A comparative study on the corrosion resistance of AA2024-T3 substrates pre-treated with different silane solutions

Composition of the films formed

A.M. Cabral a,b,∗, R.G. Duarte b, M.F. Montemor b, M.G.S. Ferreira b,c

a ISEL, Instituto Superior de Engenharia de Lisboa, Lisbon, Chemical Engineering, R. Conselheiro Emídio Navarro 1, 1950-052 Lisbon, Portugal
b Instituto Superior Técnico, ICEMS, Av. Rovisco Pais, 1049-001 Lisbon, Portugal
c University of Aveiro, Department of Ceramics and Glass Engineering, Campus de Santiago, 3810-193 Aveiro, Portugal

Received 26 April 2005; received in revised form 20 July 2005; accepted 4 August 2005

Abstract

This work reports a comparative study on the corrosion resistance of AA2024-T3 pre-treated with three different silane solutions. The silanes used for the pre-treatments of the AA2024-T3 panels were: 1,2-bis(triethoxysilyl)ethane (BTSE), bis-[triethoxysilylpropyl]tetrasulphide (BTESPT) and γ-mercaptopropyltrimethoxysilane (γ-MPS). The analytical characterisation of the silane films was performed by Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS). The corrosion performance of the pre-treated substrates was evaluated by electrochemical impedance spectroscopy (EIS). The results show that the pre-treatments based on silanes provide good corrosion protection of unpainted AA2024-T3. Painted substrates, previously pre-treated with the silane solutions also revealed improved corrosion resistance and good adhesion properties. Fatigue tests show that the silane pre-treatments do not affect the fatigue behaviour of the AA2024-T3. The work also discusses the formation of the protective silane films.

© 2005 Elsevier B.V. All rights reserved.

Keywords: AA2024-T3; EIS; XPS; Surface pre-treatment; Silanes

1. Introduction

Pre-treatments for metallic substrates, based on solutions containing hexavalent chromium, are used to provide temporary corrosion protection and improved adhesion of organic paints. Since Cr(VI) containing compounds are allergenic, very toxic and carcinogenic they are a health risk in the working environments they are normally handled. Furthermore, Cr(VI) presents strong toxicity for the environment. Thus, research with the aim of developing new surface pre-treatments, which can replace the Cr(VI) based ones, with more environmentally suited products has therefore high priority in many countries [1].

A number of promising “green” alternatives have been studied, with the objective of replacing chromates. Among them, trialkoxysilylanes (or silanes), a group of silicon-based organic-inorganic chemicals, with the general formula of X3Si(CH2)nY (where Y is the organo-functional group such as vinyl (−CH=CH2), amino (−NH2) or mercapto (−SH) and X is the hydrolysable alkoxy group, e.g., methoxy (OCH3) or ethoxy (OC2H5)), have appeared as alternative pre-treatments. The corrosion behaviour of metallic substrates pre-treated with silanes has been extensively reported in literature since early 1990s [2–18]. However, several aspects are still not very well understood. Thus, the chemistry of the interface has been discussed [13] and it was found that it is dependent on several parameters such as curing time, curing temperature and chemistry of the silane molecules. Thus, the discussion of the corrosion behaviour of silane-based pre-treatments is a field of prime technological and scientific interest.

The formation of the silane film involves a number of important steps. First the silane molecules are hydrolysed in...
alcohol- or water-based solutions before the pre-treatment of the metallic substrates. The silane solutions become “workable” when a sufficient number of silanol groups (SiOH) are generated. Fig. 1 illustrates the formation of the silane film during the pre-treatment. The silanols (Si–OH) groups establish hydrogen bonds with the hydroxyls (Me–OH) present on the native metallic surface film. The remaining silanol groups that could not approach the metallic substrate establish bonds among themselves. Upon curing or drying, these hydrogen bonds are converted in stable siloxane bonds via the following reactions [4]:

\[
\text{SiOH}_{\text{(solution)}} + \text{MeOH}_{\text{(metal surface)}} \leftrightarrow \text{SiOMe}_{\text{(interface)}} + \text{H}_2\text{O}
\]

(1)

\[
\text{SiOH}_{\text{(solution)}} + \text{SiOH}_{\text{(solution)}} \leftrightarrow \text{SiOSi} \quad \text{(silane film)} \quad + \text{H}_2\text{O}
\]

(2)

Reaction (1) occurs at the silane/metal interface, leading to covalent metallo-siloxane bonds (MeOSi) as shown in Fig. 1. The good interfacial adhesion is believed to result from the presence of these bonds. Reaction (2) forms a crosslinked silane film structure (or siloxane, SiOSi, network).

According to their chemical structures, silane molecules suitable for corrosion protection, are divided into two major categories, i.e., “mono-silanes” and “bis-silanes.” Examples of mono-silanes are vinyltriethoxysilane (VS, CH\textsubscript{2}CHSi(OC\textsubscript{2}H\textsubscript{5})\textsubscript{3}), \(\gamma\)-mercaptopropyltrimethoxysilane (\(\gamma\)-MPS, SH(CH\textsubscript{2})\textsubscript{3}Si(OCH\textsubscript{3})\textsubscript{3}), and \(\gamma\)-ureidopropyltriethoxysilane (\(\gamma\)-UPS, H\textsubscript{2}NCONH(CH\textsubscript{2})\textsubscript{3}Si(OC\textsubscript{2}H\textsubscript{5})\textsubscript{3}). Bis-silanes are similar, except that the molecules have two hydrolysable groups (Si–X\textsubscript{3}) at both ends of the chain. The bis-silanes may also have the general structure \(X_2\text{Si}(CH\textsubscript{2})\textsubscript{n}Y_m\text{Si}(CH\textsubscript{2})_nX_2\), where the functional group \(Y\) can be for example an amine group or a chain of sulphur atoms. Examples of bis-silanes are bis-1,2-[triethoxysilyl]ethane (BTSE, (C\textsubscript{2}H\textsubscript{5}O)\textsubscript{3}Si-(CH\textsubscript{2})\textsubscript{2}-Si(OCH\textsubscript{3})\textsubscript{3}) and bis-[ureidopropyl]tetrasulfide (BTESPT, (C\textsubscript{2}H\textsubscript{5}O)\textsubscript{2}Si(CH\textsubscript{2})\textsubscript{3}S\textsubscript{3}Si(CH\textsubscript{2})\textsubscript{3}Si(OCH\textsubscript{3})\textsubscript{3}), respectively. The BTESPT molecule has an average \(x\) value of 3.8 [4] These molecules have been successfully tested as corrosion resistant pre-treatments for Al alloys, cold rolled steel, and galvanised steel [3,5,11,12,14,19,20]. MPS also have been used on mild steel [16] and aluminium alloys [17].

It is the objective of the present work to compare the corrosion resistance and to assess the analytical composition of different silane films formed on AA2024-T3. Solutions of a mono-silane, \(\gamma\)-mercaptopropytrimethoxysilane (\(\gamma\)-MPS), and solutions of bis-silanes, 1,2-bis[triethoxysilyl]ethane (BTSE) and bis-[triethoxysilylpropyl]tetrasulfide (BTESPT), were used for the pre-treatment of AA2024-T3 panels. The analytical characterisation of the pre-treated substrates was performed by Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS). The corrosion performance was evaluated by electrochemical impedance spectroscopy (EIS). The results show that the pre-treatments based on silanes provide good corrosion protection both on painted and unpainted AA2024-T3 substrates.

2. Experimental

2.1. Preparation of the metallic substrates

AA2024-T3 panels were ultrasonically degreased with acetone, alkaline cleaned by immersion for 5 min at 40 °C in 30 g/l aqueous solution of TURCO 4215 (TURCO product) followed by dismutting during 4 min at room temperature in a solution of DEOXIDISER 1 (Amchem product).

Samples for Auger and XPS analysis were polished down to 1 μm diamond paste before the cleaning procedure.

2.2. Pre-treatments

2.2.1. Silanes

Bis-1,2-[triethoxysilyl]ethane (BTSE), bis-[triethoxysilylpropyl]tetrasulfide (BTESPT) and \(\gamma\)-mercaptopropytrimethoxysilane (MPS) were supplied by Sigma–Aldrich. The molecular structures of the three silanes are shown in Fig. 2.

Silane solutions (4 vol.%) were prepared by dissolving the silane in a mixture of methanol and deionised water: silane/DI water/methanol = 4/5.5/90.5 vol.%. The solutions were stirred continuously for 1h and stabilized for at least 4 days before use for maximum hydrolysis.

AA2024-T3 panels were immersed in the silane solutions for 100 s. The treated panels were then removed from the solution and dried by blowing air and cured at 120 °C for 40 min.
A standard commercial Cr(VI)-based pre-treatment (TURCOTM Accelagold) was used as reference.

Samples pre-treated with the BTSE and BTESPT were painted with commercial Polane T custom polyurethane enamel, 993AS287-4317 Enamel, from Sherwin Williams, and cured during 1 h at 35°C, to obtain a final thickness value around 75 μm. Before the enamel application the substrates pre-treated with the silanes were immersed for more 100 s in a solution of 4% of γ-APS (silane/DI water/methanol = 4/6/90 vol.%) and then cured for 15 s at 120°C. The γ-APS is a silane that promotes the adhesion of the paint to the pre-treated substrate. In this work it was applied over the previous pre-treatment with BTSE, BTESPT and MPS.

2.3. Analytical experiments

AES depth profiles, Auger mapping and XPS analysis were carried out using a scanning Auger microscope (VG Scientific) equipped with a field emission type electron gun, a concentric hemispherical analyser and a differentially pumped ion gun. Auger spectra were taken using a 10 keV, 40 nA primary electron beam, making an angle of 30° with the surface. XPS was performed using a Mg (non-monochromated) anode. Spectra were taken in CAE (constant analyser energy) mode of 30 eV.

2.4. Impedance measurements

The EIS measurements were carried out using a Gamry FAS1 Femtostat + PC4 controller board and all the measurements were performed at room temperature in a Faraday cage. A three-electrode arrangement was used. The measuring frequency ranged from 107 Hz down to 10−3 Hz. A saturated calomel electrode (SCE) was used as reference and a platinum wire was used as counter electrode. All EIS spectra were recorded after ∼10 min of immersion in 0.1 N NaCl solution, at the open circuit potential. At least two measurements were performed for each condition.

2.5. Adhesion tests

Adhesion tests were carried out using the 107 Cross Hatch Cutter, from Elcometer, following ASTM D 3359-B Standard. A 1 mm cutter was used since the total thickness of the coating was lower than 60 μm. Adhesion results were classified according Table 1.

2.6. Fatigue tests

Axial fatigue tests were carried out in order to characterize fatigue life (stress is plotted in function of the number of cycles to specimen rupture—SN curves) of AA2024-T3, and AA2024-T3 pre-treated with chromate and AA2024-T3 pre-treated with the silanes under study. To carry out the fatigue tests, a servo hydraulic Instron 8502 and a Amsler Vibrophore machines were used. The frequency of loading was from 20 to 75 Hz. For the higher frequencies lateral supports were used in order to avoid transversal vibration of the specimen during the test. All tests were performed with charge control.

Based on previous tensile testing and following the usual conditions for this kind of materials, five levels of nominal stress were selected: 350, 300, 200, 100 and 50 MPa in order
Table 1
Classification of adhesion tests results [20]

<table>
<thead>
<tr>
<th>Description</th>
<th>ISO</th>
<th>ASTM</th>
</tr>
</thead>
<tbody>
<tr>
<td>The edges of the cuts are completely smooth; none of the squares of the lattice is detached</td>
<td>0</td>
<td>5B</td>
</tr>
<tr>
<td>Detachment of flakes of the coating at the intersections of the cuts. A cross cut area not significantly greater than 5% is affected</td>
<td>1</td>
<td>4B</td>
</tr>
<tr>
<td>The coating has flaked along the edges and/or at the intersections of the cuts. A cross cut area significantly greater than 5% but not significantly greater than 15% is affected</td>
<td>2</td>
<td>3B</td>
</tr>
<tr>
<td>The coating has flaked along the edges of the cuts partly or wholly in large ribbons, and/or it has flaked partly or wholly on different parts of the squares. A cross cut area significantly greater than 15% but not significantly greater than 35% is affected</td>
<td>3</td>
<td>2B</td>
</tr>
<tr>
<td>The coating has flaked along the edges of the cuts in large ribbons and/or some squares have detached partly or wholly. A cross cut area significantly greater than 35%, but not significantly greater than 65% is affected</td>
<td>4</td>
<td>1B</td>
</tr>
<tr>
<td>Any degree of flaking that cannot be classified even by classification 4</td>
<td>5</td>
<td>0B</td>
</tr>
</tbody>
</table>

Fig. 3. Scheme of the specimens used in the fatigue tests (W = 25mm, L = 200mm, B = 1.3 mm).

3. Results and discussion

3.1. Analytical characterisation of the pre-treated substrates

The analytical characterisation of the pre-treated substrates was performed by AES and XPS spectroscopy. Fig. 4 depicts the AES depth profiles obtained on the pre-treated substrates. The depth profiles show that the films formed on the substrates pre-treated with BTSE are very rich in Si and O. The Si and O signal seem to be mixed with that of Al. The time necessary to remove Si is around 300 s. The behaviour of the substrates pre-treated with BTESPT is slightly different due to the presence of sulphur that leads to a reduction of the

Fig. 4. Auger depth profiles for AA2024-T3 alloy treated with (a) BTSE, (b) BTESPT and (c) MPS.
relative atomic content of the other elements. The time necessary to remove silicon (∼200 s) is lower than that observed for BTSE. However, the time necessary to remove sulphur is much higher (∼400 s) suggesting that sulphur remains on the surface even after carbon and silicon removal. Other studies using ex situ ellipsometry and profilometry were performed in order to measure the thickness of BTESPT films on to AA2024-T3 [21]. It was found an average value of 200 nm for the thickness of the bis-silane.

The depth profiles obtained for the substrate pre-treated with MPS reveal a very thin film deposited on the surface. Moreover, the signal of aluminium and Cu are detected on the surface. These results contrast with those obtained with the other two silanes where a silicon outer rich zone is clearly observed, hindering the detection of the substrate. Furthermore, the silane film is very poor in silicon and carbon. The AES depth profiles suggest that the bis-silanes lead to a surface film richer in Si and O when used for the pre-treatment of aluminium alloys. This behaviour is consequence of the higher number of hydrolysable groups (six) present in the bis-silane molecule (Fig. 2(a) and (b)), which doubles the number of those existing on the mono-silane molecule (Fig. 2(c)). The formation of Al–O–Si bonds at the interface is highly desirable from a good corrosion perspective. The more Al–O–Si bonds formed, the more Al–OH groups consumed, and eventually the more hydrophobic the treated surface will be. Following this concept, bis-silanes are capable of forming a high density of Al–O–Si bonds at the interface.

The spatial distribution of the different elements on the surface of the pre-treated substrates was assessed by SAM (scanning Auger mapping). In these maps the darkest areas correspond to a very low content of the element under study, whereas, the brightest areas correspond to the highest content of the element. The maps obtained on the surface pre-treated with BTESPT (Fig. 5) reveal a homogeneous distribution of Si on the surface, but a heterogeneous distribution of sulphur, which seems to be distributed in “islands”. Furthermore, these sulphur rich “islands” remain on the surface even after most of the silicon has been removed as reported in a previous work [12].

SAM obtained on the surface pre-treated with BTSE (map not shown) revealed that the distribution of Si is uniform, hindering the detection of both aluminium and copper.

The maps obtained on MPS are depicted in Fig. 6. The maps show the spatial distribution of sulphur, copper, aluminium and oxygen. The most interesting feature of these maps is that the sulphur rich areas are coincident with the location of the Cu-rich precipitates. This behaviour suggests that the thiol group present on the silane molecule seems to bind with the Cu-rich species.

The chemical identification of the different species present on the surface was assessed by XPS analysis. Fig. 7 shows the silicon ionisation obtained on the substrates pre-treated with the different silanes. It can be observed that the Si 2p main peak for BTSE has a binding energy of approximately 103 eV,

Fig. 5. BTESPT map.

Fig. 6. MPS map.

Fig. 7. Si 2p ionisation obtained on the AA2024-T3 substrates pre-treated with the different silanes.
whereas, the same Si 2p ionisation for BTESPT and MPS have binding energies around 102 eV. The O 1s main peak for BTSE also shows higher binding energy, when compared to BTESPT and MPS (Fig. 8). This difference can be attributed to the presence of the Si-O=Si and Si-OH bonds on the BTSE film, as previously reported for HDG substrates pre-treated with BTSE [22]. It may be suggested that BTESPT and MPS films formed on AA2024-T3 substrates contain less amount of non-hydrolysed molecules, when compared to the BTSE films formed on the same substrate. The existence of non-hydrolysable molecules is dependent on the silane and its solubility in water. It is known that generally the solubility of silanes in water is poor, and incomplete reactions occur. However, it does not represent a problem, because when immersed in aqueous solutions, the remaining ester groups present in the film 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 [22].

No evidence of aluminium and copper were found on the film surface of the samples treated with BTESPT and BTSE. However, these elements were detected on the surface of the sample pre-treated with MPS, as expected due to the non-uniformity and decreased film thickness, as observed in Figs. 4 and 6.

The C 1s ionisation reveals a main peak at binding energies of 285 eV, corresponding to the presence of saturated carbon groups arising from the silane molecule.

The S 2p ionisations for BTESPT and MPS are depicted in Fig. 9. For BTESPT it is possible to observe the presence of a main peak, around 164 eV (S 2p3/2), which can be attributed to the C-S bonds. Concerning MPS the S 2p ionisation reveals two main contributions. The peak observed at 164 eV results from the presence of C-S bonds. However, the existence of peaks at higher binding energies (around 165 and 169 eV) indicate that the sulphur atom of the −SH groups has recombined with more electronegative atoms. The peaks can be assigned to sulphinate (−SO3O−) and sulphonate (−SO3O−), respectively [23,24].

The analytical results show that the thickness, spatial distribution and chemical composition of the silane film is dependent on the silane molecule. Bis-silanes lead to thicker and Si-richer surface films, whereas, mono-silanes lead to more heterogeneous and thinner films. This result is consequence of the lower number of hydrolysable groups present in the mono-silane molecules.

The analytical results also show that sulphur plays an important role in the formation of the silane coating. Previous work [12] showed that the interface of the films formed with BTESPT was very rich in sulphur that could be associated with the Cu-rich precipitates. The results obtained in the present work also show that the thiol group present in the MPS molecule has strong affinity for the Cu-precipitates. Furthermore, from the S 2p spectra it can be concluded that the sulphur in the thiol group of the adsorbed mercaptosilane is partly oxidized, probably due to oxidation with ambient oxygen, into different sulphur species with lower electron density in its surrounding, giving rise to components with higher binding energy. This observation can be attributed to the characteristic of the thiol group of the silane.

3.2. Electrochemical studies on the pre-treated substrates

The corrosion behaviour of the pre-treated substrates was investigated by EIS. Figs. 10 and 11 depict the EIS plots for the three silanes under investigation after 10 min and 24 h of immersion in 0.1 N NaCl solutions, respectively. The EIS data...
are presented in the form of Bode plots, i.e. the impedance modulus plot in Figs. 10(a) and 11(a) and the phase angle plot in Figs. 10(b) and 11(b). The curves for the bare AA2024-T3 (untreated) and for the commercial chromate treatment are shown in the figures as reference. In the EIS Bode plots the impedance at lowest frequencies can be correlated with the corrosion resistance of the system. Thus, higher impedance values account for enhanced corrosion protection.

The impedance spectra show that pre-treatments with silanes provides higher impedance values comparatively to the untreated alloy and impedance values slightly higher than the commercial chromate conversion coating. This effect can be the result of a decrease on the corrosion rate of the substrate in the presence of the silane films and/or an enhanced barrier effect that increases the protection of the natural oxide film.

Some changes occur during exposure to the NaCl solution as evidenced by the phase angle plots. Initially, the silane-treated samples show a time constant in the high frequency range ($\approx 10^3$ rad/s), whereas the untreated alloy and the Cr(VI) pre-treated alloy reveal a time constant at slightly lower frequencies ($\approx 10^2$ rad/s). Concerning the silane treated substrates the high frequency time constant is associated with the response of the silane film, whereas, the one at lower frequencies is associated with the presence of an oxide film—Fig. 10(b). After 24 h of immersion a new time constant starts to develop at very low frequencies, accounting for pitting onset.

To understand these changes observed in the impedance plots the EIS results were fitted using the equivalent circuit depicted in Fig. 12 [12,15]. The equivalent circuit used in the simulation of the experimental results includes three time constants: one describing the behaviour of the system at high frequencies, which is associated with the presence of the silane film; another at around $10^2$ rad/s, accounting for the presence of an intermediate layer between the outermost
silane film and the substrate and, a third one, in the lowest frequency range associated with corrosion onset. The EIS spectra obtained for the silanes pre-treated substrates after 10 min do not evidence yet the lowest frequency time constant, since corrosion has not started. Thus, the association CPE(corr)/R(corr) was not considered in the fitting of these results. However, it was included in the fitting of the EIS spectra obtained after 24 h. The results were fitted using CPEs (constant phase element) that give an approximate value of the capacitance (if $n \approx 1$). The fitting results are presented in Table 2.

The fitting results show that the capacitance of the outermost silane film slightly increases with time, although remaining in the same order of magnitude for the BTSE pre-treated substrate. Simultaneously, the film resistance decreases by one order of magnitude for all the silanes under study. These changes are associated with water uptake by the silane film.

In the intermediate frequency range an identical trend was observed for capacitance and for the resistance. The presence of a time constant in the intermediate frequency range has been usually assigned to the development of a layer between the outermost silane film layers and the native metallic oxide [4, 5, 14, 15]. Such phase can result from the formation of stable Si–O–Al and/or Si–O–Si bonds. However, in the case of the bis-sulphur silane (BTESPT) and mono-silane (MPS) it seems to include the products resulting from the reaction of the Cu-rich intermetallics with the sulphur-containing silane.

During immersion in the aggressive solutions, electrolyte penetrates the film structure, leading to a decrease of the resistance of both layers of the thin film. However, this decrease is less pronounced for the internal layer of the film formed for BTESPT. After 24 h the time constant values at low frequencies are characterised by capacitance values between 20 and 50 $\mu$F/cm², which are typical values for corrosion processes controlled by charge transfer. The corrosion rate is also dependent on the silane. The charge transfer resistance of the substrates pre-treated with BTSE and MPS are in the same order of magnitude; however for the BTESPT pre-treated system the charge transfer resistance increases by more than one order of magnitude. Thus, the results account for higher corrosion resistance of the substrates pre-treated with BTESPT. This evidence was not expectable on the basis of the analytical characterisation of the films, showing that apart a barrier effect conferred by the silanes, other effects should also play a role, such as film porosity, formation of corrosion products and inhibiting action of the silanes.

In the case of BTESPT it may result from [12, 15]:

$$x\text{Cu} + R-S-S-S-R \rightarrow \text{Cu}_xS + R-S-S-R$$

(3)

The breakdown of the sulphur bridges of the silane molecules on the sulphide surface can occur according to:

$$n\text{Cu}_xS + R-S-S-S-R \rightarrow n_1(Cu,S)_2 + n_2(Cu,S)_3$$

(4)

where $n_1$ and $n_2$ are the corresponding stoichiometric coefficients, with $n = n_1 + n_2$.

The presence of regions with high concentration of sulphur on the alloy surface after etching, as shown in the AES depth profiles (Fig. 4) supports the formation of this sulphide phase. In the case of the mono-silane (MPS), this interface phase can include products resulting from the reaction of copper-rich intermetallics with the thiol group. The presence of sulphur areas coincident with the location of the Cu-rich precipitates, as observed in the Auger maps, supports the presence of sulphur in this phase. Thus, the pre-treated system can be described by a model that proposes an intermediate Si–O–Al and Al/Cu–S interface and an outermost Si–O–Si-rich film [12].

Table 2

<table>
<thead>
<tr>
<th></th>
<th>BTESPT 0h</th>
<th>BTESPT 24h</th>
<th>BTSE 0h</th>
<th>BTSE 24h</th>
<th>MPS 0h</th>
<th>MPS 24h</th>
</tr>
</thead>
<tbody>
<tr>
<td>CPE(sil) (n)</td>
<td>6.04E–8 (0.9994)</td>
<td>1.8E–7 (0.9306)</td>
<td>1.67E–6 (0.8291)</td>
<td>2.57E–6 (0.8097)</td>
<td>3.29E–7 (0.9441)</td>
<td>2.95E–6 (0.7542)</td>
</tr>
<tr>
<td>R(sil)</td>
<td>2.33E5</td>
<td>2.11E3</td>
<td>1.965</td>
<td>3.064</td>
<td>1.31E5</td>
<td>4.41E4</td>
</tr>
<tr>
<td>CPE(int) (n)</td>
<td>1.26E–7 (0.8000)</td>
<td>9.81E–6 (0.9421)</td>
<td>1.40E–6 (0.7643)</td>
<td>2.83E–6 (0.7500)</td>
<td>7.89E–7 (0.6989)</td>
<td>1.60E–6 (0.8659)</td>
</tr>
<tr>
<td>R(int)</td>
<td>3.26E5</td>
<td>1.47E5</td>
<td>1.8E6</td>
<td>5.96E5</td>
<td>2.11E6</td>
<td>6.47E4</td>
</tr>
<tr>
<td>CPE(corr) (n)</td>
<td>3.32E–5 (0.7110)</td>
<td>5.56E–5 (0.75)</td>
<td>2.37E–5 (0.80)</td>
<td>2.37E–5 (0.80)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>R(corr)</td>
<td>8.94E4</td>
<td>3.42E3</td>
<td>2.8E3</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
3.3. Corrosion behaviour of the painted systems

Fig. 13 depicts the EIS Bode plots obtained for the painted substrates that previously were pre-treated with BTSE and BTESPT, after different times of immersion in 0.1 N NaCl solutions (the longer one corresponding to 135 days). During the first days of immersion the spectra correspond to a RC network, where \( C \) is ascribed to the capacitance of the coating and \( R \) to the resistance of the pores of the coating. For longer immersion times the evolution of the impedance shows that the corrosion behaviour of the systems treated with BTSE and BTESPT is identical. The EIS spectra show that the resistance of the painted system decreases with time due to electrolyte uptake. As the immersion time elapses, a new time constant appears on the EIS spectra and it can be assigned to the presence of the protective silane pre-treatment. Corrosion onset could not be observed on the substrates at the end of the immersion tests.

The electrochemical behaviour of the coated systems shows that the pre-treatment with silanes are compatible with the painting systems. The results also indicate that the corrosion behaviour of the painted system is very good. When the coating resistance is above \( 10^6 \ \Omega \text{cm}^2 \), it is generally assumed that it behaves as a protective organic coating, as proposed in literature for steel substrates [25].

3.4. Adhesion tests

Adhesion is a key parameter in what concerns the corrosion protection of painted systems. Thus, adhesion tests were carried out on painted substrates in order to study the adhesion of the polyurethane coating to the BTSE and BTESPT pre-treated AA2024-T3. Both BTSE and BTESPT pre-treated coated panels were classified as level 1 (ISO), according to Table 1, which represents a good adhesion result.

3.5. Fatigue tests

Fig. 14 shows the SN curves obtained for the AA2024-T3 and for the same substrate pre-treated with silanes and chromate. The Cr(VI) treated sample shows a little increase in the fatigue life, when compared to the AA2024-T3 sample at all nominal stress levels, except at 100 MPa. At this nominal stress the fatigue life of the AA2024-T3 and the Cr(VI) pre-treated samples were observed to be \( 3.5 \) and \( 4.4 \times 10^5 \) cycles, respectively.

Samples pre-treated with BTESPT, BTSE and MPS showed an increase in the fatigue life, when compared with both the blank AA2024-T3 and Cr(VI) pre-treated samples. The higher value of fatigue life for BTESPT and BTSE samples was observed at 100 MPa (\( 6.7 \) and \( 5.4 \times 10^6 \) cycles, respectively).

Figures 13 and 14 show the BN curves obtained with bare and pre-treated AA2024-T3 substrate.
4. Conclusions

The thickness of the protective silane film and its chemical composition are dependent on the nature of the silane. Bis-silanes lead to thicker and more homogeneous films, whereas the mono-silane leads to thinner and more heterogeneous films. The former also have higher capability to form Al–O–Si bonds at the interface.

The presence of sulphur in the silane molecule helps to the formation of the silane film via the Cu-rich precipitates. The ac impedance results show that silane films provide protection to the substrate. For short time the performance is even better than that conferred by the chromate reference treatment. However, the corrosion behaviour is dependent on the nature of the silane. Comparing the silanes under study, all provide effective protection. However, for the BTESPT pre-treated system the charge transfer resistance is more than one order of magnitude higher than for BTSE and MPS. These results account for higher corrosion resistance of the substrate pre-treated with BTESPT.

Long time performance of painted systems was evaluated for AA2024-T3 substrates pre-treated with BTESPT and BTSE and then coated with commercial polyurethane enamel. The systems showed good corrosion protection behaviour and good adhesion properties. Fatigue tests showed that the silane films contribute to enhanced fatigue life of AA2024-T3 substrate.

Taking into consideration the above, pre-treatments using silanes could be considered as promising alternatives to Cr(VI)-based solutions for the AA2024-T3.

Acknowledgements

Iniciativa Comunitária PME (IC-PME), Agência de Inovação, Portugal.

References