional adhesion tests. Results are similar or better than the requirements of international quality standards such as FROSIO, NACE, GSB, Qualicoat and Qualisteelcoat.

The product has been tested in combination with the most common paint systems of leading paint suppliers in Europe.

Example test results and application method

One layer powdercoating (1000 h NSS)

Manually blasted Reference

Manually blasted MM31

Steel, powdercoating (500 hr NSS)

One layer (80 µm) Polyester coat

Double layer (120 µm) Epoxy primer Polyester coat

MM31 Not pretreated

Steel cylinder with a brass crane, one layer powder coating.

CASS TEST Fraunhofer institut

MM31 / 480h Test passed

Ohmic VBH / 240h Test stopped

MM31 standard procedure

MM31 procedure for heavy contaminated surfaces

MM31 procedure chemical pretreatment

Results powdercoating (500 h/ASST)

Aluzinc Aluminum Zinc coated steel Carbon steel

Steel (blasted), 300 µm zincprimer

1000 h NSS Reference

MM31

9 mm 5 mm

In-situ incorporation of nanocontainers during Plasma Electrolytic Oxidation

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Topic: WP14_5: Self-healing and Smart Coatings

Plasma electrolytic oxidation (PEO) is a surface treatment technique employed to light metals to enhance their properties such as heat, wear, and corrosion resistance. The coating comprises of inner thin layer and a porous outer layer. The inner layer provides passive protection separating the substrate from the surrounding environment. However, the presence of the porous outer layer allows the propagation of aggressive ions towards the substrate initiating localized corrosion.

This study aims to functionalise PEO coating by incorporating corrosion inhibitors encapsulated into nanocontainers in a single-step process. The inhibitors will be released when detecting electrochemical activity associated with corrosion initiation, providing corrosion protection on demand. The incorporation of nanocontainers in a single step allows the homogenous distribution of the nanocontainers through the coating matrix, but the integrity of the nanocontainers might be compromised due to the high temperatures developed at microdischarge sites. To prevent this, the thermodynamic conditions of the plasma process will be optimised by establishing the soft spark regime at the earliest stage of the PEO process, which allows the non-reactive incorporation of nanocontainers.

The presence of nanocontainers in PEO coating was confirmed by scanning electron microscopy and the corrosion behaviour of PEO coating was assessed by electrochemical impedance spectroscopy.

LDH conversion coatings for active corrosion protection of LPSO Mg alloys

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Layered double hydroxides (LDH) coatings with incorporated inhibitors were synthesized on Mg alloys containing long period stacking order (LPSO) phases. Different coating systems were synthesized on WZ31 and GZ61 alloys and combined with several corrosion inhibitors. Specimens were investigated in terms of morphology and composition using optical microscopy, scanning electron microscopy and X-ray diffraction. The corrosion behaviour was evaluated using electrochemical impedance spectroscopy in sodium chloride aqueous solution. Additional properties, such as surface roughness and water contact angle were also evaluated. The corrosion of specimens with an artificial defect was also investigated with the aim of evaluating the self-healing properties of the best systems.

Self- healing analysis of corrosion on Mg alloy with microcapsules PU/PUa/ IPDI

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Self-healing materials are no longer an illusion. Instead it is an evolving area with significant importance, and in increased development and modernization, enabling to obtain materials with new properties. These materials can restore their original shape or integral structure when damaged. Virtually, all materials are susceptible to natural or artificial destruction and degradation over time. In the case of construction materials, a long-term degradation process leads to the formation of micro-cracks, which consequently cause the failure of the device. Therefore, repair of the material is then necessary to increase their reliability and service life. Recently, there has been an increased interest in the study of magnesium (Mg) alloys for application in engineering sciences or as biomaterials. Nevertheless, corrosion is still a serious problem, and a great effort has been put on the minimization of its rate. Here we report on the use of self-healing microcapsules (MCs) to be used as a solution to solve and minimize corrosion phenomena.

The present work aims to study the occurrence of corrosion by means of potentiodynamic and EIS tests on a magnesium alloy AZ31 as well as the performance of MCs as a self-healing layer. The emulsion stabilizer, gum arabic (GA), was obtained from LabChem. The active H source compounds, namely, poly(ethyleneimine) (PEI) aqueous solution (Mw 60,000, 50 wt% in H₂O) and triethoxy(octyl)silane (n-OTES), were supplied from Sigma-Aldrich. The isocyanate to be encapsulated, isophorone diisocyanate (IPDI, with 98% purity), with the commercial name of Desmodur® I, was obtained from Covestro. A polyisocyanate with the commercial name Desmodur® RC, used as shell formation agent, was kindly supplied by CIPADE S.A.. The MCs were

produced by an oil-in-water (O/W) micro-emulsion system in combination with interfacial polymerization processing.

The open circuit potential (OCP), polarization curve (Tafel plot) and impedance (EIS) of the coatings on AZ31 with MCs were measured using an Atlas 0531 potentiostat (Atlas-Sollich, Rebiechowo, Poland) with a frequency Response Analyzer (FRA), in an area of 5 cm². Neutral 0.5 M NaCl solutions were used for the OCP potentiodynamic tests. EIS tests were carried out using the same solution, with a pH value 6.8 at room temperature after 1 h and 150 h of soaking. The amplitude of the sinusoidal signal was 10 mV versus the open circuit potential, and the frequency span was 100 kHz–0.01 Hz. The Bode and Nyquist plots were presented in the impedance spectra.

SEM microscopy was used to recognize the self- healing regions. It was concluded that the MCs are able to be used as a self-healing system when there is a crevice corrosion.

In situ LDH growth on bare and PEO coated magnesium alloys in the presence of chelating agents

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A promising direction of corrosion protection for magnesium alloys are LDH-based conversion treatments. However, there are a number of drawbacks of the current LDH formation process, which prevent a larger scale industrial application. The two most critical points are the use of autoclave conditions and the formation of passive non-functionalizable LDH-carbonate. However, a new approach using a carbonate-free LDH treatment bath was developed, preventing those major drawbacks. In the presence of chelating agents, the possibility of LDH formation on the surface of bare AZ91 at elevated temperatures (or even down to room temperature) and ambient pressure was demonstrated. Results of different chelating agents, such as ethylenediaminetetraacetic acid (EDTA), disodium salt of nitrilotriacetic acid (NTA) and pentasodium salt of diethylenetriaminepentaacetic acid (DTPA), on the LDH formation on bare and PEO-treated magnesium surfaces will be shown. Overall, DTPA was selected as the most promising compound based on its complexing and environmentally friendly behavior. The possibility of anionic exchange reaction with different corrosion inhibitors was checked for all LDH conversion coating and the corrosion protection was investigated, revealing a significantly increase of the corrosion resistance of the LDH-conversion treated magnesium-based substrates.

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Development of novel coating with self-healing properties under immersion in NaCl solution

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In offshore structures, when the coating is damaged, its maintenance is a common problem because its execution is often difficult and involves high associated costs. Self-healing coatings have shown attractive to provide autonomous anticorrosion protection. Epoxy resin and its hardener are considered as potential healing agents because of their excellent mechanical, physical and chemical properties. Once they are encapsulated and incorporated into a commercial paint, when a damage occurs, both microcapsules would break and release their content which react to form a new healing film in the damaged site. Literature usually considers the self-healing for atmospheric environment exposure and when the film has been formed, it is submerged in an electrolyte to evaluate its performance. In this context, the main goal of this work is to develop an epoxy dual component system, incorporating it into a commercial paint and evaluate its performance when the damage occurs under immersion in NaCl solution, simulating painted carbon steel in offshore structures. Two types of microcapsules were obtained and characterized visual, chemical and morphologically. One capsule shell of poly (melamine-urea-formaldehyde) containing epoxy resin in its core and other of polymethylmethacrylate shell containing epoxy hardener which is a fast-reactive amine. Emulsion/in situ polymerization and emulsion/solvent evaporation techniques were used as methods of synthesis, respectively. The self-healing and barrier properties of the coating were evaluated under immersion using the electrochemical impedance spectroscopy. Corrosion performance of the coatings was assessed by immersion corrosion test (1056 h) with scratched and undamaged coated samples. Corroded areas around the scribes were calculated. In both tests, a NaCl 3.5% solution was used, referring to the salinity of sea water. The results obtained showed that a new polymeric protective film can be formed even under immersion, however, the stability of the polymeric film is affected by the saline solution. The self-healing coating can retard the inevitable corrosion process,

improving its lifetime. Samples without microcapsules presented more than twice the corroded area compared to the samples with microcapsules.

Keywords: corrosion, self-healing, under immersion, epoxy dual component, polymeric microcapsules.

A Case Study on the Damage Types of Duplex Stainless Steel by Various Corrosion Environments in Refinery

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ABSTRACT

Duplex stainless steel (DSS) is widely used in the refinery because of their economical combination of strength and corrosion resistance. DSS are often used in lieu of austenitic stainless steels (ASS), in services where the ASS would have problems with chloride and/or H₂S. Various forms of damage may occur to the DSS depending on the concentration of chloride, H₂S, water, and temperature. This report presents the analysis results of failure cases occurring in various environments of the refinery. The operation condition and corrosion environment of the two heat exchangers made of DSS were compared, and the inspection results for tube defects, and the analysis results for defects were summarized. Heat exchangers in the CDU (Crude Distillation Unit) shows different defect pattern depending on mainly operating temperature, and especially one exchanger was damaged by crack within just few months of use. Heat Exchangers in SWS shows the pattern of deep pit and crack coexisting under it. And Air fan cooler header box in MDU (Middle Distillation Unit) suffers from a crack due to wet H₂S environment.

Key Words

Duplex Stainless Steel (DSS), Chloride SCC (Stress Corrosion Crack), Sulfide Stress Cracking (SSC), Chloride Corrosion

Introduction

Duplex stainless steel (DSS) has been implemented during 1980s ~ early 2000s at Ulsan refinery complex in South Korea as it has great resistance on both corrosion and stress corrosion. Many applications have been successful; however, some failures have encountered in the recent years. The failure mechanisms were chloride stress corrosion cracking, and sulfide stress cracking at weldment. In this paper, each damage mechanism will be briefly discussed and share plant experience of the DSS failures in the following section.

Damage Mechanisms

Chloride Stress Corrosion Cracking (Cl-SCC)

Cl-SCC appearance is characterized microscopically by a transgranular cracking that branches out in multiple directions when stainless steel of various types is exposed to an aqueous solutions containing chloride ions above a critical temperature [1,2]. Although there are other factors (e.g., stress level, materials surface condition, heat treatment, salt formation) to be considered for the given alloy composition, temperature is typically considered as the first criterion of the materials selection for Cl ion aqueous solution application for the simplicity. For 300-series austenitic stainless steels (ASS), the critical temperature is known to be 50~60°C [1-4]. When an exposed temperature is 50~150°C, duplex stainless steel (DSS) has been the next choice [3]. A better Cl-SCC resistance of DSS is often attributed to the nearly equal amount mixture of ferrite and austenite. Generally, this better Cl-SCC resistance is explained by the different electrochemical potential to form the crack among phases at the given crack tip environment [1,2]. Namely, if the electrochemical potential set by the surrounding environment favors to form and extend the crack in the ferrite, it will initiate and grow in the ferrite. Once the crack reaches to the austenite, it is likely difficult to propagate due to the unfavored electrochemical potential to form the crack in the austenite unless stress is high or the electrochemical potential changes greatly [2]. Although DSS clearly exhibits a better Cl-SCC resistance as compared to 300-series ASS, it is not perfectly immune [5-8]. As Cl ion containing solution is acidified (ex, pH ~1.5), the Cl-SCC resistance of DSS is greatly impaired and then a critical temperature of Cl-SCC will be lowered, which is not clearly known yet [1-4]. In addition to chloride aqueous solution, as the salt formation occurs on the DSS surface in wet-dry condition, the critical temperature for Cl SCC can be lowered to 70~80°C [7]. In refinery, the Cl-SCC failure of DSS 2205 has been reported in crude unit overhead and top pump around system [5,6,8]. For example, CDU overhead top pump around heat exchanger experienced Cl-SCC on DSS 2205 Tube. The Cl-SCC was initiated from the outside surface of the tube. Shell side of the heat exchanger had a service of liquid naphtha having MEA hydrochloride salt at 148°C. This salt caused Cl-SCC. Also, additional failure was reported in the pump and piping by the same causes [6]. Although DSS is a great alternative material when ASS cannot be used, it still suffers from Cl-SCC when DSS is exposing to high corrosive environment such as acidic salt formation.

Sulfide Stress Cracking (SSC)

SSC is one of hydrogen embrittlement that normally occurs at high hardness region when DSS is exposed to wet H₂S environments combination with an applied stress [1-3]. Similar to the carbon steels or Ni based alloys, the SSC resistance of DSS also depends on the partial pressure of H₂S, pH, chloride concentration and temperature. Among several factors, it has been shown that SSC occurrence has the highest probability at 100°C approximately [2]. As the partial pressure of H₂S and Cl concentration increase and pH level lowers, the SSC resistance of DSS deteriorates just like the Cl-SCC resistance of DSS [2]. Although there are

several factors to be considered to implement DSS under wet H₂S service, the first criterion is the hardness requirement that is well documented in NACE MR0103 [9]. For a wrought product, the maximum hardness is 28 HRC for PREN $\leq$ 40 and 32 HRC for PREN $>$ 40 [3,9,10]. And also, for the welded DSS, the average hardness shall be below 310 HV and any individual values shall not exceed 320 HV [3,9,10]. In addition to that, the area fraction ferrite of weldment shall be within the range between 35 % and 65 % [3,9,10]. Although phase fraction and hardness requirement of plate or weld have been well established over decades, MTI study and other report show that the thick walled DSS2205 (>25mm) weld part exhibits a high SSC susceptibility in reactor effluent air cooler (REAC) header box and its associated parts (e.g., Weld attached nozzle, tubesheet-tube weld) when the environment is H₂S partial pressure $>$ 1000psig and/or NH₄SH $>$ 3.5wt%. The high susceptibility of SSC was attributed to the failure to meet the hardness and ferrite fraction requirement [6,10-13]. Thus, welding DSS needs a great care as well as a thorough nondestructive inspection after welding according to MTI work, and they also suggest the in-service inspection method [10].

Failure Cases Studies

[Case 1] CDU Overhead Top Pump Around Heat Exchanger DSS Tube Failure

Heat exchanger DSS tube was failed after 4 months service. It was a very unexpected failure since DSS tube has been used for 5~10 years in the similar service. To understand the premature failure of the DSS tube, the metallurgical failure analysis was carried out by OM (Optical Microscope), EDS (Energy Dispersive Spectroscopy), EBSD (Electron Backscattered Diffraction). The outer of the failed DSS tube was exposed to the circulating naphtha at 60~110°C and inner side was experienced crude. The more operating information of heat exchanger and the simplified process flow diagram are in Table 1.

Table 1: CDU Overhead Top Pump Around Heat Exchanger

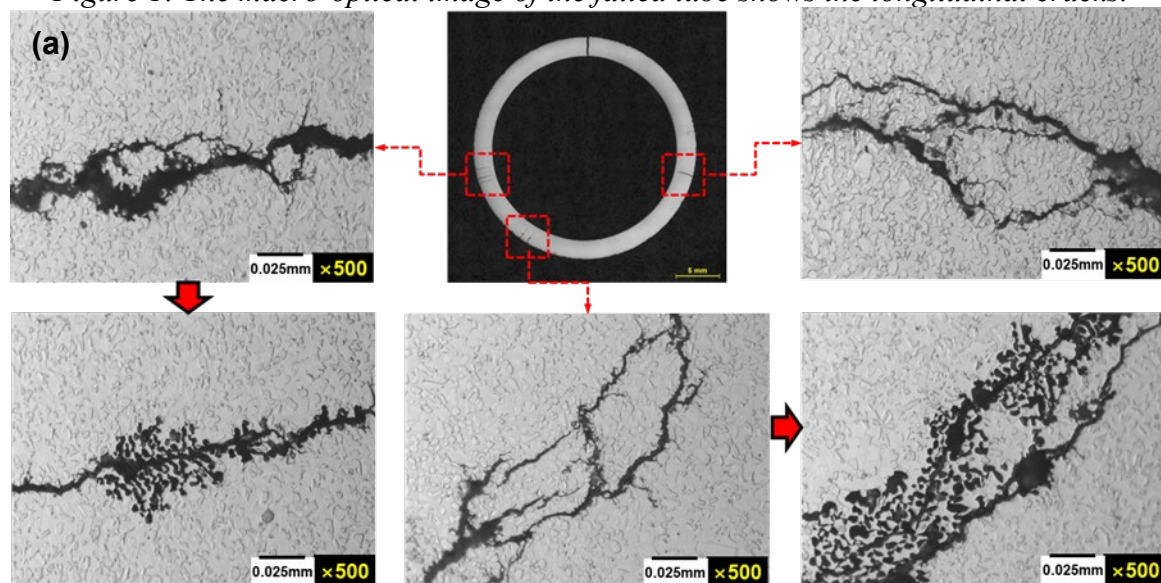
Item Desc	Column Reflux/Crude Exchanger		Naph Pump Around/ Splitter Feed Heat Exchanger	
Part	Tube	Shell	Tube	Shell
Service	Crude	Cir. Naph	Split. Feed	Cir. Naph
Oper. Pressure (kg/cm ²)	27.4	16.3	4.2	16.3
Oper. Temp (°C)	10(In) / 84.5(Out)	115(In) / 61.6(Out)	84.6(In) / 93.4(Out)	114(In) / 89.4(Out)
Tube Material	SA-789 S31803			

The crack was observable by a visual inspection with an insignificant pitting, and an example macro-optical image is shown in Figure 1. The crack was straight and parallel to the longitudinal direction of the tube. To examine the crack morphology, the cross-section sample was taken perpendicular to the crack direction from the failed tube. Figure 2a shows that the crack initiated from the outer surface of the tube with the branched trans-granular crack

morphology. Additionally, EDS results in Figure 2b revealed a high amount of chloride (6~10 w.t.%) inside of the crack. Due to the crack morphology and the presence of chloride in the crack, it is obvious that the failure mechanism is a chloride stress corrosion cracking.



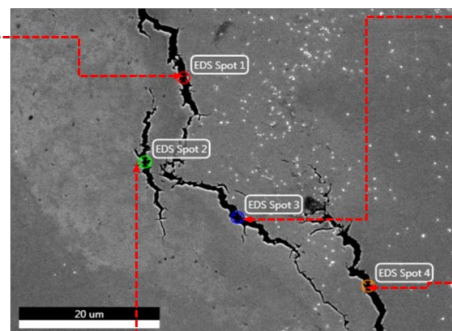
Figure 1: The macro-optical image of the failed tube shows the longitudinal cracks.



(b)

Element	Weight %
O	31.99
Si	0.29
S	2.70
Cl	7.22
Cr	43.56
Fe	14.24

Element	Weight %
O	29.80
Si	0.25
S	2.16
Cl	6.70
Cr	40.73
Fe	20.36



Element	Weight %
O	31.80
S	2.43
Cl	9.96
Cr	37.22
Fe	18.59

Element	Weight %
O	31.45
S	1.95
Cl	9.17
Cr	40.00
Fe	17.43

Figure 2: (a) The optical images of the cross-sectional sample and (b) EDS measurement results inside of the crack.

Further experimental results are illustrated in Figures 3 & 4. The various morphologies of the surface damages were observed as shown in Figure 3; the left image shows the surface cracks with a slight surface deformation, and the right image typifies the severe surface damage with a small crack. And these types of damage on the tube surface were not common based on authors experience suggesting the manufacturing defects since the tube failure occurred only after 4 months. Figure 4 illustrates the EBSD Kernal average mis-orientation (KAM) map, which often uses to show a local plastic deformation (or a local stain distribution) [14]. The degree surface deformation of the failed and normal tube was compared, and the surface deformed layer thickness was $\sim 10\ \mu\text{m}$ and $\sim 2\ \mu\text{m}$ for the failed and the normal DSS tube, respectively. This observation clearly revealed that the large extent of plastic deformation existed on the surface of the failed tube relative to that of the normal tube. According to the literature [15], the surface deformation degrades the CI-SCC resistance of DSS. This is often attributed to the surface tensile residual stress. Reasonably, the present premature CI-SCC can be ascribed to the tube surface deformation occurred during the manufacturing processes.

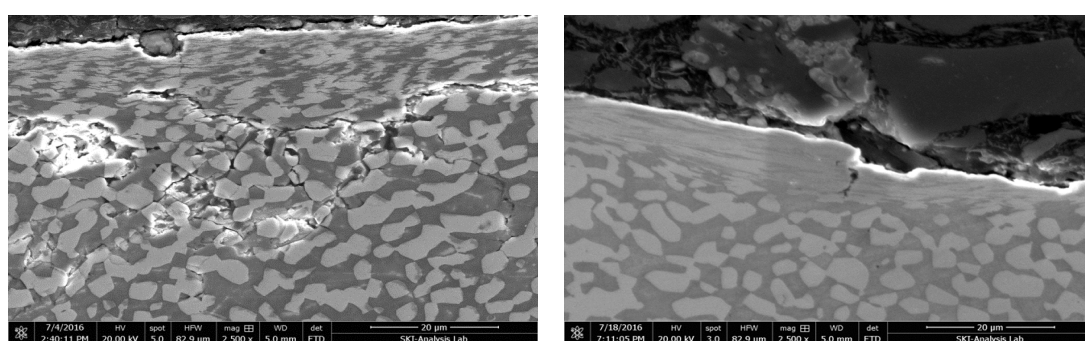


Figure 3: The SEM micrographs of the surface damages.

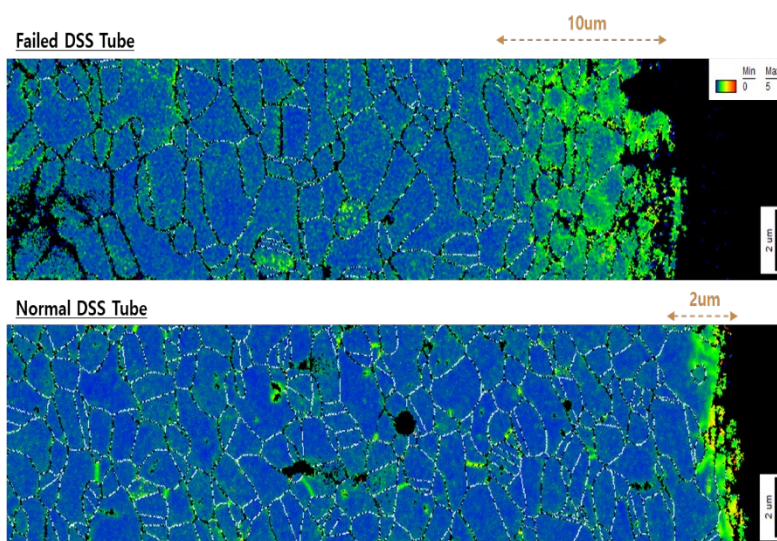


Figure 4: EBSD Kernal average mis-orientation (KAM) map comparison between the failed and normal DSS tube surface.

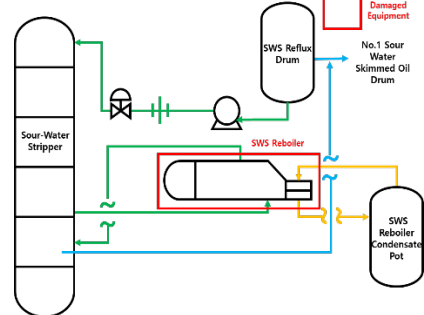
[Case 2] Sour Water Stripping Tower Reboiler DSS Tube Failure

Sour water stripping tower reboiler (heat exchanger) DSS tube replaced after 12 years service as it had many deep pits on the outside of the tubes. The outer of the replaced tube was exposed to the sour water at $\sim 125^\circ\text{C}$ and inner side was low pressure steam at $\sim 140^\circ\text{C}$. The

more operating information of the reboiler and the simplified process flow diagram are in Table 2.

Table 2: Sour Water Stripping Tower Reboiler

Part	Tube	Shell
Service	LP Steam	Sour Water
Oper. Pressure (kg/cm ²)	3.1	1.39
Oper. Temp (°C)	152(In) / 144(Out)	125.8(In) / 126.2(Out)
Tube Material	SA-789 S31803	



The diagram illustrates the process flow for the Sour Water Stripping Tower Reboiler. It features a vertical Sour-Water Stripper column on the left, connected to a horizontal SWS Reboiler. The reboiler is shown with a bundle of tubes and is highlighted with a red box, indicating it is damaged equipment. The reboiler is connected to three main components: an SWS Reflux Drum at the top, a No.1 Sour Water Skimmed Oil Drum on the right, and an SWS Reboiler Condensate Pot at the bottom. The flow is indicated by green lines for the reboiler and blue lines for the reflux drum and condensate pot. A red box labeled 'Damaged Equipment' is placed near the No.1 Sour Water Skimmed Oil Drum.

Two different morphologies of pit were observed from the replaced tubes, as shown in Figure 5a. One was a valley-shaped pit (A in Figure 5a) and the other was a round-shaped (B in Figure 5a). The severe pits were likely due to the large amount of foulants outer tube surface as shown in Figure 5b. The cross-sectioned samples were taken out from the location A and B indicated in Figure 5a. The optical image in Figure 6 revealed that both pits contained the branched trans-granular cracks underneath. Additionally, the crack “B” contained ~1.4 w.t.% chloride inside of the crack according to the EDS measurement in Figure 6. Based on the experimental results, the following failure mechanisms can be withdrawn; during 12 years’ service, a fouling outside of the tube causes a severe deep pitting corrosion. and such deep pits act as a stress riser. Consequently, chloride stress corrosion cracking occurs although a bulk temperature was below 140~150°C that is the typical limit of DSS [3,4].

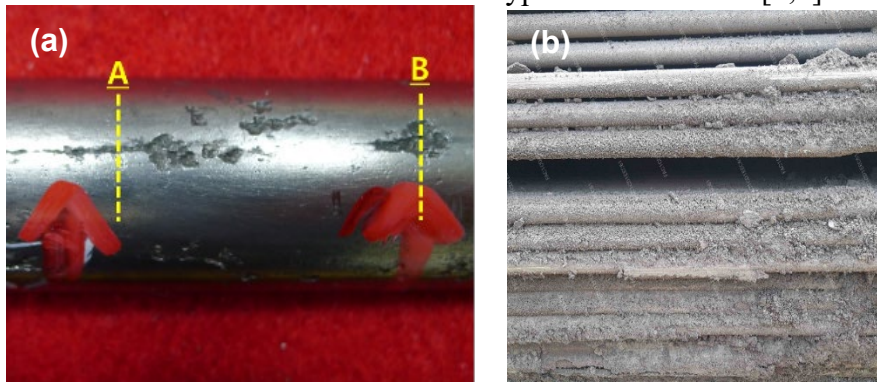


Figure 5: (a) The optical image of pits on the tube surface and (b) the photograph of the severe fouling on the tube bundle.

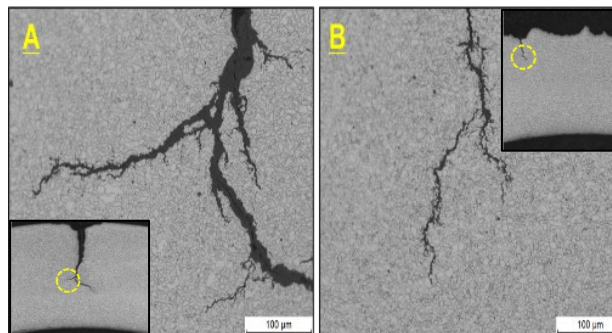


Figure 6: The optical image of the crack morphology underneath of each pit is shown. A & B on the image correspond to the A & B in Figure 5a, respectively. Inset of each optical image shows the overall pit shape with the crack underneath it.

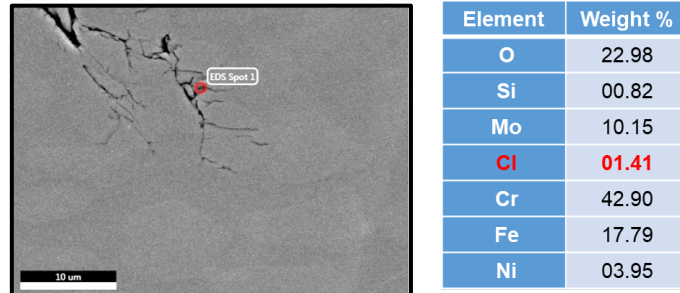


Figure 7: EDS results inside of the crack B

[Case 3] MDU Reactor Effluent Air Cooler (REAC) Header Box Weldment Crack Analysis

During the recent turn-around, 26 years serviced reactor air cooler DSS header box was inspected by PAUT (Phased Array Ultrasonic Test), and a defect in the weldment of the header box was detected as shown in Figure 8a. The crack location was the root pass weld. In addition, penetration dye test (PT) was applied through a tube hole, and then a linear surface crack along the weldment was observed in Figure 8b. In the process stream, a H₂S partial pressure was approximately 31.3 psia and a tube inlet temperature is 120~130 °C. Since it is a middle distillate hydrodesulfurization unit, the operating pressure and the H₂S content is low compared to the atmospheric residue hydrodesulfurization unit. The more operating information of the header box and the simplified process flow diagram are in Table 3.

Table 3: MDU Reactor Effluent Air Cooler

Part	Tube	
Service	Reactor Effluent	
Oper. Pressure (kg/cm ²)	40	
Oper. Temp (°C)	158(In) / 66(Out)	
Tube Material	SA-789 S31803	

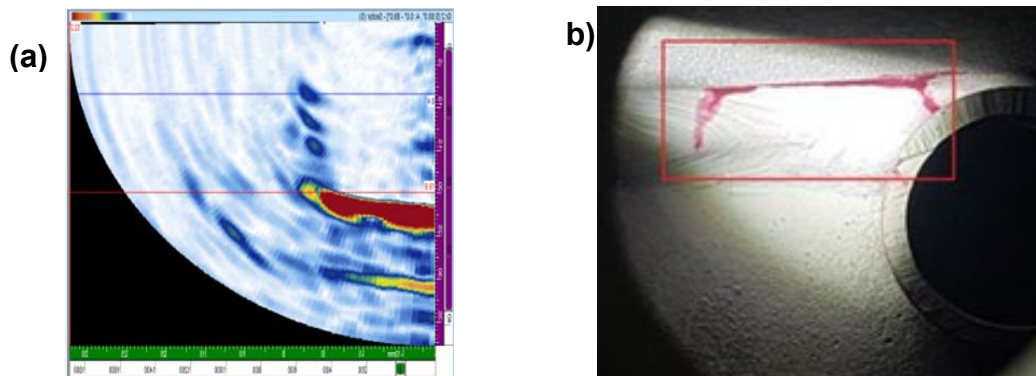


Figure 8: (a) PAUT result indicates the presence of a defect inside of weldment in header box and (b) PT result shows the surface defects.

The cracked region was taken out to examine the microstructure around the crack. The sample was etched by using Beraha II at 70°C [13] to investigate the duplex weld microstructure. In addition, Micro Vickers hardness (load = 1kgf) measurement was conducted. Figure 9 shows that the 10 μ m depth crack located in the weldment and initiated from the inside of the header box. The overall view of the crack in weldment and the ferrite ratio and hardness values were summarized in Figure 9a. And the color etched weld microstructure morphology (black: ferrite, white: austenite) with phase fraction map (red: ferrite, green: austenite) were illustrated in Figure 9b. All hardness values were within the specification whereas the ferrite contents were not always within the specification. The highest hardness value was 295 HV, and the location was at the initiation site. This was satisfied with the specification of average value of 310 HV (no single value > 320 HV); however, the ferrite content was 76% at the crack initiation site, in Figures 9a-b, and it was outside of range of 35~65 % [9]. According to the literatures, the SSC resistance was degraded when DSS has either a high hardness or the outside the range of optimum ferrite content [6,10-13]. Consequently, sulfide stress corrosion cracking was the cause of the crack formation due to the high ferrite content region exposed to relatively high H₂S content environment. In addition, the weld deposit shape at the crack initiation site was smaller and different than other weld passes suggesting that two repair weld passes were likely conducted during manufacturing due to an unknown reason at this moment. It appears that the hardness values are able to meet to the specification; however, it is not able to produce proper ferrite content perhaps due to the difficulty in controlling a cooling rate of the small size repair welding against the larger area.

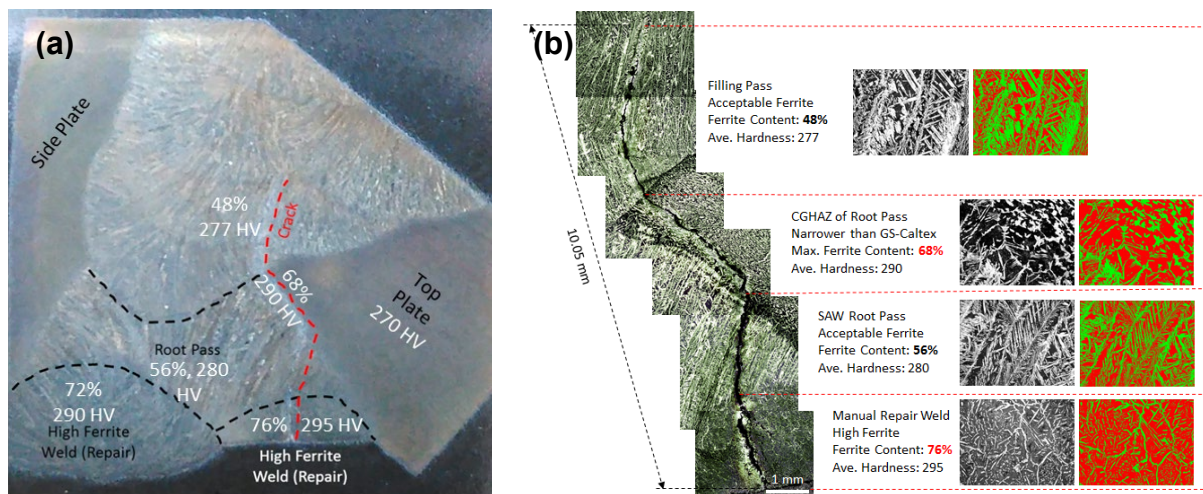


Figure 9: (a) The overall cross-sectional view with the crack location and ferrite number with hardness values, (b) the detailed crack morphology with the color etched optical image (black: ferrite, white: austenite) and phase map (red: ferrite, green: austenite).

Summary

Chloride SCC and corrosion

As previously stated, the susceptibility of commercial DSS to chloride SCC is influenced by several variables, including chloride concentration, temperature, and pH, as well as the surface deformation (i.e., a residual stress). In both Case 1 and 2, Duplex 2205 tubes were utilized, and the following features were observed.

- In both cases, the cracks originated outside of the tube exposed to the naphtha and sour water.
- For Case 1, Cl-SCC occurred prematurely with a trivial pitting corrosion. The premature Cl-SCC was ascribed to the tube surface deformation occurred during the manufacturing processes. Therefore, the surface quality control during manufacturing is critical for DSS tube employed in Cl containing solution.
- For Case 2, deep pitting corrosion was observed initially, followed by Cl-SCC beneath the pits. This case study suggests the following damage mechanisms; during 12 years' operation, a deep pitting corrosion on the tube surface had occurred due to the heavy deposits. This stress concentrated location causes Cl-SCC underneath of pits.

Sulfide Stress Cracking (SSC)

According to the MTI report [10], DSS has low susceptibility to SSC when an operating condition is well below 1000 psi (70.3 kg/cm²) and 3.5 w.t.% NH₄HS. For Case 3, MDU REAC was operating at 569 psia (40 kg/cm²) and 0.14 w.t.% NH₄HS, which is a relatively mild condition. However, deep SSC was confirmed in the REAC header box DSS weldment by PAUT and the microstructural analysis.

- The cause of the SSC was attributed to the inadequate ferrite/austenite ratio at the localized weld, which was suspected that a repair welding was carried out during manufacturing.
- Ascertaining the quality of the welding in the field is a challenging task and sometimes impractical. And hence, it is essential to conduct thorough preliminary verification of the repair method including WPS (Welding Procedure Specification) during the manufacturing process. In addition, the periodic NDE (Non-destructive Evaluation) is required to avoid the failure during the operation.

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Predicting Acid Gas Dew-Point Corrosion At Sulfur Recovery Units Through Proactive Corrosion Management

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Abstract

Deviating from established corrosion control measures could lead to a leak, rupture, or potential catastrophic failure if not attended to properly. Thus, switching from reactive to proactive corrosion management in gas plants is essential to enhance plants' reliability and availability. Saudi Aramco has developed an in-house web-based technology known as the "Corrosion Management Solution" (CMS), an integrated solution for monitoring corrosion parameters through real-time data. Through this solution, Saudi Aramco was able to determine chronic issues related to reactive corrosion management. This paper discusses a protocol adopted and applied by Saudi Aramco on several gas plants to predict Acid Gas Dew-Point corrosion at Sulfur Recovery Units (SRU) utilizing CMS. Noncomplying with the minimum recommended operating temperature of the acid gas preheater led to severe localized corrosion for associated downstream piping in several facilities. This damage mechanism occurs when weak acids are formed due to the absorption of H_2S and CO_2 in water under its saturation temperature. This phase is highly corrosive to bare carbon steel components. Naturally, the corrosion will become more pronounced in locations where the aqueous acid phase is likely to accumulate. CMS alerted the concerned facilities about the possible risk and advised them to conduct a Non-destructive Inspection (NDT) that confirmed the prediction.

Failure Analysis Of Crack On Subang CO₂ Removal Absorber Column And Repair Methods

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Abstract

CO₂ Absorber is the main equipment of Subang CO₂ Removal Plant, operated since 2003 at a design pressure of 600 psig and a design temperature of 100 °C, with aMDEA as the absorbent to absorb CO₂ in natural gas from 23% mol to a maximum of 5% mol of CO₂. The pressure vessel is of welded construction, vertical cylindrical, 3.26 meters in diameter, and 55 mm in shell thickness with ASTM A516-Gr.70N as material.

At Turn Around in 2015, a crack with a depth of up to 10 mm was found on the inside of the top of the Absorber (on the welding overlay area) which indicates that this part had experienced thinning and welding was carried out to increase the thickness of the shell.

Based on the FFS (Fitness For Service) calculation method, the equipment is not feasible to operate because the MAWP (Maximum Allowable Working Pressure) for the remaining wall thickness is less than the operating pressure of 520 psig.

The crack has a branching pattern and its propagation cuts through transgranular and intergranular materials which indicates the crack occurred due to stress corrosion cracking (SCC) and mixed martensite-widmanstatten ferrite phases were found.

Based on ASME PCC-2, Butt Weld Insert Plate were chosen as repair methods. Repairs were carried out using a full penetration butt-welded joint and continued with PWHT at a temperature range of 593–649 °C and a holding time of 125 minutes.

The result is that no martensite phase was found and hardness values are uniform which is less than 200 BHN. After 6 years of operation, there was no indication of a crack.

Keywords

“CO₂ Removal”, “Absorber”, “SCC”, “PWHT”

Introduction

CO₂ Removal is one of the Gas Processing Plant owned by PT Pertamina EP located in Subang, Indonesia. CO₂ removal Plant processes natural gas from around Subang field with a composition of CO₂ 23 % mol into sales gas with a maximum CO₂ composition 5% mol. Feed gas composition can be seen at table 1.

Table 1. Feed Gas Composition

CO ₂	N ₂	CH ₄	C ₂ H ₆	C ₃ H ₈	nC ₄	C ₅	C ₆	H ₂ S	Ops Pressure
% mol									(Psig)
23	6,50	66,97	1,80	1,14	0,27	0,12	0,2	0,0004	520

CO₂ Removal Subang has a design capacity of 98.97 MMscfd with a process flow as shown in Figure 1.

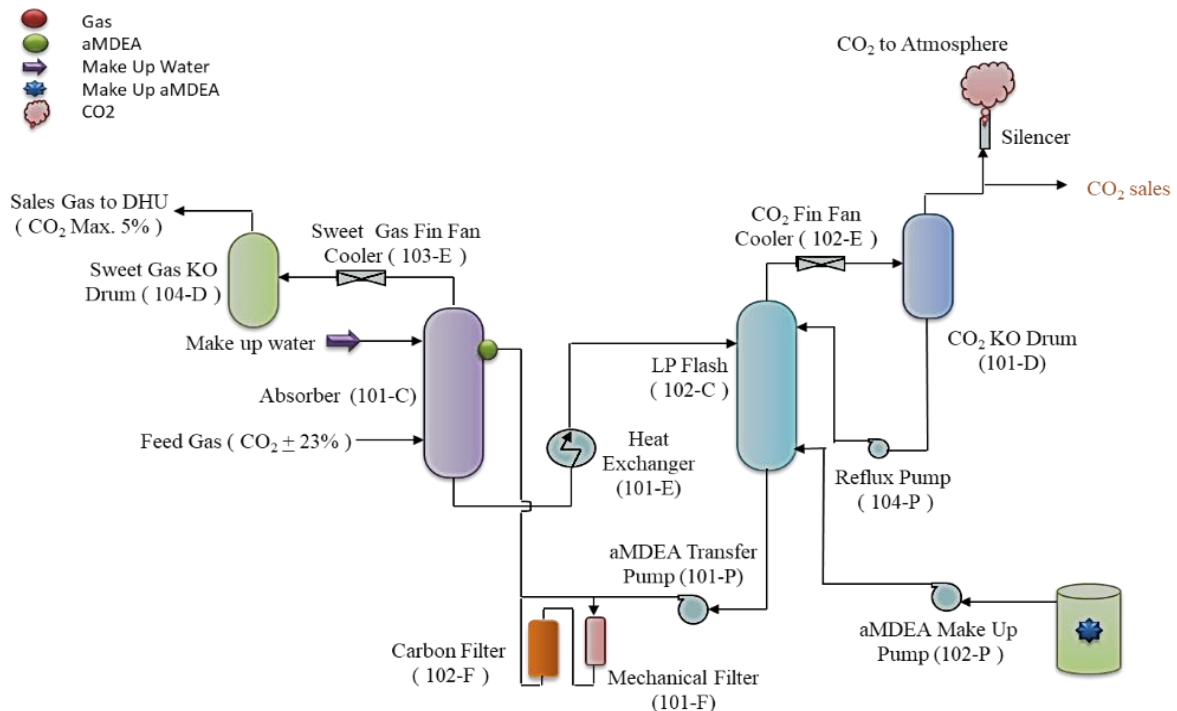


Figure 1. Feed Gas Composition

The process of purifying natural gas in the CO₂ Removal Subang uses the absorption principle, in which natural gas with a high CO₂ content is transferred to the absorber column and contacted with aMDEA (activated Methyl Diethanolamine) as an absorbent to absorb CO₂. Natural gas with a composition of CO₂ that meets the specification will be transferred into the DHU system and then sold to the consumer, while the rich aMDEA (containing high CO₂) will be transferred to the LP Flash Column for regeneration. The CO₂ gas that has been released from aMDEA is partly sold and the rest is discharged into the environment.

At Turn Around 2015, indications of crack and thinning (see Fig. 2) were found in the weld overlay area inside the top of the absorber column (at a height of 32 meters) (see Fig. 3). The CO₂ absorber column specification is a welded vertical cylindrical pressure vessel, 3.26 meters in diameter, 33 meters in height, and 55 mm of shell thickness, with ASTM A516-Gr.70N carbon steel as material.

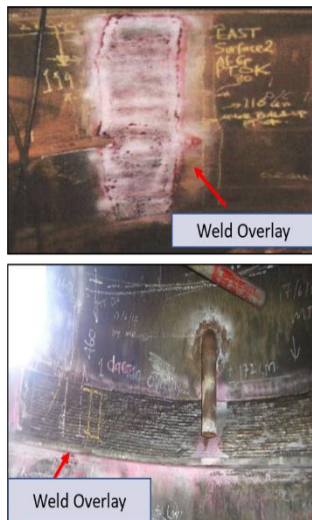


Figure 2. Weld Overlay and Thinning Area

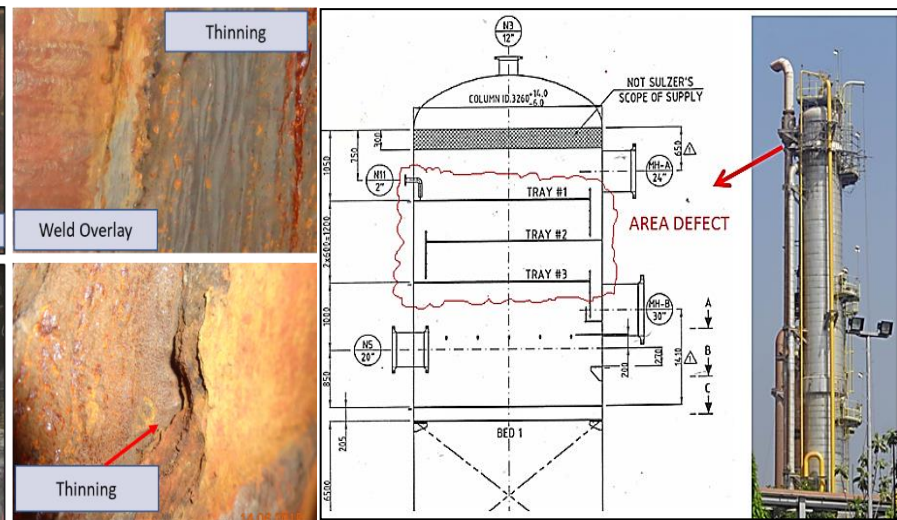


Figure 3. Crack Location

Inspection and Testing

There are cracks and thinning on the absorber shell, consequently a complete inspection and testing is required to determine the severity of the cracks, the impact on the operation of the CO₂ removal unit and the correct method of repair.

Visual Inspection

Visual inspection is essential in analyzing an indication or finding, especially in this case where the aim is to obtain the actual condition of surface, cracks and thinning. The result of visual observation is the presence of four weld overlay areas (Fig. 4) on the inner top of the absorber shell. This demonstrates that the shell has undergone thinning and welding has been applied to increase the shell thickness so that the absorber can operate according to the operating pressure.

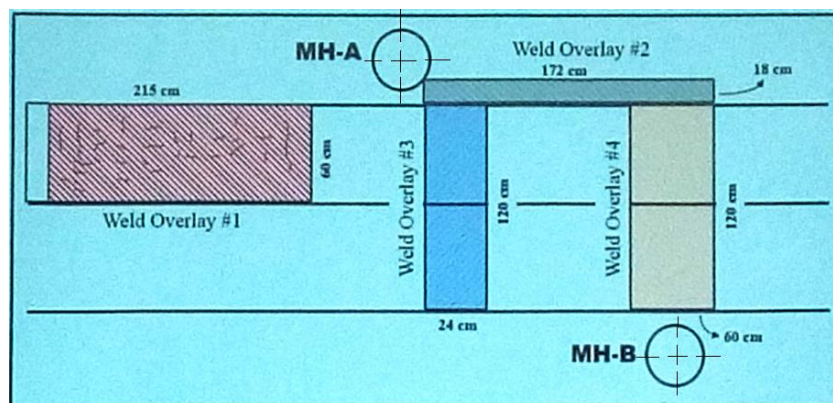


Figure 4. Weld Overlay Areas

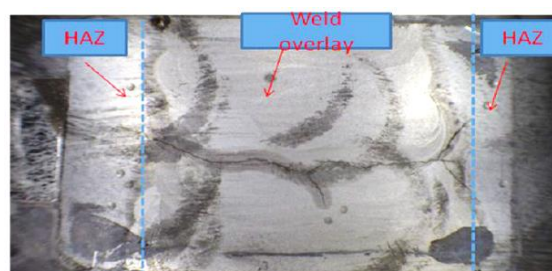


Figure 5. Visual inspection on crack at weld overlay #1

On weld overlay #1 (after smooth grinding), it's found that crack occurred from weld area and propagated to HAZ area and also make some branches, as seen on figure 5.

Non Destructive Test

NDT is especially necessary in this case because it aims to detect the cracks that occur on the absorber wall, including their patterns, spreading, and severity, as well as the residual thickness of the absorber shell around the defect.

a. Magnetic Particle Testing (MPT)

There are multiple subsurface cracks that are branched and spread along the weld overlay area (Fig. 6).

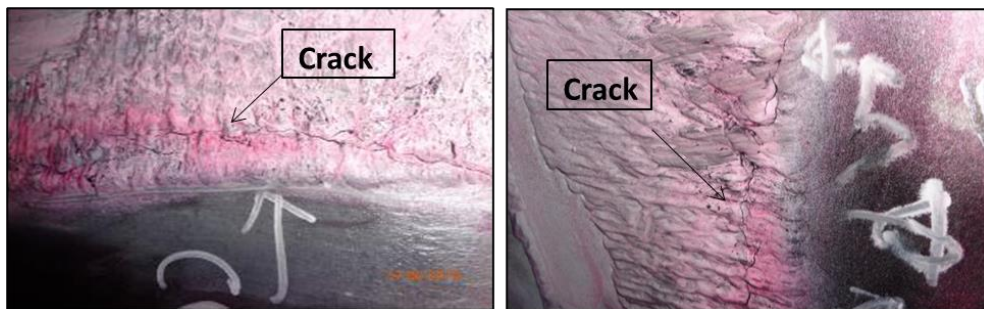


Figure 6. Crack Area by MPT

b. Phased Array Ultrasonic Test (PAUT)

Cracks are found up to a depth of 10 mm from the internal shell of the absorber, with a crack length of up to 340 mm (Fig. 7).

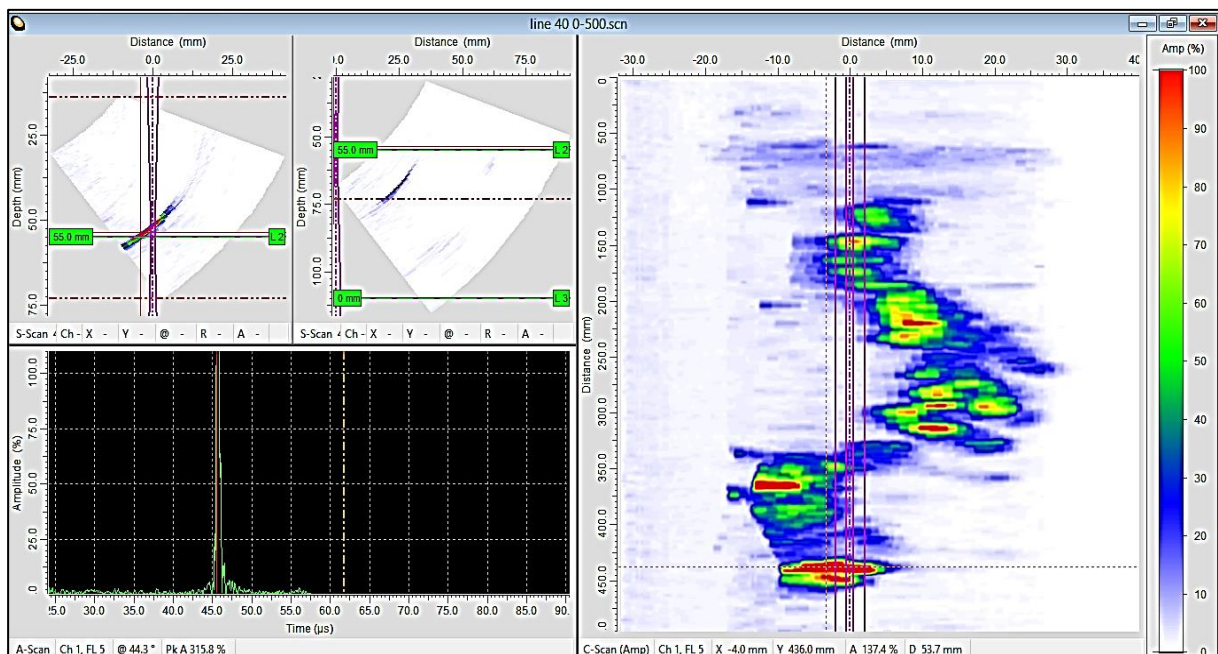


Figure 7. PAUT Result

c. Ultrasonic Test (UT)

The minimum thickness around the overlay welding area is 51,33 – 52,37 mm (Fig. 8). While the minimum design thickness is 53.8 mm. The actual thickness of the absorber wall is already less than the thickness required for the operating pressure, which is 520 psig.



Figure 8. UT Result

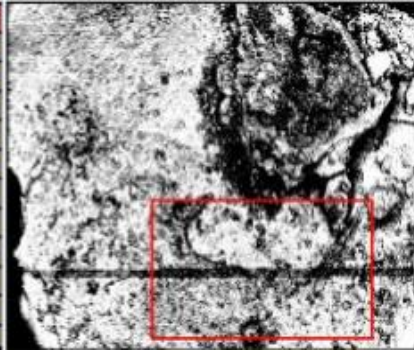
Rust Composition Analysis

In this case, the rust composition is also analyzed in order to determine the cause of the thinning that occurs on the absorber shell.

The EDAX method is used for rust analysis, and it can be noted that Fe (48,69%), O (37,19%), and C (8,38%) have unusually high amounts of content when compared to others. The rust that has formed on the absorber shell is yellow-brown in color.

Table 2. Rust Composition

Element	Wt%	At%
CK	08.38	17.20
OK	37.19	57.32
AlK	00.92	00.85
PK	01.05	00.84
SK	01.91	01.47
ClK	00.06	00.04
CrK	00.92	00.43
MnK	00.07	00.03
FeK	48.69	21.50
CuK	00.81	00.32
Matrix	Correction	ZAF



In-situ Metallography Examination

In-situ metallography examination was performed in the crack analysis on this absorber column to determine the mechanical properties of the absorber shell material, including grain size, formed phases, and microstructure crack patterns, in order to obtain more detailed information and treatment that the absorber shell has received.

The results of the in-situ metallography test show the presence of coarse martensite and widensmentatten ferrite structures in the heat-affected zone (HAZ) area (Fig. 9). The crack has a branching pattern, and its propagation cuts through the grain (transgranular) and grain boundaries (intergranular) (Fig. 10).

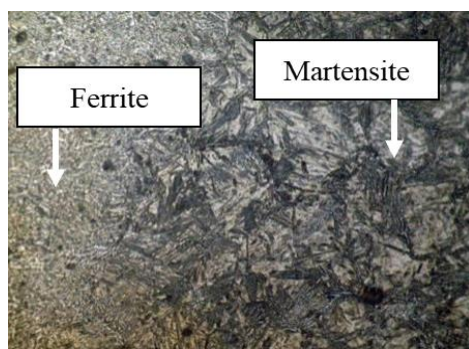


Figure 9. In-situ Metallography Result

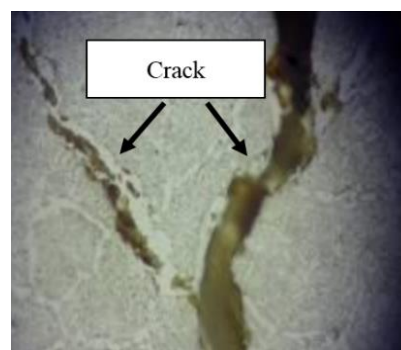


Figure 10. Crack Pattern

Hardness Test

In this case, the hardness test also attempts to identify the mechanical properties and treatment that have been applied to the absorber shell material. The results of the hardness test demonstrate that the base metal and weld overlay areas have distinct hardness values (Table 3).

Table 3. Hardness Test Result

Weld Overlay 1		Weld Overlay 2	Weld Overlay 3		Weld Overlay 4	
Base (Near Weld)	Weld	HAZ	Base (Near Weld)	Weld	Base (Near Weld)	Weld
144	223	129	142	203	143	211
146	211	130	142	192	139	202
149	213	134	141	181	140	210
155	213	137	143	190	135	198
159	218	-	140	196	135	197
160	204	-	137	195	133	209

Note : unit in Hardness Brinell (HB)

Fit For Service (FFS) Analysis

FFS analysis is performed to determine whether an absorber column with cracks may still be used under current operating conditions or if it needs to be repaired.

The initial analysis was performed using a level 1 assessment by examining the actual condition of the cracks and the result show that the actual crack length (340 mm) was more than the maximum permissible crack length at level 1 assessment (200 mm)[1], hence the assessment was advanced to level 2. As a result, the FAD values obtained from FFS simulations exceed the allowable limits, resulting in an absorber column with extended surface crack conditions in a welded section that is unsafe to operate (Fig. 11).

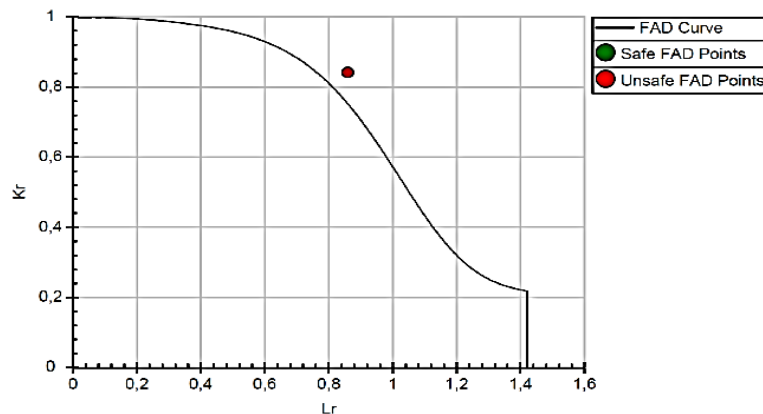


Figure 11. FFS Simulation Result

Analysis of Failure

From the testing and printing performed on the crack area of the absorber column, information and analysis can be obtained as follows:

- The CO₂ Absorber has thinned as a result of amine corrosion, which is indicated by a yellow-brown corrosion product with a high concentration of Fe, C, and O in its composition. This indication showed that the compounds that were formed were siderite (FeCO₃). Amine corrosion is typically localized corrosion that occurs principally on carbon steel in amine treating processes which is corrosion is not caused by the amine itself but results from dissolved acid gases CO₂ and other contaminant [2], water (H₂O). The partial pressure of CO₂ is 112 psig, indicating a corrosive environment.
- The crack that occurs in the CO₂ Absorber is caused by amine stress corrosion cracking (SCC) characterized by [2]:
 - cracks appear in the HAZ and / or the weld area

- cracks develop parallel to the weld and there are multiple cracks
 - by metallographic analysis, crack has a branching pattern and its propagation cuts through the grain (transgranular) and grain boundaries (intergranular).
- c. The majority of the weld area had a hardness value greater than 200 HB as a result of the hardness test on weld overlays. According to API 945, to reduce the risk of amine SCC, the weld hardness of carbon steel equipment shall not exceed 200 HB [3]. The difference in hardness primarily produces a high residual stress, which may result in crack formation.
 - d. The CO₂ Absorber has gone through a welding process without PWHT which is characterized by a high difference in hardness between the base metal and the weld area and the presence of a martensite structures in the weld area.
 - e. The CO₂ absorber column should be repaired based on the results of the FFS simulation, where the absorber column is not safe to operate under current operating conditions.

Repair Methods

Based on the failure analysis and refer to ASME PCC-2, Butt Weld Insert Plate was chosen as the repair method [4] with the consideration as follows :

- a. material has been subjected to repeated heating
- b. applicable to wide range defects
- c. reduce the risk of crack propagation
- d. as a permanent repair [5]

This improvement is also continued with the PWHT process, with the following considerations :

- a. According to ASME VIII Div 1, the plate thickness of the Absorber is 55 mm, which exceeds 1.5 inches, requiring PWHT to reduce residual stress [6].
- b. According to API RP 571 and API RP 945, the amine flowing in the absorber column made of carbon steel has a tendency to cause amine stress corrosion cracking. As a result, PWHT is required during repair in order to reduce residual stress in the welded area and significantly lower the risk of amine SCC [3].

Construction

- a. Make a cutting plan for shell that will be replaced (Fig. 12)
- b. Make a temporary support in the replacement shell area to sustain the load when replacing the plate and during PWHT (Fig. 13).

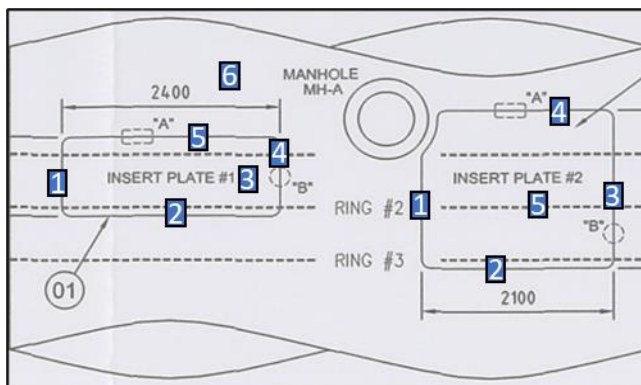


Fig. 12 Cutting Plan & Hardness Test Location

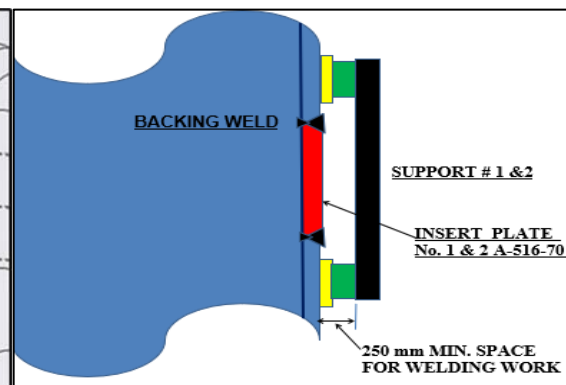


Fig. 13 Temporary Support Plan

- c. Cut the existing shell in accordance with the cutting plan, then continue with welding the new plates.

- d. PWHT is performed onsite at a temperature range of 593 – 649 °C, using an Internal High Velocity Gas Fired Technique (Fig 14) with a holding time of 125 minutes. Then, at a rate of no more than 100°C per hour, gradually cool to a temperature of 400°C. It continued to cool down to a temperature of 200°C. Then the insulation can be opened. The actual temperature of PWHT process can be seen at Fig. 15.
- e. After the PWHT work is completed, cut the temporary support.

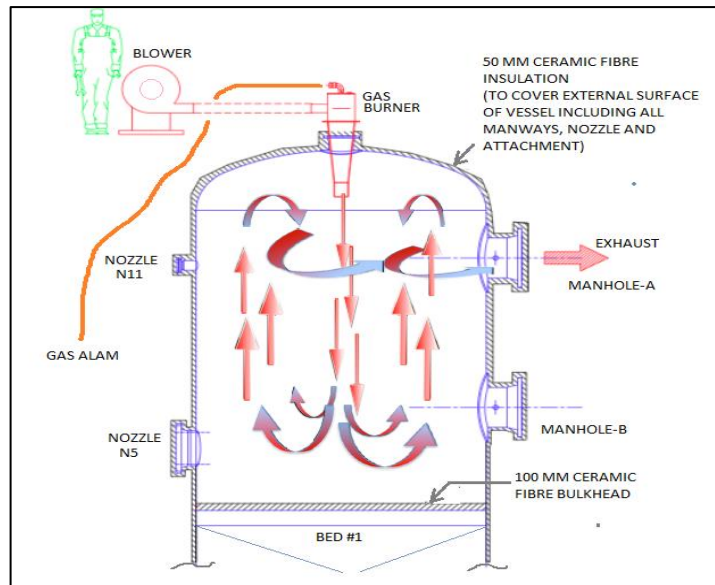


Fig. 14 PWHT Process

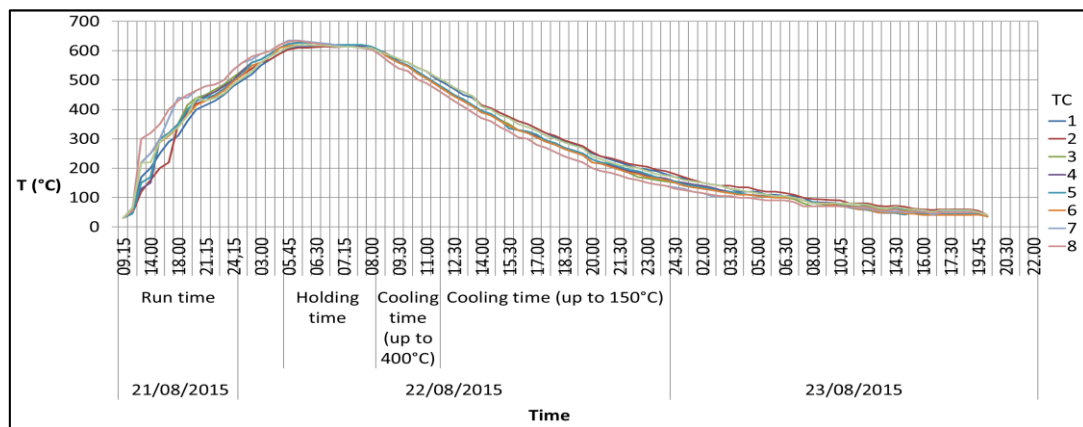


Fig. 15 Actual Temperature of PWHT Process

Inspection and Testing After Repair

After replacing the absorber shell, perform inspection and testing to confirm that the repair results were in compliance with the standard and no defects or flaws were discovered in the repair area.

Non Destructive Test (NDT)

There is no indication of a defect after shell replacement using Magnetic Particle Testing and Phased Array Ultrasonic Testing (Fig. 16).

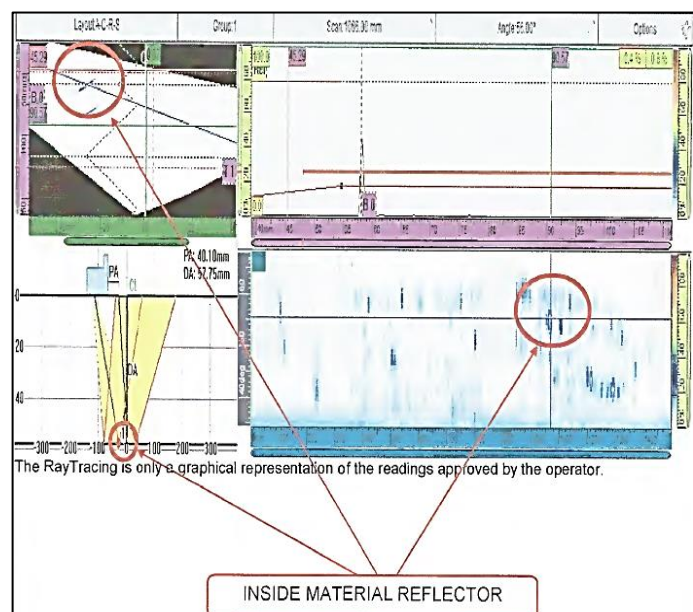


Fig. 16 PAUT Result After Repair

In-situ Metallography Examination After Repair

The in-situ metallography examination results show that the martensite structure does not form in the weld area (Fig. 17), indicating that the PWHT process was successful.



Fig. 17 In-situ Metallography Result After Repair

Hardness Test After Repair

The results of the hardness test at the weld area show that a hardness value is less than 200 HB and is nearly uniform (Table 4).

Table 4. Hardness Test Result After Repair

	Plate 1						Plate 2				
	1	2	3	4	5	6	1	2	3	4	5
Base Metal 1	136	128	128	140	156	137	113	125	126	139	125
HAZ 1	145	157	123	132	150	143	147	137	147	136	138
Weld	163	190	120	163	173	150	135	156	170	158	121
HAZ 2	149	134	106	159	166	148	120	136	137	143	118
Base Metal 2	114	137	109	157	123	155	125	114	140	140	125

Monitoring After 6 Years Operation

After six years of absorber operation after repair, a monitoring inspection was performed on the insert plate weld area using a phased array UT and the result was no indication of a defect (Fig. 18).

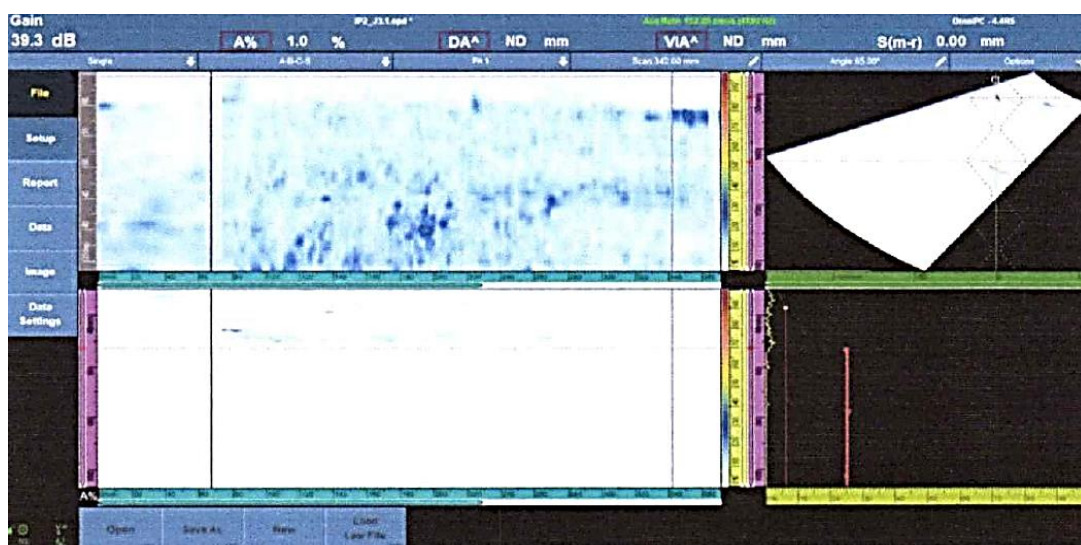


Fig. 18 PAUT Result After 6 Years Operation After Repair

Conclusions

1. The crack on Subang CO₂ removal absorber column is caused by amine stress corrosion cracking (SCC) generated by a combination of the corrosive environment and the residual stress on the absorber shell material.
2. The most effective repair method is the butt weld insert plate followed by the PWHT process to prevent repeated failures on the Subang CO₂ Removal Unit, which uses amine as an absorbent and carbon steel material.

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The Investigation of Correlation between Corrosion and Lap shear Strength on Steel and Al Joints

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As lightweighting through the use of Al has been increasing in the automotive industry for fuel efficiency and reduction of pollutant emissions, interest in a joint characteristics of aluminum and conventional carbon steel has been also increasing. Thus, it has been very important how to protect or suppress the joint between Al and steel from galvanic corrosion and crevice corrosion. Especially, because the change in joint strength of bimetallic joints due to corrosion could be directly related to durability, experimental case studies on various combinations of steels and Al have been needed. In this study, a variation of joint strength between steels (Uncoated cold-rolled, Zn or ZnMgAl coated steels) and Al (6014 Al alloy) changed by an accelerated corrosion test were measured on several joint methods such as resistance-spot-welding, clinching, and self-piercing-rivet (SPR). A corrosion depth of overlapped area and lap shear strength were measured for each specific duration points of accelerated corrosion test. As a result, the lap shear strength of ZnMgAl steel-Al joints on SPR changed the least and increased slightly. It might be inferred that this had contributed to strengthening the joint strength of the contact area as the corrosion product acts like an adhesive, more than the weakening of the strength due to the resulting volume expansion in the contact area.

Keywords

ZnMgAl steel, Bimetallic corrosion, Accelerated corrosion test, Joint strength

Corrosion and tribocorrosion characterization of a novel cast quasicrystal aluminum alloy

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In the automotive industry, there is a high trend of using lighter materials with improved strength and corrosion properties that are fully recyclable. With this aim, within the framework of the EIT Raw Materials CastQC project, we are developing an aluminum alloy that is reinforced with quasi-crystals and is suitable for the high-pressure die casting process. The purpose of the development of this alloy is to replace the standard DIN 226 Al alloy with a lighter, stronger and cheaper one and thus contribute to the European Green Deal.

Results of investigation have shown that developed quasi-crystalline aluminum alloy has improved mechanical properties.

The main purpose of this study was to investigate and compare the corrosion and tribocorrosion properties of the developed quasi-crystal aluminum alloy with a conventional aluminum alloy in accordance with the DIN 226 standard. It is assumed that the presence of quasi-crystals affects the corrosion and tribocorrosion properties of the quasi-crystal aluminum alloy.

Key words: quasicrystals, aluminum alloy, lightweight, automotive, corrosion, tribocorrosion

The Investigation of Tungsten Carbide-Cobalt Coatings Behaviour Subjected to Mechanical Forces and Stresses

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Keywords: Tensile, Bending, Fatigue, Porosity, Tribocorrosion.

This research presents the behaviour of Tungsten Carbide-Cobalt metallic coatings when subjected to mechanical forces and stresses. It focuses on producing coating materials that provide superior mechanical properties. The aim was to identify a single thermal spray method and coating material combination capable of producing a multi-layer coating by blending micro and nano tungsten carbide cobalt powders with AMDRY powders, deposited by the HVOF and Plasma spray equipment onto carbon steel substrates. This research addresses issues in the oil and gas industry, such as material degradation because of applied mechanical forces, tensile strength, bending, fatigue, and post corrosion effects. The results showed that the use of HVOF with a spray powder combination of 60 wt.% nano-sized WC-12Co and 40 wt.% Micro-sized AMDRY 9954 had enhanced mechanical properties in comparison to other powder combination used in this study. It yielded high elasticity (15 GPa), high tensile strength (300 MPa), low porosity (1.3%), and high corrosion resistance. Thus this coating is ideal for applications where a component is subjected to corrosion, corrosion under load, tension under corrosion, fatigue under corrosion, and bending applications.

Evaluation of a new multi-component aluminium alloy applied as a low-density thermal barrier for corrosion, wear and hydrogen applications

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Abstract

Since few years ago more complex alloys are being developing, such as the new high and medium entropy metal alloys (HEAs) or multi-component alloys. Aluminium casting alloys obtained based on the multicomponent alloy concept have been demonstrated to provide improved static mechanical properties and wear resistance¹.

Recently, the development of multi-component coating using the capabilities of the thermal spray process is becoming more and more attention by offering new possibilities for new and thicker coating for corrosion and more extreme wear conditions².

¹ I. Vicario, J.J. Trujillo, G. Arruebarrena, I. Hurtado, M. T. Guraya, J. Albizuri, E. Villanueva, Development of Multicomponent Cast Alloys by High Pressure Die Casting, 74th WFC (2022).

² C. Lin, Y. Yao, Corrosion-Resistant Coating Based on High-Entropy Alloys, Metals 2023, 13, 205. <https://doi.org/10.3390/met13020205>

The high cooling rates obtained during the thermal process, in addition to the powder milling process, allow greater solubility and the formation of more fine-grain structures. Consequently, thermal sprayed multi-component coatings can possess different characteristics with an improved combination of strength and ductility. In addition, and compared to the matrix composites, thermal sprayed multi-component coatings present particles of oxides with a higher hardness which can also act as self-lubricating materials during the sliding process³.

In this research, thermal sprayed coatings based on a new multicomponent AlSiMgCu alloy have been deposited over A6061 aluminium alloy used as the material substrate. To compare tribological properties and wear mechanisms, ball-on-disc tests were performed over the A6061 aluminium base alloy with and without the multi-component AlSiMgCu coating.

The results have demonstrated that the new multicomponent AlSiMgCu thermal spray coating helped to reduce the friction coefficient from the value of $\mu=0.52$ to $\mu=0.42$. SEM/EDS analysis showed that the sub-mechanisms of wear changed from micro abrasion and plastic deformation in the A6061 aluminium substrate alloy to cleavage abrasion in the new coated material. It agrees with other works reported in the bibliography focused on thermal barrier coatings for aluminium alloys⁴. The new multi-component coating contributes to reducing the plastic deformation in the A6061 alloy and therefore the adhesion wear. The combination of reduced adhesion with microcleavage abrasion resulted in a lower wear rate. Finally, the values for the specific wear rate were determined demonstrating that in the case of newly coated material, the specific wear rate decreased by around 88% of its initial value.

A further investigation will be assessed for evaluating its behaviour as barrier in H₂ transport and use applications.

³ R. Bhaskaran, R. Supekar, S. Morteza, W. Wang, Y. Zou, A. McDonald, J. Mostaghimi, P. Stoyanov, High-Entropy Alloy Coatings Deposited by Thermal Spraying: A Review of Strengthening Mechanisms, Performance Assessments and Perspectives on Future Applications, *Metals* 2023, 13, 579. <https://doi.org/10.3390/met13030579>

⁴ M. L. Bañuelos, A. Díaz, D. Rodríguez, I. I. Cuesta, A. Fernández, J. M. Alegre, Influence of Atmospheric Plasma Spray Parameters (APS) on the Mechanical Properties of Ni-Al Coatings on Aluminum Alloy Substrate, *Metals* 2021, 11, 612. <https://doi.org/10.3390/met11040612>

Anti-corrosive composite coatings based on PVB/ZnO:Co and PVB/HAP:Co

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Recently we have developed polymer/ceramic composite coatings based on poly(vinyl butyral), hydroxyapatite and zinc oxide-based nanostructured powders (PVB, HAP:Co and ZnO:Co, respectively). Prepared composite coatings showed good both adhesions to metal and glass surfaces and camouflage properties, thus can be used to improve combat capability of military equipment.

An essential demand of new materials in the military industry is to be multifunctional. Accordingly, the aim of this study was to examine corrosion activity of the PVB/ZnO:Co and PVB/HAP:Co coatings in saline solution as a function of immersion time. The ZnO:Co and HAP:Co nanostructured powders were synthesized by hydrothermal processing of a precipitate. To adjust optical properties, synthesized powders were annealed at 400, 800 and 1000 °C. Annealed powders were mixed with PVB: each powder was dispersed in ethanol with the aid of an ultrasonic probe, successively PVB powder was added in dispersion, in 10 wt.% regard to ethanol, and stirred on a mechanical stirrer to completely dissolve. Prepared solution was coated on stainless steel substrate and dried at room temperature for 72 hours to form solid coating. The corrosion activity of the coatings was measured by potentiodynamic polarization technique in the potential range from –0.8 to –0.2 V vs SCE, with the scan rate of 10 mVs⁻¹. The measurements were performed using a conventional three-electrode cell in 3% NaCl water solution as the electrolyte. Platinum foil, a standard calomel electrode (SCE) and coated stainless steel were used as the counter, reference and working electrode, respectively. We found that all examined coatings have lower corrosion activity than bare stainless steel or stainless steel coated with pure PVB. Differences in corrosion activity between the coatings are explained by different textural and opto-electronic properties of ceramic powders modified by the annealing procedure.

Towards Sustainable Waste Management: Enhancing Recycling of Multi-material Waste using 'Green' Solvents

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Abstract

Recycling flexible packaging materials such as blister packs, laminates, food packaging etc. is critical if we are to reduce the severe environmental effect of plastic waste. The figures are alarming - less than a fifth of plastic packaging is currently collected for recycling globally, with the remainder ending up in landfills, waterways, and oceans. It is time for a paradigm shift in our approach to packaging waste, and recycling flexible, multi-material packaging systems is a key part of the solution. Recycling such systems would have significant potential advantages, such as lowering greenhouse gas emissions and saving resources to providing new job possibilities, and promoting a circular economy. We can no longer afford to ignore the issue of plastic waste; it is time to act, beginning with recycling.

To address the above challenge, the SolRec² project funded by the EU (under grant agreement number 101003532) is looking at developing 'green' solvents for multi-material recycling. Several aspects of multi-material system recycling are covered in the project. However, the purpose of the experimental work was to look into the usage of non-toxic, stable, deep eutectic solvents (DES) and ionic liquids (ILs) for the separation of polymer-aluminium laminates. The study focused on determining the efficacy of these 'green' solvents in delaminating the multi-material systems. The findings also revealed that some DESs and ILs were successful in dissolving certain polymers, resulting in separation of the aluminium layer. However, this approach required additional steps for the recovery of the polymer. The systems that were able to accelerate delamination were studied further. These systems also resulted in

excellent aluminium recovery. The corrosion or dissolution of aluminium in the DESs and ILs studied were limited, at least in the short-term tests.

Finally, this work illustrates the possible application of DESs and ILs for polymer-aluminium laminate separation. The use of these solvents resulted in effective separation and excellent recovery of the laminate constituents. Nevertheless, if this procedure is scaled-up, more study is needed to understand the influence of DESs and ILs on the corrosion performance of aluminium. This study has significant implications for the development of long-term and effective recycling procedures for laminates containing multi-material systems.

Acknowledgements



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Study on the Corrosion Potential of Cast Iron in Distilled Water:

Effects of Sample Thickness and Type of Surface Exposure

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Introduction

This technical paper is part of a collaborative project with Thames Water to fully understand cast iron and how mitigation can be utilized to improve the longevity of the network, and how applying external mitigation can influence the adjacent unprotected areas on the external surface and the opposing internal surface. Corrosion investigations typically look at isolated microclimates to see the effects of specific environment conditions or types of mitigation on a given surface area. Cast Iron is a unique material in the space of corrosion as previous studies have indicated that graphite flake network influences the corrosion process. The graphite flake network is believed to increase conductivity of the two sides of a sample, hence resulting in the idea that the environment on one side of the could impact the other side. Following the same interpretation, the thickness could influence this connectivity, depending on how the flakes span between the two faces.

Objectives

The objective of this study is a baseline to investigate the relationship that corrosion rate has on bilateral samples that are exposed to isolated microclimates, through testing samples based on thickness and whether the sample is exposed to distilled water on one side or both. The proposed questions are that in cast iron:

- Is the corrosion rate influenced by the thickness of a sample?
 - Through comparing data from single exposed samples
- Is the corrosion rate isolated to the microclimate a set surface area is exposed to or is it influenced by the microclimate on the opposing face?
 - Through comparing data between single exposed samples against double exposed samples for a given thickness
- If there is discrepancy between single and double exposed samples, is this relationship influenced further by the thickness of a sample?
 - Through comparing each pair of thickness data

Methods

To fulfill the initial objectives, a H-cell with a thin cast iron working electrode clamped between two vessel chambers was utilized. The H-cell could be filled with one side or both sides for a comparison between single and double exposed samples. The thickness of the cast iron working electrodes included 1mm, 3mm, 5mm, 10mm, giving 8 total test specimens to be evaluated through open-circuit potential (OCP) and linear polarization resistance (LPR) over a 1cm² area. These are the initial iterations that monitor data over a weeklong period, with LPR taken once a day after the first 24 hours. Figure 1 shows an example of the cell with double exposure.



Figure 1 - Double Exposure of 3mm Cast Iron Working Electrode

Results

Results have found that thicker samples have less corrosion potential than thinner samples and double exposure cells have more corrosion potential than their corresponding single exposure counter parts. The influence that this result has is that for cast iron, corrosion rate isn't isolated to just the surface area exposed to an environment but is affected by the thickness of the sample and the environment on the other side. These are baseline observations that will be analyzed further in the form of useful, quantitative data in the coming months.

Conclusion

The conclusions that can be drawn from this initial experiment iteration is that corrosion rate isn't isolated to the microclimate but can be influenced by the microclimate acting on the opposite side. The thickness impacts how large this effect is, which can be attributed by the conductivity of the graphite flake network, with thinner samples having singular flakes that can span the full thickness.

The implication of this work is that it establishes that there is a relationship between the two faces of a sample and that corrosion potential can be influenced by the microclimate on the opposing side to the one that's being monitored. The bigger picture of the project is to investigate this relationship in terms of a mitigation perspective, which is the focus of the coming months.

Environment-friendly treatment of rusted steel for the conservation of historical heritage

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Europe has a rich cultural heritage, which is a significant component of the European identity –this shows not only the history of industrial and technological advances but also the history of a period and society-. Atmospheric corrosion of metals and deterioration of protective coatings is a serious problem for the protection of cultural heritage. Conservation research in the field of metals is relatively new when compared to other fields of metals testing related to industry; for obvious reasons, conservation science has been using practices developed for the metals industry.

Before a conservation professional decides on introducing a new material or technique to diagnose, treat or protect an object, they need to be assured that the material or technique is suitable for their purposes –and respectful for the cultural asset- in order to make proper decisions, which also requires understanding of the costs involved as well as the available resources.

In the development of conservation methods, attempts have been made to prevent further corrosion of rusty steel without previous removal of corrosion products (patina), treating the oxide scale in such a way as to prevent any active corrosion process continuing underneath. For this purpose, and considering environmental and health issues, the attention has been turning into the application of environment-friendly (“green”) products –non-toxic and natural organic compound, among others- for the preservation of steel and iron historical objects.

This work shows the comparative performance of novel, non-toxic (“green”) products (Neem oil and nettle extract) in combination with an acrylic resin for the protection of rusted carbon steel by means of electrochemical (OCP) and weathering corrosion tests.

By assessing the rust index (Ri), it was observed that both natural products improved the performance of the acrylic resin after 24 h in weathering conditions; on the other hand, the electrochemical tests showed differences in performance of the three products applied to a rusted carbon steel surface.

Musical Instruments in Museum Collections – A Challenge in Metal Conservation

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In museum collections, contact corrosion is a challenge in musical instrument conservation. Steel strings of stringed instruments, as well as keyboard instruments, are affected. The metal strings corrode in contact with other materials of the instrument's sounding body. When mounted close to materials, such as damping felt, damping leather or bridges of wood or plastic, the strings tend to corrode and crack (*Figure 1*). Our project aims to investigate causes and to mitigate this corrosion process.

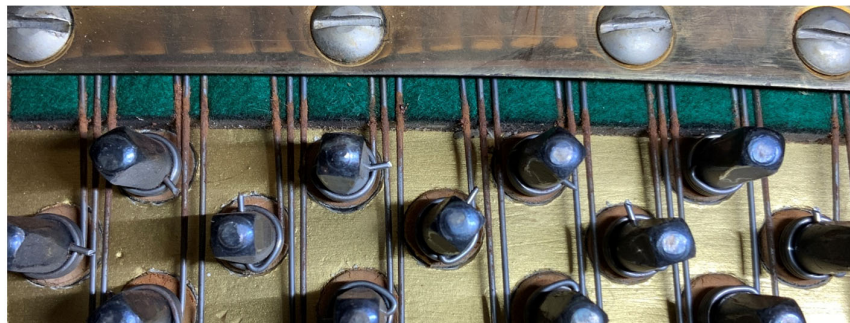


Figure 1 Corrosion on piano strings in contact with piano fabric

In a survey conducted in several musical instrument collections within this project, we documented the occurrence of this contact corrosion in numerous examples. Instruments produced around 1800 and later are the focus of this research. The keyboard instruments of this time period still contain most of their primary material. It is, therefore, of high significance to find ways to conserve those materials today.

The relative humidity and temperature of a storage room's environmental conditions have been monitored. The air quality has also been analyzed for the presence of formic acid, acetic acid, nitrogen dioxide and ozone. We observed contact corrosion even if all threshold values were under the critical values. Besides a possible earlier impact of high relative humidity, we presume that compounds emitting from the organic material in contact accelerates the corrosion.

The analysis of steel sheets in contact with cotton and wool piano fabric showed typical signals for the presence of long-chain carboxylic acids in laboratory experiments. The decomposition of cellulose of the cotton through reaction with oxygen can partly explain the existence of carboxylates. Interestingly, in contrast to the samples in contact with the fabric, lab-exposed reference samples that had not been in contact with the textile fabric showed visible signs of corrosion.

Techniques used to investigate the surface of the steel sheets were grazing incidence infrared reflectance absorbance spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS).

We have explored three different SAMs (organic thin-film layers) to protect the surface of the steel: Octadecyltrimethoxysilane (ODTMS), octadecylphosphonic acid (ODPA), stearic acid (SA). The FTIR spectrum of ODTMS showed a successful modification of the surface. We plan to conduct further work to determine SAMs' suitability for the corrosion protection of musical instrument strings.

More experiments forcing corrosion by artificial aging of strings are planned. For the choice of representative material for the experiments, we investigate both samples of historical strings and contemporarily produced facsimile strings. The microstructure and surface are analyzed by scanning electron microscopy with energy-dispersive X-ray analysis (SEM-EDX) and XPS. An analysis of a selection of organic materials, which have been observed at contact corrosion, will also be done. The piano fabric and leather will be investigated according to their compounds of, for example, dyes or dyes or tanning agents.

We will evaluate the explored conservation methods to their suitability for practical use in conservation, keeping in mind questions regarding conservation ethics, such as reversibility.

Assessment of Pitting Corrosion in Anodized 2xxx Aluminum Alloys

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This work focus on the characterization of pitting corrosion initiated in 2xxx Al alloys anodized in Tartaric Sulphuric Acid (TSA), specifically the 2024-T3 alloy substrates, and the 2198, in the T8 and T851 tempers. The results were compared to that of anodized pure Al (99.99 wt.%). The pitting corrosion resistance of the anodized samples was tested by potentiodynamic polarization in 0.1 mol L⁻¹ NaCl solution. The tested surfaces were then characterized by optical microscopy, optical profilometry, scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), and image analysis by ImageJ. The polarized samples presented pits of different sizes. Some pits presented diameters of several hundred microns, with the anodic films remaining as pit covers. The pits in all anodized samples showed similar characteristics, such as, a continuous pit cover with a central hole or a pit cover detached from the substrate in some small areas. The central hole serves as a diffusion channel for dissolved species within the pits. Detachment of the pit cover occurs due to accumulation of corrosion products within the pits leading to swelling of the anodic film and its detachment from the substrate. The results showed that pit size and depth analysis measured by optical profilometry can be misleading. Depth assessment should be carried out after removal of the anodic layer followed by cross-section of the anodized sample. The pits developed under highly occluded conditions. It was also observed that in the anodized alloys, as opposed to pure Al, pits are related to the defects in the anodic films due to dissolution of micrometric intermetallic particles during the anodizing process. Pitting attack propagation occurred according to the microstructure characteristics of the tested material.

Corrosion development in hybrid joins in C5 environment using advanced FEM modeling

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Hybrid steel joints with light metal alloys and/or non-metallic components offer opportunities to create new structures with reduced weight. However, aggressive saline environments (e.g. C5 according to BS EN ISO 12944-2) can lead to corrosion related damage and loss of integrity. The process can lead to stress-corrosion-cracking (SCC) or subsequent material loss or accumulation of corrosion products which significantly contributes to service-life shortening of the hybrid joint. Physics-based, transient simulation of the effects would enable local damage prediction and durability assessment under given environmental and mechanical conditions. On the macro-scale, mechanical loading induces a local strain-rate-related corrosion acceleration which can further affect the joint integrity. A model of hybrid steel joints were created using FEM, taking into account galvanic corrosion and mechanical damage. For these models, an analysis of the joint stress state were carried out and its characteristics will be determined depending on the level of development of corrosion defects, as well as the external load.

Effect of diatomite surface modification on the loading and release of organic corrosion inhibitors from anti-corrosive coatings

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In previous works, we introduced the use of diatomite (mineralized microalgae exoskeletons) as an efficient nanoporous microcarrier for the incorporation of organic and inorganic corrosion inhibitor salts in anticorrosive coatings. The strategy reduced the interaction of inhibitors (cerium salts and 2,5-dimercapto-1,3,4-thiadiazole (DMTD)) with the surrounding matrix and significantly increased the efficiency to protect large damages (1 mm wide, 400 μ m depth) in coated AA2024 for long immersion times (>30 days) and wet-dry cycles using very low amounts of cerium salts [1-2]. However, the incorporation of DMTD in diatomite led to lower protection degrees than theoretically possible with such an efficient inhibitor.

In this work, we studied how to increase the loading of DMTD in diatomite, reduce the negative interactions with an epoxy amine coating matrix and increase the release and active corrosion protection at damaged locations. To this aim, we selected three silanes based on the expected inhibitor-silane alkyl chain interactions and used them to modify the diatomite microparticles surface using wet chemistry and gas deposition techniques (CVD). Surface functionalization was studied through Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDX), and X-ray photoelectron spectroscopy (XPS). The loading and release capacity of DMTD as a function of the diatomite surface functionalization was studied by in-electrolyte ultraviolet-visible spectroscopy (UV-Vis). The modified carriers were then successfully embedded in epoxy-amine matrices showing high levels of dispersion and low levels of negative interaction. The inhibitor release from the coating and its active corrosion inhibition efficiency at damaged locations was evaluated using in-situ Opto-electrochemical set-up and UV-Vis. The results show an effective strategy to load organic corrosion inhibitors in coatings in an efficient manner through the use of diatomite silica microcarriers.

Reference

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Influence of Surface Roughness and Post-Processing on the Corrosion Properties of additive manufacturing AlSi7Mg Alloys

Produced by LPBF

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Additive manufacturing of metals is increasingly used in industry to produce complex-shaped parts. However, the surface of additively manufactured metallic parts often has high roughness ($R_a > 10 \mu\text{m}$ for as produced surfaces), which can negatively impact their mechanical or corrosion resistance. To address this issue, protective coatings and post-processes such as chemical or electrochemical etching are typically necessary to increase the substrate's corrosion resistance and reduce the surface roughness of additively manufactured parts respectively.

The objective of this study is to present both the influence of roughness on AlSi7Mg alloys produced by Laser Powder Bed Fusion (LPBF) and the influence of surface post-processing on corrosion properties in a neutral NaCl environment.

For this purpose, a CrVI-free conversion process was used as a protective coating, and chemical etching was used as a roughness-reduction post-processing. The surfaces have roughness values gradually ranging from $R_a=10$ microns for as-built surfaces to a mirror-polished surface for the least rough. The behavior of the AlSi7Mg alloy was assessed using polarization curves in 3.5% NaCl solution and the durability of the alloy was characterized by neutral salt spray test.

The open circuit potential and pitting corrosion potential were measured and discussed as a function of surface roughness and the presence or absence of CrVI-free conversion. The results showed the impact of both roughness and post-processing on the corrosion resistance and durability of the AlSi7Mg alloys.

Acknowledgments:

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Effect of Be addition on the microstructure morphology and corrosion behavior of an Al-Cu aeronautical alloy

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Abstract

Aluminum alloys have been one of the main materials of aircraft structural components, due their consolidated and reliable characteristics in performance, design methods, manufacturing, and inspection techniques. The addition of beryllium (Be) in Al-Cu alloys enables thermal stability of mechanical properties, as well as influences on their corrosion resistance. This work aims to develop an experimental analysis concerning the effects of cooling rates on the microstructure development and corrosion behavior of the Al-5wt.%Cu-1wt.%Si-0.5wt.%Be alloy. Experimental results including microstructural characterization, electrochemical impedance spectroscopy (EIS) test and potentiodynamic polarization test. Was observed an essentially dendritic morphology for all cooling rates analyzed. The final microstructural arrangement was characterized by an α -Al matrix plus eutectic compound (Al + Al₂Cu+Si), no intermetallic phases containing Be were observed, and the Be was concentrated in the interdendritic regions. It was observed that the addition of Be and the high cooling rate contributed to a refinement of the alloy. The corrosion results, in 0.06M NaCl solution, showed that the Al-5wt.%Cu-1wt.%Si-0.5wt.%Be alloy presented greater resistance to corrosion than the Al-5wt.%Cu alloy.

Keywords: Al-Cu alloys, Microstructure, Corrosion Behavior, Corrosion Resistance.

Introduction

The relationship between microstructural parameters and the ultimate application properties is vital for the metallurgical pre-planning of a metallic component for structural or mechanical application. To effectively strategize the behavior of a metallic alloy during service, a thorough analysis of its microstructure is required. This analysis encompasses assessing the grain size, quantifying phase fractions, and evaluating the microstructural arrangement. Additionally, it entails defining key application properties like mechanical strength and corrosion resistance. Parameters such as tensile strength and corrosion resistance have been largely correlated with the microstructural parameters associated with solidification[1]–[6], such as dendritic or cellular spacing.

In the aerospace sector, correlating microstructural factors with corrosion behavior is essential for the initial analysis of alloy properties. This is justified because each process exposes the metal to potentially harmful environmental conditions [7], [8]. With the advancement of studies in this field, the gradual substitution of steels with aluminum alloys has garnered attention, primarily due to their positive engineering outcomes, such as weight

reduction and increased corrosion resistance. Aluminum-based lightweight alloys offer improvements in various areas, as their intrinsic characteristics generally result in better fuel efficiency and superior corrosion resistance.

It is essential to highlight that corrosion resistance and mechanical strength do not always exhibit similar behavior concerning microstructural parameters such as grain size and phase fraction [5], [9]. Regarding the mechanical aspect, the impact of grain size and intermetallic phases can be significant. On the other hand, in corrosive analysis, the correlation between phase distribution, electrochemical properties of these phases, and their interaction in forming galvanic couples holds greater significance.

The microstructural morphology of aluminum alloys in their as-cast state is determined by the dynamics of the solid/liquid interface as latent heat is released [10]. As the alloy solidifies, there is a transition in the growth morphology from planar to cellular and dendritic structures [11]. The spacing between these growth forms, as well as the morphology, size, porosity, and distribution of intermetallic phases, among other factors, are microstructural parameters that have a direct impact on the mechanical properties [2].

Azarbarmas et al. [12] conducted a study investigating the impact of Beryllium on the microstructure and mechanical properties of the Al-15%Mg₂Si composite. The authors found that increasing the Be content led to a reduction in the average size and volume fraction of primary Mg₂Si particles. Additionally, they observed that the alloy without Be exhibited the formation of coarse primary Mg₂Si crystals, which grew in hollow forms. In contrast, the alloy containing Be demonstrated the formation of finer Mg₂Si particles without this void morphology, which was considered advantageous as the presence of voids within particles can serve as potential sites for crack initiation. Furthermore, the researchers confirmed that the addition of Be improved both the ultimate tensile strength (UTS) and elongation values.

The aerospace industry has a keen interest in developing new aluminum alloys by incorporating elements like beryllium. These alloys offer the potential to achieve exceptional specific strength and thermal stability. Furthermore, alloys with favorable microstructural morphology, which exhibit excellent mechanical strength, without compromising corrosion resistance. Hence, the primary objective of this study was to develop an Al-5wt.%Cu-2wt.%Si-0.5wt.%Be alloy and investigate the influence of cooling rate on its microstructural morphology, mechanical strength, and corrosion behavior.

Materials and Methods

The Al-5wt.%Cu-2wt.%Si-0.5wt.%Be alloy was fabricated by incorporating a copper-based alloy with a beryllium content of 10wt.% and commercially pure silicon. Initially, the aluminum was melted in a muffle furnace at a temperature of 850 °C using a silicon carbide crucible internally coated with a refractory mass based on alumina. Following that, all solute elements were introduced into the molten liquid and held in the furnace for 60 minutes at 800 °C to facilitate solute incorporation into the alloy through diffusion. Prior to pouring the alloy, it was homogenized using a stainless-steel rod. Finally, the alloy was cast into a staggered bronze ingot mold, which featured four different diameters (10, 15, 25, and 40 mm) as shown in Figure 1.

The microstructural analysis was conducted on samples taken from the cross section of each in relation to the vertical axis of the bronze ingot mold. The samples were prepared by grinding with sandpapers and polishing using 1μm diamond paste, eliminating the need for chemical etching to reveal the microstructure. Optical microscopy was performed using a ZEISS Axiolab 5 microscope. Secondary (λ_2) dendritic arm spacings were measured from optical images of the samples. The intercept method was employed for measuring λ_2 . A minimum of 50 measurements were conducted for each sample. The intermetallic compounds

(IMCs) were characterized using scanning electron microscopy (SEM) micrographs and analyzed with an Energy Dispersive Spectrometer (EDS) model OXFORD X-MAX, which was incorporated into a ZEISS Scanning Electron Microscope (ZEISS-EVO-MA15).

To measure the solidification cooling rate, a total of four (4) fine type K thermocouples with a wire diameter of 0.2 mm were strategically positioned at the geometrical center of the cylindrical cavity for each section of the bronze ingot mold (Figure 6). These thermocouples were connected to a data logger (Fieldlogger Novus) via coaxial cables and interfaced with a computer. The setup allowed for the automated recording of temperature data at a frequency of 5 Hz.

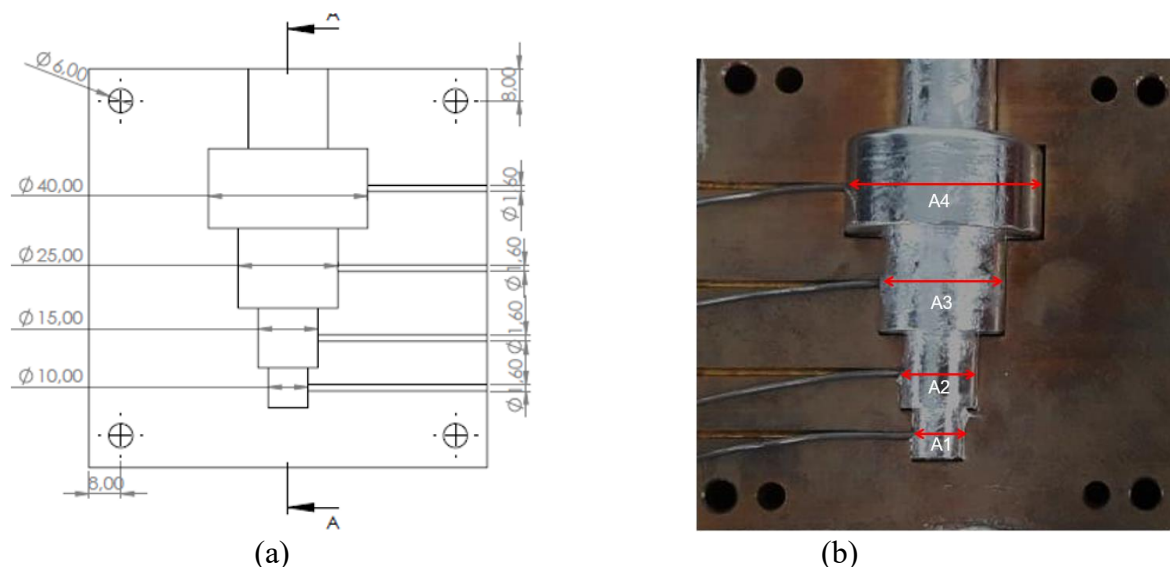


Figure 1. a) Layout of the bronze ingot mold used; b) Position of samples and sections of cuts. Dimensions in mm.

Electrochemical Corrosion Tests

To conduct electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization (POL) analyses, a three-electrode electrochemical cell setup was utilized. The cell comprised an Ag/AgCl 3M KCl reference electrode, a platinum plate counter electrode, and the Al-5wt.%Cu-2wt.%Si-0.5wt.%Be alloy samples under investigation as the working electrode [2]. Specimens for the electrochemical tests underwent metallographic preparation, including sanding and polishing, similar to the process employed for microstructural characterization. No chemical etching was performed on the specimens. Both corrosion tests were carried out in triplicate using a potentiostat/galvanostat Autolab PGSTAT128N.

All electrochemical tests were conducted at room temperature ($25^{\circ} \pm 2^{\circ} \text{C}$) using a 0.06 M NaCl solution. The choice of this diluted saline solution was motivated by the inhibitory effect and aggressiveness often observed in electrolytes with higher concentrations, such as the standard 0.5 M solution. Both potentiodynamic polarization (POL) and electrochemical impedance spectroscopy (EIS) analyses were performed under naturally aerated conditions. The working electrode, with a circular area of 0.503 cm² and a surface finish achieved using 1- μm diamond paste, was exposed to the electrolyte solution. Additionally, an Autolab Faraday cage was employed to shield EIS measurements and POL scans from any external sources of electromagnetic interference. Before starting POL analysis, the sample was measured at open circuit potential (OCP) for 2400 seconds. Linear polarization assays were then performed at a

sweep rate of 0.167 mV/s from -0.200 mV to +0.250 mV versus OCP. Corrosion current density (i_{corr}) values were calculated for all samples exposed to the electrolyte by means of Tafel strapolation [13].

EIS analysis was conducted with amplitude adjusted to 10mV in relation to the peak-to-peak open circuit potential with six points per decade in a frequency range from 100 mHz to 100 kHz with AC signal. The impedance spectroscopy assays resulted in Bode, Bode Phase and Nyquist curves.

Results and Discussions

In this research study with an Al-5wt.%Cu-2wt.%Si-0.5wt.%Be alloy, bronze cylindrical molds of varying diameters (10, 15, 25, and 40 mm) were used to induce different cooling rates. The smallest diameter facilitated cooling rates of over 70 K/s. Microstructural analysis revealed the presence of an α -Al matrix with a predominantly dendritic morphology, Fig. 2. To comprehensively characterize the solidification process, the secondary dendritic spacing (λ_2) was carefully measured and subjected to parametric analysis. A strong correlation between the values of λ_2 and the solidification rate was significantly established. By applying linear regression to the experimental data, a discernible growth law was derived, indicating a more refined growth pattern than other alloys in the Al-Cu system. These empirical insights contribute to a deeper understanding of the influence of cooling rates on the microstructure of bronze ingots and provide valuable insights into the growth behavior of the specific Al-Cu alloy system under investigation.

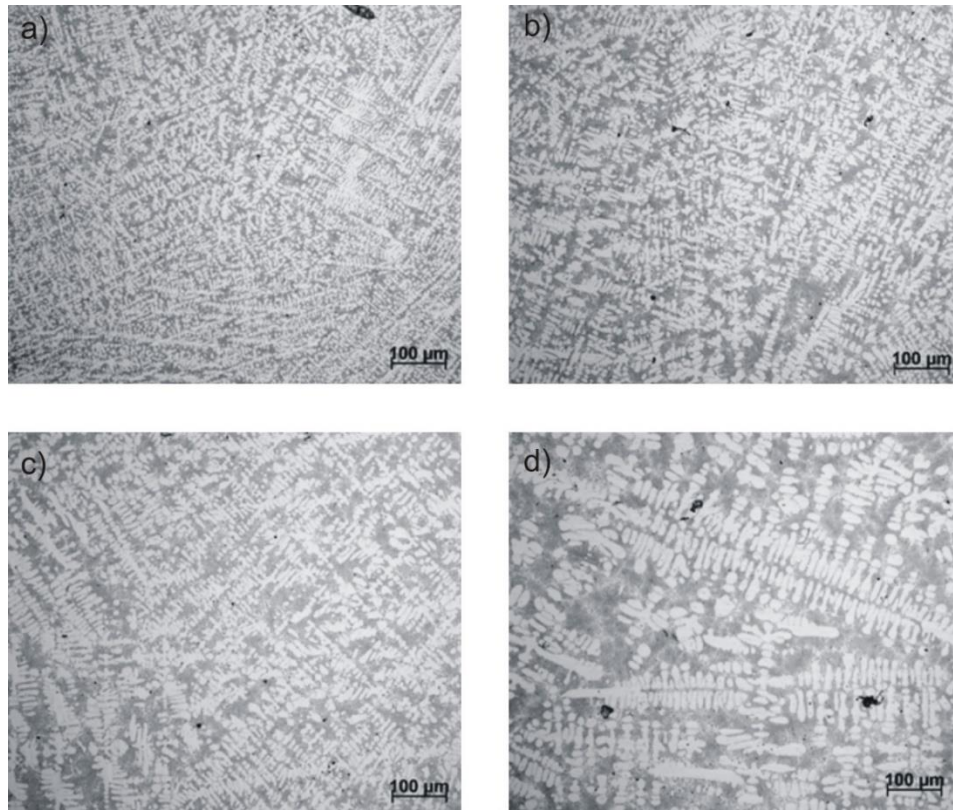


Figure 2. Micrographs obtained by optical microscopy for: a) sample A1 ($\dot{T} = 71.5$ K/s) b) sample A2 ($\dot{T} = 39.5$ K/s); c) sample A3 ($\dot{T} = 18.5$ K/s); d) sample A4 ($\dot{T} = 16.5$ K/s).

The evolution of the microstructure was quantified as a function of secondary dendritic spacing (λ_2), i.e., an experimental growth law of the type $\lambda_2 = 26 \dot{T}^{-1/3}$ was proposed describing the λ_2 evolution as a function of the cooling rate, as shown in Fig. 3. Solidification in a cylindrical mold promotes two-dimensional heat extraction. However, it can be assumed that in the regions close to the mold wall there was a unidirectional heat extraction. This hypothesis can be supported by the established growth law, since the use of the exponent $-1/3$ in this equation suggests that the growth pattern is of a system with unidirectional solidification [14]. This same exponent has been used to correlate λ_2 with $\dot{T}$ in binary and ternary Al-Cu alloys [1], [15], [16]. The curves that represent the secondary dendritic growth for Al-5wt.%Cu [15], Al-5wt.%Cu-1wt.%Ni [1], and Al-6wt.%Cu-1wt.%Si [16] alloys are shown in Figure 3 for the purpose of comparison.

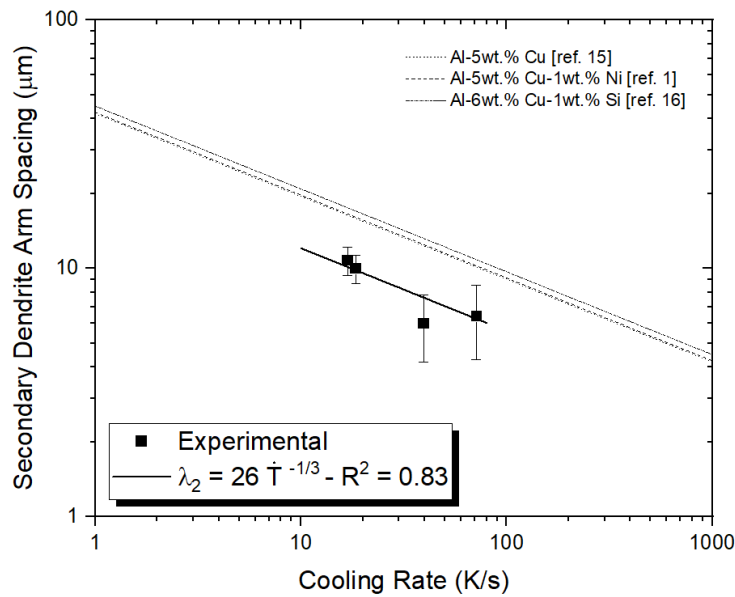


Figure 3. Graph of Dendritic Spacing (μm) by Cooling Rate (K/s) of Al-5wt.%Cu-2wt.%Si-0.5wt.%Be alloy.

During dendritic growth in steady state conditions, solute elements such as Cu, Si, and Be may segregate preferentially along the dendrite arms or in the interdendritic regions. This segregation can affect the overall corrosion resistance of the alloy, as the composition of the corroding regions differs from the bulk alloy composition. The levels of cooling rates obtained during the solidification of the Al-5wt.%Cu-2wt.%Si-0.5wt.%Be alloy contributed to the formation of a Cu supersaturate solid solution (SS) in the dendritic matrix of α -Al [17] with about 1.35wt.% of copper, Fig. 4. With the use of the EDS (dispersive energy spectroscopy) technique, it was possible to observe the intermetallic phases, and these were basically constituted of the Si and Cu-rich phases. Fig. 4b shows the details of the distribution of solute elements in each phase, and presents the composition values obtained by EDS. The presence of dendrites introduces microstructural heterogeneity in the alloy. Regions with different compositions and crystal structures can exhibit varying susceptibility to corrosion. Some regions might be more prone to corrosion attack than others, leading to non-uniform corrosion patterns.

The EIE and linear polarization tests on the analyzed samples were conducted with a milder chloride solution, in order to better understand the initial percussion means of the corrosive process. Fig. 5a graphically presents the measurements of Impedance in steady state by the Nyquist graph. Fig. 5b presents the impedance and phase angle modules as a function of

frequency, defined as Bode and Bode Phase curves, respectively. Electrolyte resistance was analyzed at high frequencies. At medium frequencies, a maximum phase angle of 70° was observed associated with a frequency of 30 Hz. The slope of the impedance module suggests the distance from the ideal capacitor. At low frequencies, it is possible to check the surface characteristics of the sample.

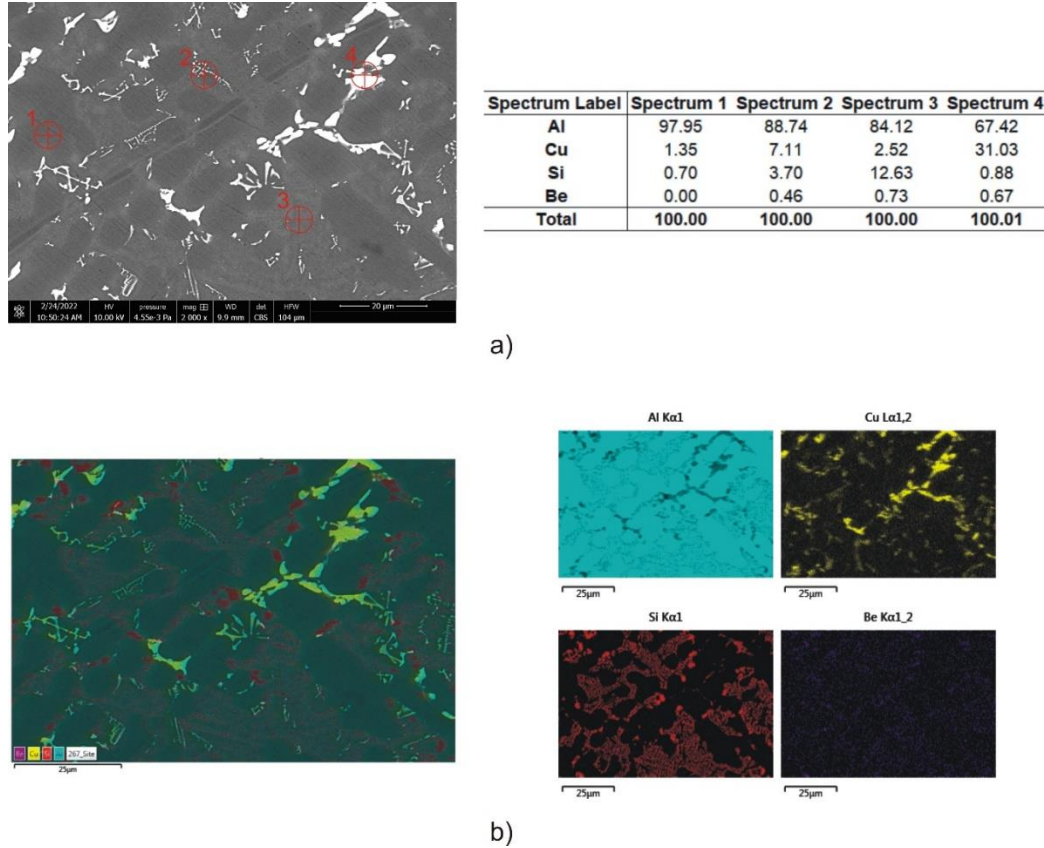


Figure 4 - SEM/EDS analysis and mapping element (EDS), in a solidified sample at a cooling rate of 18.5 K/s.

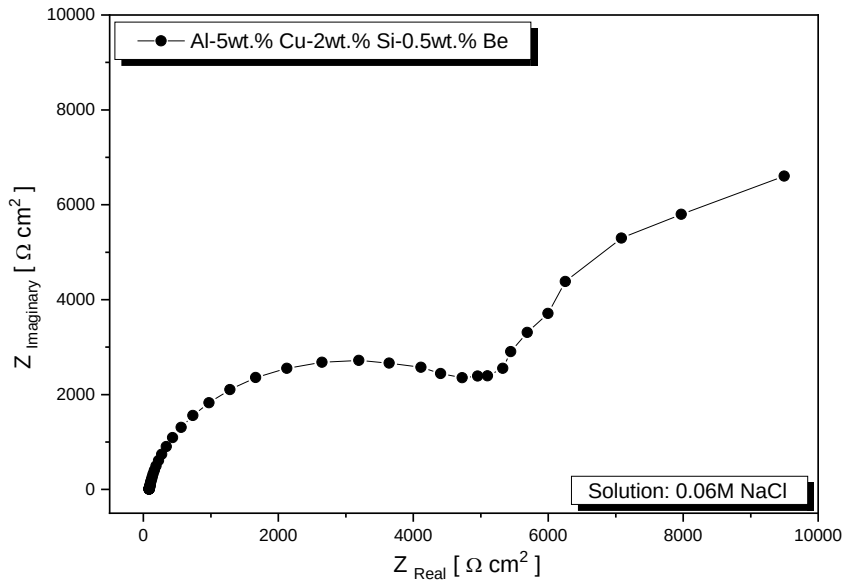
Figure 6 shows the experimental linear polarization profile of an Al-5wt.%Cu-2wt.%Si-0.5wt.%Be alloy sample solidified at a cooling rate of about 18.5 K/s. The polarization profiles allowed the values of corrosion current densities (i_{corr}) and corrosion potentials (ϕ_{corr}) in a solution of 0.06 mol/L NaCl at room temperature, 25 °C, to be determined by extrapolation from Tafel's plots considering both the anodic and cathodic branches of the polarization curves. The ϕ_{corr} was about -0.537 V (vs Ag/AgCl), and i_{corr} was about 2.4×10^{-6} A/cm². The polarization profiles were obtained by applying a small potential perturbation to the sample and measuring the resulting current change. The values of ϕ_{corr} and i_{corr} can be used to assess the corrosion resistance of an alloy. A comparison of this value with other literatures was possible using literatures [1], [4], [15], [16], in which there are also electrochemical tests and analyzes of microstructural parameters in Al-Cu alloys. The ϕ_{corr} value of the Al-5wt.%Cu-2wt.%Si-0.5wt.%Be alloy is relatively low, indicating that it is a relatively corrosion-resistant alloy. The i_{corr} value is also relatively low, indicating that the rate of corrosion is also relatively low.

The corrosion tendency of the Al-Cu alloys can be ranked as follows:

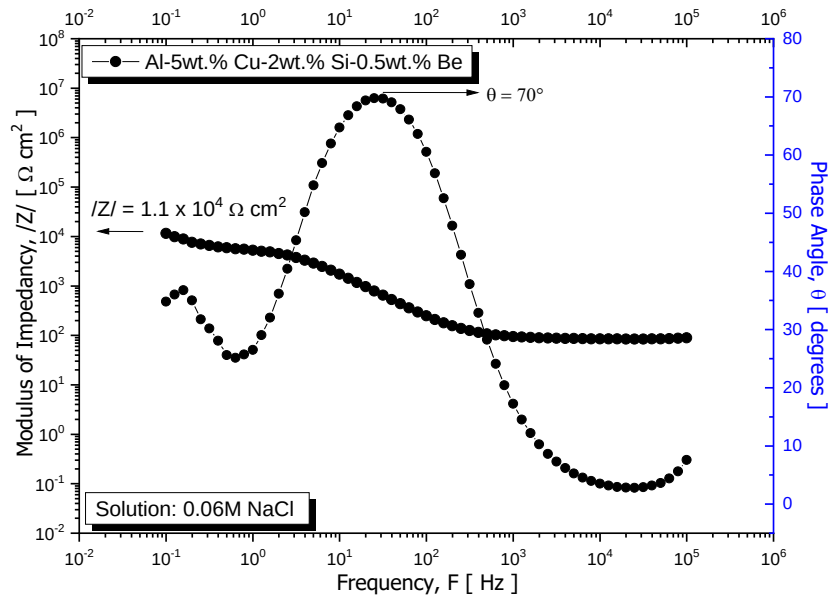
Al-5wt.%Cu-1wt.%Ni < Al-5wt.%Cu-2wt.%Si-0.5wt.%Be < Al-5wt.%Cu < Al-6wt.%Cu-1wt.%Si

The corrosion current density values in Table 1 show that the Al-5wt.%Cu-1wt.%Ni alloy has the lowest i_{corr} value, indicating that it is the most corrosion-resistant alloy. The Al-

5wt.%Cu-2wt.%Si-0.5wt.%Be alloy has a relative higher i_{corr} value, but it is still lower than the i_{corr} value of the Al-5wt.%Cu alloy. The Al-6wt.%Cu-1wt.%Si alloy has the highest i_{corr} value, indicating that it is the least corrosion-resistant alloy.



(a)



(b)

Figure 5. a) Nyquist curve; b) Bode and Bode Phase curves of Al-5wt.%Cu-2wt.%Si-0.5wt.%Be alloy in 0.06M sodium chloride solution.

The corrosion potential (E_{corr}) of the Al-5wt.%Cu-2wt.%Si-0.5wt.%Be alloy is also more noble than the E_{corr} values of the other two alloys. This indicates that the Al-5wt.%Cu-2wt.%Si-0.5wt.%Be alloy is less susceptible to corrosion. The results of this study suggest that the addition of Be and Ni to the Al-5wt.%Cu alloy can improve the corrosion resistance of the alloy.

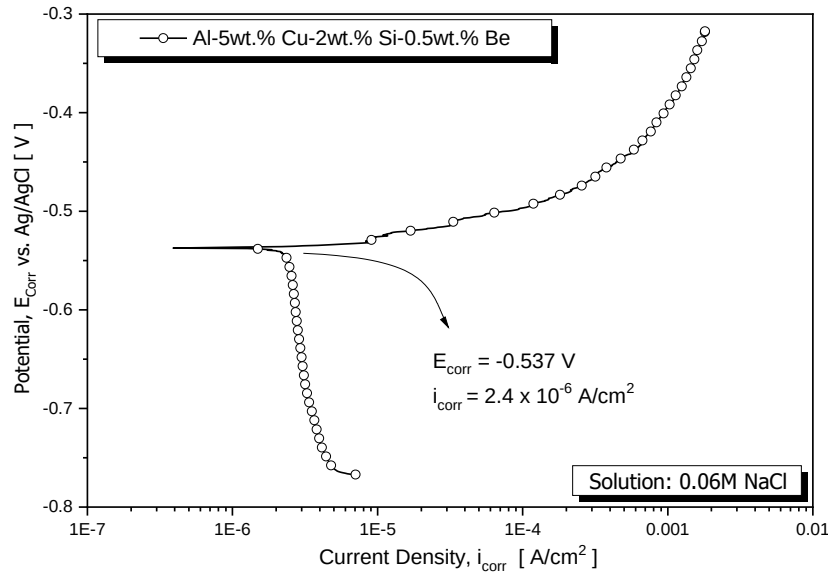


Figure 6. Potentiodynamic polarization Graph of Al-5wt%Cu-2wt.%Si-0.5wt.%Be Alloy in 0.06M sodium chloride solution.

The corrosion rate (CR_y) [18] is a significant parameter employed to assess the corrosion behavior of metallic alloys, Table 1. This metric facilitates the transformation of corrosion rates obtained through electrochemical techniques into current density units ($\mu\text{A}/\text{cm}^2$) corresponding to penetration depth per unit time ($\mu\text{m}/\text{year}$). The determination of CR_y values can be accomplished following the guidelines outlined in the ASTM G102–89 Standard. The calculation process involves the utilization of specific equations, enabling researchers to effectively quantify the rate of corrosion for the given metallic alloy under investigation:

$$CR_y = K_1 \frac{i_{corr}}{\rho} W_E \quad (1)$$

$$W_E = \frac{1}{\sum \frac{n_i f_i}{W_i}} \quad (2)$$

where CR_y is the corrosion rate ($\mu\text{m}/\text{year}$), $K_1 = 3.27 \times 10^{-3} \text{ mm} \cdot \text{g}/(\mu\text{A} \cdot \text{cm} \cdot \text{year})$, i_{corr} is the corrosion current density ($\mu\text{A}/\text{cm}^2$), and ρ is the density of the alloy (g/cm^3); W_E is the alloy equivalent mass, n_i is the valence of the i_{th} element of the alloy, f_i is the mass fraction of the i_{th} element in the alloy and W_i is the atomic mass of the i_{th} element of the alloy.

Table 1. Comparative table of cooling rate, average dendritic spacing, corrosion current density and corrosion potential of different Al-Cu alloys

Alloy	$\dot{T}$ [K/s]	λ_2 [μm]	i_{corr} [$\frac{\mu\text{A}}{\text{cm}^2}$]	E_{corr} [V]	CR_y [$\mu\text{m} \cdot \text{year}^{-1}$]
Al-5wt.%Cu-0,5wt.%Be	16.5	10.0	2.40	-0,537	28.9
Al-5wt.%Cu [15]	9.8	24.3	4.15	-0,678	46.9
Al-5wt.%Cu-1wt.%Ni [1]	12.6	10.5	0.15	-0,525	1.7
Al-6wt.%Cu-1wt.%Si [16]	13.5	10.2	4.36	-0,620	47.2

When assessing the corrosion characteristics of as-cast hypoeutectic alloys, a comprehensive understanding of the electrochemical properties of the constituent phases forming the matrix and eutectic is paramount in determining the cathodic-to-anodic area

(A_C/A_A) ratio. The A_C/A_A ratio plays a critical role in influencing the CR_y , wherein an increase in the A_C/A_A ratio leads to a corresponding increase in i_{corr} , resulting in reduced corrosion resistance of the material [8]. Based on the nobility and corrosion rate of the alloying elements involved [19], the dendritic matrix should be less noble than the eutectic region. However, due to the supersaturated Cu content in solid solution in the matrix, the α -Al matrix also has a nobler nature. The presence of Cu in the α -Al matrix caused a modification in the A_C/A_A configuration within the microstructure of the Al-5wt.%Cu-2wt.%Si-0.5wt.%Be alloy.

Fig. 7, shows that pitting corrosion starts at the Al-eutectic phase and then moves towards the Cu-depleted region. This behaviour is like the intergranular corrosion mechanism, for which the corrosion is caused by a difference in the electrochemical potentials between the bulk of the grain and the grain boundaries, where intermetallic phases precipitate.

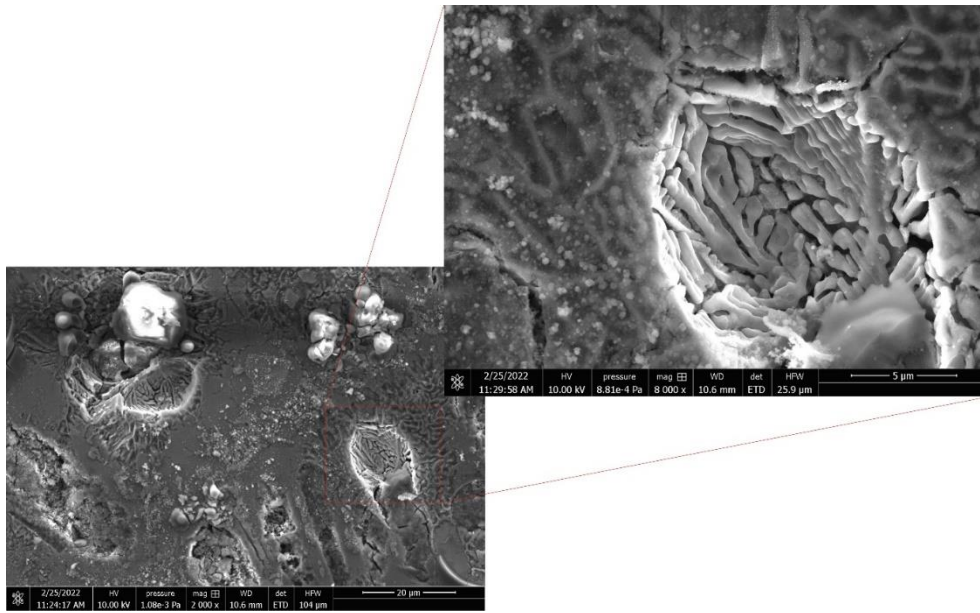


Figure 7. Typical SEM images illustrating the corrosion effect after the linear polarization test in 0.06M NaCl solution

Conclusions

The evolution of λ_2 in the Al-5wt.%Cu-2wt.%Si-0.5wt.%Be alloy directionally solidified in steady state follows the following experimental law, $\lambda_2 = 26 \dot{T}^{-1/3}$, where λ_2 is the secondary dendritic spacing, $\dot{T}$ is the cooling rate, and the constant 26 is the growth exponent. The addition of Be and the high cooling rate contributed to a refinement of the Al-5wt.%Cu-2wt.%Si-0.5wt.%Be alloy. This is likely since Be is a strong nucleating agent, and the high cooling rate promotes the growth of fine dendrites. Based on corrosion resistance values (CR_y), the addition of Be also resulted in a higher corrosion resistance when compared to the Al-5wt.%Cu alloy. This is likely due to the formation of a protective layer on the surface of the alloy.

Acknowledgments

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Environmental assisted cracking of friction stir welded UNS S32750 super duplex stainless steel in chloride media

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Abstract

Super duplex stainless steel UNS S32750 exhibits superior corrosion resistance and mechanical properties than conventional austenitic stainless steels and therefore is employed in demanding applications such as oil and gas industries. The presence of austenite and ferrite offers a combination of good mechanical properties and stress corrosion cracking resistance (SCC) in chloride environments, which is not possible in the case of austenitic stainless steels. Generally, this stainless steel is welded using fusion techniques for fabrication of components and this causes a significant loss to these properties. Friction stir welding (FSW), a novel solid-state welding technique can be beneficial as it can overcome the formation of some of the intermetallic phases and also maintain the phase balance. However, it is not clear how friction stir welding influence the SCC behaviour of this stainless steel. In the present work, the influence of FSW on the SCC behaviour of UNS S32750 was investigated. FSW joint was done with an optimized rotational speed of 800 rpm and 100 mm.min⁻¹ traverse speed, using W-25%Re tool. The FSW joint so obtained had fine grains without affecting the phase balance of the base metal. Further, grain boundary distribution after FSW was found to be significantly different in both the phases from the base metal. Slow strain rate tests (SSRT) carried out at 3.5x10⁻⁶ s⁻¹ strain rate in boiling MgCl₂ solution showed SCC susceptibility indices of 0.43 and 0.2 respectively for the base metal and the weld. The fracture surfaces of both the base metal and weld revealed typical transgranular cleavage features. FSW has exhibited higher SCC resistance than the base alloy due to the grain refinement.

Corrosion behavior of pipeline materials under the supercritical condition of CO₂ with the addition of H₂O

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| Introduction

Recently, CO₂, a greenhouse gas generated by the use of fossil fuels, has been noted as the biggest cause of global warming, and various efforts are being made mainly in developed countries to reduce CO₂. Among them, CCS technology is in the spotlight. Carbon capture and storage (CCS) refers to a technology that captures CO₂ by chemical methods and stably stores it in marine and onshore gas layers. With the recent increase in CCS infrastructure, the importance of CO₂ transport, which is responsible for connecting each part, is increasing. In other words, no matter how efficiently CO₂ is captured, it can face huge challenges without safe CO₂ transportation.

In North America, about 8,000 km of CO₂ transport pipelines are already used in enhanced oil recovery technology (EOR: Enhanced Oil Recovery)[1~3]. EOR is a technology that increases the recovery of oil by injecting CO₂ into the oil layer. CO₂ used in EOR has a higher purity than CO₂ in a CCS environment and does not contain various impurities. But in CCS, the situation is completely different. CCS facilities contain various impurities because CO₂ is artificially captured by chemical methods in pre- and post-combustion processes. CO₂ used in EOR is limited to a very strict level of contamination. Due to the interaction of various impurities, the sulfur content in CO₂ is limited to 1,500 ppm or less in EOR. CCS proposes the delivery of completely sulfur-free gases. Various discussions are being made on how much impurities should be controlled because the economic aspect should be considered[4~7].

Then, what is the most important cause of corrosion in CO₂ pipeline? Moisture (H₂O) has been reported to have a very large effect on CO₂ corrosion. The presence of H₂O forms hydrates in the pipe, and the formed hydrates can cause corrosion by creating highly acidic salts (pH ~3). Almost all pipelines used for EOR are made of carbon steel, and it is known that in pure CO₂ steel is generally not corrosive. However, in the presence of H₂O, the corrosion rate in humid CO₂ is about 1cm per year. In the case of short-distance transportation, if CO₂ containing H₂O must be transported inevitably, CRA (corrosion resistance alloy) steel, which is resistant to corrosion, must be used. However, at a time when CCS infrastructure is expanding globally, long-distance transportation must be considered. Considering long-distance transportation, CRA is considerably less valuable than carbon steel in terms of price. In the case of using carbon steel, the prevailing opinion is that the content of H₂O in the CO₂ pipeline should be adjusted to 600 ppm or less after CO₂ capture and H₂O treatment equipment, and that if impurities such as sulfides are present, it should be limited to 500 ppm. Since there is no exact standard for the H₂O content in pipelines yet, it is necessary to evaluate the quantitative corrosion according to the H₂O content of carbon steel for safe CO₂ transport.

In this paper, corrosion tests were conducted to assess whether carbon steel was safe as a material for CO₂ transport pipes. The degree of corrosion due to the addition of H₂O in CO₂ was evaluated by a 24/100/500-hour test, and SUS 316L with high corrosion resistance was used as a comparison group.

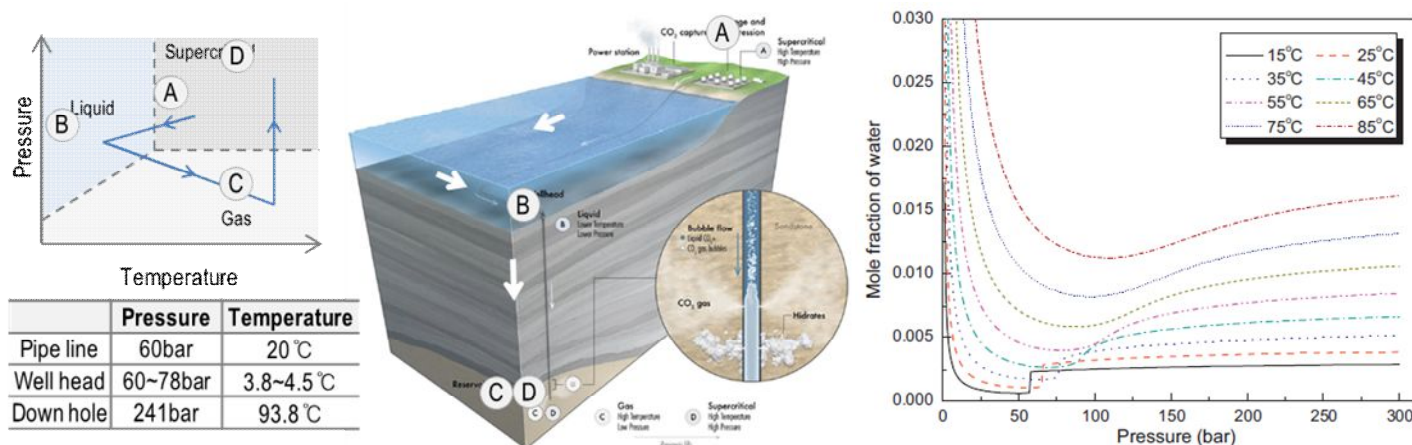


Fig. 1. CO₂ pipeline environment(left) CO₂/H₂O solubility(right)

| Experiment

5-types of material were used in this study. Four carbon steels, which are widely used in the United States as materials for CO₂ piping, and stainless steel with high corrosion resistance were selected. The chemical compositions of the alloys were analyzed by the inductively coupled plasma (ICP) method, and the results are listed in Table 1. corrosion tests were conducted to assess whether carbon steel was safe as a material for CO₂ transport pipes. The degree of corrosion due to the addition of H₂O in CO₂ was evaluated by a 24/100/500-hour test, and SUS 316L with high corrosion resistance was used as a comparison group.

Table.1. Chemical compositions of test materials (in wt. %).

Wt.%	Fe	C	Si	Mn	Cu	Nb	Ti	V	Ni	Cr	Mo
A (52 ksi)	Bal.	0.062	0.17	1.05	-	Nb + Ti + V ≤ 0.15			-	-	-
B (52 ksi)	Bal.	0.052	0.15	0.8	-				-	-	-
C (70 ksi)	Bal.	0.071	0.19	1.54	-				0.1↓	0.1↓	0.1↓
D (70 ksi)	Bal.	0.054	0.17	1.1	0.3				0.1↓	0.1↓	0.1↓
E (316L)	Bal.	0.017	0.59	1.05	0.03	-	-	-	12.6	17.6	2.38

| Results

Fig. 2(a) shows the weight change results for each material in a high-pressure (10MPa) distilled water environment over 24/100h time. As a result of the test, it was possible to confirm the high corrosion resistance of stainless steel, as is well known. In the case of carbon steel, when it meets water, Fe₂O₃ and Fe₃O₄ are formed, and corrosion is actively performed on the surface. Therefore, it can be confirmed that the weight increase and decrease are greater than those of stainless steel. Fig. 2(b) shows the weight change results for each material CCS pipeline environment over 24/100/500h time. The test results showed high corrosion resistance regardless of the type of steel in a water-treated environment below the saturated solubility of H₂O in CO₂. In the case of carbon steel, it is known that corrosion hardly occurs in a pure high-pressure CO₂ environment. However, if water is present in the pipe for any reason, as shown in the test results, carbon steel becomes vulnerable to corrosion. Therefore, if carbon steel piping is to be used, it must be water treated after CO₂ capture and prior to transport (Fig. 2(b))[8~11]. The saturation solubility, which is the amount of H₂O that CO₂ can hold, changes depending on the change in temperature/pressure of CO₂. If H₂O content higher than the saturation solubility is added(Fig. 2(a)), it will exist as water and surface corrosion in the pipe will become active.

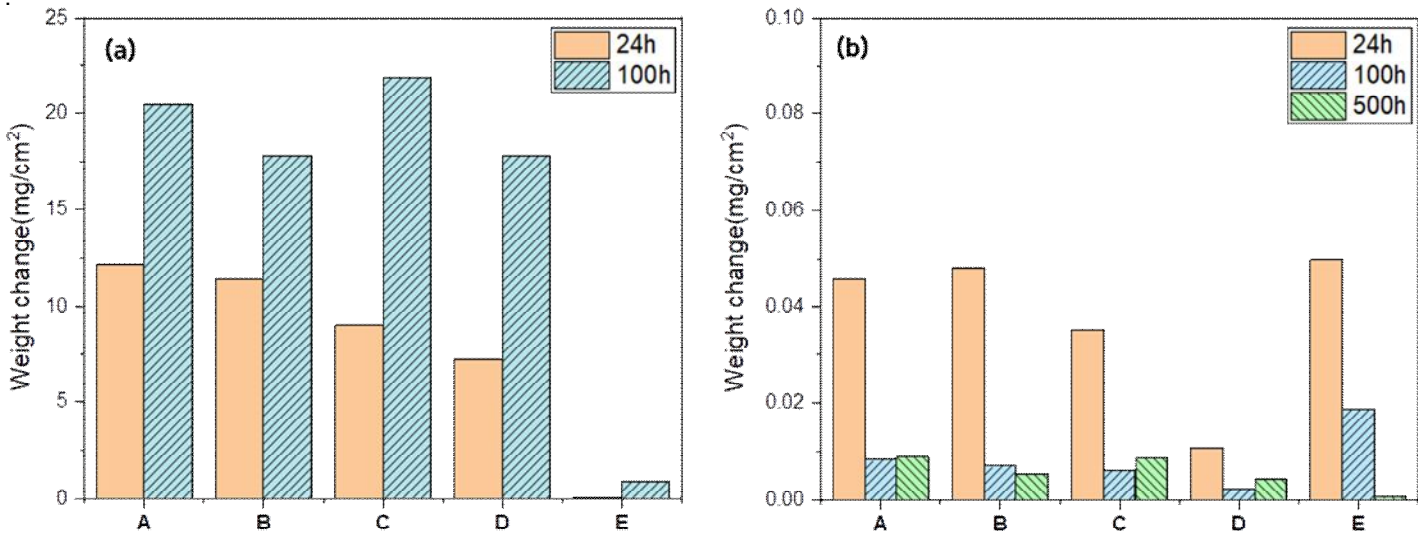


Fig.2. Results of weight gain in (a) distilled water (b) S-CO2/distilled water(1,000 ppm) environment.

| Conclusion

As the global CCS infrastructure expands, the demand for long-distance transportation between countries/continents increases, and the demand for CO₂ pipelines is expected to increase. If you use stainless steel, which is already well known for its high corrosion resistance, there will be no problem. But the cost of materials will be high. In order to utilize relatively inexpensive carbon steel as a material for CCS piping, H₂O pretreatment is essential. According to the results of the corrosion test in which the H₂O content in CO₂ was managed below the saturated solubility, if the H₂O content is controlled below the saturated vapor pressure, there seems to be no problem in using carbon steel instead of stainless steel for piping.

| Further work

Through this test, basic corrosion evaluation of materials for CO₂ pipelines was performed. In order to develop materials that can be applied to actual CCS projects, (1) evaluation of materials applied to demonstration projects (2) additional tests simulating actual piping environments are being planned. Various conditions such as pressure, temperature, impurities, flow rate will be evaluated. Based on this, the final goal is to develop a material for a safe CO₂ transport pipe by evaluating the material's marginal integrity.

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Stainless steel selection in specific environments

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Abstract

EN 1993 “Eurocode 3. Design of steel structures” gives the design guidelines for buildings and civil engineering works in steel. In Part 1-4 “General rules. Supplementary rules for stainless steels”, additional provisions to ferritic, austenitic and austenitic-ferritic stainless steels are found. In the Annex A, a procedure for the selection of materials for structural applications is provided, taking into account the environmental corrosivity.

Using EN 10088 – 1 “Stainless Steels. Part 1: List of stainless steels”, pitting resistance equivalent (PRE_{Mn} taking into account the negative effect of the manganese) is calculated from the chemical composition of the materials referred to in EN 1993 – part 1-4.

In this paper, a correlation between the corrosion resistance requirements established in EN 1993-1-4 and the PRE_{Mn} of stainless steels can be seen.

Keywords

“EN 1993-1-4”, “environmental corrosivity”, “PRE_{Mn}”, “corrosion resistance class”.

Introduction

The material selection for a particular application is highly influenced by the environment in which the material is exposed, and in turn, the severity of the environment depends on several factors, such as humidity, temperature, salinity, pollution, maintenance and cleaning operations, etc. For structural applications, these aspects are taken into account in Annex A of EN 1993-1-4 to establish different ambient factors, which related to each other give a Corrosion Resistance Factor (CRF), from which the environmental corrosivity is categorized by Corrosion Resistance Class (CRC).

Although to select the most appropriate material for an application, factors as surface finish, joining methods or strength required, the procedure established in the standard gives a useful guideline to the selection of materials for structural applications exposed to external environments.

Methodology

Evaluation of environmental corrosivity

For structural applications, EN 1993-1-4 gives the guideline to the selection of materials.

The procedure set out for the selection of materials implies to calculate the Corrosion Resistance Factor (CRF), which depends on the environment severity. To calculate CRF the followings factors are evaluated:

- F1: risk of exposure to chlorides from salt water or deicing salts,
- F2: risk of exposure to sulfur dioxide,
- F3: cleaning regime or exposure to washing by rain.

Tables 1 – 3 show the values for each factor in relation with the exposition to each parameter.

F1		M: distance from the sea S: distance from roads with deicing salts
1	Internally controlled environment	
0	Low risk of exposure	$M > 10 \text{ km}$ $S > 0.1 \text{ km}$
-3	Medium risk of exposure	$1 \text{ km} < M \leq 10 \text{ km}$ $0.01 \text{ km} > S \leq 0.1 \text{ km}$
-7	High risk of exposure	$0.25 \text{ km} < M \leq 1 \text{ km}$ $S \leq 0.01 \text{ km}$
-10	Very high risk of exposure	Road tunnels where deicing salt is used or where vehicles might carry deicing salts into the tunnel
-10	Very high risk of exposure	$M \leq 0.25 \text{ km}$ North Sea coast of Germany and all Baltic coastal areas
-15	Very high risk of exposure	$M \leq 0.25 \text{ km}$ Atlantic coastline of Portugal, Spain and France. English Channel and North Sea Coastline of UK, France, Belgium, Netherlands and Southern Sweden. All other coastal areas of UK, Norway, Denmark and Ireland. Mediterranean Coast

Table 1. F1 index (risk of exposure to chlorides from salt water or deicing salts).

F2		
0	Low risk of exposure	$< 10 \mu\text{g}/\text{m}^3$
-5	Medium risk of exposure	$10 - 90 \mu\text{g}/\text{m}^3$
-10	High risk of exposure	$90 - 250 \mu\text{g}/\text{m}^3$

Table 2. F2 index (risk of exposure to sulfur dioxide).

F3 (If $F1 + F2 \geq 0$, then $F3 = 0$)	
0	Fully exposed to washing by rain
-2	Specified cleaning regime
-7	NO washing by rain or NO specified cleaning

Table 3. F3 index (cleaning regime or exposure to washing by rain).

Once determined each factor, Corrosion Resistance Factor is evaluated by equation 1, and classified according to table 4.

$$\text{CRF} = \text{F1} + \text{F2} + \text{F3}$$

Equation 1

Corrosion Resistance Class (CRC)							
CRC I	CRF = 1	EN 1.4003	EN 1.4016	EN 1.4512			
CRC II	$0 \geq \text{CRF} > -7$	EN 1.4301	EN 1.4307	EN 1.4311	EN 1.4541	EN 1.4318	EN 1.4306
		EN 1.4567	EN 1.4482				
CRC III	$-7 \geq \text{CRF} > -15$	EN 1.4401	EN 1.4404	EN 1.4435	EN 1.4571	EN 1.4429	EN 1.4432
		EN 1.4162	EN 1.4662	EN 1.4362	EN 1.4062	EN 1.4578	
CRC IV	$-15 \geq \text{CRF} \geq -20$	EN 1.4439	EN 1.4462	EN 1.4539			
CRC V	$\text{CRF} < -20$	EN 1.4565	EN 1.4529	EN 1.4547	EN 1.4410	EN 1.4501	EN 1.4507

Table 4. Corrosion Resistance Class.

Correlation of environmental corrosivity and nobility of materials

To assess the nobility of materials, PRE_{Mn} is calculated by equation 2 [3], based on the medium composition values expressed in EN 10088-1.

$$\text{PRE}_{\text{Mn}} = \% \text{Cr} + 3.3\% \text{Mo} + 30\% \text{N} - \% \text{Mn}$$

Equation 2

The PRE_{Mn} values for each material in table 4 are represented in figure 1, grouped according to their CRC category to which they belong, and the correlation in table 5 is established.

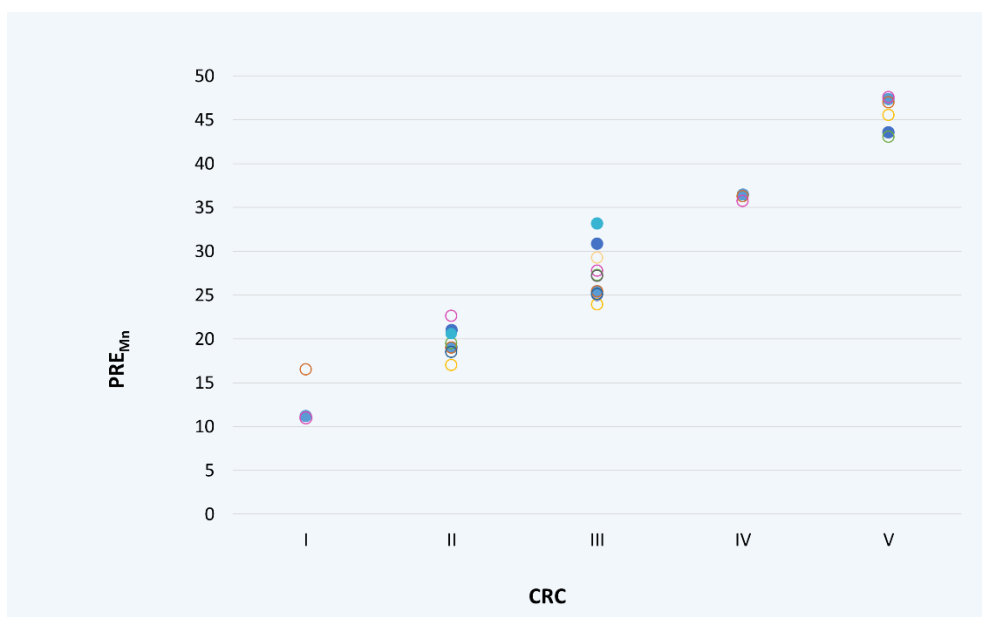


Figure 1. PRE_{Mn} vs CRC.

Categoría	PRE_{Mn}
I	< 17
II	$17 \leq PRE_{Mn} < 23$
III	$23 \leq PRE_{Mn} < 34$
IV	$34 \leq PRE_{Mn} < 40$
V	≥ 40

Table 5. Correlation $PRE_{Mn} - CRC$.

Conclusions

A correlation between PRE_{Mn} and CRC is established, finding PRE_{Mn} values that mark the limits between each category.

References

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Prediction of corrosion product thickness by DOProC method

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Abstract

Corrosion coupon analysis is a crucial factor in the proper design of a steel structure's service life. Corrosion coupons should be exposed for a longer amount of time (such as 10 years or more) if a long-term estimation of corrosion losses is needed. Therefore, when designing steel structures exposed to corrosion damage, designers usually use corrosion prediction models or derived corrosion maps. Average annual temperature, average annual relative humidity, average yearly deposition of chloride ions and sulfur dioxide, or average annual concentration of dust particles are usually the main input parameters for these models. This paper presents a stochastic approach to corrosion prediction models. The thickness of the corrosion products after one year of exposure is then determined by processing the input parameters using stochastic methods. The comparison with in-situ measurement data at sites near roadways is also included in the article.

Keywords

Chloride ions; steel; corrosion losses, ISO 9223, Multi-Assess, UN ECE ICP

Introduction

When designing and assessing structures, designers may be faced with problems related to the accurate prediction of corrosion processes. This is applicable, for example, in the design of new structures made of weathering steel or in the assessment of the reliability and residual life of in-service structures. If the corrosion loss projection is inaccurate, the structure's durability may be greatly reduced, or its maintenance costs may be significantly higher than average during its lifetime.

Utilizing corrosion maps [1], [2] allows for the simplest forecast of corrosion losses. According to ISO 9223 [3], corrosion losses after one year of exposure may be calculated if the engineer has knowledge of the typical deposition of sulfur dioxide ions and chloride ions. These two mentioned corrosion stimulants are now considered the main ones. However, this is not the only possible approach. There are several further prediction models, including those from the UN ECE ICP Effect on Materials project [4, 5] and the Multi Assess project [6]. The factors on the following list have an impact on how well each of the various approaches fits:

- average annual temperature,
- average annual relative humidity,
- average annual deposition of chloride ions,
- average annual deposition of sulfur dioxide ions,
- total annual rainfall,
- average annual pH of rainfall,
- average annual concentration of PM₁₀ particulates (maximal diameter = 10 µm).

The variables listed above are not deterministic. Since their values might change, all of the variables are random. There are two methods for calculating corrosion losses. In the first approach, corrosion losses are predicted deterministically using average values. Following this method, there is just one number of predicted corrosion losses without any knowledge of the quantity's variation. A probabilistic method for predicting corrosion losses is the second choice. Using this method, variables may be entered as random values depending on the measured data. The prediction of corrosion losses at theoretically extreme values of environmental influences is the outcome of the work [7]. However, a simplified description of the random input parameters is given only due to a limited duration of exposure (one year).

Numerous probabilistic approaches, like the Direct Optimized Probabilistic Calculation (DOProC) described in the article [8] or the SBRA, which applied the Monte Carlo method [9], may be used to calculate results given the input of random variables. There is a large number of input variables, and their combinations resulting in a large number of alternative inputs to solve; thus, the DOProC technique is picked. The number of equations to solve and the time required to answer all scenarios can be reduced with this approach since it can be tuned for the input volume of the data set [8].

Corrosion loss has been investigated for a long time by many corrosion engineers around the world. Historically, in inland Europe, the main corrosion stimulant was sulfur dioxide (SO₂). These days, its emissions are highly reduced by, e.g., desulfurization units in the industry. On the other hand, the deposition of chloride ions increased. The influence of this factor is also increasing as a result of the continuous increase in road traffic. In inland areas, the main source of chloride ions is roads and the deposition of de-icing salt and brine in the winter season. The prediction of corrosion losses is constantly changing according to the actual situation of corrosion stimulants in the atmosphere, chloride emitters (traffic), and the global climate.

Determining corrosion losses can be done in a variety of ways. The direct approach is based on the location of the existing or intended structure. This is due to the fact that structural engineers often lack relevant long term measured data from the site of the structure exposure. Corrosion losses may be calculated for a specific circumstance if measurable data on the concentration and deposition of corrosion stimulants are available.

The research builds upon the work [7] is focused on the estimation of the thickness of the corrosion products after one year of exposure with the processing of the input parameters using stochastic methods with an improved description of the probability density function of the input parameters. In the work [7] only normal distributions are used. Other possible distributions with greater tightness fit to the original data are used in this paper. The comparison with in-situ measurement data at sites near roadways is also conducted as well based on the data from the deposition of chlorides and corrosion losses.

Prediction models for determination corrosion losses

Currently, there are three main approaches to predict corrosion losses after one year of exposure. There are ISO 9223 [3], UN ECE ICP Effect on Materials [4, 5] and Multi-Assess [6]. The resulting value is used to determine the environment's aggressiveness. It is necessary to have the correct input values, see introduction. In the following paragraphs, equations for both one-year and multi-year corrosion losses are given. Throughout the text, one-year corrosion losses are used, with one year of exposure being substituted into the equation where appropriate.

The following legend is used for the following text:

r_{corr} – average annual corrosion rate for the first year of atmospheric exposure (μm),
 P_d – average annual SO_2 deposition rate ($\text{mg}/(\text{m}^2\text{day})$),
 P_c – average annual SO_2 concentration (mg/m^3),
 S_d – average annual Cl^- deposition rate ($\text{mg}/(\text{m}^2\text{day})$),
 RH – average annual relative humidity (%),
 RH_{60} – average annual relative humidity – if $RH \leq 60\%$, then 0%, else RH (%),
 T – average annual air temperature ($^\circ\text{C}$),
 $RAIN$ – sum of annual rainfall (mm),
 $[H^+]$ – hydrogen molar concentration (mg/l),
 pH – potential of hydrogen (-),
 V – volume (l),
 M – molar mass (g/mol),
 PM_{10} – average annual particulate matter smaller than $10 \mu\text{m}$ (mg/m^3),
 t – time of exposure (years),
 e – Euler's number.

ISO 9223

Currently, the standard ISO 9223 [3] equation is used to calculate corrosion losses. The equation for carbon steel is:

$$r_{corr} = 1.77 * P_d^{0.52} * e^{0.02 * RH + f_{st}} + 0.102 * S_d^{0.62} * e^{0.033 * RH + 0.04 * T} \quad (1)$$

where

$$f_{st} = 0.150 * (T - 10) \text{ when } T \leq 10^\circ\text{C}, \text{ otherwise: } -0.054 * (T - 10) \quad (2)$$

It is important to convert concentration to deposition rate since CHMI (Czech Hydrometeorological Institute) detects SO_2 concentration at their stations. The following equation is introduced in ISO 9223 standard for this conversion to deposition rate:

$$P_d = 0.8 * P_c \quad (3)$$

UN ECE ICP Effect on Materials

Between 1987 and 1995, the UN ECE ICP Effect on Materials was realized [4, 5]. This study produces an equation that accounts for the rate of sulfur dioxide deposition when calculating corrosion losses for weathering steel. The formula for the equation is:

$$\ln(r_{corr}) = 3.54 + 0.33 * \ln(t) + 0.13 * \ln(P_c) + 0.02 * RH + f_{st} \quad (4)$$

from which it follows:

$$r_{corr} = P_c^{0.13} * t^{0.33} * e^{0.02 * RH + f_{st} + 3.54} \quad (5)$$

where

$$f_{st} = 0.059 * (T - 10) \text{ when } T \leq 10^{\circ}\text{C}, \text{ otherwise: } -0.036 * (T - 10) \quad (6)$$

Multi-Assess

Project Multi-Assess was completed between 1970 and 2005 [6]. In 50 locations across Europe, corrosion coupons were exposed. Years throughout the realization era include those during which the press to ecology and desulfurization units in the industry and energy sector have lowered SO₂ deposition. The corrosion losses brought on by SO₂'s action are also declining [10]. Compared to the two others previously described equations, the equation from the Multi-Assess project includes more environmental acts. It goes as follows:

$$r_{corr} = 29.1 + (21.7 + 1.39 * P_c^{0.6} * RH_{60} * e^{f_{st}} + 1.29 * RAIN * [H^+] + 0.593 * PM_{10}) * t^{0.6} \quad (7)$$

where

$$f_{st} = 0.150 * (T - 10) \text{ when } T \leq 10^{\circ}\text{C}, \text{ otherwise: } -0.054 * (T - 10) \quad (8)$$

$$[H^+] = \frac{10^{-pH}}{V} * M * 1000 \quad (9)$$

Input parameters

Input values as the original measured data were analyzed using the HistAn program [8] and the histograms with the highest tightness fit are used in the following text. The data are taken from the CHMI database [12]. Chloride ion deposition and measured corrosion losses after one year of exposure are the authors' own measurements over a period of four years (2019 to 2022).

Due to the difficulty of measuring all input variables, it is not possible to measure all environmental parameters directly at the exposure site. Therefore, the nearest relevant CHMI station to the Hrabyně location under investigation is always selected for this case.

Average annual air temperature

The information is taken from years between 1961 and 2022 at the CHMI station in Opava, site Otice [12]. The graph in Fig. 1 displays an upward trend. On the data set, linear regression with Laplace distribution was applied, and the final equation is:

$$T = 0.027 * Year - 46.06 \quad (10)$$

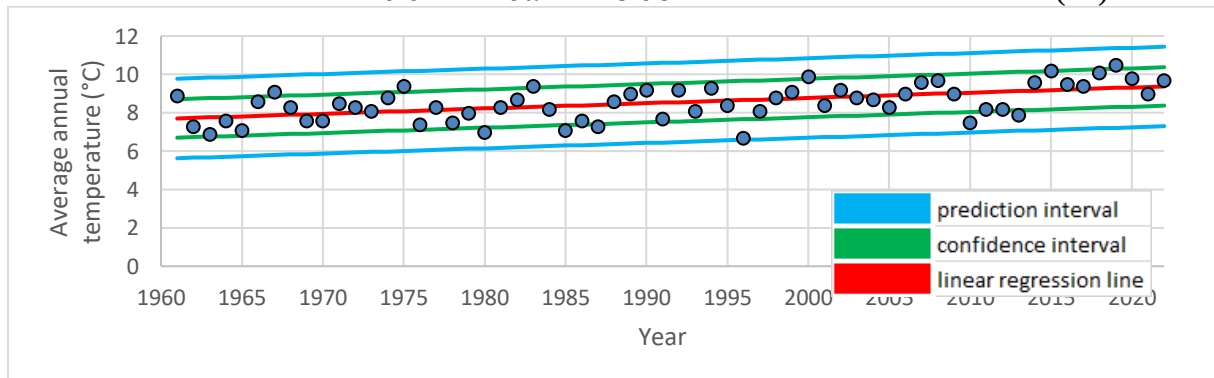


Fig. 1 : Average annual temperature - confidence and prediction interval

Average annual relative humidity

The data comes from the CHMI station at Opava, site Otice [12], and spans the years 1961 to 2022. A declining tendency may be seen in the graph in Fig. 2. The data set performed linear regression with Laplace prediction distribution. The resulting equation is:

$$RH = -0.12 * Year + 318.46 \quad (11)$$

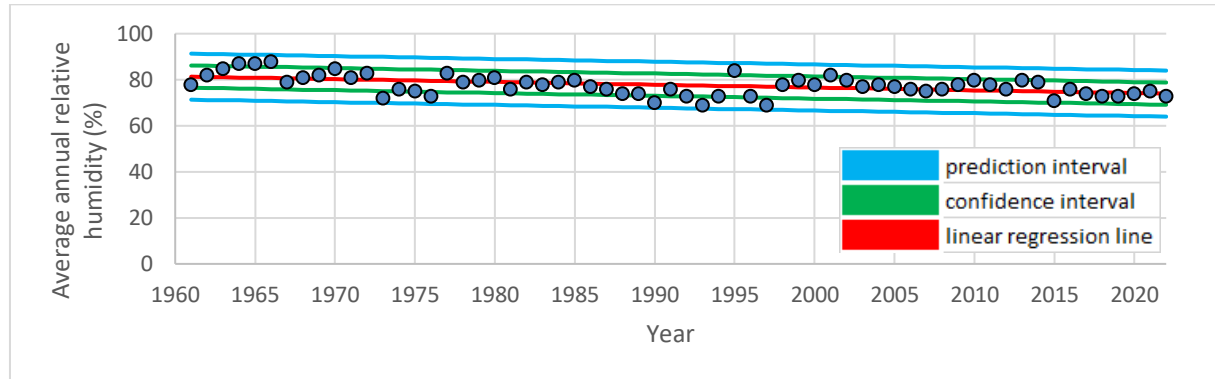


Fig. 2 : Average annual relative humidity - confidence and prediction interval

Average annual concentration of sulfur dioxide

In the past, sulfur dioxide (SO₂) had a key role in causing steel structures to corrode [13]. Data on SO₂ concentrations are taken from Ostrava-Poruba/CHMI [14] station data from 2011 to 2022. The linear regression with Rayleigh distribution are presented in Fig. 3.

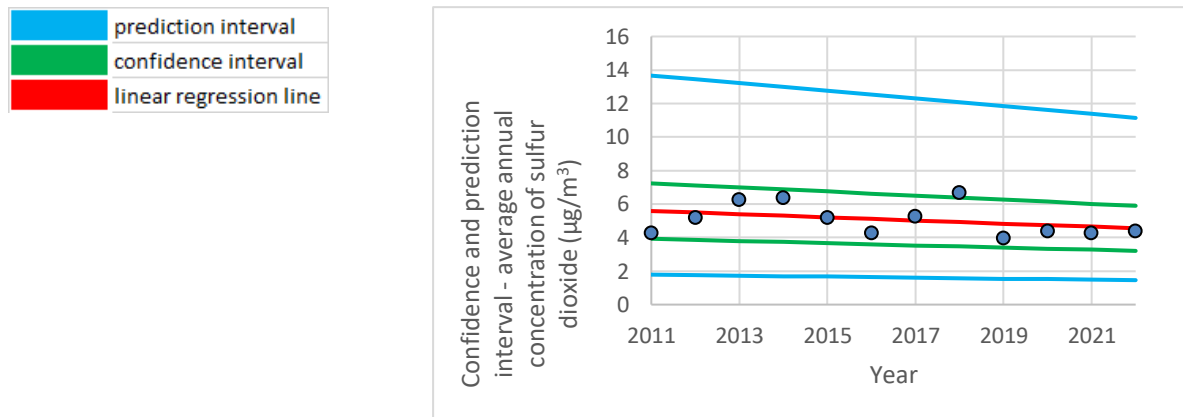


Fig. 3 Average annual concentration of sulfur dioxide - confidence and prediction interval

Average annual deposition of chloride ions

Three stations are selected near I/11 at Hrabyně - Josefovce locality (site map - Fig. 4) between years 2019 and 2022. Data was collected according to the ISO 9225 standard. The authors' measurements include four-years data (four average annual values). This means, confidence and prediction interval of data has limited predictive value. Another necessary information is, that deposition of chloride ions cannot be smaller than 0,0 µg/m². This information is mentioned on the Fig. 5, Fig. 6 and Fig. 7 for illustration. For itself computation is taken nonparametric distribution of the dataset. The original values are used for the analysis, not their interpretation by histograms. Collective of authors carries out further measurement to refine the results.

Site B1

The location of this site is closest to a road. The location is 7 meters away from the guidance strip on the road cut's crown. Measured information is displayed in the Fig. 5.

Site B3

The site is 45 meters away from the guide strip on the summit of the road cut. Measured data is displayed in the Fig. 6.

Site B5

This location is further from the road. The site is 180 meters away from the guide strip. Measured data is displayed in the Fig. 7.

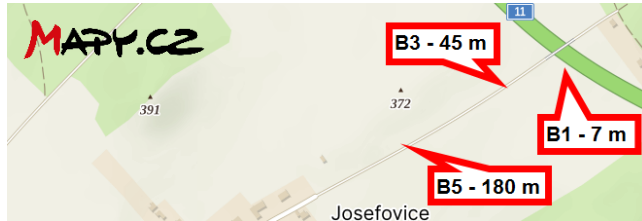


Fig. 4 : Site map – Hrabyně – Josefovce (source: mapy.cz)

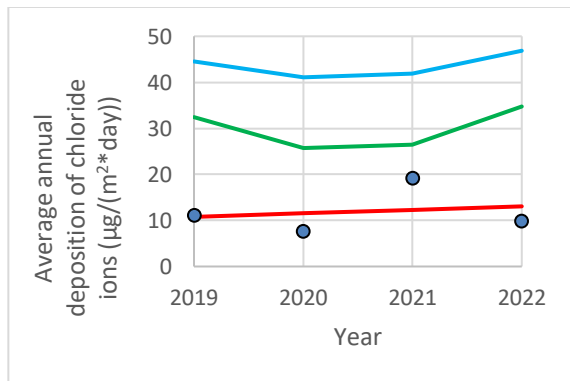


Fig. 5 : Average annual deposition of chloride ions - Hrabyně, site B1, wet candle method - confidence and prediction interval

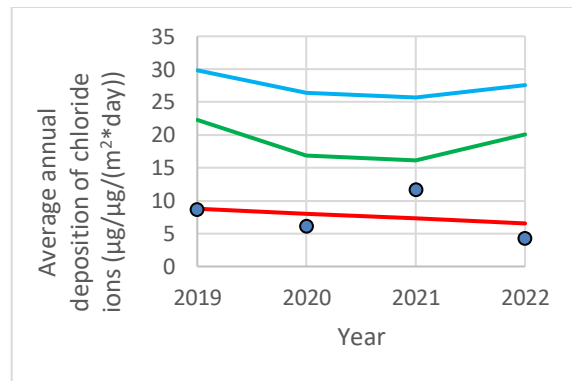


Fig. 6 : Average annual deposition of chloride ions - Hrabyně, site B3, wet candle method - confidence and prediction interval

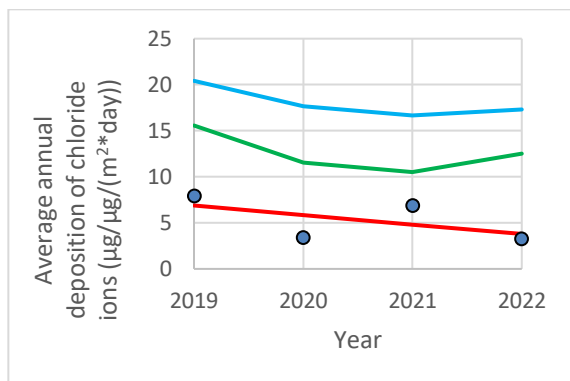
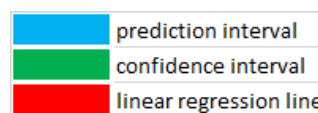


Fig. 7 : Average annual deposition of chloride ions - Hrabyně, site B5, wet candle method - confidence and prediction interval



PM₁₀

Dust particles can carry chloride ions. The average annual deposition of PM₁₀ particles is taken from CHMI, site Opava, site Kateřinky [14], from 2011 to 2022. Progress and confidence and prediction interval with Rayleigh prediction distribution are shown in the Fig. 8.

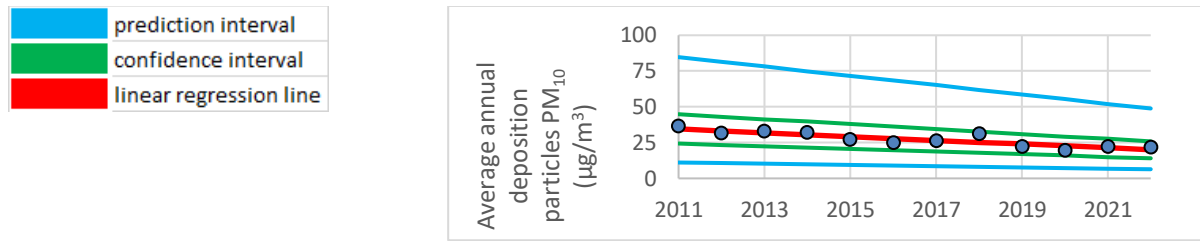


Fig. 8 : Average annual deposition particles PM_{10} - confidence and prediction interval

Annual rainfall

Data about annual rainfall are from CHMI for site Opava, site Otice [12], from 1961 to 2022. The progress of annual rainfall is shown in Fig. 9.

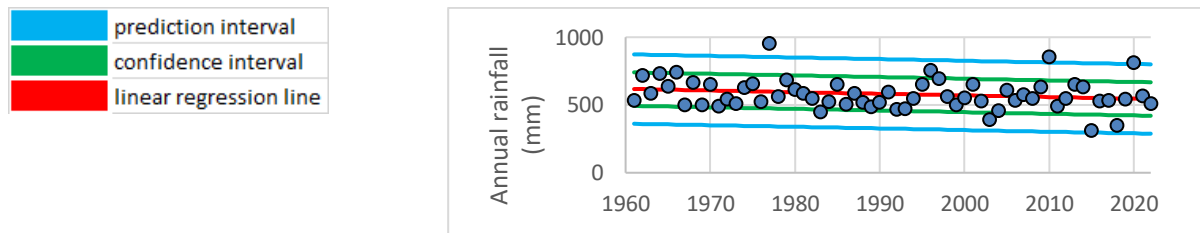


Fig. 9 : Sum of annual rainfall - confidence and prediction interval

Rainfall pH

The rainfall pH is determined based on the knowledge of [15, 16, 17]. It is a parametric model of normal distribution with a mean value of 5.82 and a standard deviation of 0.63. There is no pH measurement data. It is used data from the literature [15, 16, 17].

Histograms

HistAn software [18] is used to produce histograms from input variables data sets with the best possible tightness (correlation coefficient). In this instance, 64 intervals are handled for maximum tightness and the histograms are made for 2022. The chosen distribution has the tightness specified in the Tab. 1 and Tab. 2. Normal distribution is used only for the rainfall pH, see previous chapter. The pH rainfall distribution is specified in the Tab. 3. For the chloride ion deposition value, one constant annual average predicted value for 2022 based on a linear regression analysis is considered.

Tab. 1: Rayleigh distribution

	Intervals	μ	σ - coef. of distribution
PM_{10}	64	16.51	5.482
SO_2	64	3.247	0.946

Tab. 2: Laplace distribution

	Intervals	μ	β
RH	64	77.867	3.392
Rainfall	64	586.457	86.752
Temperature	64	8.583	0.703

Tab. 3: Normal distribution

	Intervals	μ	σ
pH	64	5.82	0.63

Direct Optimized Probabilistic Calculation method – prediction of corrosion losses

The Direct Optimized Probabilistic Calculation method (DOProC) is used for the corrosion losses prediction. The method is implemented in the ProbCalc software [18]. With reference to previous prediction models, input parameters such as relative humidity or rain are random variables. All input parameters are therefore in the form of histograms. The main goal is to determine a prediction of a 95% reliability value for the corrosion losses at each site.

In all three of these methods, it's important to take temperature into account. Checking the RH value is necessary for the MultiAssess method. The Delphi 7 based script is used in ProbCalc takes this into account. The resulting values based on equations (1),(4) and (7) are shown in the Tab. 4. The 95% quantile is chosen because corrosion attacks the surface and therefore reduces the cross-sectional area. It is therefore appropriate that the predicted value is in the 95% quantile so that the actual attack is less than the predicted value. There is also included the 5% quantile in the Tab. 4.

Tab. 4: Prediction average corrosion loss values r_{corr} [$\mu\text{m}/\text{year}$] for 2022

		min	max	mean	5% reliability value	95% reliability value
ISO 9223	B1	6.69	53.43	23.43	15.72	32.14
	B3	4.78	49.32	20.62	12.49	28.93
	B5	3.76	47.11	19.14	11.09	27.33
UN ECE ICP		7.75	26.24	14.25	13.89	20.53
Multi-Assess		8.60	96.26	38.61	20.53	56.79

Measurement corrosion losses in situ

The corrosion losses are measured on vertically and horizontally oriented corrosion coupons. The main reason why vertical and horizontal corrosion coupons are used is the realistic orientation of the surfaces on the structures, see e.g. [10]. The exposition time of coupons is one year. The measured average data is from four one-year deposited corrosion coupons for 2022 and can be seen in the Tab. 5. There is a quantile value too representing the probability that measured corrosion loss is lower than the numerically simulated value.

Tab. 5: Average corrosion losses of one-year exposed corrosion coupons in locality Hrabyně, from exposition in years from 2022 and quantile value (three valid digits) representing the probability that measured corrosion loss is lower than the numerically simulated value

Site/Orientation		r_{corr}		ISO9223	UN ECE ICP	Multi-Assess
		($\text{g}\cdot\text{m}^{-2}$)	(μm)	(-)	(-)	(-)
B1	horizontal	141.47	18.0	0.157	0.659	0.0185
	vertical	144.33	18.4	0.178	0.730	0.0206
B3	horizontal	112.45	14.3	0.108	0.0742	0.00410
	vertical	77.65	9.9	0.0107	0.000328	0.0000478
B5	horizontal	121.15	15.4	0.242	0.182	0.00687
	vertical	91.32	11.6	0.0635	0.00375	0.000978

Comparison of the numerical model and in-situ measurement

Tab. 5 shows the quantile value of average measured data from four years in the prediction models. In the design practice the respected quantile value equals to 5% (0.05) or 95% (0.95). In this case 95% quantile is important, because it has similar effect to steel coupons as the load on the structure with respect to the reliability assessment point of view.

The ISO 9223 approach gives acceptable results (~ 0.01 - 0.24) for all measured stations if it considers input values from different weather stations. For all mentioned situation is the equation from the standard ISO 9223 have good reliability value. This equation does not show some dangerous prediction situation.

The UN ECE ICP Effect on Materials approach gives values with quantiles with very low value (~ 0.00033) in some cases, but on the other hand with high values (0,659 or 0,730). These values of the quantile are not dangerous (still lower than 0,95), but it is important to keep this information in mind in case of usage of the UN ECE ICP approach.

The Multi-Assess approach has a reliability of less than 95% quantile in all cases. On the other hand, the average measured values are very small, with quantile values smaller than ~ 0.02 quantile. This approach is not risky to use, but it can produce values with greater predicted corrosion losses. It means the designed structure used more material for construction, and it will have more additional weight.

Conclusion

From the presented data, it can be observed that using the POPV method and input data in the form of histograms of environmental parameters, it is possible to achieve satisfactory results for the normative approach according to ISO 9223 and the UN ECE ICP method give result on statistically acceptable level. The predicted values are smaller than 95% quantile limit and their usage are considered safe for the data in question. It is necessary to extend values of the real-world corrosion losses and check 95% quantile in more cases than only for 2022. Collective of authors will make additional measurements and validation of this.

Another situation occurs with the Multi-Assess approach. Predicted values at the 95% quantile are greater in all cases considered. However, there is a downside. The predicted value is too high in all cases, quantile of average corrosion loss measured data is smaller than 0.02. This means predicted values are higher than they can be, and for the design of the structures, this is not a good situation either. If the engineer considers higher corrosion losses, he needs to use greater thicknesses of the profiles or plates. This will use more material than is strictly necessary and may result in an uneconomical design.

It is necessary to say that the only ISO 9223 approach consider Cl^- ions. UN ECE ICP and Multi-Assess approaches do not use Cl^- ions to determine the prediction corrosion losses. These days, roads are a bigger source of chloride ions because of the use of de-icing salt and brine in the winter. At the same time, chloride ions are nowadays the main corrosion stimulant. To neglect it, is therefore, incorrect.

Due to the limited amount of some long-term data (e.g., average annual chloride deposition), the result may be affected by this fact. Another parameter of minor inaccuracy may be the fact that different data are taken from different meteorological stations, which may be influenced by the local climate. The distance between stations is about 20 kilometers. The authors will continue to

monitor the sites for the extension of the chloride deposition data and the corrosion losses on the corrosion coupons.

Acknowledgement

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Study of Ce oxidation mechanisms

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Cerium is usually used for applications as oxide CeO₂; this oxide is largely studied in the literature. However, Ce oxidation was considered by a few rare studies [1,2] that have only shown the high reactivity of pure Ce at temperatures going from ambient to 320°C and any identification of the oxidation mechanism was not performed.

The present work aims to thoroughly study pure Ce oxidation between room temperature and 200°C in dry atmosphere with different oxygen partial pressures. In addition, the influence of water vapor presence in the exposure atmosphere will equally be addressed.

Two kinds of studies are performed. On one hand, the first oxidation instants are investigated by XPS analysis. On the other hand, the scale growth kinetics is followed and shows that after parabolic step, breakaway occurs at time dwells depending on the temperature and atmosphere composition. Surface and cross section SEM characterizations and XRD analyses are performed in order to determine the scale composition before and after breakaway. The phase responsible for breakaway was equally studied by *in-situ* XRD. The results are used in order to discuss Ce oxidation mechanisms in the considered exposure conditions.

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Electrochemical characterization of patinated bronzes exposed to outdoor atmosphere

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Bronze sculptures that are exposed to outdoor environment are usually artificially patinated after casting in order to protect underneath metal substrate and to achieve aesthetic appearance. The patinas are then covered with protective coating, usually waxes or resins. Protective coatings deteriorate over time and bronze and patina are affected by intense atmospheric corrosion.

Due to the air pollution, significant decay of bronze cultural heritage is observed over the years. In this work, we compared the results of measurements taken three years apart on bronze sculptures exposed to outdoor atmosphere in the city of Zagreb and on bronze samples artificially patinated in our laboratory and then exposed to outdoor Zagreb atmosphere. The aim of this work was to observe the difference in the corrosion stability and the composition of patina on real objects and laboratory prepared samples.

The electrochemical cell with aqueous electrolyte is difficult to apply to real objects with curved geometry. Therefore, electrochemical impedance spectroscopy (EIS) with a gel-electrolyte electrochemical cell was used to determine the corrosion stability of bronze and bronze patina. The measurements were conducted on several points on each sculpture in order to determine the impact of exposure of a particular part to different conditions (sun and rainfall), while on laboratory prepared samples it was measured in one point. The composition of the patina was determined by ATR-FTIR spectroscopy.

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Effect of artificial patination on Atmospheric Corrosion of Weathering Steel and Bronze

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Most metal sculptures and monuments for outdoor use are made of bronze or weathering steel (Cor-Ten), mainly because of their ability to form beautiful and protective oxide layers when exposed to a mild urban atmosphere, but this formation is a slow process that requires many years and special environmental conditions. For aesthetic reasons, some sculptors accelerate the patination process by treating it with various oxidising agents. This acceleration is artificial and does not correspond to the original conception of this material, so it could compromise the protective effect of the patina and thus jeopardise the long-term preservation of the artwork.

In this study, the effects of sulfuric acid patination on Cor-Ten and patination of bronze with sulphuric liver were investigated as the most commonly used artificial patination processes. The samples were exposed to the mild urban atmosphere of Zagreb for 1.5 years, together with weathering steel and bronze samples without artificial patination, the so-called natural patinas. Corrosion behaviour was evaluated by electrochemical impedance spectroscopy (EIS) using a paste electrolyte cell specifically designed for in situ measurements. Exposure conditions (humidity and temperature) are monitored, and samples are periodically characterised using spectroscopic techniques. Laboratory results were compared with in situ measurements on actual Cor-Ten and bronze sculptures.

This work has been fully supported by Croatian Science Foundation under the project Development of new solutions for characterization and protection of bronze cultural heritage exposed to outdoor environment IP-2019-04-5030.

Identification of Critical Details of Weathering Steel Bridges

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Introduction

The atmospheric corrosion of weathering steel had been studied in the Czech Republic since 1970ties not only on atmospheric test sites with typical environmental conditions but also on the real bridge structures. The most intensive program started in 2013. The standard samples were withdrawn after 1 and 3 years and now after 9 years from bridge structures, resp. 14 years from atmospheric test sites.

Materials and methods

The standard samples of weathering steel Atmosfix 52A (eq. Corten A) with 100x150 mm dimensions were exposed on the racks and under shelter at the atmospheric test sites according to ISO 8565 and directly on the specific areas of bridge structures (beam wall, upper and bottom flange, etc.) – Figure 1.



Figure 1 – Example of sample exposures

During whole exposure period the environmental parameters significant for atmospheric corrosion were measured. Since 2016 the chloride deposition according to ISO 9225 was measured too. After exposure the weight gain, corrosion product

layers' thickness, color of corrosion product layers, corrosion product layers' macrostructure (adhesion), corrosion mass loss and chemical composition of corrosion products had been evaluated by standard methods. On samples exposed to leakage from bridge deck the pitting corrosion was evaluated.

Results

Corrosion mass loss of weathering steel reduced due to decreasing of the air SO₂ pollution since 1970ies. In the contemporary atmospheric environments, the corrosivity was evaluated as category C2 for weathering steel according to ISO 9223 except the specific areas of bridges' structures. Practically all evaluated parameters of patina and corrosion mass loss from samples exposed at the atmospheric test sites and on the bridge structure area with suitable conditions for patina forming were the same (Figure 2). On the bridge structures the values of corrosion loss was ca double on the critical bridge structures' areas as upper are of bottom flange, bottom area of upper flange, etc., but these values still correspond to C2 corrosivity category. The higher values were estimated for bridges with the intensive traffic bellow the structure. These results are used for determination of critical details of bridge structures. The effect of corrosion losses on the reliability of the structure should be analyzed using probabilistic reliability analysis, taking into account the randomness of load and resistance effects.

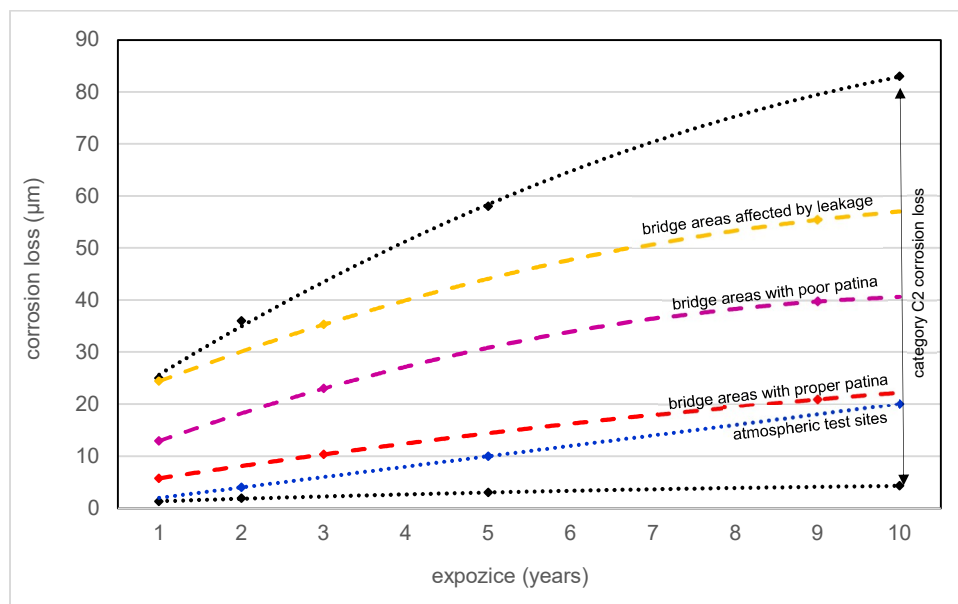


Figure 2 – Example of long-term corrosion loss from bridge structure

Influence of phosphonic acid monolayers on atmospheric corrosion of Al2024-T3 under outdoor conditions

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Aluminum alloys of the series 2XXX possesses high strength and good damage tolerance and are hence typically used for aerospace applications. The aluminum alloy 2024 as an important aerospace alloy is known to be susceptible to localized corrosion promoted by intermetallic phases (IMPs).^[1] As this specific kind of corrosion is fundamentally well understood, the development of new corrosion-inhibition strategies is of distinct interest. One possible approach to achieve these goals, might lay in the intrinsic inhibition properties of self-assembled monolayers (SAMs).^[2–5]

The presented paper focusses therefore on the influence of monolayers based on organophosphonic acids on the atmospheric corrosion kinetics.

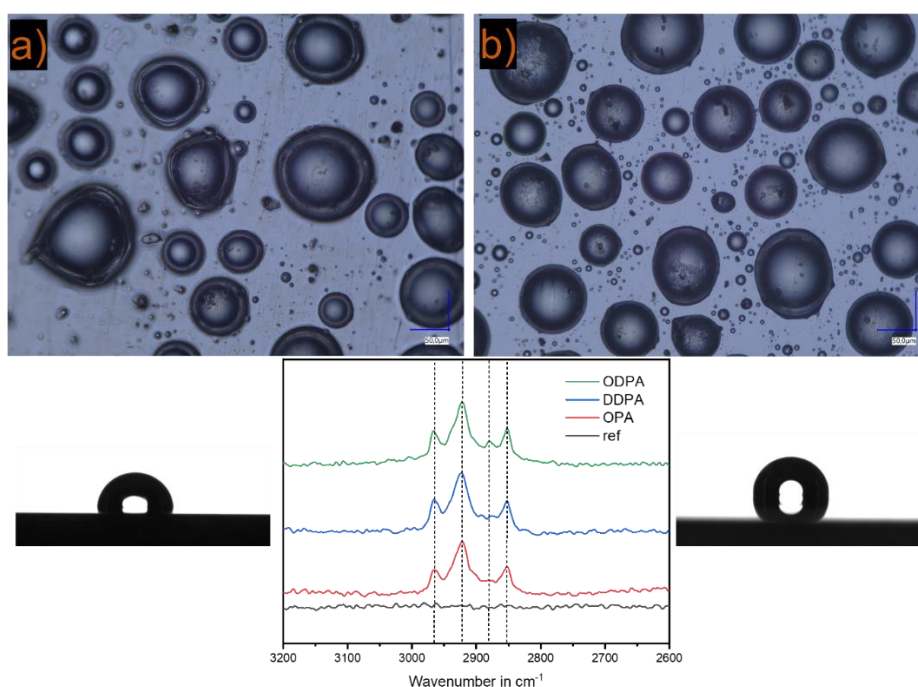


Figure 1: a) In-situ microscopic image of a salt-loaded Al 2024 surface without a phosphonic acid monolayer during high humidity exposure. b) shows a salt-loaded Al 2024 surface with a phosphonic acid monolayer under same exposure conditions as in a). The bottom panel shows respective contact angles and PM-IRRAS results verifying successful adsorption of an ordered monolayer.

Phosphonic acid monolayers with different chain lengths, state of ordering, and defect density are comparatively studied with regard to the change in surface energy, electrochemical properties and resulting atmospheric corrosion kinetics.

The monolayers are analyzed by complementary surface analytical methods such as X-ray photoelectron spectroscopy (XPS) and FTIR spectroscopy under grazing incidence (FT-IRRAS). The progress of corrosion is monitored by means of in-situ digital microscopy and Scanning Kelvin Probe measurements. A correlation is established between the structure of the monolayer and the progress of corrosion under atmospheric conditions.

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Challenges in assessing atmospheric corrosion performance of anticorrosive coatings with accelerated cyclic corrosion tests

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Application of anticorrosive coatings is an essential method to delay corrosion of metals. There exists two common ways to select an appropriate coating system based on the environment in which the system is exposed. One is testing the system in the field, being a fairly accurate technique but a very tardy process. The other is testing the system in accelerated corrosive environments. The latter method is reasonably quick, but the corrosive environment may not resemble well the actual corrosive environment, resulting in inaccuracies in assessing the durability of the developed coating systems.

A primitive, but very popular, accelerated corrosion test is ASTM B117 which sprays salt continuously on the samples. However, this is a condition that does not naturally occur in the field and the obtained results may not be reliable enough to assess the durability of the coating system in the actual corrosive environment. Besides, ASTM B117 is often used as a screening test to rank coatings designed for exposure to corrosive environments but does not provide information on the actual performance or mechanism of failure.

In the natural atmosphere, condensation and evaporation of electrolyte, pollutants, ultraviolet, temperature change, etc. may control the atmospheric corrosion rate of coatings. Therefore, over decades, accelerated cyclic corrosion tests have been developed to resemble more realistic conditions to natural atmosphere. Despite that,

there are still challenges in terms of assessing the durability of coating and correlating the accelerated cyclic test results to natural atmospherically corroded samples. This paper will discuss such challenges.

Wet CO-CO₂ Stress Corrosion Cracking in CCS Pipelines

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Carbon capture and sequestration (CCS) is gaining greater importance in the industry transition to meet climate goals reducing carbon intensity. As the source of CO₂ captured for sequestration widens to many more applications from oil and gas productions, power plants, refineries, chemical plants, steel manufacturing and other industries, the composition of the captured gas stream for sequestration sees various components. Some of the common impurities particularly from combustion processes are carbon monoxide, oxygen, SO_x, NO_x and others. Understanding the effect of presence of the various chemical species on material limits and maximum tolerance limits are crucial for safe operations of the assets. In one of the recent projects, there was a presence of CO in the CO₂ stream, and it was imperative to identify the effect of this on the existing carbon steel pipeline. The pipeline was of X65 steel and fabricated for natural gas transmission. Wet CO-CO₂ cracking is a reported degradation mode particularly as the CO concentration increases beyond 200 ppm in gas phase or at partial pressures above 0.3 bar. This study is a combination of literature review of current state of art with respect to CO-CO₂ cracking in carbon steel in presence of impurities and also laboratory testing of welded X65 specimens exposed to CO concentration in dense phase up to 1000 ppm and also in the presence of small concentrations of oxygen that also replicates some of the expected conditions in the project. The tests clearly indicate that the risk of CO-CO₂ cracking is not significant up to the concentrations tested.

Effect of pure ammonia gas on surface behavior of stainless steel and Ni base alloys above 500 degC

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Hydrogen is of great interest as a key means for carbon-neutralization conversion in various industrial areas. Since hydrogen is low energy density per volume, an effective way of storage and transport of hydrogen needs to be developed.

Ammonia should be an important candidate as hydrogen carrier. Ammonia is environmentally friendly because it is nothing with carbon. Ammonia has a high hydrogen content (17.8% by weight and a volumetric density of 121 kg H₂ m⁻³ at 10 bar) and can liquefy at low pressure, 8.6 bar and 1 bar, at 20 °C and -33 degC, respectively. Moreover, ammonia is widely used in many industrial areas and its transport and marketing infra are already available. Its transport and storage are relatively easy and require a low amount of energy. However, no commercial grade of process facilities are available in the world so far; thus, research activities are required for developing commercial scale plant of hydrogen production from ammonia. Since high concentration of ammonia existing in the hydrogen production from ammonia decomposition is very toxic and fatal, the design and construction of safe plant is the most important issue. Nitriding is the formation of a hard, brittle surface layer on some alloys due to exposure to high-temperature process streams containing high levels of nitrogen compounds such ammonia under reducing conditions.

Considering that the target operation temperature of hydrogen production from ammonia decomposition would be above 500 degC, nitriding is found to be a critical damage mechanism in the given process condition. It is found few studies have been reported about long term exposure behavior of high temperature metals at the given service condition. In the present work, phase transformation and physical property

change of stainless steel and nickel base alloys are aimed to study in the high concentration ammonia gas at high temperature. The root cause of the change is aimed to figure out; in addition, impact of nitriding on material selection of the process design for commercial grade plant is discussed in detail.

Key words: Ammonia, Gas nitriding, Stainless steel, Ni based alloy, process design

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Influence of laser beam welding related to corrosion of 316L stainless steel

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Laser beam welding allows for joining two metallic plates together in a very fast and industrial scalable manner, and is applied for the production of metallic bipolar plates of proton exchange membrane fuel cells (PEMFCs). One of the challenges regarding the performance, and more crucially the durability of a PEMFC is the corrosion of the metallic bipolar plates made of 316L stainless steel (SS). Where the ribs of the bipolar plate are usually covered with a coating, the channels defining the reactants flow field are not. Therefore, the corrosion preferentially takes place within the channels, where the weld seams are located. The weld seams could be a significant contributor to 316L SS bipolar plate corrosion. Therefore, an in depth study of the differences between the weld seams and the blank/unmodified steel is needed in order to depict the chemical/structural modifications occurring at the steel upon the welding process to further correlate these modifications to the corrosion properties of the metallic bipolar plates.

We will show the segregation of manganese and silicon at the edge of the weld seams by a combination of secondary electron microscope images and chemical analysis using energy dispersive x-ray spectroscopy (EDX). The passive layer, the main contributor to corrosion protection, was characterized using X-ray photoelectron spectroscopy and time of flight - secondary ion mass spectrometry. Silicon oxide and enrichment of manganese oxide could be detected for the passive layer of the weld seams, which is consistent with our EDX results. Furthermore, a change in the depth profile for the iron and chromium oxide layer could be also detected.

For the electrochemical characterization, performed under conditions relevant for fuel cell applications, classical corrosion studies via polarization curves will allow for the determination of the corrosion current and of the passive potential range. The apparent second anodic peak, at ca. 0.40 V_{RHE} may be attributed to sensitization, which is an indicator of susceptibility towards intergranular corrosion and/or intergranular stress corrosion cracking [1]. In addition to that, a non-invasive technique such as cyclic voltammetry applied around the open circuit/corrosion potential offer the possibility of

extracting the corrosion current without modifying/reducing the passive layer after the laser beam welding [2].

Lastly, the semi-conducting characteristics of the oxide layer, arising from its defective structure, were probed by means of electrochemical impedance spectroscopy. The Mott-Schottky plots describe the behavior of a p-n heterojunction [3] and allow for the determination of the charge carrier densities. The charge carrier density is the main contributor to the passive film's electrical conductivity and likely, one of the descriptors of the changes in the corrosion currents.

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Degradation of functionalised zinc biomaterials in advanced in vivo models

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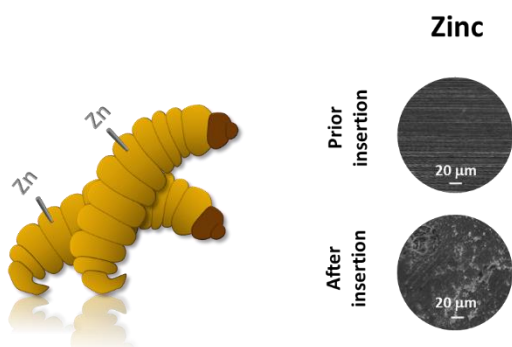
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Medical Implants and Devices



Metallic zinc has been widely studied as a biomaterial due to its biocompatibility and biodegradability properties. Zinc is a biocompatible metal that promotes bone growth and prevents bacterial infection, making this a promising biomaterial for medical applications in wound healing and tissue engineering. Upon degradation,

zinc ions can stimulate osteoblasts activity, the cells responsible for bone formation, and promote bone tissue mineralisation. This stimulating activity leads to improved implant integration and faster healing times. Another benefit of metallic zinc is its ability to inhibit the growth of many bacteria causing implant infections, including methicillin-resistant *Staphylococcus aureus* (MRSA) and *Pseudomonas aeruginosa* in their planktonic and biofilm forms.

Despite the promising results of these studies, there are still some challenges that need to be addressed before metallic zinc can be widely adopted in biomedical

applications. One of these challenges is the development of biocompatible coatings that can improve zinc functionality inside the body, including bone growth and regeneration, antimicrobial activity, or create new functionalities for anticancer applications. With it, further research is needed to understand the effects of functionalised zinc on the body, including degradation rates and the corrosion layers formed.

So far, the *in vitro* degradation of metallic zinc has been shown to occur through a combination of corrosion and surface reaction with body fluids, leading to the formation of zinc oxide, hydroxide and hydrochloride, and calcium phosphate-derived compounds. These compounds are non-toxic and have been shown to favour cell growth and wound healing. *In vivo* degradation of metallic zinc has been studied using different mammals and found to follow similar degradation mechanisms as *in vitro*; however, intrinsic factors, such as pH and the presence of other ions, must be addressed.

The greater wax moth (*Galleria mellonella*), a commonly used *in vivo* model, must be explored for the degradation of metallic zinc. Its ability to produce enzymes capable of breaking down zinc compounds, its high tolerance to zinc exposure, and its ability to study the effects of different forms of zinc make it an ideal model for this purpose.

ELECTROCHEMICAL BIODEGRADABLE BEHAVIOUR AND SURFACE TREATMENT OF MAGNESIUM ALLOY ZK60

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Plasma Electrolytic Oxidation (PEO) is a surface modification technique that enhances the properties of magnesium alloys, particularly the biodegradable alloy ZK60. In the biomedical field, biodegradable alloys have gained increasing attention due to their ability to be absorbed by the body after fulfilling their purpose. However, their intrinsic corrosion resistance is limited. To improve this, researchers are exploring ways to enhance the corrosion resistance of these alloys, one of which is by applying a polymer coating to the surface after PEO treatment. This helps to fill the pores in the PEO layer and forms a protective layer that prevents corrosion and improves the long-term stability of the material.

The evolution of voltage during the PEO process was recorded and graphically presented to understand its formation mechanism. The morphology and thickness of the PEO coating, as well as its corrosion resistance, were evaluated through electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization (PD) measurements after 1 hour of exposure to a simulated body fluid solution of 0.9% NaCl. Results showed a considerable increase in corrosion resistance of the biodegradable ZK60 alloy sample treated with PEO.

The study also investigated the application of an organic polymer coating as a post-treatment method after the PEO process. The PEO process was performed in DC mode with a constant current density of 0.05 A/cm^2 for 14 minutes. The results of the EIS and PD measurements confirmed the effectiveness of the polymer coating in increasing the corrosion resistance of the PEO-treated sample.

In conclusion, the combination of PEO treatment and polymer coating is a promising approach for improving the corrosion resistance of biodegradable magnesium alloys,

making them a more suitable option for use in biomedical applications. The biodegradable magnesium alloys can be used with confidence for a wide range of medical applications, offering a safe and sustainable solution for the future

Characterization of the microstructure and corrosion behavior of electrodeposited FeMn films for bioabsorbable implants applications

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Abstract

Corrosion of biodegradable implants is not supposed to be avoided, but controlled to reach a target biodegradation rate [1-4]. Implants made of Fe or its alloys have been studied for this type of applications; however, they have some drawbacks as low corrosion rates for this application, accumulation of bulky corrosion products and ferromagnetic properties, which might be a problem for MRI exams [1-4]. Some improvements have been proposed in the literature, such as using electrodeposition to produce thin strut walls of Fe (or alloys) with high purity and using FeMn alloys (with high concentrations of Mn) that can form an antiferromagnetic phase with higher corrosion rates than pure Fe [1-6].

In the first part of this work, thin films of FeMn alloys were electrodeposited from sulfate electrolytes. The effects of additives and electrodeposition current density were evaluated through electrochemical techniques. The microstructure of the electrodeposited films was characterized by SEM/EDX and XRD. The surface finishing and magnetic properties were evaluated by AFM/MFM techniques. The results showed that FeMn films with a maximum concentration of 18 wt% of Mn were obtained at an applied cathodic current density of 80 mA/cm² (close to the limiting current density) for a 1:5 ratio of Fe²⁺ and Mn²⁺ in the electrodeposition bath. These films were mainly composed of alfa-FeMn phase that still showed magnetic response on MFM analysis. The use of additives such as buffer, surfactant, and leveling resulted in a more homogenous film with improved surface finishing. In the second part of this work, the biodegradation rate of the electrodeposited film will be evaluated through immersion and electrochemical techniques in simulated body fluids.

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Effect of patient factors on the corrosion properties of biomedical implants

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Changes in the local chemistry and physical forces (micromotions, load, friction) may contribute to the corrosion (degradation involving chemical processes) of metallic orthopedic implants. It has been debated, and in some case studies shown, that some conditions, especially autoimmune conditions, diabetes, infection, and inflammation, contribute negatively to the corrosion process or could even be deteriorated by the corrosion process. For example, periprosthetic infection and diabetes have been reported to cause a very aggressive chemical environment, attacking the implant material. Other patient factors affect the physical environment of the implant: for example, weight, height, and degree of physical activity. It is almost certain that all these patient factors and comorbidities are strongly dependent on gender and sex. The rationale behind this study is to improve musculoskeletal health for patients with and without pre-existing conditions, by identifying comorbidities and patient factors that are likely to influence the corrosion-related clinical outcome and survival length of a total hip or knee arthroplasty. Optical microscopy and scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy were used to analyze the types and extent of surface damage due to corrosion and wear for 235 retrieved hip and knee implants (Western's Implant Retrieval Lab). The results were categorized and scored according to a standardized method. This quantified and categorized corrosion data was then correlated by statistical methods to the above patient factors, and corrected for confounders (length of implantation, implant type). Tribocorrosion was found to be the most prevalent type of corrosion.

Effect of Pearlite on HAC Behavior of Pipeline Steel at Different Strain Rates

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Abstract: In this work, the mechanical properties of pearlite pipeline steel under different strain rates were comparatively studied by the tensile test with and without hydrogen charging. The fracture and microcrack distribution were observed by SEM, and the influence of pearlite structure on hydrogen induced crack propagation and hydrogen diffusion in pipeline steel under different strain rates was discussed. The results show that hydrogen induced cracks are easy to initiate at the ferrite/ pearlite interface and propagate along with the ferrite/ pearlite interface without external stress. Under the condition of hydrogen charging, when the strain rate is large, the diffusion time of hydrogen in steel is limited, the diffusion degree is low, the movement speed of dislocation is fast, and the hydrogen atom cannot move with the movement of dislocation. At the same time, the hydrogen concentration finally enriched in pearlite is low, the material is not prone to generate hydrogen induced crack, and the plastic loss is relatively small. When the strain rate is low, the hydrogen atoms entering the test steel would have sufficient time to diffuse and gather at pearlite. In addition, the hydrogen concentration at the ferrite/ pearlite interface is high, which leads to the reduction of the strength of the two interfaces, and easily to produce secondary cracks. Then it will trigger the crack to expand along with the ferrite/ pearlite boundaries. Thus, the material is more vulnerable to hydrogen induced fracture, and the plastic loss is more obvious.

Subtopic –Pipeline steel, Microstructure, Hydrogen assisted cracking.

High-Performance Copper-Base Alloys for a Safe Operation in Hydrogen Containing Environments

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Hydrogen will become one of the most important elements for regenerative power generation. As producer of high-performance materials, Materion has investigated the susceptibility for hydrogen embrittlement of several alloys in hydrogen or hydrogen bearing environments.

Three different, commercial available high strength copper alloys had been loaded with hydrogen in aqueous and gaseous atmospheres. The composition of the alloys, the test conditions as well as the measured hydrogen contents are summarized in Table 1.

		Weight %						Hydrogen Content [ppm]	Hydrogen Content [ppm]
Alloy	Temper	Be	Ni	Si	Cr	Sn	Rest	Dechema	Ruhr University Bochum
Alloy 25	AT	1,8 – 2,0					Cu	< 1	< 0,1
PerforMet	MM-V		6,5 – 7,5	1,5 – 2,0	0,75 – 1,25		Cu	< 1	< 0,1
ToughMet	TS 95, TS 120U, TS 160U		14,5 – 15,5			7,5 – 8,5	Cu	> 1	> 1

Table 1 – Chemical composition of measured copper alloys, hydrogen content after pre-loading (measured by Thermal Desorption Analysis (TDA)). All samples kept at -192°C (liquid nitrogen) after pre-loading. Dechema – Hydrogen pre-loading in Devanathan-Stachurski-cell, NaOH/As₂O₃-solution, cathodic polarization at room temperature over 192h; Ruhr University Bochum – Pre-loaded in gaseous hydrogen in an autoclave at 300°C and 275 bar for 21 days

It is well known that face-centered cubic crystal structures, as found in copper alloys, have much lower diffusion coefficients for hydrogen than body centered structures.

The investigations at the Dechema Institute, where samples had been electrochemically pre-loaded in cathodic pre-charged thin discs (0,2 mm thick), demonstrated that hydrogen penetrate into the material but apparently remains close

to the surface since any diffusion (or permeation) through the material could not be detected even after long term exposure. In contrast, ferritic martensitic materials become saturated by hydrogen within a few hours with measurable currents on the oxidation side.

At higher temperatures and pressures (pre-loading test conditions at the Ruhr University Bochum via gaseous hydrogen) hydrogen contents had been determined in the same order of magnitude. Whether or not the internal distribution of hydrogen is more homogeneous was not investigated and thus could not be answered. These samples had been subsequently tested regarding their mechanical properties in slow strain rate tensile tests. The results and the SEM-investigations of the fractured surfaces are given in Table 2 (for CuBe).

CuBe – Rod AT	Yield strength [MPa]	UTS [MPa]	Elongation [%]	Reduction of area [%]
Condition I	1098	1229	7	14
Condition II	991	1158	9	21
Condition III	977	1137	8	17

Table 2:

Mechanical Strength and Ductility of CuBe (AT-temper) in various testing conditions (I = as delivered, II = after 21 days at 300°C/275 bar without hydrogen, III = after 21 days at 300°C/275 bar in hydrogen), results mean value from 3(2) tests in each condition

As a general rule of thumb, materials with yield strength > 800 MPa are likely to be prone with respect to hydrogen embrittlement when exposed to hydrogen or hydrogen bearing environments. This type of material damage occurs usually with an unpredictable incubation time and may lead to fatal failure of the parts (sudden rupture or delayed fracture). Use of these materials requires therefore proof of compatibility in hydrogen under realistic scenarios in their final application. All results determined from our investigations point in the direction that CuBe and PerforMet are immune in hydrogen and hydrogen bearing environments (under given test conditions).

The copper alloys, and especially CuBe with a yield strength of 1100 MPa, are thus suitable for the safe use in high strength applications. In addition, engineers may utilize the high strength properties to design for smaller parts (i.e. miniaturization) given all other positive properties of copper alloys (i.e. spark freedom, cryogenic properties, wear characteristics etc.).

Sensitization of Nickel-base Alloy 690 and the Role of Hydrogen during Oxidation by Water – An Experiment-guided First-principles Study

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Here we explore possible oxidation-driven sensitization processes that would precede stress corrosion cracking (SCC) in Ni-base alloy 690 due to water chemistry under light-water reactor (LWR) conditions. Enhanced susceptibility to SCC result from the composition of the oxide scale formed at steady state becoming increasingly non-uniform, consisting of an inner chromia film (Cr_2O_3) in conjunction with an outer layer composed of $\text{Cr}_2(\text{Ni,Fe})\text{O}_4$ spinel, Fe_2NiO_4 , $\text{Ni}(\text{OH})_2$, and NiO [1-3]. These oxides were experimentally observed at the water-oxide interface owing to the continuous dissolution of elements into the reactor water, particularly chromium [4]. Here, only the inner chromia scale thickness is considered to be at steady state, i.e., at a constant thickness, being controlled by: (a) the chromium activity in the alloy and the effective oxidation potential reflected by the activity of the $\text{Ni}(\text{OH})_2$ and NiO fractions in the overlaying scale, here “nominal $\text{Ni}_2\text{O}(\text{OH})_2$ ”; and (b) the chromium dissolution process taking place at the interface between inner and outer layers.

In as much as H_2O constitutes the *a priori* oxidant by forming the chromia scale, it displays an enthalpy of formation that is similar to the nominal $\text{Ni}_2\text{O}(\text{OH})_2$. During chromium oxidation, this pathway involves NiO acting as a water conveyer, i.e.,



followed by



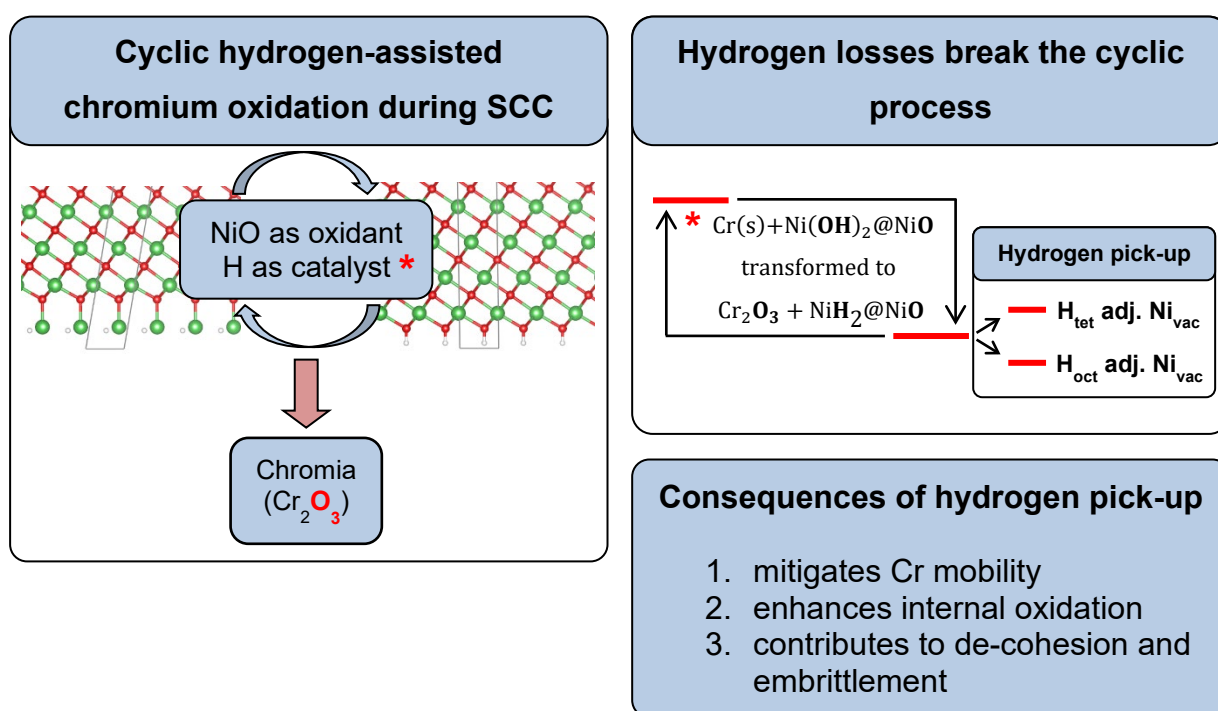
where the fates of hydrogen may include hydrogen evolution, hydrogen absorption in the oxide scale or in the alloy grain boundaries.

In a second oxidation pathway, NiO present in the complex non-protective oxide scale may also act as the oxidant towards chromium, forming, besides the observed chromia scale, elemental nickel precipitates [5], i.e.,



Indeed, R.3 should be energetically more favorable than reaction pathway 1, but it may be kinetically hindered.

In the present study, we explore how the NiO reduction pathway (R3) may be activated by the suggested water conveyer mechanism (R.1 and R.2) and how the residual hydrogen may take a catalytic role in this process. Our results are based on experiment-guided density functional theory calculations. We find that hydrogen may act as a catalyst for the chromia formation at alloy-oxide interfaces. This reaction channel is terminated if hydrogen becomes picked-up by the alloy or forms nickel hydride in the scale. In case of hydrogen pick-up, sensitization towards SCC results from chromium mobility loss favoring internal oxidation along alloy grain boundaries.



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Hydrogen permeation testing parameter exploration for high-entropy alloys

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Abstract

Hydrogen permeation testing standards for metallic materials, such as ASTM G148 and ISO 17081, refer to the use of Devanathan-Stachursky cell-like electrochemical setups. This type of setup consists of two electrochemical cells separated by the testing specimen, that acts as a membrane. One of the cells is aimed to load one side of the specimen with a constant surface hydrogen concentration. The second cell is aimed to oxidize the hydrogen at the other side and monitor the rate at which the hydrogen effuses across the membrane. Both the working parameters at each cell and the membrane thickness are highly material and electrolyte dependent.

The standards and scientific literature guide the effective permeation testing conditions according to the membrane material and the electrolyte. Thorough studies may be found on common industrial alloys, such as iron, stainless steels, or nickel alloys. However, the development of high-entropy alloys (HEAs) offers a wide range of alloying options whose conditions for testing are not always covered by literature. These alloys are composed of several major elements and may show unexpected properties. Behavior of equiatomic and non-equiatomic CoCrFeMnNi alloy in hydrogen environments has been explored in recent years with promising results. This suggests

that HEAs could be used as hydrogen barriers, but each new alloy combination is a new experimental challenge.

To contribute to the study of hydrogen permeation across different HEA families, a consortium composed of two universities, three research institutes, two metallic product manufacturers and an industry-oriented cluster is developing a research project (more information available at <https://www.h2matproject.com/>). As stated above, one of the problems that are being faced is the determination of an effective set of permeation testing parameters for the alloys under study in the project. The aim of this contribution to Eurocorr 2023 is sharing with the rest of the scientific community the advances achieved up to now by the consortium, covering:

- Microstructural and X-Ray diffraction analysis of the manufactured materials.
- Electrochemical study of the alloys to explore the permeation test conditions.
- Hydrogen permeation test results under the testing parameters defined.

Microstructural and corrosion characterization of different types of High Entropy Alloys

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Abstract

In order to storage and transport hydrogen at its required conditions (temperature, pressure, etc.), carbon fiber composites and lower carbon or stainless steels are being used at the moment. However, due to the high capacity of hydrogen to diffuse within the material that contains it, ensuring a high resistance against hydrogen embrittlement still remains a challenge.

High Entropy Alloys (HEAs) were first introduced by Yeh et al.¹, and compositionally defined as alloys that contain at least five or more major metallic elements, each of which has an atomic percentage varying from 5 to 35%. The term high entropy refers to random solid solutions that prevail over intermetallic compounds due to the high configurational entropy arising as a result of mixing multiple components. Unlike steels and other types of alloys, HEAs show outstanding properties in presence of hydrogen, enhancing their strength resistance and ductility, as registered by the literature². Nevertheless, the industrial use of HEAs is limited by both the complexity of the route of processing and its cost.

The aim of this study is to determine the basic corrosion parameters of several HEAs, based in Cantor³ and a Ni-based alloy, as exploratory research of their potential use in the energy industry. To do so, UPV/EHU and other partners from Basque Network of Science, Technology and Innovation are developing these alloys using CALPHAD method, to determine the phases of the multicomponent system. The purpose is to achieve a single-phase solid solution of all the elements, supposedly being the FCC lattice the best structure for hydrogen containing environments; and to establish the optimum melting and casting processes conditions. Once the HEAs are obtained, work will continue with a microstructural and corrosion characterization for each of them. The tests performed include determination of conventional corrosion parameters (OCP, corrosion rate, critical pitting potential and others) determined by electrochemical techniques, using NaCl as electrolyte as suggested by bibliography⁴. Depending on the alloying elements, it is likely to find different behaviors towards corrosion resistance. The project emphasizes in the effect of Al content and the corrosion behavior through the lattice (for instance, interdendritic spaces) for the Cantor HEA; and the performance of the Ni-based HEAs when compared to the previous one.

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Evaluation of hydrogen embrittlement of X65 pipeline steel in high pressure hydrogen gas using tubular samples

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In order to evaluate the suitability of gas pipeline steel structures to safely transport the hydrogen, it is necessary that some appropriate testing methods would be developed to investigate the mechanical properties of steel when exposed to high pressure hydrogen gas. Thus, in this study, a test setup is proposed which allows applying a slow strain rate condition on tubular samples when the internal hole of the sample is exposed to high pressure gas. Different sections of this setup were shown and explained in this research. Slow strain rate tests were carried out in presence and absence of high pressure hydrogen gas to ensure proper interpretation of the material behavior. Tests have been carried out on API5L X65 samples obtained from commercial 12.7 inch pipe. Results of stress-strain curves showed a considerable decrease in total elongation percent after fracture when the sample was tested in high pressure hydrogen gas. Fracture surfaces were analyzed at macro and micro scales, and evaluation of the results after testing in high pressure hydrogen proved a quite brittle fracture with many pores and micro cracks as well as less percent of area reduction compared to sample tested without hydrogen. In overall, current research showed that hydrogen embrittlement of pipeline steels can be successfully studied using tubular sample test setup, and reduce the costs, risks, and complexity of testing in high pressure environments like autoclave.

Tackling corrosion under insulation by retrofitting pipelines with fiber optic sensors

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Objectives

Corrosion Under Insulation (CUI) of insulated pipelines is a widespread industrial problem where Distributed Fiber Optic Sensing (DFOS, [1]) provides a promising alternative to existing monitoring techniques. The monitoring system CUI-CONTROL was specifically developed by Fluves for continuous monitoring of CUI for every meter of pipeline and for easy installation by the plant owner.

A fiber optic cable is attached to the outer cladding of the insulated pipeline. This offers the advantage that the insulation or cladding does not need to be dismantled to install the monitoring system. With a fiber optic cable, Distributed Sensing of both acoustic and temperature events can be done along the entire fiber optic cable.

In this paper, we present the components and functioning of the CUI-CONTROL monitoring system, as well as a case study for BASF.

Results

BASF is one of the frontrunners in applying technological innovations for detecting CUI problems on their plants. A pilot test of CUI-CONTROL was executed at the BASF Antwerp (Belgium) site on a 300 m insulated MDI pipeline section (Figure 1 - left). To monitor the pipeline, a fiber optic cable was attached to the outer cladding of the pipeline. The pipeline has been continuously monitored since August 2021.

Soon after installation, the CUI-CONTROL software detected several potential corrosion spots along the pipeline. Besides pinpointing the spots with a 1 m accuracy, the detection system also provides an estimate of the severity of the corrosion. In April 2022, a BASF team removed the cladding and insulation on the monitored section and inspected the locations that were identified by Fluves' CUI-CONTROL system. The corrosion risk and location matched perfectly with the CUI-CONTROL predictions (Figure 1 - right).

CUI-CONTROL can be applied to other type of infrastructure, such as tanks or reactors. The deployment of CUI-CONTROL on a large storage tank at the Lanxess site in Antwerp (Belgium) illustrates how CUI-CONTROL can be applied to infrastructure other than pipelines.

Conclusions

The current energy crisis exacerbates the need for pipeline corrosion and leak detection for insulated pipelines. Inspection and monitoring should focus on existing pipelines, since these are more prone to problems than newly constructed assets, meaning that the ability to retrofit is crucial. Fluves has developed a monitoring system (CUI-CONTROL) for continuous monitoring of every meter of pipeline on CUI risks, that can be retrofitted at the outside of the pipeline cladding.

During blind tests at the BASF Antwerp site, CUI-CONTROL was able to find the exact locations of potential corrosion sites. The system is able to measure the degree of risk at corrosion with great precision, and the system has the added advantage that it can be applied on the outer layer of the jacketing, without having to dismantle anything. CUI-CONTROL can also be applied to other type of infrastructure, such as tanks or reactors, as is illustrated by the Lanxess case in Antwerp.

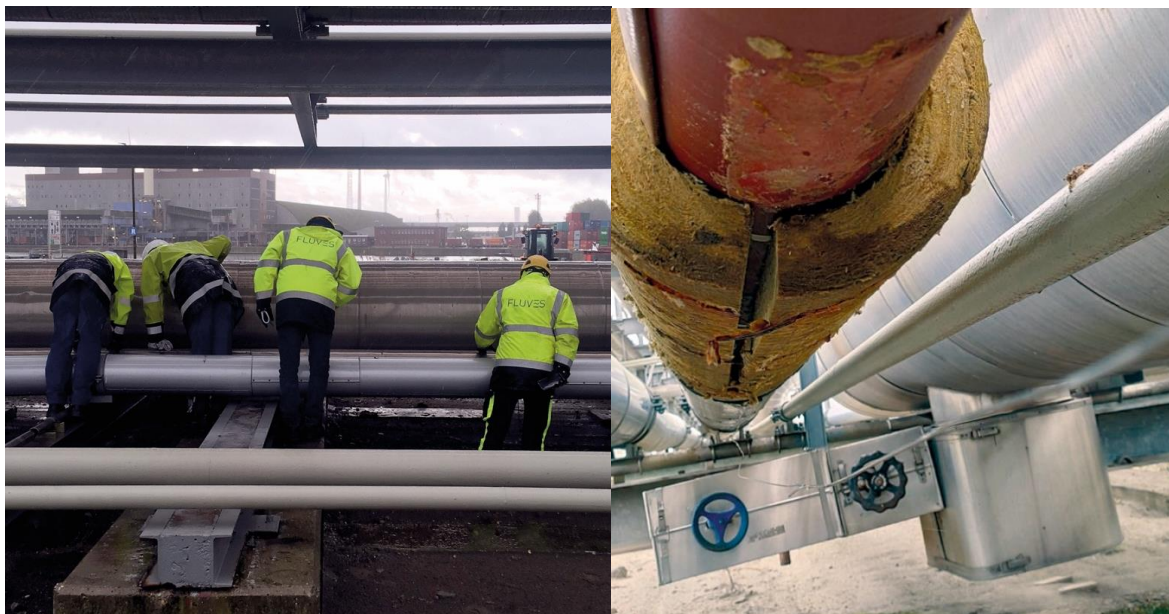


Figure 1: Left: Fluves engineers installing the sensing system on the MDI pipeline at BASF. Right: Corrosion was detected on the exact points that the CUI-CONTROL system pointed out.

Acknowledgements

We gratefully acknowledge BASF for their enthusiasm and support during the whole pilot process and the further roll out of the CUI-CONTROL system.

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(Microbial) Corrosion and cathodic protection of steel sheet pilings in a harbor in The Netherlands

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MIC is the deterioration of metals as a result of metabolic activity of microorganisms. Different genera of microorganisms convert nutrients which are available in soil and water into acids and other corrosive by-products that change the environmental conditions and may accelerate corrosion processes. MIC can be recognized very well by its typical tubercles or corrosion products, being relatively soft layered structures consisting of orange iron hydroxide products and black products containing iron sulfide. These layers are only weakly attached to the steel surface; underneath this the steel is shiny with pits, craters and holes. To protect structures such as sheet piles in marine and harbour environments, a thorough failure analysis and diagnosis is essential to conclude if MIC is really the root cause of the damage observed. On basis of the results of a comprehensive failure analysis package proper recommendations for appropriate mitigation methods can be given.

During inspection works in a harbor in the Netherlands pits and full perforations were detected in steel sheet pilings in an older part of the harbor, whereas structures that were recently installed in this same harbor showed no damages. Next to holes, reddish brown spots on the surface of the steel sheet pilings were found. A complete failure analysis, including material cross sections, SEM analyses, microbial investigations and wall thickness measurements was carried out to clarify the reason for the present failure. Additionally, potential measurements were done to investigate the performance and protective capacity of sacrificial anodes which are placed on various parts of the structure. Results of this failure case investigation will be presented.

Insight into the interaction between chemical groups in polymer matrices and organic inhibitors

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Anti-corrosion coating formulations are usually made to have two functions: passive and active protection. Active protection is normally provided by additives in the form of corrosion inhibitors which are released when needed, e.g. at damaged locations exposing the underlying metal surface. The number of reported efficient corrosion inhibitors in solution is relatively large. Nevertheless, (direct) incorporation of inhibitors, and more significantly organic inhibitors, in organic coatings has proven complex thereby leading to unsatisfying corrosion efficiencies. A probable explanation for this effect is the negative cross-chemical reactivity of the binder and the inhibitor which limits the inhibitor release potential from the coating. However, the specific interactions are not well reported or understood. As a potential strategy to overcome this, we proposed in previous works [1] the creation of internal networks with reduced matrix-inhibitor interactions and increased inhibitor transport properties. Of particular interest within the myriad of organic corrosion inhibitors are those containing S-H, N-H and O-H groups

In this work, we used the versatility of polymethacrylate chemistry to introduce a range of chemical moieties and study the interactions with 2,5-Dimercapto-1,3,4-thiadiazole (H-DMTD) and 1,3,4-Thiadiazole-2,5-dithiol dipotassium salt inhibitors (K-DMTD) and the level at which these interactions affect the inhibitor release. To this aim, we also controlled the state of the inhibitor in the matrix (molecularly dispersed vs. micron size phase separation) and studied its impact on inhibitor release and active corrosion protection at damaged locations on coated-AA2024 alloys. Morphological analysis using Laser confocal microscopy, Raman and μ -FTIR mapping and the corresponding release behaviour using real-time UV/Vis spectroscopy analysis and electrochemistry unveiled the effect of basic main-chain interaction with small inhibitor molecules and phase segregation affecting inhibitor release.

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Hot corrosion behaviors of Inconel 718 superalloy and its aluminide coating under environments containing solid NaCl and water vapor

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Abstract:

Inconel 718 alloy is a typical Ni-based superalloy that has been widely used as key components in gas turbine and aerospace engines due to its outstanding mechanical properties and oxidation resistance at elevated temperature. However, with the increase in human activities in marine environment, it has been found that the corrosion of turbine engines is much more severe in marine environment than that in inland areas due to the fact of the air in marine environment is humid and contains large amounts of sea salts, mainly composed of NaCl. In such an environment, the internal cooling passages of turbine blade are quite susceptible to corrosion during service, leading to clogging and overheating. In order to slow down the corrosion attack induced by the solid NaCl and water vapour, there is an urgent requirement for a protective coating can be applied to the internal cooling passages.

In this study, the aluminide coating was deposited on the Inconel 718 alloy using CVD method. After depositing NaCl film on samples, hot corrosion tests were conducted in air and water vapour at 750 °C, respectively. For the sake of comparison, tests on Inconel 718 alloy were also carried out under the same conditions. The results indicate that the substrate alloy shows poor corrosion resistance in both corrosive environments, particularly in air + NaCl environment. The corrosion products formed on the surface are mainly composed of porous and less protective NiO and Fe₂O₃. In contrast, the aluminide coating performs well and provides relatively good protection for the substrate alloy. In air + NaCl environment, a thin layer of α -Al₂O₃ developed on the coating surface in the early stage of corrosion. Over time, severe internal corrosion was observed beneath the corrosion scale, but the coating could still act as a barrier to mitigate the attack of NaCl to a certain extent. In air + NaCl + water vapor environment, the corrosion attack suffered by the aluminide coating is alleviated instead. The coating beneath the corrosion

zone is basically intact with no visible defects, and it can still provide protection for the substrate alloy. Based on the analyses of the microstructure of corrosion products, the corrosion mechanism of the Inconel 718 substrate and its aluminide coating in both corrosive environments was discussed.

Comparative study on high temperature oxidation behavior of deformable austempered ductile iron with and without protective Al rich coatings

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Coupons of Deformable Austempered Ductile Iron (DADI) were coated with the slurry of two compositions: pure Al and Al doped with Cr, composed of the micro sized particles of those metals. 60mg/cm² of coating applied provided quite thick overlay surface layer. Subsequent high temperature annealing, using a specially elaborated scheme of treatment, developed the protective aluminized diffusion layers on the studied substrates. High temperature oxidation properties of bare (uncoated), Al and AlCr coated DADI were comparatively studied at 650°C in air for up to 200 hours. Discontinuous oxidation kinetics showed that the weight gain of Fe rich substrates of DADI with pure Al coatings on them have decreased higher than by the factor of 30 when compared with the bare DADI. Cr dopped Al slurry coatings performed considerably worse than the pure Al coatings, and improved high temperature resistance of the substrate only by the factor of 4. Oxygen uptake expressed in the respective weight gain values are given on the Fig. 1.

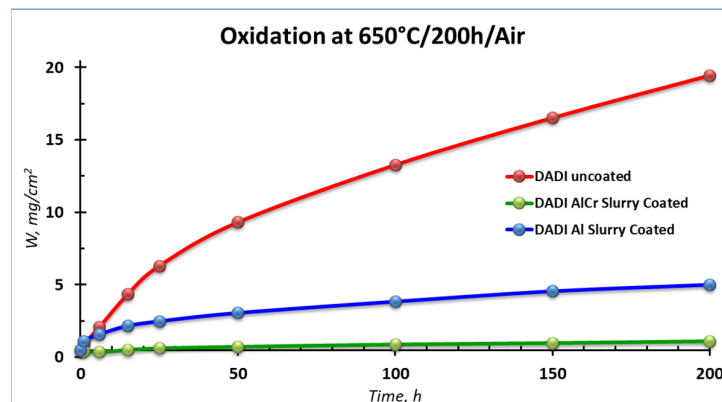


Fig. 1. Weight gain vs. time dependence for uncoated, Al and AlCr coated DADI specimens after oxidation in air for 200 hours at 650°C.

When oxidized the uncoated DADI formed exclusively iron oxides (Fe_2O_3 , Fe_3O_4), which are known to be fast growing, insufficiently dense and thus non-protective

oxide species. Pure Al slurry coatings developed a decent thickness of aluminized zone on the top of DADI, which induced formation of mostly Al containing oxides (Al_2O_3 , Al_3O_4). AlCr coating's less favorable performance is attributed to Al content in the coating that was decreased on the expense of adding Cr powder to the slurry, which at the annealing as well as oxidation temperatures adopted did not contribute, rather acted as a natural barrier for Al to diffuse into the iron substrate. Thus, protective abilities of the latter coating was not as profound as pure Al one's.

To study the microstructural peculiarities of the developed oxide layers (surface and cross sections) SEM/EDS and XRD methods were utilized. The objective of this recent work was the attempt to improve high temperature oxidation resistance of DADI, which was uncarefully accomplished. DADI is a type of cast iron, possessing outstanding mechanical properties paired with not that of a great chemical resistance when exposed to the elevated temperatures. As a summary of an experimental work performed, it is worth mentioning that aluminization with the pure Al slurry using the spherical microparticles of the latter brings out the best of the substrate material, rather than when it is doped with Cr.

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Corrosion resistance of additively manufactured high strength aluminum alloys

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In this study, the corrosion resistance of two newly designed additively manufactured (AM) Al-Mn alloys was investigated in artificial (sodium chloride 3.5 wt%) and natural seawater. Electrochemical and immersion techniques were used to assess the short-term and long-term corrosion behavior of these new alloys and compared it to a benchmark alloy of Al-Si-Mg. The corrosion resistance of the Al alloys was investigated in three different environments/exposure scenarios: continuously immersed in artificial sea water, continuously and alternatively immersed in natural seawater. The alloys were evaluated as-printed and after heat-treatment. A combination of electrochemical and gravimetric analysis was utilized for assessing the corrosion protection.

In all environments Al-Mn alloys have a higher corrosion resistance than Al-Si-Mg regardless of the assessment technique used or exposure environment. The passive film resistance and corrosion current densities for the Al-Mn alloys were two orders of magnitudes higher than the tested Al-Si-Mg alloy. All materials were sensitive to pitting corrosion but the critical pitting potentials for the Al-Mn alloys were higher than the Al-Si-Mg alloy. The evolution of the passive film electrochemical impedance spectroscopy response was different for continuous immersion in natural seawater compared to alternate immersion and continuous immersion in artificial seawater. This means the surface of the alloys is behaving differently in one of the environments compared to the other two. A significant shift in open circuit potential was also observed for continuous immersion in natural seawater but not in the other two.

These results showed promising corrosion resistance of new AM high-strength Al-Mn alloys and highlighted the importance of knowledge on corrosion protection capability in more than continuously immersed environments.

Effect of build orientation on the corrosion behaviour of additively manufactured 316L stainless steel on 316L stainless steel

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Abstract

The corrosion behaviour of 316L stainless steel made through laser powder bed fusion was studied with respect to building orientation. The samples were printed at various angles (0°, 45°, 90°) and microstructures were characterized through X-Ray Diffraction (XRD) analysis, Scanning Electron Microscopy (SEM), and Optical Microscope (OM). The electrochemical results using 3.5% NaCl solution revealed that both horizontal and vertical samples displayed remarkable corrosion resistance due to the higher amount of β phase and lower presence of acicular α martensite. The mechanical properties of all samples were determined through hardness tests, and the sample with a building orientation of 45° showed the highest hardness. Therefore, the different build orientations resulted in a distinct anisotropy.

3D Printed Stainless Steel Biomedical Implant Corrosion Resistance Study

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The technologies of Additive Manufacturing AM continue to evolve making it the dominant manufacturing method of several products in different industries including biomedical metallic implants manufacturing. The purpose of this paper is to study the corrosion resistance performance and requirements of AM biomedical implants as well as to characterize the corrosion behavior of Additive Manufactured 316L stainless steel in simulated physiological environment. The corrosion performance and mechanical properties of additive manufactured 316L stainless steel material in simulated physiological environment was studied. As a revolutionary manufacturing process, additive manufacturing creates three-dimensional objects by the fusion of successive layers of metallic powder using computer-controlled heat sources such as lasers or electron beams. Geometries with high complexity patterns can be produced using this net-shape manufacturing process. It brings solutions to a wide spectrum of applications in different industries such as aerospace, energy production and medical devices. However, the material properties produced by the repetitive powder deposition and curing process has a major impact on the reliability of the additive manufactured devices; especially at aggressive environments. In the efforts of improving the reliability of Additive Manufactured biomedical devices, this research focuses on studying the corrosion, microstructural and mechanical properties of Additive Manufactured 316L stainless steel. It evaluates corrosion resistance through characterizing the corrosion behavior using cyclic anodic polarization tests in simulated physiological environment. In this experiment, the properties of 316L stainless steel parts manufactured using Selective Laser Melting SLM technique have been studied. Cyclic potentiodynamic polarization test indicated that additive manufactured materials had lower corrosion resistance than the wrought stainless steel parts of the same grade. This was evident by the difficulty of regenerating a stable and protective passive oxide layer at room temperature as well as the instability of passivation at higher temperatures. Moreover, the additive manufactured samples showed a higher yield strength than the wrought samples but lower values for elongation and ultimate tensile stress.

Corrosion of LD Converter Gas Pipe in Condensate Environment

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Abstract

In the steel production process, a large amount of by-product gas is generated depending on the process. By-product gases generated are classified into coke oven gas (COG), blast furnace gas (BFG) and Linze Donawitz gas (LDG) according to each process.

Recently, steelworks are recovering such by-product gas and using it again as an energy source to reduce electricity consumption and cost saving. However, on the inner surface of these pipelines, corrosion is slowly developed by corrosive environment, and corrosion can be accelerated under special conditions.

In case of LDG pipelines, corrosion is occurred by carbon dioxide contained in a converter gas and cooling water for decreasing temperature of gas. In particular, corrosion of LDG pipelines is occurred to be due to acidification of the condensate water. It is because a large amount of mist generated during cooling process by water absorbs CO₂ that is one of the main components of LDG.

For this reason, in order to use the pipelines stably for a long period of time, it is necessary to identify the corrosive environment to which it is exposed, in addition, anticorrosion technology that can control the corrosion the internal corrosion of pipelines is required.

In this study, the corrosion level of actual LDG pipelines was identified and the experiment was conducted by simulating the corrosion environment in order to analyze the cause of the internal corrosion of LDG pipelines. So as to improve LDG pipelines corrosion problems, the corrosion rate according to pH change was measured, and the degree of coating deterioration according to the epoxy coating thickness was analyzed. In addition, the effect of weld zone which are vulnerable to corrosion was also evaluated. As a result, the factors causing the internal corrosion of LDG pipelines were verified, and the optimal management range that could inhibit corrosion was confirmed by controlling the pH of the condensate water and the thickness of the epoxy coating.

The impact of fluoride ion on the local corrosion of stainless steel in a phosphoric medium: An electrochemical investigation

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The corrosion of stainless steel (SS) equipment during phosphoric acid production is a significant concern in this industry. The main corrosive species in this environment are highly reactive halides, such as fluoride ions due to their specific physical and chemical characteristics. This study utilized electrochemical methods, such as cyclic polarization to identify the influence of F^- on parameters associated with pitting corrosion (E_{pit} , E_{rep} , etc.), and electrochemical impedance spectroscopy to gain a thorough comprehension of the aggressive impact of fluoride ions at the metal/solution interface. Using cyclic potentiodynamic polarization, F^- has been shown to increase critical and passive currents and shift the pitting corrosion potential to lower values. These results indicate that the presence of fluoride in the phosphoric acid solution reduces the resistance to pitting. Furthermore, electrochemical impedance spectroscopy demonstrated that the film resistance significantly decreased with the introduction of fluoride ions. This was attributed to the aggressive behavior of F^- ions in destabilizing the passive film, thus reducing its protective capacity.

Effect of fluoride ion concentration on pitting resistance

The presence of aggressive ions in corrosive media, such as halides, may cause the breakdown of the protective film of austenitic stainless steel, resulting in pitting as a form of localized corrosion. The purpose of this research is to investigate the effect of F^- on the pitting of SS by increasing the concentration of fluoride ions in the phosphoric medium.