The influence of a Zr-based conversion treatment on interfacial bonding strength and stability of epoxy coated carbon steel

Sababi, M.; Terryn, H.A.; Mol, J. M C

DOI
10.1016/j.porgcoat.2016.11.016

Publication date
2017

Document Version
Final published version

Published in
Progress in Organic Coatings

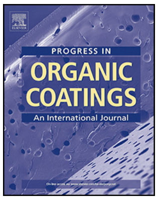
Citation (APA)
Sababi, M., Terryn, H. A., & Mol, J. M. C. (2017). The influence of a Zr-based conversion treatment on interfacial bonding strength and stability of epoxy coated carbon steel. *Progress in Organic Coatings*, *105*, 29-36. https://doi.org/10.1016/j.porgcoat.2016.11.016

Progress in Organic Coatings 105 (2017) 29–36

Contents lists available at ScienceDirect

Progress in Organic Coatings

journal homepage: www.elsevier.com/locate/porgcoat



The influence of a Zr-based conversion treatment on interfacial bonding strength and stability of epoxy coated carbon steel

M. Sababi [a,b], H. Terryn [b,c], J.M.C. Mol [b,*]

[a] Materials Innovation Institute (M2i), Elektronicaweg 25, 2628 XG Delft, The Netherlands
[b] Delft University of Technology, Department of Materials Science and Engineering, Mekelweg 2, 2628 CD Delft, The Netherlands
[c] Vrije Universiteit Brussel, Department of Electrochemical and Surface Engineering, Pleinlaan 2, B-1050 Brussels, Belgium

ARTICLE INFO

Article history:
Received 21 July 2016
Received in revised form 21 October 2016
Accepted 10 November 2016
Available online 8 January 2017

Keywords:
Zr-based treatment
Fusion bonded epoxy
Carbon steel
Interfacial bonding
Scanning Kelvin probe
ATR-FTIR

ABSTRACT

The effect of a zirconium (Zr)-based pretreatment on interfacial bonding properties of a fusion bonded epoxy (FBE) coating on carbon steel is investigated. The initiation and kinetics of delamination of epoxy coatings applied on differently pretreated carbon steel surfaces is studied with scanning Kelvin probe (SKP). In-situ attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) is applied to study interfacial coating-oxide chemistry changes upon electrolyte diffusion towards the buried interface. Corresponding coating degradation is analyzed with the use of electrochemical impedance spectroscopy (EIS). pull off experiments showed a clear beneficial effect of the Zr-based pretreatment improving the dry and wet adhesion properties of the fusion bonded epoxy coating to the carbon steel surface particularly upon exposure to wet and corrosive conditions. This increase in interfacial bonding stability is confirmed by the ATR-FTIR and EIS experiments and delayed and slower delamination was observed in the SKP measurements.

1. Introduction

Carbon steels are amongst the most widely used structural material in a wide variety of industries due to a good combination of strength, ductility, weldability and reasonable cost in comparison to alternative structural materials. On the other hand, bare carbon steels show low corrosion resistance in corrosive operating conditions and in those cases need to be applied together with additional protective methods such as cathodic protection [1–5], inhibitors [6–10] or organic coatings [11–15] depending on the application.

Organic coatings can significantly improve the corrosion resistance of the underlying metal by providing a passive barrier layer between the protected metal and corrosive environment. When exposed to an aqueous corrosive environment, water and corrosive species may diffuse and migrate through the coating and, especially once the coating is damaged, show mobility along the metal/polymer interface causing loss of adhesion and delamination which is considered to be one of the most important mechanisms of polymer protection failure [16–21]. The loss of adhesion is directly related with (electro)chemical degradation at the metal/polymer interface [19,22,23]. Surface chemistry modification of the metal can increase the chemical binding energy between coating and substrate as well as the electrochemical reaction energy needed for delamination at the metal/polymer interface and consequently improve the interfacial bonding under dry, wet and corrosive conditions [24].

Generally, phosphating is the most common pretreatment for coated carbon steel, but in the last decade there is more concern about the energy cost, disposal and environmental impact related with this process [25]. Zirconium (Zr)-based surface treatment is considered to represent a viable replacement which showed promising results for improving adhesion between organic coating and carbon steel [26–29]. Cerezo et al. [30–33] performed a thorough study about Zr-based conversion layer formation on different metals such as aluminum alloy, galvanized steel and mild carbon steel. They have studied mechanisms and kinetics of Zr-based conversion layer formation from hexafluorozirconic acid-based solution. It was shown that the convection in the conversion bath and the initial metal surface chemistry can be a controlling factor on Zr-based conversion layer formation for different metals but carbon steel showed to be less influenced by these factors. This is promising for industrial application aiming for a robust and reproducible process. Khun et al. [28,29] studied the effect of hexaflurozirconic acid treatment on corrosion protection and adhesion strength of polyurethane and epoxy coatings applied on carbon steel and zinc showed that the Zr-based pretreatment resulted in enhanced cor-

---

* Corresponding author.
E-mail address: J.M.C.Mol@tudelft.nl (J.M.C. Mol).

http://dx.doi.org/10.1016/j.porgcoat.2016.11.016
0300-9440/© 2017 Elsevier B.V. All rights reserved.

rosion protection and adhesion performance of the organic coatings [34].

In order to understand the effect of the Zr-based layer chemistry on durable adhesion of fusion bonded epoxy coating on carbon steel in more detail, an ATR-FTIR system in Kretschmann configuration is used [35]. In this technique a thin layer of metal is deposited on an internal reflection element (IRE), covered with an organic coating and exposed to an electrolyte subsequently. The buried metal/polymer interface can be reached with an IR beam passing through the thin deposited metal layer. IR peak intensities are recorded in-situ with time of exposure and can be correlated to chemical changes at the metal/polymer interface [36–39]. The IR beam penetration at the metal/polymer interface can be controlled by some analysis parameters e.g. the infrared wavelength, angle of incidence and the media refractive index [36] and can be considerably decreased due to the presence of the deposited layer at the interface [40]. Scanning Kelvin probe (SKP) is used to measure delamination kinetic at the metal/polymer interface and to study the effect of the Zr-based conversion treatment on delamination kinetic of epoxy coating from a carbon steel surface. In this technique, a metallic reference electrode vibrates in the vicinity of the surface and allows to measure corrosion potential with high spatial resolution even under the insulating organic coating without touching or destruction of the surface [41–45]. Corrosion potential distributions have been measured with this technique from an artificial defect in order to investigate the delamination mechanism and kinetics which could be affected by Zr-based conversion treatment. Moreover, electrochemical impedance spectroscopy (EIS) is used to study deterioration and corrosion of coated metals. This technique works based on the application of a small continuous perturbed electrical voltage and measures current response without changing the steady state condition of the system. EIS is very useful because it is a non-destructive method which can provide several system parameters such as organic coating resistance, capacitance and charge transfer reactions at the metal/polymer interface upon coating degradation [46,47].

Overall, the research approach and results presented in the manuscript provides (*i*) chemical information of key chemical compounds at carbon steel/fusion bonded epoxy interface and chemical disbonding due to water and aggressive ions at the interface; (*ii*) delamination propagation rates at the carbon steel/fusion bonded epoxy interface from artificial defects exposed to a corrosive environment; (*iii*) degradation of the fusion bonded epoxy. In addition, the effect of the Zr-based treatment is investigated with similar techniques to assess the effect of the treatment on durability of fusion bonded epoxy coatings to carbon steel.

2. Experimental

2.1. Materials

Cold rolled carbon steel ($C \leq 0.1$ wt.%, $Mn \leq 0.50$ wt.%, $P \leq 0.030$ wt.%, $S \leq 0.035$ wt.%, balance Fe) was used as a substrate. The Zr-based chemical conversion solution containing dihydrogen hexafluorozirconate, MAVOMcoat 1742 CC, was supplied by MAVOM Chemie BV, The Netherlands. A commercial fusion bonded epoxy resin, Resicoat R-556, was supplied by AkzoNobel.

2.2. Coating preparation

Prior to application of the coatings, the carbon steel surfaces with a dimension of 2.5 cm × 2.5 cm × 0.2 cm were abraded with SiC grinding paper up to 1200-grit, followed by final polishing using alumina suspension with particle size of 3 and 1 μm respectively, then cleaned ultrasonically in acetone for at least five minutes, rinsed with ethanol and dried with a gentle stream of nitrogen gas. Substrates were polished in order to eliminate an additional mechanical interlocking effect between epoxy coating and substrate, enabling to examine the chemical effect of the Zr-based treatment only.

The Zr-based pretreatment was performed by immersion (dip application) of carbon steel samples in the conversion bath. The bath was prepared to contain almost 100 mg/L zirconia, pH adjusted to ∼5 and it was magnetically stirred at 300 rpm to establish a uniform distribution of chemical components in the solution. The carbon steel specimens were immersed in the bath for one minute at room temperature and rinsed thoroughly with deionised water to remove the remaining Zr-based solution from the surfaces, then dried with a gentle nitrogen gas stream.

The epoxy coating was prepared by casting epoxy powder on the substrate. Then, it was cured in the oven for 2 min at 225 °C, and cooled down to ambient temperature. The initial thickness was around 300 μm which afterwards was gently abraded back to appropriate thickness. The final coating thickness was measured by using a magnetic flux thickness meter, Gaussmeter HT201, to be 10 ± 0.7 μm for all of the coatings.

2.3. Testing methods and equipment

2.3.1. Scanning Kelvin probe (SKP)

The SKP delamination measurements were performed on coated steel as shown in Fig. 1. A part of the epoxy coating was pulled off made possible by putting a thin adhesive layer at one side of the carbon steel prior to the application of the fusion bonded epoxy coating. Silicon rubber was applied at the edge of the pulled area to create a reservoir which could contain almost 1 cm^3 of a sodium chloride aqueous solution during the experiment. The sample was placed in the humidity chamber of the Kelvin probe instrument (SKP5050) for at least two hours and allowed to equilibrate at a humidity of 85%. Afterwards, 0.1 M sodium chloride solution was added to the defect to initiate delamination. The SKP probe was scanned over the epoxy coating along a 10 mm line from the defect edge towards the intact area. The probe was set to vibrate at a 68 Hz frequency and amplitude of 30 μm, the probe diameter was 50 μm. The height was controlled with high-gain current to voltage convertor and set to 300 ± 5 μm to maintain equal distance from the surface over the scanning line. Prior to each SKP experiment, the probe was calibrated in order to avoid a potential shift of the probe. A $Cu/CuSO_4$ reference electrode was used and the measured potential was converted to the standard hydrogen electrode potential (0.316 V vs SHE). The calibration procedure is explained in detail elsewhere [42]. All of the SKP measurements were performed at room temperature and controlled humidity of 85%.

2.3.2. In-situ attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR)

The interfacial bonding stability at the fusion bonded epoxy/carbon steel interface was measured with ATR-FTIR in Kretschmann configuration as shown schematically in Fig. 2. Carbon steel was used as deposition source and deposited on a Ge crystal target with a Balzers BAE 250 high vacuum evaporating system in order to mimic similar chemical composition of carbon steel on the crystal. The film thickness as determined by atomic force microscopy was found to be 15 ± 2 nm. Subsequently, the deposited layer was Zr-treated under similar Zr-based pretreatment conditions explained in the coating preparation section, or it was not treated (reference sample). Afterwards, a thin layer of fusion bonded epoxy was applied on treated and untreated substrates under similar conditions explained in the coating preparation section. The coating thickness was controlled

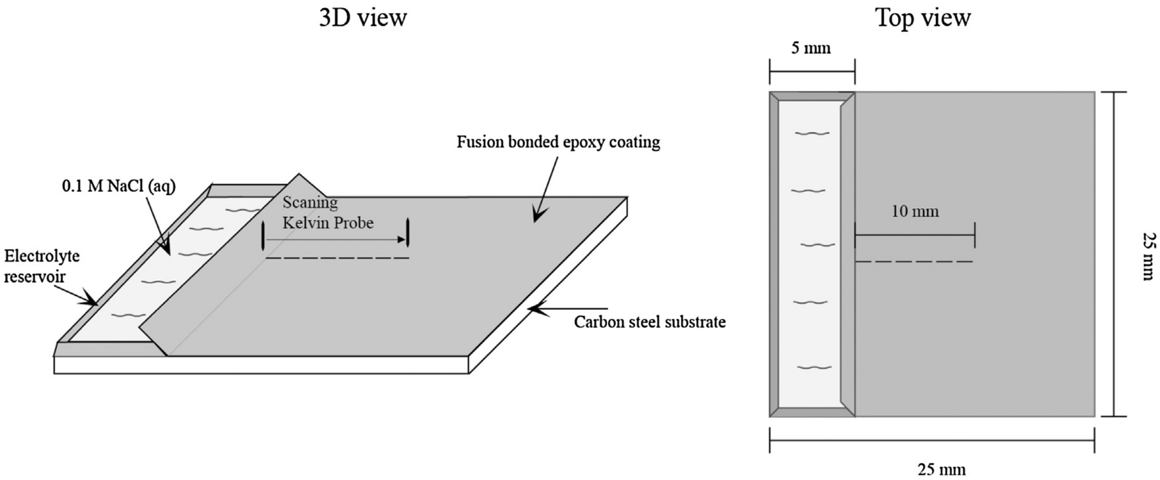


Fig. 1. Schematic illustration of the scanning Kelvin probe specimen configuration and measurement set-up.

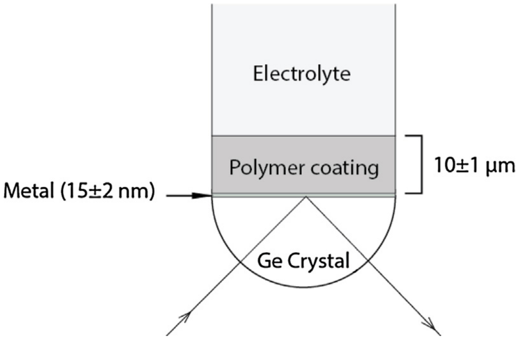


Fig. 2. Schematic setup for analysing interfacial bonding chemistry at the metal/polymer coating interface with an ATR-FTIR experimental method based on Kretschmann geometry.

to be 10 ± 1 µm. The IR measurements were performed with a Thermo Nicolet Nexus Fourier transform infrared spectroscope (FTIR) with mercury-cadmium-telluride as a liquid nitrogen cooled detector. The measuring chamber was purged with nitrogen gas. A Seagull multipurpose reflection accessory was used for ATR measurements in Kretschmann geometry configuration. The incident angle of p-polarized IR radiation was set to 65° with a of KRS-5 wire grid polarizer. The spectra were collected in the region of 4000–600 cm^{-1} at a resolution of 8 cm^{-1} and 1000 scans per spectrum. The spectrum is collected in absorbance format, $-\log(R/R_0)$, where R and R_0 are the reflectance from sample and background respectively. The background spectrum was collected before exposing the coated sample in the electrolyte. A Smart SAGA^{TM} (Specular Apertured Grazing Angle) accessory with fixed incident angle of 80° was used for infrared reflection absorption spectroscopy (IRRAS). The spectra are recorded in absorbance mode and polished carbon steel surface was used for background collection.

2.3.3. *Electrochemical impedance spectroscopy (EIS)*

EIS was performed to evaluate the electrolyte penetration based degradation of the coating systems. A three-electrode electrochemical cell with a saturated calomel electrode (SCE) reference electrode and a Pt mesh counter electrode was used. The exposed area was 1 cm^2. A Solartron Potentiostat/Galvanostat 1287A with a frequency response analyser 1255 instrument was used for the EIS measurements in a frequency range of 10^4 to 10^{-2} Hz at voltage amplitude of 10 mV. The exposure was executed in a 0.1 M NaCl solution. Measurements were repeated at least three times to confirm the reproducibility.

2.3.4. *De-adhesion test*

The adhesion of the epoxy coating was evaluated with an Elcometer 510 automatic pull off adhesion gauge. The pull rate was set to its lowest possible value, 0.1 MPa/s, in order not to introduce any imbalance and sudden breakage. Dollies with a 10 mm diameter were used for adhesion test. Dollies were attached with Araldite standard two-part epoxy and cured at room temperature for three days. At least three measurements were performed for each sample condition.

3. Results and discussion

3.1. *SKP*

The SKP potential measurements were performed to study the effect of Zr-based treatment on delamination initiation and kinetics of the epoxy coating from the carbon steel. In Fig. 3 the potential profiles as a function of time for Zr-treated and untreated samples are shown. The recorded profiles have the typical form for cathodic delamination reported in previous works [48,49]. In general, two potential levels can be observed: a potential in the delaminated area and a potential at the intact, coated interface. In Fig. 3a potential level for the delaminated area of the reference sample without Zr-based treatment reach lower than $-0.4\,V_{SHE}$ within an hour upon addition of the aqueous sodium chloride solution to the defect area. Subsequently, the position of the potential step shifts further into the initially intact part of the epoxy coated surface. The potential profiles exhibit different potential regions. The potential range just next to the coating defect area shows almost similar potentials to the corrosion potential of bare carbon steel and its potential slightly increases towards the still adhering part of the coating [50–52]. It is followed by a sharp increase in potential related to the position of the delamination front, followed by a plateau potential indicating the presence of a non-delaminated coating [53]. The delamination front is moving forward, away from the coating defect with time. A similar potential profile measurement was performed for the epoxy coated Zr-treated sample. Fig. 3b shows a different potential profile as a function of time for a Zr-treated sample in comparison with a sample without treatment (Fig. 3a). It is clear that after one hour of exposure, the potential right next to the coating defect higher for the Zr-treated sample in comparison with that for the untreated sample (Fig. 3a). Furthermore, the potential value next to the defect area decreases with time but still remains higher than that for the untreated sample after one day. This is related to the delay time for corrosion driven coating delamination

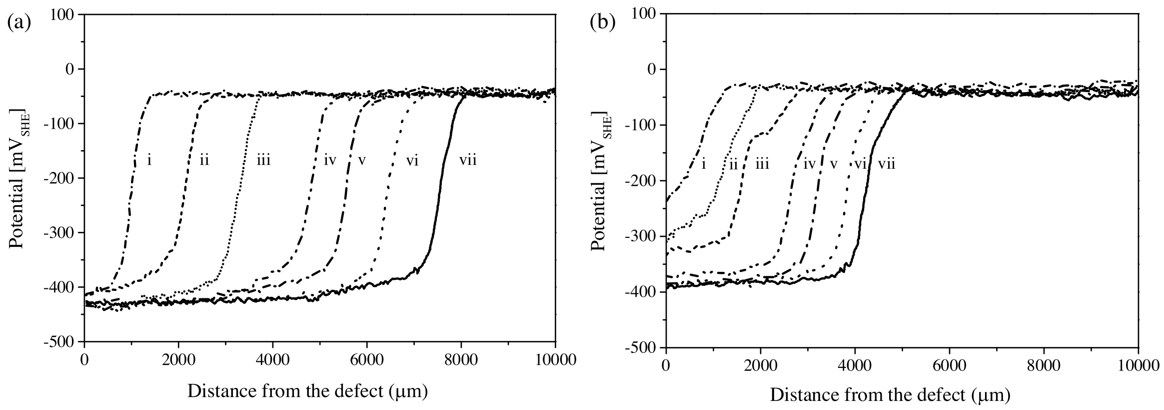


Fig. 3. Potential distribution vs. distance from the defect edge for different times as indicated; (a) epoxy coated carbon steel, (b) epoxy coated carbon steel with Zr-based conversion layer at the interface. Measuring time: i = 1, ii = 7, iii = 18, iv = 25, v = 35, vi = 45 and vii = 56 h. Electrolyte concentration in the defect is 0.1 M NaCl and test environment humidity 85%.

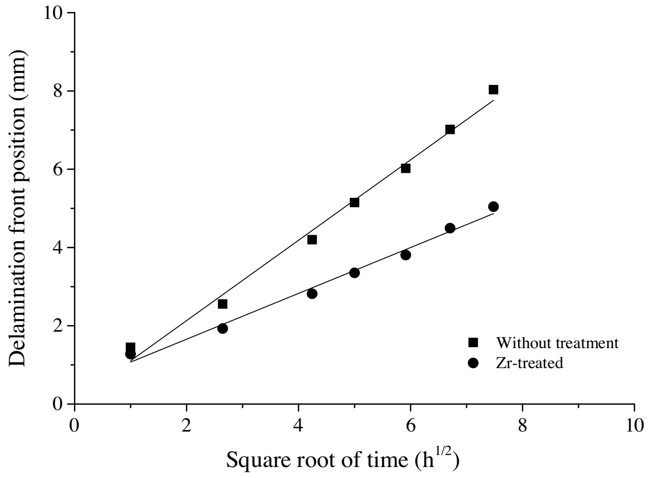


Fig. 4. Delamination front position vs. square root of time, for Zr-treated (●) and untreated samples (■).

at the pretreated and hence durable metal-polymer interface prior to local electrochemical activity [42,48,54]. Also, the potential in the delaminated area shows a difference between the untreated and Zr-treated samples. The potential in the delaminated area for the Zr-treated sample shows a higher potential of $-237 \pm 3\,\mathrm{mV_{SHE}}$ in comparison with $-413 \pm 3\,\mathrm{mV_{SHE}}$ for the untreated sample within one hour of exposure. Moreover, the potential in the delaminated area for the Zr-treated sample decreases with the time towards the potential of the untreated sample in the defect. However, the equilibrated potential in the defect area is higher than the potential for the untreated sample ($-386 \pm 3\,\mathrm{mV_{SHE}}$ for the Zr-treated sample as compared to $-429 \pm 3\,\mathrm{mV_{SHE}}$) after 56 h of exposure. Hence the potential difference at the delamination front will be lower due to the Zr-based treatment which reduces the driving force and suppresses the delamination propagation kinetics of the coating for the Zr-treated sample.

Delamination front positions for different samples are shown as a function of the square root of time in Fig. 4. The linear relation of delamination propagation with square root of time for both samples indicates that the delamination is under control of cation ($\mathrm{Na^+}$) mobility at the interface [55]. Average delamination rates are 1025 and 585 $\mu\mathrm{m/h^{0.5}}$ for untreated and Zr-treated carbon steel respectively. The results clearly show that the Zr-based treatment effectively decreases the delamination rate of epoxy coated carbon steel samples. Therefore, the Zr-based conversion layer at the epoxy/carbon steel interface can hinder cation ($\mathrm{Na^+}$) mobility from the anodic region located at the defect area. On the other hand, the Zr-based treatment increases the corrosion potential in the delaminated area which can leads to a lower oxygen reduction rate, hence decreasing the hydroxyl ion formation at the delamination front in the cathodic region [18,48]. It is good to mention that the results presented here are in full agreement with the work of Khun et al. who studied the effect of the hexafluorozirconic acid pretreatment on cathodic delamination of epoxy coating from carbon steel substrates and showed that the treatment can improve delamination and corrosion resistance of carbon steel at neutral pH, reporting this to be due to better interfacial adhesion [28,29].

3.2. ATR-FTIR

To obtain a better understanding of the effect of Zr-based conversion treatment on buried fusion bonded epoxy/carbon steel interfaces, in-situ ATR-FTIR measurements with Kretschmann geometry setup were performed. The hidden interface between the Zr-based conversion coated carbon steel surface and epoxy coating was investigated upon exposure to sodium chloride solution. Similar experiments without a Zr-based conversion layer at the fusion bonded epoxy/carbon steel interface were performed as a reference. Fig. 5 shows selected IR-spectra for the reference sample and Zr-treated samples upon exposure to electrolyte, respectively. After exposure to electrolyte, both IR-spectra show a broad and strong band between 3700 and 3000 $\mathrm{cm^{-1}}$ which increases with exposure time. This band may be assigned to symmetric and asymmetric stretching vibration of water molecules [56], and/or arise from hydroxyl (—OH) stretching vibration due to metal hydroxide formation at the interface [57,58]. The other distinctly rising peak observed in both spectra between 1700 and 1500 $\mathrm{cm^{-1}}$ with a maximum around 1650 $\mathrm{cm^{-1}}$ is indicative of water bending vibration (H—O—H) [56]. Moreover, it is remarkable to observe the bands indicating frustrated rotation of water molecules or libration modes of liquid water molecules in the range below ~1000 $\mathrm{cm^{-1}}$ only for the untreated reference sample [59]. The comparison of these two spectra gives valuable information regarding the effect of the Zr-based treatment at the hidden fusion bonded epoxy/carbon steel interface. Fig. 5c shows the absorption peak intensity at 3450 and 1650 $\mathrm{cm^{-1}}$ corresponding to the hydroxide and water molecule vibrations as a function of time. For the reference sample, after almost seven hours of exposure, a broad band at ~3450 $\mathrm{cm^{-1}}$ appears due to stretching vibration of water molecules and hydroxyl, the latter due to the formation of hydroxide at the interface. In contrast, for the Zr-treated interface the

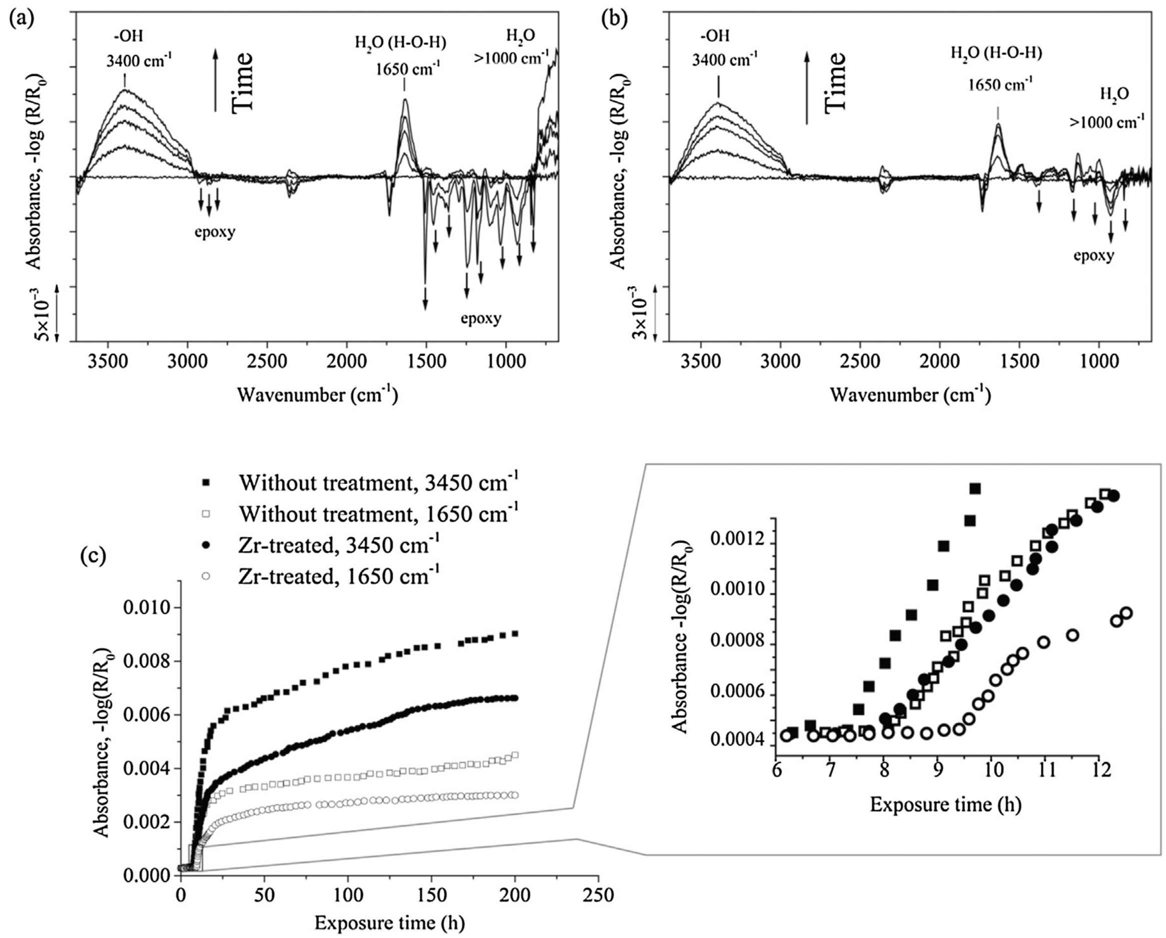


Fig. 5. ATR-FTIR Kretschamann spectra for (a) carbon steel film coated with fusion bonded epoxy and (b) Zr-treated carbon steel film coated with fusion bonded epoxy after 3, 9, 15, 70 and 190 h of exposure to 0.1 M sodium chloride solution (c) corresponding ATR-FTIR peak intensities at 3450 and 1650 cm^{-1} versus exposure time, with the zoom-in of the initial stages of the peak intensities.

identical band can be observed only after slightly longer time. A higher increase for the hydroxyl (—OH) band can be observed for the reference sample as a function of time. Furthermore, the peak intensity shows a plateau value for the Zr-treated sample after around 170 h, while the peak intensity for the reference sample increases till 200 h. This could be an indication for a higher rate of oxidation and hydration process at the interface for untreated carbon steel in comparison to Zr-treated carbon steel. In Fig. 5c, the absorbance intensities at 1650 cm^{-1} show a clear different behaviour. This peak, which is assigned to water bending vibration is indicative for water molecules entering the interfacial region, shows that the Zr-based treatment can change the effect of the presence of water presence at the interface. While the Zr-based treatment cannot change the penetration of water molecules through the coating, it can affect the destructive and resulting accumulation effect of water molecules at the interface. This peak arises after around eight hours of exposure for the reference sample, however in the case of the Zr- treated sample the presence of this peak is delayed to over 9.5 h of exposure. The clear difference can be seen in the librations of liquid water assigned to the band below ~1000 cm^{-1}, which is related to frustrated rotations of bulk/liquid water. This band can be observed clearly after almost 9 h of exposure for the reference sample, but this peak did not appear for the Zr-based sample during the whole exposure time. Therefore, the absence of a significant water band below ~1000 cm^{-1} indicates a smaller amount of bulk water at the Zr-based interface. Moreover, Fig. 5a and b shows negative bands marked with downward arrows. These peaks are in agreement with epoxy backbone functional groups at the interface. Negative bands can be related to swelling or delamination of epoxy polymer which indicates a decrease of polymer concentration within the depth of analysis because of the polymer swelling or delamination. The intensity of negative peaks is higher for the reference sample in comparison with the Zr-treated sample, which can be related to delamination of epoxy from the carbon steel surface occurring faster in the absence of the Zr-based conversion layer. Correspondingly, this effect is in line with the concurrent appearance and increase of positive bands at 1650 cm^{-1} and region bands below ~1000 cm^{-1} indicating a higher amount of water molecules at the interface for the reference sample.

3.3. EIS and adhesion evaluation

Similar to previous experiments, electrochemical tests were performed on both fusion bonded epoxy coated carbon steel as a reference sample and fusion bonded epoxy coated Zr-treated carbon steel surface. The EIS diagrams after different times of exposure to 0.1 M sodium chloride solution for these epoxy coated samples are presented in Fig. 6. For both samples, the modulus of impedance shows a plateau response in the low frequency region upon one hour of exposure to the electrolyte. This indicates that the epoxy coating possesses resistive properties, while IR bands related to stretching, bending and libration modes of water molecules in these examined systems did not appear until at least seven hours of exposure. This delay can be explained with the fact that the EIS technique

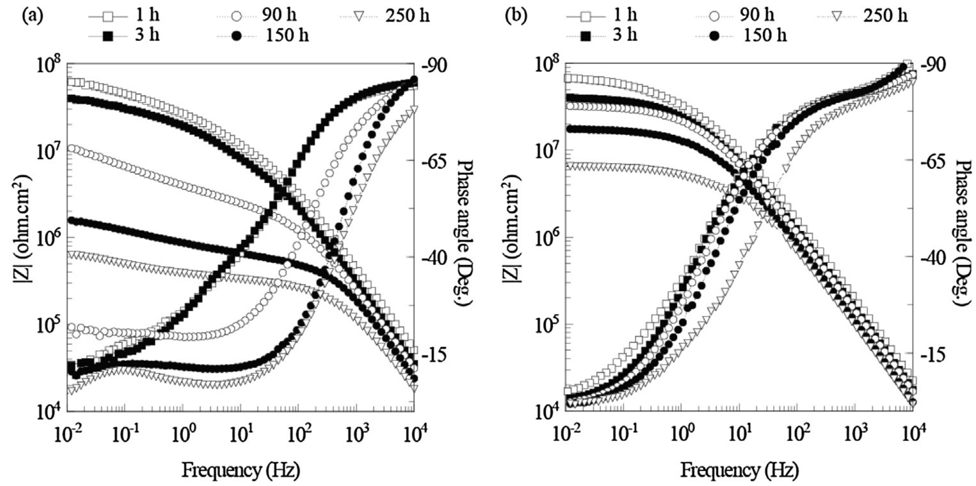


Fig. 6. EIS spectra for (a) untreated carbon steel coated with fusion bonded epoxy and (b) Zr-treated carbon steel coated with fusion bonded epoxy after 1, 3, 90, 150 and 250 h of exposure to 0.1 M sodium chloride solution.

measures the overall changes due to water uptake in the polymer network and corrosion at the interface, while the ATR-FTIR technique with Kretschmann geometry setup, probes the chemical changes close to the interfacial region only. In spite of that, the EIS response shows clear differences with exposure time for the different samples. The impedance modulus and phase angle values for the reference sample show the resistive behaviour in a lower frequency region in comparison with the Zr-treated surface. Also, the modulus of impedance at low frequencies decreases at a higher rate for the reference sample indicating lower corrosion protection. The phase for both samples reaches a plateau and almost the same value in the low frequency region, however the samples show a clear difference in the mid frequency region. This indicates that, while for both samples the impedance of the coating changes from capacitive to a predominantly resistive nature with exposure time, the limited interfacial stability and resulting enhanced interfacial corrosion reactions with exposure time for the untreated sample results in relatively low interfacial impedance and complex phase angle behaviour in the mid frequency range as compared to that for the Zr-treated sample. This observation is fully in line with the in-situ FTIR measurements shown in Fig. 5 which confirm the increase of interfacial chemical stability resulting from the Zr-based treatment. At the same time with this decrease, a new time constant can be seen at frequencies <1 Hz after almost 150 h of exposure to electrolyte. This can indicate the accumulation of water molecules at the interface which results in the delamination of the epoxy layer from the substrate and is accompanied with interfacial corrosion reactions. This is in good agreement with IR results which showed hydroxyl stretching ($3450\,\mathrm{cm}^{-1}$), water molecule bending ($1650\,\mathrm{cm}^{-1}$) and specifically librations of liquid water ($<1100\,\mathrm{cm}^{-1}$) for reference sample spectra. The modulus of impedance from the middle to high frequency region is used to estimate the water diffusion coefficient through the exposure time using the Brasher and Kingsbury equation [60]. The diffusion coefficient is estimated to be 1.25×10^{-11} and $1.21 \times 10^{-11}\,\mathrm{cm}^2/\mathrm{s}$ for the reference and Zr-treated sample respectively, which are almost identical values. This is in line with the assumption that the diffusion coefficient through the epoxy coating should not be influenced by the pretreatment procedure of the metal surface. EIS diagrams for a Zr-treated sample in Fig. 6b, shows decreasing modulus values in the low frequency region but does not show secondary time constants in the phase angle values over 250 h of exposure. This indicates increased stability of the interfacial region upon water molecule diffusion with Zr-based treatment at the epoxy/carbon steel interface. This is in line with IR spectra recorded for the Zr-treated sample.

The ATR-FTIR and EIS experiments showed that the Zr-based treatment has a beneficial effect on the interfacial bonding stability between fusion bonded epoxy and underlying carbon steel substrate. Traditional pull off tests were performed in order to evaluate the adhesion strength and stability and the effect of the Zr-based treatment after short and longer times of exposure in a corrosive electrolyte. Fig. 7a shows the adhesion failure stress valueswe for the epoxy coating from a carbon steel substrate without Zr-based treatment (reference sample) and from a Zr-treated carbon steel substrate. The failure stress measured just after application and curing of the epoxy coating on the surface is referred to as dry adhesion. Also, the failure stress was measured after a relatively short exposure time of 250 h and long exposure times of 35 and 70 days in 0.1 M sodium chloride solution referred to as wet adhesion. The failure stress in dry condition is increased around 45% in case a Zr-based treatment is applied. In addition, wet adhesion values are increased around 39, 75 and 140% as compared to those for untreated samples for exposure time of 250 h, 35 and 70 days, respectively. It can be concluded that, the Zr-based conversion treatment clearly increased dry and wet adhesion. After immersion in electrolyte, the pull off tests show that the adhesion between epoxy and underling substrate reduced more for the reference sample, in contrast to that of the Zr-treated carbon steel surface showing no significant reduction in adhesion value for the short exposure time of 250 h. The effect of the Zr-based treatment is even more significant after longer times of exposure. The adhesion value for the reference sample dropped more than half of the initial value after 70 days of exposure; however, the adhesion value for the Zr-treated sample is more stable and decreased around 20% only. It is good to mention, that all samples showed adhesive (interfacial) failure. Subsequently, IRRAS spectroscopy was performed on the underlying substrates. IRRAS is working based on the reflection of the polarized light from the metal surface at the grazing angle which due to enhancement of the electrical field perpendicular to the surface is a very surface sensitive technique which can reveal possible residues of an organic film on the surface [61]. Fig. 7b shows the IR spectrum for reference and Zr-treated samples after being exposed 70 h in electrolyte and pull off tested. The signal-to-noise ratio is very low for the spectra but there are clear peaks assigned to sp^3 C—H stretching in the $3000–2850\,\mathrm{cm}^{-1}$ region. This indicates that small remnants of epoxy polymer on the Zr-treated carbon steel surface after adhesive bonding testing are present

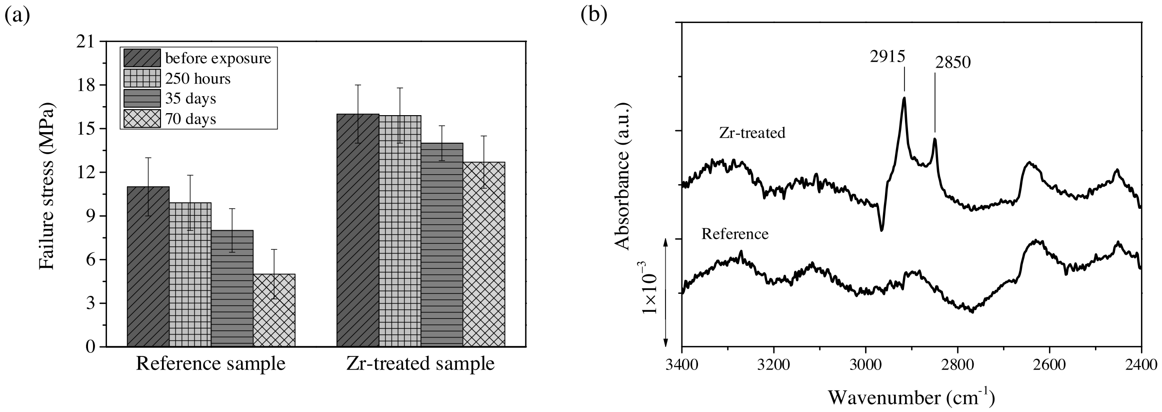


Fig. 7. (a) Adhesion measurements (pull off testing) for samples without (reference) and with Zr-based treatment of the fusion bonded epoxy/carbon steel interface before exposure, 250 h, 35 days and 70 days after exposure in 0.1 M sodium chloride electrolyte (b) IRRAS spectra for 70 days exposed reference and Zr-treated sample surfaces after pull off testing.

which may be due to better adhesion of the fusion bonded epoxy layer; it is however good to emphasize that the remnants of epoxy polymer cannot be detected visually and the failure mechanism is still classified as adhesive breakdown.

4. Conclusions

Stability and adhesion strength of the fusion bonded epoxy to carbon steel were evaluated for Zr-treated steel in contrast to untreated steel. SKP measurements were performed in order to study the potential distribution and delamination kinetics in the vicinity of an artificial defect. It is shown that a Zr-based treatment can decrease the potential difference at the delamination front causing a reduction in the delamination propagation rate. Also, diffusion of cations along the coating metal interface were revealed to be controlling factors in the delamination of fusion bonded epoxy from carbon steel. In-situ ATR-FTIR studies in Kretschmann geometry provide information about the chemical stability of the hidden fusion bonded epoxy/carbon steel interface upon exposure to a corrosive electrolyte. Transport of electrolyte towards the interface upon exposure to sodium chloride solution is monitored. The Zr-based conversion treatment is shown to significantly influence the water molecule interaction mechanism at the interface. Zr-based treatment can inhibit the formation of large water aggregates and prevent epoxy disbonding at the interface. EIS measurements in similar experimental conditions showed that Zr-based treatment can improve the corrosion performance of the fusion bonded epoxy for coated carbon steel. These results are in accordance with adhesion strength measurements. The Zr-based treatment can improve adhesion strength between fusion epoxy bonded polymer and carbon steel under dry conditions. Moreover, the adhesion strength under wet conditions is higher and more durable for Zr-treated carbon steel as compared to untreated samples.

It can be concluded that Zr-based treatment can significantly improve dry adhesion and moreover wet durability of fusion bonded epoxy to carbon steel upon exposure to a sodium chloride electrolyte in the presence and absence of a macroscopic coating defect.

Acknowledgements

This work is carried out under the project number M31.6.12469 in the framework of the research program of the Materials innovation institute M2i (www.m2i.nl). The authors wish to thank the European Space Agency ESA for granting permission to perform the SKP measurements on the SKP5050 equipment on loan at Delft University of Technology and Dr Antonius de Rooij for his valuable guidance. Mr Daryon van Duijn (MAVOM Chemie BV) is kindly acknowledged for his technical support in the pretreatment of the samples. The authors gratefully acknowledge Dr Peyman Taheri, Mr Peter Visser and Mrs Agnieszka Kooijman for their help and valuable discussion.

References

[1] P. Pedeferri, Cathodic protection and cathodic prevention, Constr. Build. Mater. 10 (1996) 391–402.
[2] A.W. Peabody, R. Bianchetti, Control of Pipeline Corrosion, National Association of Corrosion Engineers, 1967.
[3] M. Barbalat, L. Lanarde, D. Caron, M. Meyer, J. Vittonato, F. Castillon, S. Fontaine, P. Refait, Electrochemical study of the corrosion rate of carbon steel in soil: evolution with time and determination of residual corrosion rates under cathodic protection, Corros. Sci. 55 (2012) 246–253.
[4] J. Pacheco, R.B. Polder, A.L.A. Fraaij, J.M.C. Mol, Short-term benefits of cathodic protection of steel in concrete, Conc. Solu. (2012) 147–156.
[5] P. Refait, M. Jeannin, R. Sabot, H. Antony, S. Pineau, Corrosion and cathodic protection of carbon steel in the tidal zone: products, mechanisms and kinetics, Corros. Sci. 90 (2015) 375–382.
[6] D. Harrop, Chemical Inhibitors for Corrosion Control, Royal Society of Chemistry, Cambridge, 1991.
[7] M. Abdallah, M.M. El-Naggar, Cu + 2 cation + 3,5-dimethyl pyrazole mixture as a corrosion inhibitor for carbon steel in sulfuric acid solution, Mater. Chem. Phys. 71 (2001) 291–298.
[8] G. Trabanelli, Inhibitors. An old remedy for a new challenge, Corros. Sci. 47 (1991) 410–419.
[9] M. Şahin, G. Gece, F. Karcl, S. Bilgiç, Experimental and theoretical study of the effect of some heterocyclic compounds on the corrosion of low carbon steel in 3.5% NaCl medium, J. Appl. Electrochem. 38 (2008) 809–815.
[10] L. Yohai, W. Schreiner, M. Vázquez, M.B. Valcarce, Phosphate ions as effective inhibitors for carbon steel in carbonated solutions contaminated with chloride ions, Electrochim. Acta 202 (2016) 231–242.
[11] M. Stratmann, R. Feser, A. Leng, Corrosion protection by organic films, Electrochim. Acta 39 (1994) 1207–1214.
[12] G. Grundmeier, W. Schmidt, M. Stratmann, Corrosion protection by organic coatings: electrochemical mechanism and novel methods of investigation, Electrochim. Acta 45 (2000) 2515–2533.
[13] P.A. Sørensen, S. Kiil, K. Dam-Johansen, C.E. Weinell, Anticorrosive coatings: a review, J. Coat. Technol. Res. 6 (2009) 135–176.
[14] J. Li, L. Ecco, M. Fedel, V. Ermini, G. Delmas, J. Pan, In-situ AFM and EIS study of a solventborne alkyd coating with nanoclay for corrosion protection of carbon steel, Prog. Org. Coat. 87 (2015) 179–188.
[15] I. Santana, A. Pepe, E. Jimenez-Pique, S. Pellice, I. Milošev, S. Ceré, Corrosion protection of carbon steel by silica-based hybrid coatings containing cerium salts: effect of silica nanoparticle content, Surf. Coat. Technol. 265 (2015) 106–116.
[16] H. Leidheiser, W. Wang, L. Igetoft, The mechanism for the cathodic delamination of organic coatings from a metal-surface, Prog. Org. Coat. 11 (1983) 19–40.
[17] G. Fourche, An overview of the basic aspects of polymer adhesion. 1. Fundamentals, Polym. Eng. Sci. 35 (1995) 957–967.
[18] J. Wielant, R. Posner, R. Hausbrand, G. Grundmeier, H. Terryn, Cathodic delamination of polyurethane films on oxide covered steel – combined adhesion and interface electrochemical studies, Corros. Sci. 51 (2009) 1664–1670.

[19] M. Santa, R. Posner, G. Grundmeier, Wet- and corrosive de-adhesion processes of water-borne epoxy film coated steel, J. Electrochem. Soc. 158 (2011) C36–C41.
[20] T.A. Al-Khaldi, S.B. Lyon, The effect of interfacial chemistry on coating adhesion and performance: a mechanistic study using aminobutylphosphonic acid, Prog. Org. Coat. 75 (2012) 449–455.
[21] S.M. Cambier, R. Posner, G.S. Frankel, Coating and interface degradation of coated steel, part 1: field exposure, Electrochim. Acta 133 (2014) 30–39.
[22] R. Posner, K. Wapner, M. Stratmann, G. Grundmeier, Transport processes of hydrated ions at polymer/oxide/metal interfaces Part 1. Transport at interfaces of polymer coated oxide covered iron and zinc substrates, Electrochim. Acta 54 (2009) 891–899.
[23] R. Posner, K. Wapner, S. Amthor, K.J. Roschmann, G. Grundmeier, Electrochemical investigation of the coating/substrate interface stability for styrene/acrylate copolymer films applied on iron, Corros. Sci. 52 (2010) 37–44.
[24] G. Fourche, An overview of the basic aspects of polymer adhesion. 2. Application to surface treatments, Polym. Eng. Sci. 35 (1995) 968–975.
[25] T.S.N.S. Narayanan, Surface pretreatment by phosphate conversion coatings – a review, Rev. Adv. Mater. Sci. 9 (2005) 130–177.
[26] L. Fedrizzi, F.J. Rodriguez, S. Rossi, F. Deflorian, R. Di Maggio, The use of electrochemical techniques to study the corrosion behaviour of organic coatings on steel pretreated with sol–gel zirconia films, Electrochim. Acta 46 (2001) 3715–3724.
[27] S. Adhikari, K.A. Unocic, Y. Zhai, G.S. Frankel, J. Zimmerman, W. Fristad, Hexafluorozirconic acid based surface pretreatments: characterization and performance assessment, Electrochim. Acta 56 (2011) 1912–1924.
[28] N.W. Khun, G.S. Frankel, Composition and corrosion protection of hexafluorozirconic acid treatment on steel, Mater. Corros. 66 (2015) 1215–1222.
[29] N.W. Khun, G.S. Frankel, Effect of hexafluorozirconic acid pretreatment on cathodic delamination of epoxy coatings from steel substrates, Corros. Sci. 71 (2015) 277–284.
[30] J. Cerezo, I. Vandendael, R. Posner, K. Lill, J.H.W. de Wit, J.M.C. Mol, H. Terryn, Initiation and growth of modified Zr-based conversion coatings on multi-metal surfaces, Surf. Coat. Technol. 236 (2013) 284–289.
[31] J. Cerezo, P. Taheri, I. Vandendael, R. Posner, K. Lill, J.H.W. de Wit, J.M.C. Mol, H. Terryn, Influence of surface hydroxyls on the formation of Zr-based conversion coatings on AA6014 aluminum alloy, Surf. Coat. Technol. 254 (2014) 277–283.
[32] J. Cerezo, I. Vandendael, R. Posner, J.H.W.d. Wit, J.M.C. Mol, H. Terryn, The effect of surface pre-conditioning treatments on the local composition of Zr-based conversion coatings formed on aluminium alloys, Appl. Surf. Sci. 366 (2016) 339–347.
[33] J. Cerezo, R. Posner, I. Vandendael, J.H.W. de Wit, H. Terryn, J.M.C. Mol, The effect of conversion bath convection on the formation of Zr-based thin-film coatings on multi-metal surfaces, Mater. Corros. 67 (2016) 361–367.
[34] P. Taheri, P. Laha, H. Terryn, J.M.C. Mol, An in situ study of zirconium-based conversion treatment on zinc surfaces, Appl. Surf. Sci. 356 (2015) 837–843.
[35] E. Kretschmann, H. Reather, Radiative decay of nonradiative surface plasmons excited by light, Z. Nat. 23a (1968) 2135–2136.
[36] M. Ohman, D. Persson, C. Leygraf, In situ ATR-FTIR studies of the aluminium/polymer interface upon exposure to water and electrolyte, Prog. Org. Coat. 57 (2006) 78–88.
[37] M. Ohman, D. Persson, C. Leygraf, A spectroelectrochemical study of metal/polymer interfaces by simultaneous in situ ATR-FTIR and EIS, Electrochem. Solid State 10 (2007) C27–C30.
[38] P. Taheri, J.H.W. de Wit, H. Terryn, J.M.C. Mol, In situ study of buried metal-polymer interfaces exposed to an aqueous solution by an integrated ATR-FTIR and electrochemical impedance spectroscopy system, J. Phys. Chem. C 117 (2013) 20826–20832.
[39] P. Taheri, M. Ghaffari, J.R. Flores, F. Hannour, J.H.W. de Wit, J.M.C. Mol, H. Terryn, Bonding mechanisms at buried interfaces between carboxylic polymers and treated zinc surfaces, J. Phys. Chem. C 117 (2013) 2780–2792.
[40] Y. Nakao, H. Yamada, Enhanced infrared Atr spectra of surface-layers using metal-films, Surf. Sci. 176 (1986) 578–592.
[41] M. Stratmann, A. Leng, W. Fürbeth, H. Streckel, H. Gehmecker, K.H. Groβe-Brinkhaus, The scanning Kelvin probe; a new technique for the in situ analysis of the delamination of organic coatings, Prog. Org. Coat. 27 (1996) 261–267.
[42] A. Leng, H. Streckel, M. Stratmann, The delamination of polymeric coatings from steel. Part 1. Calibration of the Kelvin probe and basic delamination mechanism, Corros. Sci. 41 (1999) 547–578.
[43] B. Reddy, M. Doherty, J.M. Sykes, Breakdown of organic coatings in corrosive environments examined by scanning Kelvin probe and scanning acoustic microscopy, Electrochim. Acta 49 (2004) 2965–2972.
[44] A. Nazarov, T. Prosek, D. Thierry, Application of EIS and SKP methods for the study of the zinc/polymer interface, Electrochim. Acta 53 (2008) 7531–7538.
[45] A. Nazarov, M.G. Olivier, D. Thierry, SKP and FT-IR microscopy study of the paint corrosion de-adhesion from the surface of galvanized steel, Prog. Org. Coat. 74 (2012) 356–364.
[46] F. Deflorian, L. Fedrizzi, S. Rossi, P.L. Bonora, Organic coating capacitance measurement by EIS: ideal and actual trends, Electrochim. Acta 44 (1999) 4243–4249.
[47] K. Jüttner, Electrochemical impedance spectroscopy (EIS) of corrosion processes on inhomogeneous surfaces, Electrochim. Acta 35 (1990) 1501–1508.
[48] G. Williams, H.N. McMurray, Chromate inhibition of corrosion-driven organic coating delamination studied using a scanning Kelvin probe technique, J. Electrochem. Soc. 148 (2001) B377–B385.
[49] Y.Z. Luo, A. Vimalanandan, X.H. Wang, M. Rohwerder, Study of the buried interface between zinc and emeraldine base coating, Electrochim. Acta 161 (2015) 10–16.
[50] J. Liu, Y. Lin, X. Yong, X. Li, Study of cavitation corrosion behaviors and mechanism of carbon steel in neutral sodium chloride aqueous solution, Corros. Sci. 61 (2005) 1061–1069.
[51] L. Cáceres, T. Vargas, L. Herrera, Determination of electrochemical parameters and corrosion rate for carbon steel in un-buffered sodium chloride solutions using a superposition model, Corros. Sci. 49 (2007) 3168–3184.
[52] R. Vera, R. Schrebler, P. Cury, R. Río, H. Romero, Corrosion protection of carbon steel and copper by polyaniline and poly(ortho-methoxyaniline) films in sodium chloride medium. Electrochemical and morphological study, J. Appl. Electrochem. 37 (2007) 519–525.
[53] M. Stratmann, A. Leng, W. Furbeth, H. Streckel, H. Gehmecker, K.H. GrosseBrinkhaus, The scanning Kelvin probe; a new technique for the in situ analysis of the delamination of organic coatings, Prog. Org. Coat. 27 (1996) 261–267.
[54] A. Leng, H. Streckel, K. Hofmann, M. Stratmann, The delamination of polymeric coatings from steel. Part 3: effect of the oxygen partial pressure on the delamination reaction and current distribution at the metal/polymer interface, Corros. Sci. 41 (1999) 599–620.
[55] A. Leng, H. Streckel, M. Stratmann, The delamination of polymeric coatings from steel. Part 2: first stage of delamination, effect of type and concentration of cations on delamination, chemical analysis of the interface, Corros. Sci. 41 (1999) 579–597.
[56] P.A. Thiel, T.E. Madey, The interaction of water with solid-surfaces – fundamental-aspects, Surf. Sci. Rep. 7 (1987) 211–385.
[57] V.C. Farmer, The Infrared Spectra of Minerals, Mineralogical Society, London (41 Queen's Gate, SW7 5HR), 1974.
[58] J. Majzlan, C.N. Alpers, C.B. Koch, R.B. McCleskey, S.C.B. Myneni, J.M. Neil, Vibrational, X-ray absorption, and Mössbauer spectra of sulfate minerals from the weathered massive sulfide deposit at Iron Mountain, California, Chem. Geol. 284 (2011) 296–305.
[59] Y. Maeda, M. Ide, H. Kitano, Vibrational spectroscopic study on the structure of water in polymer systems, J. Mol. Liq. 80 (1999) 149–163.
[60] D.M. Brasher, A.H. Kingsbury, Electrical measurements in the study of immersed paint coatings on metal. 1. Comparison between capacitance and gravimetric methods of estimating water-uptake, J. Appl. Chem. 4 (1954) 62–72.
[61] H. Antony, S. Peulon, L. Legrand, A. Chaussé, Electrochemical synthesis of lepidocrocite thin films on gold substrate—EQCM, IRRAS, SEM and XRD study, Electrochim. Acta 50 (2004) 1015–1021.