The early corrosion behaviour of hot dip galvanised steel pre-treated with bis-1,2-(triethoxysilyl)ethane

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Abstract

The present work aims at correlating the evolution of the analytical composition of bis-1,2-(triethoxysilyl)ethane films formed on hot dip galvanised steel substrate during immersion in NaCl solution with the corrosion performance of the pre-treated substrates. The electrochemical tests were carried out by electrochemical impedance spectroscopy and the analytical characterisation was performed by X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES) and infrared spectroscopy (FT-IR). The electrochemical results show that the functional silane provides temporary corrosion protection for hot dip galvanised steel during immersion in NaCl-containing solutions. The analytical results show that the chemical composition of the silane film changes during immersion in the aggressive solution. During the first days of immersion these changes improve the corrosion resistance of the pre-treated substrate.
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1. Introduction

The corrosion resistance of several metals and alloys can be improved by pre-treatments based on silanes. These have become matter of research during the last years and attracted the interest of industry since they contribute for increased adhesion of organic coatings and for improved corrosion protection of the substrate. Furthermore, these pre-treatments are easy to apply, are not expensive and comply with the actual environmental concerns.

A large number of silanes and derivates from silanes can be used for the pre-treatments. One class of these molecules are the bis-functional silanes. These molecules are characterised by the presence of six hydrolysable groups (R') in the main organic chain: $(R')_3$–Si–R–Si–$(R')_3$. One example is bis-1,2-(triethoxysilyl)ethane (BTSE). This silane has been successfully tested and it shows promising results for cor-

rosion protection of galvanised steel, steel and aluminium alloys [1–4]. In previous works [1,2] the corrosion behaviour of steel substrates pre-treated with BTSE was compared with that of substrates pre-treated with a mono-functional silane and it was shown that the bis-silane leads to a considerable reduction of the corrosion rate of steel substrates immersed in NaCl solutions. This behaviour was attributed to the highest number of hydrolysable groups (six) on BTSE compared to the aminosilane (three). The protective properties of the BTSE films were also studied by Franquet et al. [5–8]. These works show that the thickness and porosity of the films are dependent on the concentration of the silane solution. These works also report that the curing procedure decreases the film porosity, enhancing its anti-corrosion behaviour.

Other bis-functional silanes such as BTESPT (bis-(triethoxysilylpropyl) tetrasulfide) have also been considered very promising pre-treatments. Previous studies [8–12] show that BTESPT provides corrosion protection of galvanised steel substrates and aluminium alloys. The methacryloxypropylmethoxysilane (MAOS) was also studied with

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good results for corrosion protection of aluminium alloys [13,14].

It is generally accepted that the silane films provide protection due to the formation of a dense silicon oxide-rich hydrophobic network that hinders the access of aggressive species. However, very little is known on the chemical changes occurring in the film during exposure to aggressive solutions and how these changes affect the temporary corrosion protection of the substrate. Thus, the present work aims at correlating the analytical composition of bis-1,2-(triethoxysilyl)ethane (BTSE) films deposited on hot dip galvanised steel (HDG) substrate during immersion in dilute NaCl solutions with the corrosion resistance of the pre-treated substrate. The study aims at discussing the mechanisms involved in the early corrosion behaviour of the BTSE films. The electrochemical study was performed using electrochemical impedance spectroscopy (EIS) and the chemical composition of the silane film was assessed by X-ray photoelectron spectroscopy (XPS), Auger depth profiling and Infrared spectroscopy (FT-IR). The results show that the composition of the film changes during the first days of contact with the solution, improving the corrosion protection of the substrate.

2. Experimental

2.1. Substrate cleaning

The hot dip galvanised steel substrate (zinc coating $275 \, g \, m^{-2}$ with 5% Al) was degreased using an alkaline cleaner (NOVOMAX[®] 187 U supplied by Henkel). The cleaner was prepared as a 3% (v/v). solution, which was maintained at $60°$. Following cleaning the panels were washed with distilled water and dried in air.

2.2. Pre-treatment

The silane solution was obtained by dissolving the silane (4% (v/v)) in methanol (90.5% (v/v)) and deionised water (5.5% (v/v)).

The hot dip galvanised steel substrate was immersed in the silane solution for 10 s. The excess of solution was removed by blowing air tangentially to the surface. After immersion the pre-treated samples were cured in an oven at $120°C$ for 40 min.

2.3. Techniques

2.3.1. Electrochemical techniques

The EIS measurements were performed at room temperature in a Faraday cage using a frequency response analyser and an electrochemical interface connected to a personal computer. A three-electrode electrochemical cell arrangement was used, consisting on the working electrode ($3.15 \, cm^2$ of exposed area), a saturated calomel electrode as reference and Pt as counter electrode. The measuring frequency ranged from $10^5 \, Hz$ down to $10^{-3} \, Hz$. All the experiments were performed at the corrosion potential after stabilisation ($\sim 10 \, min$). The experiments were performed in 0.005 M NaCl solutions at least in triplicate samples.

2.3.2. Analytical techniques

AES and XPS analysis were carried using a 310 F Microlab (VG Scientific). The XPS spectra were taken in CAE mode (30 eV), using an Mg (non-monochromated) anode. Auger spectra were obtained using a 10 KeV and $\sim 40 \, nA$ primary electron beam. The Auger depth profiles were obtained using a differential pumped ion gun with an ion beam accelerated at 2 keV. The etching current was around $0.8 \, \mu A/mm^2$. In these conditions the sputtering rate of Ta/Ta_2O_5 is around 12 nm/min.

The FT-IR spectra were recorded by using a Perkin-Elmer Spectrum. One spectrometer fitted with a variable angle specular reflectance accessory (RAIR) from Graseby Specac. The spectra were recorded from 4000 to $450 \, cm^{-1}$ by measuring 16 scans with a resolution of $4 \, cm^{-1}$ at an incident angle of $45°$. A MCT detector was used in the RAIR measurements.

3. Results

3.1. Electrochemical results

Fig. 1 shows the EIS spectra obtained on HDG pre-treated with BTSE. The spectra show the presence of two well-defined time constants: one in the high frequency range and
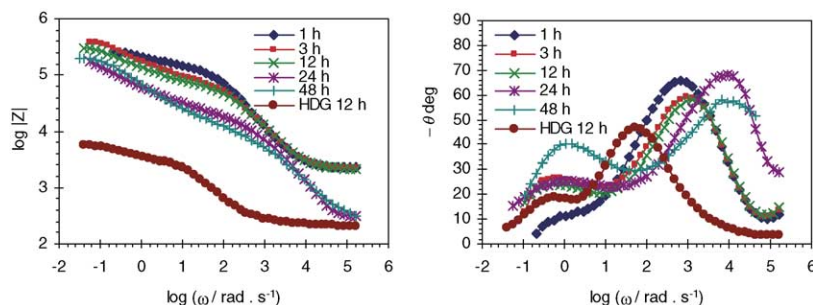

Fig. 1. EIS Bode plots obtained after different immersion times in 0.005 M NaCl.
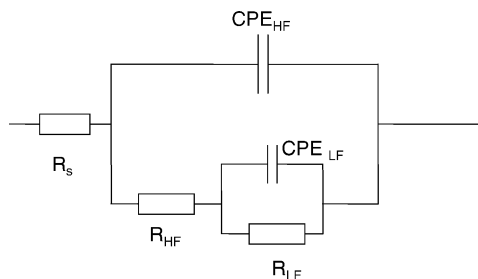
Fig. 2. Electrical equivalent circuit used for numerical simulation of the EIS results obtained after different immersion times.

another one in the low frequency range. Fig. 2 depicts the equivalent circuit used for the numerical fitting of the EIS spectra presented in Fig. 1. The equivalent circuit includes two time constants: (i) the association (R_{HF}-CPE_{HF}) accounts for the presence of an organic film and (ii) the association (R_{LF}-CPE_{LF}) that accounts for the presence of an intermediate process, which nature will be discussed later. Both time constants are described by a non-ideal frequency dependent capacitance (CPE), which can be attributed to heterogeneity of the substrate. The parameter R_s corresponds to the resistance of the electrolyte.

A typical fitting is depicted in Fig. 3 and the values of resistance and CPE obtained on the pre-treated substrates after different immersion times are presented in Figs. 4 and 5. The results clearly show that there is a decrease of the high frequency resistance with time. At the same time the capacitance associated with this time constant increases. These changes account for an increase of the water uptake through the organic layer.

The low frequency time constant is characterised by resistance values, which show an increase during the first hours of immersion. Then the resistance stabilises, being approximately constant during 48 h. The CPE associated with this time constant shows a very small decrease during the first hours of immersion, but later it increases again. Compari-
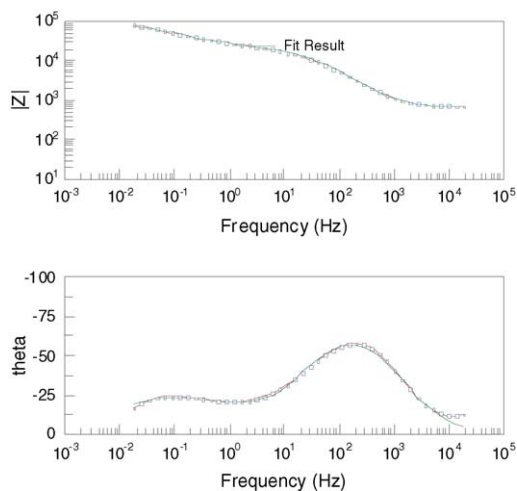

Fig. 3. Numerical fitting of the EIS Bode plots obtained after 12 h of immersion in 0.005 M NaCl.

son with the reference substrate (non-treated HDG) reveals that the pre-treatment increases the impedance by about two orders of magnitude–Fig. 1. After 72 h of immersion (not shown) the impedance started to decrease as consequence of the corrosion onset. After this period small corrosion spots could be observed at naked eye on the pre-treated substrate.

3.2. Analytical results

The XPS analysis gives information on the evolution of the chemical composition of the pre-treated surface during immersion in the aggressive solution. Figs. 6–8 depict the XPS ionisation spectra obtained for C1s, Si2p and O1s after different immersion times. The analysis of the C1s ionisation reveals the following information: (i) the binding energy of the main peak (attributed to the presence of C−H bonds) does not change and (ii) new peaks appear in the higher binding energy side after immersion in NaCl. After 3 h a peak becomes evident at 287 eV, suggesting formation of C−O bonds. After 24 h a new peak appears at 289 eV. This can be attributed to the presence of C=O bonds. The behaviour of the C1s spectra after different immersion times reveals degradation of the outer layers of the organic film due to oxidation of some carbon groups.

The Si2p ionisation shows, with time, a shift towards lower binding energies. Initially the Si2p peak has a binding energy of 103 eV, however after 3 h of immersion the peak position is around 102 eV. This shift can be attributed to a change in the film composition. For the same time the binding energy of the O1s ionisation also decreases. For 24 h of immersion the peak energies keep the same values.

Initially, the binding energy of both oxygen and silicon account for the presence of Si−OH$_x$ and SiO$_2$ bonds. The latter peak position of Si suggests an interaction with an electropositive element instead of an anion. This behaviour shows that changes occurred in the chemical composition of the film during immersion.

The in-depth distribution of the different elements was evaluated by AES depth profiling. Figs. 9–11 depict the Auger depth profiles obtained before immersion, after 3 h and 24 h of immersion, respectively.

Before immersion the AES depth profiles reveal an external layer very rich in carbon (content above 50%) containing oxygen and silicon. The sputtering procedure, revealed a more internal plateau (after ∼100 s) containing carbon, oxygen and silicon. This sputtering time necessary to remove this plateau was approximately 250 s. After this sputtering time the contents of C, and Si show a strong decrease. The time necessary to remove all silicon and carbon was around 500 s. The profiles suggest the presence of two layers in the film: one outer layer very rich in carbon and a more internal plateau where the contents of the different elements are stable. The maximum Si content detected in the internal plateau is around 20%, whereas the O content is slightly higher. After 3 h of immersion the carbon content in the outer layers shows a sharp decrease after the first 50 s of sputtering, whereas the
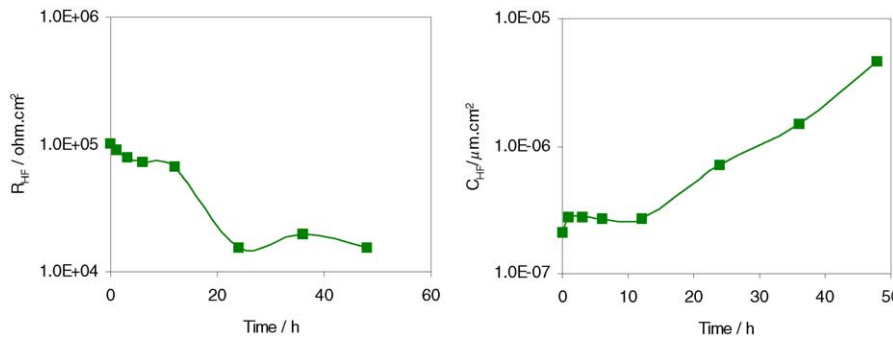
Fig. 4. Fitting results showing the evolution of the resistance and capacitance for the high frequency time constant.
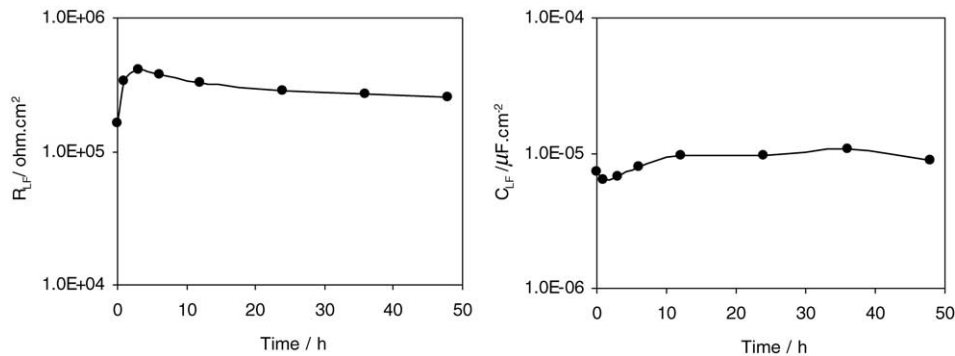

Fig. 5. Fitting results showing the evolution of the resistance and capacitance for the low frequency time constant.

plateau rich in Si and O become evidenced. The amount of silicon in this plateau increases relatively to the values observed in Fig. 9 and the O/Si ratio becomes lower than one (∼0.8). After 24 h the carbon content drops faster, evidencing the Si and O rich layer. One interesting feature of the AES depth profiles has to do with the Zn profile. Before immersion Zn was detected only after approximately 200 s, however for the longer immersion time important amounts of Zn were detected closer to the surface, revealing that zinc seems to be present in Si and oxygen rich film.

FT-IR analysis of the pre-treated substrates before immersion is depicted in Fig. 12. Table 1 depicts the wavelength of the different peaks observed in the spectra. The most intense peaks observed in the spectrum are due to: OH- groups (∼3349 cm^{-1}), CH$_2$ and CH$_3$ (∼1413 cm^{-1}), C–O (∼1272 cm^{-1}), Si–O–Si (∼1150 cm^{-1}) and Si–O–C (∼920 cm^{-1}). The presence of OH groups also accounts for a large number of silanol (Si–OH) species in the film, in agreement with the XPS data. On the other hand silicon is present in the form of Si–O–Si and Si–O–C. The presence of Si–O–C bonds show that part of the silicon existing
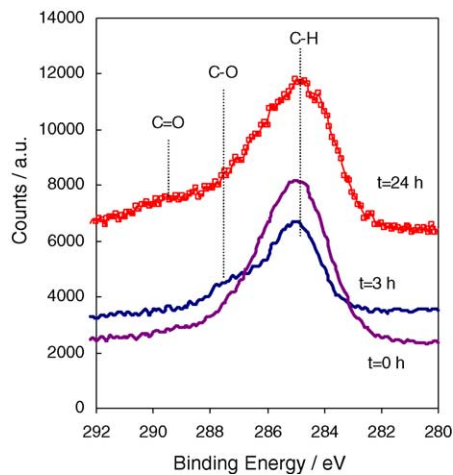

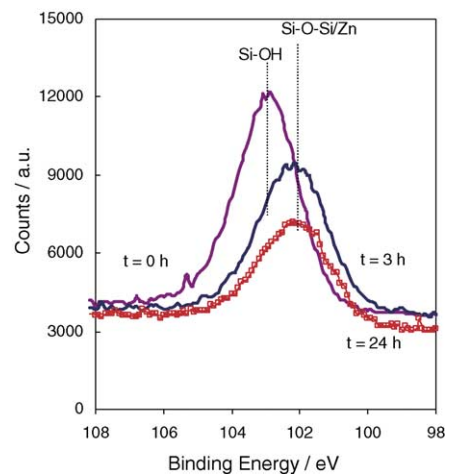
Fig. 6. XPS spectra for the C1s ionization.
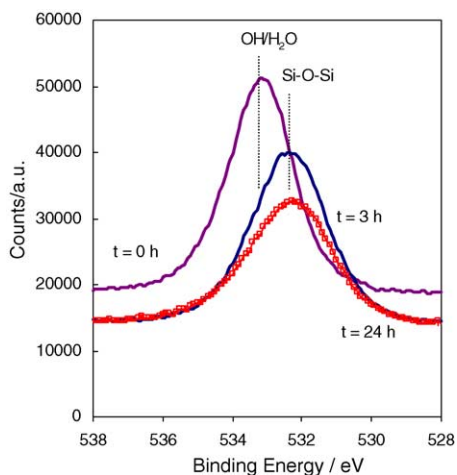

Fig. 7. XPS spectra for Si2p ionization.

Fig. 8. XPS spectra for O1s ionization.

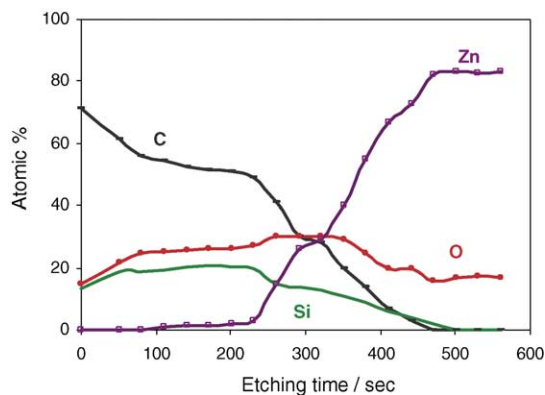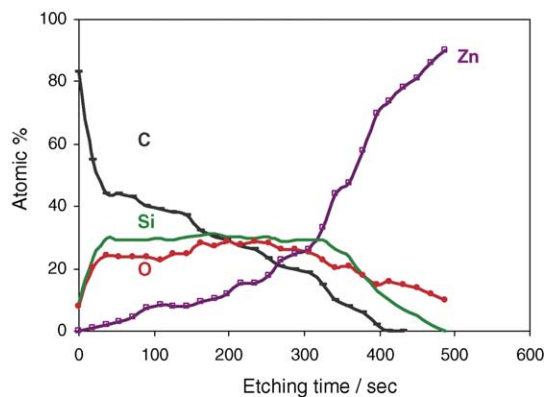Fig. 9. Auger depth profile before immersion.
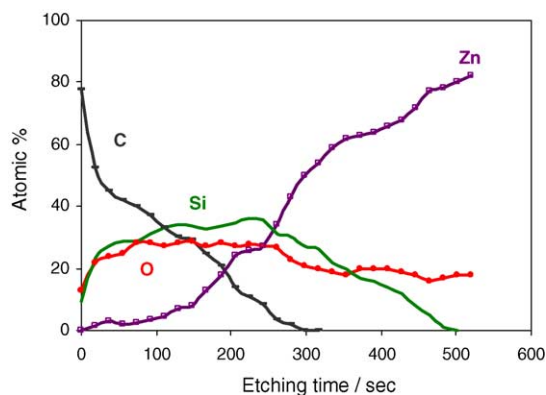

Fig. 10. Auger depth profile after 3 h of immersion.

Fig. 11. Auger depth profile after 24 h of immersion.
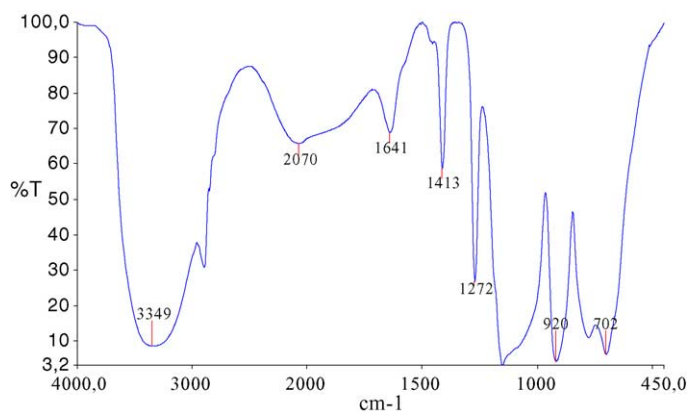
Fig. 12. FT-IR analysis obtained before immersion.

(1) Hydrolysis:

$$R\text{–}Si(OR')_3 \quad \rightleftarrows \quad R\text{–}Si(OR')_2(OH)$$
$$\downarrow\uparrow$$
$$R\text{–}Si(OH)_3 \quad \rightleftarrows \quad R\text{–}Si(OR')(OH)_2$$

(2) Condensation and polymerisation

$$-SiOH + HOSi- \quad \rightleftarrows \quad Si\text{–}O\text{–}Si + H_2O$$
$$-SiOH + ROSi- \quad \rightleftarrows \quad Si\text{–}O\text{–}Si + ROH$$
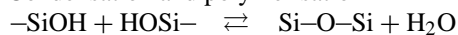
These equilibrium reactions proceed at rates that depend on the nature of the substrate, functional groups existing in the silane molecules, water content in the organic solution, pH of the silane solution and temperature and curing time. All these parameters have been investigated and found to play an important role in the film formation [1–7].

Table 1
FT-IR results

Wavelength (cm^{-1})	Groups
3300–3400	OH
2900–3000	C–H
1650	C=C
1300–1400	CH$_2$ + CH$_3$
1240–1270	C–O
1000–1150	C–O or Si–O–Si
900–950	Si–O–C
700–800	C–H

in the film prior to immersion is still in the form of an ester.

4. Discussion

The formation of silane films occurs according a number of steps, the most important being [15]:
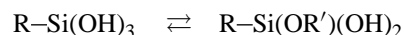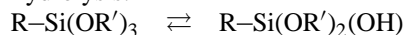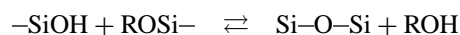
Alkaline etching of the galvanised steel substrate facilitates the formation of $Zn(OH)_2$ species. During dipping into the pre-treatment solution the $Si(OH)_3$ groups of the silane molecules approach the substrate where a very large number of hydroxyl groups formed after etching are available for binding. The silanol groups establish hydrogen bonds with the zinc hydroxides, leading to the formation of some monolayers covering the entire substrate. The silanol groups that could not bind with the substrate are able to form hydrogen bonds between them, creating a network of silane molecules through Si−O−Si bridging.

The curing step has an important role in the condensation/polymerisation reactions since it allows the conversion of the hydrogen bonds into more stable covalent bonds. However, this process is slow and dependent on the curing time. Previous works [6] showed that the amount of siloxane bonds increased with curing time. This effect was observed for curing times ranging between one minute and three hours. Small changes, were, however observed after thirty minutes. This behaviour suggests that some silanol groups and/or nonhydrated silanes molecules may be present on the film after the curing step.

The analytical results obtained in this work evidence some important chemical changes occurring in the silane film during immersion in dilute NaCl solutions. The FT-IR results and the XPS results clearly show a significant number of hydroxyl groups after film formation film (and prior to immersion). Furthermore, FT-IR evidences the presence of ester groups (Si−O−C), revealing that some silane molecules are not totally hydrolysed. After immersion in the NaCl solution these remaining ester groups start to react and the hydrolysis process continues within the film. Simultaneously, the hydroxyl groups also react further leading to the formation of Si−O−Si bonds, as evidenced by the XPS spectra. The AES depth profiles suggest that after immersion the silane film becomes richer in Si and poorest in oxygen and carbon. After 24 h of immersion the strong drop of the carbon signal during the first seconds of sputtering suggest an important loss of the outer layers of the film. These external layers also become more oxidised as observed by XPS analysis. The evolution of the Si and O profiles with time suggests the presence of a stable layer deposited upon the Zn substrate. This layer is very rich in Si−O−Si and/or Si−O−Zn species and protects the substrate from corrosion onset. Fig. 13 depicts a structural scheme that can be suggested to describe the behaviour of the silane film formed with
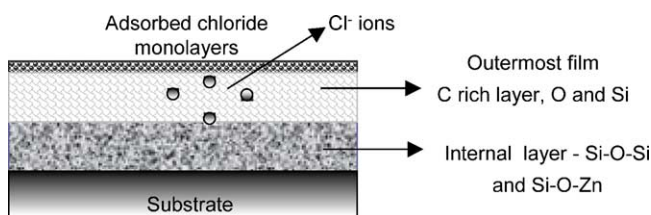
BTSE on HDG substrate during immersion in dilute NaCl solutions.

The analytical results help to understand how the silane film confers corrosion protection to the substrate. After film deposition and cure there are molecules, which were not hydrolysed, and molecules that did not condensate. After immersion in the NaCl solution the chloride ions adsorb on the surface and start to penetrate into the first layers of the film, which are porous and not very protective due to incomplete polymerisation. The electrolyte uptake within this layer leads to a decrease of the high frequency resistance observed in the EIS spectra. But, as soon as the electrolyte reaches the film a number of reactions start, and the condensation/polymerisation reactions proceed at an important rate. These reactions are likely to be initiated in the ester groups and silanol groups that remain in the film. This leads to a degradation of the carbon rich outer layers and to the build up of a Si rich intermediate layer, which becomes more resistive with time. This evolution is reflected in the EIS results, which showed an increase of the resistance of the intermediate layer during the first hours of immersion. Thus, in spite of chloride and water uptake and deterioration of the first layers of the film, the more internal layer becomes more protective with time.

The presence of a significant amount of zinc within the intermediate layer accounts for a mixed Si−O−Zn oxide interface. In fact the low content of oxygen when compared to Si and Zn suggests that this element acts as a bridge between the silane film and the substrate. Later on, the penetration and accumulation of chloride ions at this interface leads to the initiation of the corrosion process. This was detected in the EIS spectra after approximately 3 days of immersion.

The results obtained in this work show that the silane film is not completely cross-linked after the pre-treatment because some ester and silanol groups were detected in the film. It was suggested [16] that the silane pre-treatment solution should be a water - based solution rather than an alcohol-based solution in order to avoid incomplete hydrolysis. However the low solubility of some silanes in water limits the application of this procedure. Moreover, the incomplete reactions are not avoided, since a number of silanol groups (resulting from hydrolysis) are still present in the film. However, the presence on non-hydrolysed groups is not deleterious because the hydration and polymerisation reactions proceed during immersion leading to the formation of a resistant Si-rich interface. The present results also show that the silane film delays corrosion onset, when the substrate is exposed to environments with low concentration of chlorides. This behaviour has important implications because the main problems with corrosion of galvanised steel occur during storage and transportation (before paint application), where the environmental conditions are generally not very aggressive. Thus, pre-treatments using BTSE seem to be a good choice for temporary corrosion protection, since the protective behaviour is likely to increase during the early lifetime of the film.

Fig. 13. Scheme of the film formed on HDG.

5. Conclusions

After the pre-treatment the silane film formed on galvanised steel substrate is very rich in carbon, oxygen and silicon and contains a significant number of ester and hydroxyl groups.

The presence of an aqueous environment promotes the reaction of the silanol and ester groups with water converting them into stable Si–O–Si bonds. This process results in the formation of an intermediate layer, mainly composed by Si–O–Si bonds. The presence of an important amount of zinc, suggests that this element is also present within this layer. Thus it seems that there is an interaction between silicon and the metallic substrate through the formation of a Si–O–Zn bonds.

The resistance of the silicon rich intermediate layer increases during the first hours of immersion, leading to an increase of the total impedance of the system and improved corrosion protection. Thus, bis-1,2-(triethoxysilyl)ethane can be used for temporary corrosion protection of galvanised steel in environments contaminated with low chloride contents.

Acknowledgement

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