Modification of bis-silane solutions with rare-earth cations for improved corrosion protection of galvanized steel substrates

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Abstract

Chemical formulations based on silane solutions are currently used for the pre-treatment of metallic substrates. These pre-treatments provide corrosion protection of the metallic substrates due to the good barrier properties of the silane films that form on the surface. The corrosion protection of silane-based pre-treatments can be improved by adding dopants to the silane solutions. The dopants must present corrosion inhibition properties and must keep or improve the barrier properties of the silane film without modification of surface functionality and bulk properties.

The present work aims at assessing the corrosion behaviour of hot dip galvanised steel substrates pre-treated with bis-[triethoxysilylpropyl]-tetrasulfide and bis-1,2[triethoxysilyl]ethane silane solutions doped with cerium nitrate or doped with lanthanum nitrate. The effect of the dopants on the barrier properties of the silane film and its corrosion-inhibition ability is studied via electrochemical impedance spectroscopy. Complementary studies using atomic force microscopy and surface analysis were also performed. The results show that the corrosion resistance of substrates pre-treated with the silane solutions doped with the rare-earth cations increases by more than one order of magnitude when compared with the non-doped pre-treatments. The results also show that the protective behaviour of the pre-treatment is dependent on the dopant and on the silane film. The work discusses the role of the dopant on the anti-corrosion properties of the pre-treated substrates.

Keywords: Silanes; Corrosion; Cerium; Lanthanum; Galvanised steel

1. Introduction

Silane-based chemical formulations are currently used for the pre-treatment of different metallic substrates, such as galvanised steel, steel, aluminium and its alloys, copper and magnesium [1–20]. These pre-treatments have attracted industrial interest because they can provide chemical functionality to the pre-treated surface, improving adhesion to painting systems.

The most important feature of the silane pre-treatment is the formation of a very dense self-assembled silicon and oxygen rich network—the silane film. This film is usually very homogeneous, presents chemical stability and resists to water uptake and chemical attack in addition to thermal stability. Thus, silane films present very good barrier properties that lead to improved corrosion protection of the pre-treated substrates. However, small defects such as pinholes or cracks can be present in the silane film. These defects constitute preferential pathways for electrolyte uptake and consequently for corrosion onset. Thus, it is of paramount importance to develop procedures to inhibit the corrosion processes as soon as they start. Typically, the silane film plays an “inert role”, i.e., it provides corrosion protection because it constitutes a physical barrier. Thus, in order to improve its protective performance it is necessary to introduce corrosion inhibition ability in the silane film. This can be done by adding to silane solutions chemical species with corrosion inhibition properties. These species must inhibit the corrosion process without negative impact on the barrier properties and functionality of the silane film.

Among the most effective anti-corrosion species, rare-earth salts present good corrosion inhibition properties in addition to environmental friendliness.

Cerium nitrate has been successfully tested for corrosion protection of galvanised steel substrates either as aqueous corrosion inhibitor or as conversion film [21–26]. The modification of
thin organic coatings through the addition of cerium nitrate was tested for hybrid sol–gel coatings, which revealed improved corrosion protection of aluminium and zinc substrates [27–29]. The corrosion inhibition properties of cerium have been explained assuming that cerium inhibits the cathodic reactions [30–32].

Lanthanum ions have been used as aqueous corrosion inhibitor for corrosion protection of aluminium, magnesium and steel [33–35]. Corrosion protection of galvanized steel substrates in the presence of La ions was attributed to the formation of a film composed of La2O3 and La(OH)3 and small quantities of Zn(OH)2 and ZnO [30,36].

Following previous studies [37–41], the present work investigates the electrochemical behaviour of galvanised steel substrates pre-treated with bis-[triethoxysilyl)propyl]tetrasulfide (BTESPT) and bis-1,2(triethoxysilyl)ethane (BTSE) silanes doped with cerium nitrate or lanthanum nitrate. The electrochemical study was performed via electrochemical impedance spectroscopy (EIS). The results show that the addition of cerium or lanthanum improves the corrosion resistance of the silane pre-treated substrates.

Atomic force microscopy (AFM) experiments and time-of-flight secondary ion mass spectrometry (TOF-SIMS) analyses were also used to study the modified silane films.

2. Experimental procedure

2.1. Pre-treatments

The silane (Sigma/Aldrich product) solutions were prepared by dissolving 4% (v/v) of silane in methanol (90.5%, v/v) and aqueous solutions of the inorganic salt (5.5%, v/v). Aqueous solutions of 1 × 10−3 M of Ce(NO3)3 and La(NO3)3 were used for the preparation of the pre-treatment solutions. The pretreatment silane solutions, having a final concentration of rare earth cation of 5.5 × 10−5 M, were stirred during 1 h and kept for 3 days before use.

The substrate was galvanised steel, having a zinc coating weight of approximately 140 g/m2 and a thickness of approximately 10 μm. The substrates were degreased using an alkaline cleaner, washed with distilled water, dried in air and immersed in the doped silane solution for 10 s. The panels were cured in a Memmert oven at 120 °C for 40 min.

2.2. Techniques

The electrochemical impedance spectroscopy (EIS) measurements were performed using a three-electrode electrochemical cell, consisting of the working electrode (3.15 cm2 of exposed area), saturated calomel electrode (SCE) as reference and platinum as counter electrode. The measuring frequency ranged from 102 Hz down to 10−2 Hz. The r.m.s. voltage was 10 mV. The EIS experiments were performed during immersion of the pre-treated substrates in solutions of 0.005 M NaCl and 0.5 M NaCl at least in duplicate samples. The experiments performed in the most diluted NaCl solution aimed at monitoring the changes on the properties of the film (resistance and capacitance), whereas the experiments performed in 0.5 M NaCl aimed at accelerating the corrosion process and at assessing the inhibiting effect of the dopants. Spectra were treated using the Z-view Software.

The morphology of the silane films was assessed by Atomic Force Microscopy using a Nanoscope Digital Instruments with a NanoScope III controller with a silicon tip covered with PtIr5 in tapping mode to prevent scratching of the pre-treated surface.

The TOF-SIMS experiments were performed using a PHI TRIFT II apparatus. The High-mass-resolution spectra were taken in positive secondary ion mode over the mass range 2–1650 amu (atomic mass unit) and were acquired using a Ga primary ion source with a voltage of 15 kV and a primary ion current of 600 pA. The acquisition time for the samples was 2 min and the time per channel was 138 picoseconds. The ion dose was 3.36 × 1011 ions/cm2. The analysis depth was less than 2 nm and the area analysed around 150 μm × 150 μm. Two measurements were made per sample.

3. Results

The EIS spectra obtained for the BTESPT films doped with Ce (Fig. 1) are characterised by a capacitive response in the high frequency range and a resistive response at lower frequencies. For the substrates immersed in the most diluted solution the total impedance of the system were kept constant (~2 × 107 Ω cm2) during all the immersion period—1 week. This response reveals that these silane films are very protective and that corrosion could not develop. When the substrates are immersed in the most aggressive NaCl solution, the low frequency impedance values shows a pronounced drop from values around 1 × 108 Ω cm2 to values around 1 × 106 Ω cm2. At low frequencies a new time constant starts to develop, being more visible after 2 days of immersion. At the end of the tests the signs of corrosion activity were very weak as can be observed in Fig. 7.

The spectra obtained for the BTESPT films doped with La (Fig. 2) are slightly different from those obtained for the Ce-doped film. In the most diluted solution, the spectra show the presence of two time constants, one in the high frequency range and another one in the low frequency range. When the samples are immersed in the most aggressive solution identical behaviour could be observed, although the high frequency time constant is not so well-defined. At very low frequencies the phase angle suggests the presence of diffusion controlled mechanisms associated with the development of the corrosion processes. After 1 week of immersion these substrates revealed the presence of corrosion attack (Fig. 7).

The addition of Ce and La to the BTESPT silane solutions increases the total impedance of the pre-treatment for about two orders of magnitude comparatively to the non-doped BTESPT film. Cerium is more effective then lanthanum, Fig. 3.

For the substrates pre-treated with BTSE (doped and non-doped) there are always two well-defined time constants in the EIS spectra, Figs. 4–6. The impedance of the BTSE doped films is slightly higher then that of the non-doped BTSE films, Fig. 6.

For the BTSE systems doped with Ce and La, immersed in the most diluted solution, the EIS spectra are very similar and the total impedance values are very close, decreasing with time from...
values around $1 \times 10^6 \, \Omega \cdot \text{cm}^2$ to values around $1 \times 10^5 \, \Omega \cdot \text{cm}^2$. When the BTSE doped systems are immersed in the most aggressive solution, the film doped with La shows a strong drop of the impedance values. At the end of the tests, it can be observed that the BTSE system doped with La shows evident corrosion attack, whereas that doped with Ce shows only few localised corrosion spots, Fig. 7.

The high frequency time constant observed in the EIS spectra for the different silane systems can be attributed to the presence of the silane film, whereas the time constant at lower frequencies can be attributed to different processes: a surface oxide or/and the corrosion processes. These processes have identical relaxation times, appearing in the same frequency range. The EIS plots depicted in Figs. 3 and 6 include the spectra for untreated HDG substrates, which reveals a time constant in the same frequency range (approximately between 1 and 10 rad s$^{-1}$) of that observed for the silane pre-treated substrates. Since the untreated substrates are under corrosion activity, it is reasonable to assume that the low frequency time constant includes the corrosion processes.

The interpretation of the EIS results obtained during immersion in the NaCl solutions was performed by numerical fitting, using the equivalent circuit depicted in Fig. 8. In this equivalent circuit, constant phase elements were used instead of pure capacitors. This equivalent circuit includes the film capacitance and resistance ($R1$–$Q1$) and a second relaxation process ($R2$–$Q2$) that simulates the behaviour of the spectra at lower frequencies. For the silane films doped with La and immersed in the most aggressive solution there is an extra feature, at very low frequencies that is probably related with diffusion controlled processes. This time constant was simulated by adding a Warburg to the equivalent circuit.

The fitting parameters are depicted in Figs. 9–12. Fig. 9 shows the evolution of the silane film capacitance and film resistance, for the substrates immersed in the most diluted NaCl solutions. The results show that the addition of dopant leads to a decrease of the capacitance. The BTESPT doped films present lower capacitance values when compared to the corresponding BTSE doped films. The Ce-doped BTESPT films present capacitance values around $5 \times 10^{-9} \, \text{F/cm}^2$, whereas the capacitance of the Ce-doped BTSE films increases from $1 \times 10^{-8}$ to $1 \times 10^{-7} \, \text{F/cm}^2$.

The addition of dopant to the BTESPT pre-treatment solutions leads to an important increase of the resistance of the silane film. Comparatively to the non-doped BTESPT films, the addition of Ce leads to an increase of more than two orders of magnitude in the film resistance, from $5 \times 10^4$ to $1 \times 10^7 \, \Omega \cdot \text{cm}^2$, whereas the addition of La leads to an increase of about one order of magnitude, from $5 \times 10^4$ to $1 \times 10^5 \, \Omega \cdot \text{cm}^2$. The changes observed both on the capacitance and resistance of the doped films shows that the barrier properties of the doped films are improved in the presence of cerium ions.
For the BTSE doped films there are also important changes in the film capacitance and film resistance, but the effects are not as pronounced as observed for the BTESPT films. The capacitance of the BTSE doped films decreases approximately one order of magnitude. The resistance of BTSE doped films increases comparatively to the non-doped film, especially during the early stages of immersion. The resistance values for both doped BTSE films are identical, being slightly higher in the presence of cerium. For example, after about 2 days of immersion the resistance of the non-doped BTSE film is $1 \times 10^4 \, \Omega \, \text{cm}^2$, about 5 times lower than that of the Ce doped film ($5 \times 10^5 \, \Omega \, \text{cm}^2$).

The evolution of the film capacitance and resistance for the substrates immersed in the most aggressive solution is depicted in Fig. 10. The parameters were only estimated for the doped films, since the non-doped films revealed important degradation during the early stages of immersion. The results are in good agreement with the trends observed in Fig. 9 and, once more,
Fig. 4. EIS Bode plots obtained on galvanized steel substrates pre-treated with BTSE solutions doped with Ce(NO$_3$)$_3$ during immersion in (A) 0.005 M NaCl and (B) 0.5 M NaCl.

Fig. 5. EIS Bode plots obtained on galvanized steel substrates pre-treated with BTSE solutions doped with La(NO$_3$)$_3$ during immersion in (A) 0.005 M NaCl and (B) 0.5 M NaCl.
the results show that the BTESPT doped films provide better barrier properties. The BTSEPT film doped with cerium shows resistance values about one order of magnitude above that of the La-doped films. For the BTSE films this difference is not so marked. The resistance values are closer, being slightly higher for the Ce-containing films.

The results obtained from the numerical simulation of the EIS spectra in the high frequency range show that the barrier properties of the silane film depend on the silane and on the dopant. The most protective pre-treatment is based on BTESPT.

The addition of dopant improves the barrier properties of the films; Ce being more effective than La.

The evolution of the corrosion processes was studied only in the most aggressive solutions. As explained before the low frequency time constant seems to include more than one relaxation processes. This time constant was always observed in the BTSE systems, since the early stages of immersion in the most diluted solutions, for which the corrosion activity was much reduced. The low frequency time constant was also observed in the most aggressive solutions, but in this solution here there is corrosion.
activity, as confirmed in Fig. 7. Thus, it can be assumed that the charge transfer resistance associated with the corrosion processes is included in the low frequency time constant, being the predominant response in the most aggressive solutions. The parameters used in the numerical simulation of the EIS results are depicted in Figs. 11 and 12. The presence of the dopant affects both the low frequency resistance and the low frequency capacitance. The addition of dopant leads to lower capacitances and the most important decrease is observed in the presence of cerium.

The evolution of the low frequency resistance can be used to assess the corrosion rate of the substrates. Higher resistances account for lower corrosion activity. For the BTSEPT doped films (Fig. 11) it is clear that the presence of dopant leads to an increase of the low frequency resistance. The effect is more pronounced in the presence of cerium. This dopant increases the low frequency resistance by about two orders of magnitude. The beneficial effect of La can also be observed, and it is possible to see that the resistance increases by about 5 times comparatively to the non-doped film, especially during the earlier stages of immersion.

For the BTSE doped films (Fig. 12) the most effective anti-corrosion dopant is also cerium, which increases the low frequency resistance comparatively to the non-doped system. The presence of La also tends to increase the low frequency resistance, but the effects are not as clear as those observed for Ce.

From the interpretation of the low frequency impedance, it can be observed that the presence of Ce reduces the corrosion activity of the substrates. The addition of La is also beneficial but not as marked as cerium.

The EIS results clearly show that the presence of dopant has beneficial effects both on the barrier properties and on the anti-corrosion performance. The most effective pre-treatment is BTESPT doped with cerium nitrate.

Figs. 13 and 14 show the AFM scans obtained on the BTESPT films doped with cerium (the most protective doped film) and on
the BTSE film doped with La (the doped film with the poorest performance) before and after 1 week of immersion in the most diluted NaCl solution, respectively.

The “as prepared films” present similar morphology, being very uniform as can be observed in the 20 μm scan, Fig. 13. The detailed analysis of the surface (1 μm scan) reveals that the BTESPT film doped with cerium is more organised, evidencing a nanostructured surface film.

After 1 week of immersion (Fig. 14) the BTESPT film doped with cerium still shows a very uniform surface, however blistering can be observed. Contrasting with such behaviour, the BTSE film doped with La shows non-covered areas, where the film was completely released.

The AFM results clearly show that the BTESPT film doped with Ce is more uniform and more resistant to deterioration under aggressive environment than the BTSE film doped with La.

One of the most important properties of the pre-treatments based on silane films is their surface functionality, which should not be much affected by the presence of the dopant. The chemical composition of the pre-treated surface was assessed by TOF-SIMS and XPS analysis.

The mass spectra were measured from three spots (150 μm in diameter) for two minutes time for each sample, recording both positive and negative ions. The mass for Lanthanum is 138.906 amu (99.9%) and for Cerium 139.905 amu (88%). For the silane films doped with cerium it was not possible to detect this element with acceptable certainty. This result suggests that cerium is not present in the outer layers of the surface film. For the samples doped with La, the amount of La was very reduced, but detectable, Fig. 15.

The TOF-SIMS spectra reveal that the distribution of La and Ce at the film surface is slightly different. La is present in the outermost layers, whereas Ce is probably located deeper in the inner layers of the film. The XPS analysis of the doped films revealed the presence of carbon, oxygen and silicon on the surface of the film. For the BTESPT doped films sulphur was also observed. Zinc was not detected revealing that the surface coverage was uniform. Neither cerium nor lanthanum could be detected in the as formed films. However, XPS analysis performed on BTESPT films doped with a higher amount of cerium nitrate (100 times higher) revealed the presence of traces of cerium, as reported in a previous work [40]. Furthermore, in such conditions, Ce³⁺ and Ce⁴⁺-containing species were detected.

Previous results [19,42] also showed that the outer silane layers, which are richer in organic species are aged and released during immersion. The stable surface film is mainly composed
by an “oxide-type” inner layer. Thus, the following models can be proposed to explain the beneficial effect of the dopants.

The dopant ions added to the silane solution become trapped in the Si–O–Si network during the polymerisation and self-assembling of the surface film. However, La and Ce seem to have different distribution in the film. La was found in the outermost layers and it can be leached to the aggressive solution, during ageing and release of the film as observed by AFM. Thus, its amount decreases and its beneficial effects are reduced. However, the inhibition effects do not vanish completely, suggesting that La ions are also located in the more stable internal layers of the surface film. This behaviour is supported by the EIS measurements that showed that the presence of La improves the corrosion resistance comparatively to the non-doped substrates. Thus, some of these ions remain in silane film, being able to inhibit the corrosion processes.

The Ce ions added to the silane solution are probably stabilised in the inner layers of the surface film. Thus, after ageing the amount of cerium in the surface film is higher than that of La, and the inhibiting effects of Ce ions are more important. Furthermore, in a previous work [40] it was clearly demonstrated by SVET measurements that Ce ions inhibit corrosion activity when they are used as dopant in the BTESPT films.

The dopants trapped in the siloxane network can be released to the active areas, hindering the corrosion processes. Thus, the presence of inhibitor modifies the typical “inert role” of the silane film, making it “smarter” face to the corrosion process. The addition of Ce is more effective then the addition of La.

The EIS results show that the barrier properties of the silane film are also improved with the addition of dopant. It is clear that the dopant decreases the film capacitance and increases the film resistance. These effects can result from a combination of
different factors. The dopant helps to decrease the porosity of the surface film, probably blocking small defects and/or cracks in the film. Furthermore, the dopants may contribute to decrease the conductivity of the film, since their oxides are very insulating. On the other hand, the addition of dopants may increase the film thickness helping to improve the barrier properties. Results found in literature [28] indicate that the addition of increasing amounts of Ce to sol–gel films lead to increasing thickness. It is also reasonable to assume that cerium ions are able to react during the silane polymerisation reactions, becoming incorporated in the Si–O–Si network. Identical explanation was also proposed in literature [28] to interpret the improved corrosion protection of sol–gel films containing Ce.

All these factors are likely to contribute to the improved barrier properties of the doped silane film.

The results obtained in this work show that two objectives could be achieved by adding a dopant to the silane film: improved barrier properties of the silane film and corrosion inhibition ability. Among the dopants tested cerium is the most effective one, leading to film resistances that are more then two orders of magnitude higher than those of the non-doped films. This dopant also decreases the corrosion rate of the substrate by more than one order of magnitude comparatively to the non-doped silane.

The nature of the silane molecule also affects the protective performance of the film. The film resistance was higher for the BTESPT films. Assuming that the effect of the dopant is identical for both silanes, the differences can be attributed to different film thickness or different cross linking density. A fully cross linked film presents reduced porosity and is more resistant to water uptake. It is known that the Si–O–Si bonds are more hydrophobic than Si–OH or Si–O–C bonds. Previous FTIR results [19] revealed the presence of non-hydrolysed ester groups (Si–O–C) in outer BTSE silane layers. These incompletely hydrolysed groups make difficult the self-assembling growth of the BTSE film, leading to lower cross linking density in the outermost layers of the silane film and thus to slightly poorer barrier properties.

The present work clearly evidences the beneficial properties of the pre-treatments based on organofunctional silane solutions doped with cerium nitrate and lanthanum nitrate. Thus, formulations based on these doped silane solutions can be considered an effective procedure for the pre-treatment of galvanised steel substrates. Additionally, these formulations can be applied on other metallic substrates. The Ce-doped silane solutions were also used for the pre-treatment of aluminium alloys (AA2024-T3) and the results evidence improved anti-corrosion behaviour [42].

4. Conclusions

The addition of cerium nitrate or lanthanum nitrate to the silane solutions led to the formation of silane films with good barrier properties. The addition of cerium was more effective than the addition of lanthanum. Bis-[triethoxysilyl]propyl]tetrasulfide silane films doped with cerium showed film resistances two orders of magnitude above those of non-doped films.

Pre-treatments for galvanised steel based on the use of bis-[triethoxysilyl]propyl]tetrasulfide silane and bis-[triethoxysilyl]ethane silane doped with cerium nitrate showed good corrosion inhibition properties; the corrosion rate of the substrate treated with Ce-containing silanes decreased by more than one order of magnitude comparatively to the non-doped silane pre-treatments. The corrosion inhibition performance of silane films doped with lanthanum nitrate could be observed, however the effects were not so effective as those observed with cerium. Doped silane solutions are a suitable procedure to improve the corrosion resistance of pre-treated galvanised steel substrates. Improved barrier properties and enhanced corrosion inhibition performance can be achieved without negative effects on the surface functionality of the silane pre-treated surface.

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