The corrosion resistance of hot dip galvanized steel pretreated with Bis-functional silanes modified with microsilica

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Abstract

The present work aims at understanding the corrosion behaviour of hot dip galvanized steel pretreated with either bis-1,2-[triethoxysilyl]ethane silane (BTSE) or bis-[triethoxysilylpropyl] tetrasulfide (BTESPT) modified with microparticles of SiO2. The corrosion resistance was evaluated by electrochemical impedance spectroscopy, potentiodynamic polarization and by the scanning vibrational electrode technique (SVET) during immersion in dilute NaCl solutions. The films formed on the galvanized steel substrate were characterized by X-ray photoelectron spectroscopy, Auger electron spectroscopy and atomic force microscopy. The results show that the pretreatments based on silane films modified with silica particles provide corrosion protection for hot dip galvanized steel during immersion in NaCl-containing solutions.

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1. Introduction

Organo-functional silane coatings have becoming matter of research during the last years since they can provide a large variety of chemical functionalities on a huge range of substrates. The first developments in this field were performed for glass-reinforced polymers. In the organo-silicon compounds, the inorganic silicon ends are compatible with the glass surface, whereas the organic groups are compatible with the chemistry of the polymers.

Presently silanes are applied in very different fields, such as the microarray industry, where they are used for coating of glasses and immobilization of DNA molecules [1]. Recently, silane coatings have attracted the attention of the nanotechnology industry because they provide a highly uniform, robust and reliable coating with lateral resolution in the nanometer scale. These characteristics make the silane coatings also suitable for pretreatments that aim at improving the corrosion resistance of several metals and alloys. A wide variety of silane molecules has been successfully tested, and the results show that silanes provide corrosion protection of aluminium alloys, steel and galvanized steel [2–20].

Recent research works propose modified silane solutions. Zhu and van Ooij [12] investigates a mixture of bis-sulphur and bis-amino silanes for pretreatment of aluminium alloys and galvanized steel. This procedure combines the hydrophilic nature of the amino silane with the hydrophobicity of the bis-sulphur film, resulting in improved corrosion protection. Water-based mixtures of bis-amino silanes with vinyltriacetoxysilane also revealed interesting corrosion behaviour [13].

The modification of the silane films with alumina or silica particles has been used to improve the mechanical properties of the pretreated substrates. This procedure seems to increase the impact, scratch and wear resistance of the pretreated surfaces. The corrosion resistance of aluminium...
alloys pretreated with bis-sulphur silanes modified with SiO₂ also seems to increase. However, the corrosion resistance of the pretreated substrates is dependent on the concentration of silica particles in the silane coating [17].

The corrosion behaviour of hot dip galvanized steel pretreated with silane solutions modified with silica is not reported in the literature. Thus, the present work aims at assessing the corrosion behaviour of hot dip galvanized (HDG) steel pretreated with bis-1,2-[triethoxysilyl]ethane (BTSE) and bis-[triethoxysilylpropyl] tetrasulftide (BTESPT) solutions modified with particles of SiO₂. The composition and the early deterioration of the silane film in a dilute NaCl solution are also discussed. The electrochemical studies were performed using electrochemical impedance spectroscopy (EIS), potentiodynamic polarization and the scanning vibrational electrode technique (SVET). The chemical composition of the films was assessed by X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES). The evolution of surface topography was studied by atomic force microscopy (AFM). The results show that the silane pretreatments modified with microsilica particles improve the corrosion protection of the galvanized steel substrates. The analytical results show that the chemical composition and the surface topography are dependent on the silane used and on the immersion time.

2. Experimental

2.1. Pretreatment

The silanes (Sigma/Aldrich product) were dissolved in a methanol-based solution: 4%(vol/vol) of silane in methanol (90.5% vol/vol) and deionised water (5.5% vol/vol). SiO₂ particles (Hi-Sil T-700) with an average diameter of approximately 2 μm were obtained from PPG industries and were introduced in the deionised water used to prepare the silane solutions. The amount of SiO₂ in the pretreatment solution was 50 ppm.

The solutions were stirred during 1 h and stored for 3 days before use. The metallic substrate consists of galvanized steel specimens having a zinc-coating weight of approximately 140 g/m² and a thickness of approximately 10 μm. Postannealing was not performed on these substrates. The galvanized steel specimens were degreased using an alkaline cleaner. Following cleaning, the panels were washed with distilled water, dried in air and immersed in the silane solution for 10 s and cured in a Memmert oven at 120 °C for 40 min.

2.2. Techniques

2.2.1. Electrochemical techniques

The EIS measurements were performed at room temperature in a Faraday cage using a Solartron frequency response analyser and an electrochemical interface connected to a computer. A three-electrode electrochemical cell was used, consisting of the working electrode (3.15 cm² of exposed area), the saturated calomel electrode (SCE) as reference and platinum as counter electrode. The measuring frequency ranged from 10⁵ down to 10⁻² Hz.

The scanning vibrational electrode technique (SVET) measurements were performed using an applicable electronics probe. The scanned area was 1×1 mm².

The electrochemical experiments were performed in triplicate specimens under immersion in 0.03% NaCl solutions.

2.2.2. Analytical techniques

AES and XPS analyses were carried out using a 310 F Microlab (VG Scientific). XPS spectra were taken in CAE
mode (30 eV), using an Mg (nonmonochromated) anode. The spot of the X-ray beam was around 3×3 mm.

Auger spectra were obtained using a 10-KeV and ~40-nA primary electron beam. The Auger depth profiles were obtained using an argon ion beam accelerated at 2 keV. The etching current was around 0.8 μA/mm². In these conditions, the sputtering rate of Ta/Ta₂O₅ is around 12 nm/min.

Atomic force microscopy measurements were performed using nanoscope digital instruments (NanoScope III) operated in taping mode to prevent scratching of the pretreated surface.

3. Results

3.1. Corrosion evaluation

The corrosion behaviour of the pretreated substrates was assessed by EIS. Figs. 1 and 2 depict the EIS spectra obtained for substrates pretreated with BTSE and BTESPT solutions modified with SiO₂ particles, respectively. Spectra for the untreated HDG (after 12 h of immersion) and spectra for substrates pretreated with silane without particles (after 24 h of immersion) are also included for comparison.

For the bare sample, the EIS spectrum obtained after 12 h of immersion is characterized by two well-defined time constants: one at frequencies around 10² rads⁻¹ and another at lower frequencies. The time constant at higher frequencies can be assigned to the presence of an oxide/hydroxide film existing on the galvanized steel substrate, whereas the time constant at lower frequencies can be assigned to corrosion activity. The total impedance of the bare substrate after 12 h of immersion is lower than 10⁴ V cm². At this stage, the untreated surface shows a significant amount of corrosion products. For the substrates pretreated with BTSE modified with SiO₂, the spectra are also characterized by the presence of two time constants. The low-frequency time constant develops at around 10 rad/s, and the high frequency time constant appears at 10⁴ rad/s. The pretreatment modified with SiO₂ increases the low-frequency impedance of the system by about two orders of magnitude, comparatively to the untreated HDG substrate. The pretreatment with BTSE only (without SiO₂) reveals, after 24 h of immersion, impedance values below those of the pretreatment modified with SiO₂. Moreover, for the BTSE pretreated samples (without silica addition), the total impedance values starts to decrease after 24 h of immersion [18], whereas for BTSE doped with SiO₂, the total...
impedance increases during the first 3 days of immersion (Fig. 1). However, later on, there is an important decrease of the impedance values. The first signs of corrosion activity were detected between the 4th and 5th day of immersion. Nevertheless, the impedance values are more than one order of magnitude higher than those for the untreated sample.

For the substrates pretreated with BTESPT and SiO$_2$, the impedance spectra do not evidence the presence of two time constants (Fig. 2). The spectra are characterized by a broad time constant, which may include two superimposed processes with identical relaxation times.

During the first stages of immersion, the total impedance of the system BTESPT plus SiO$_2$ is more than two orders of magnitude above the impedance of the untreated HDG and about one order of magnitude above the impedance of the substrate pretreated with BTESPT only. The visible signs of corrosion activity were detected between the 3rd and the 4th day of immersion.

Comparison of BTSE and BTESPT (both doped with SiO$_2$) reveals that BTESPT leads to the highest impedance values during the first 3 days of immersion. For the substrates pretreated with BTSE and SiO$_2$, the impedance shows an important increase during the first 3 days of immersion, whereas for BTESPT and SiO$_2$, it slowly increases during the first 24 h and later on starts to decrease. This behaviour suggests that, although initially, the protection conferred by the BTESPT-containing film is higher, it deteriorates more rapidly than the BTSE-containing film.

The presence of two time constants in the impedance spectra obtained for metallic substrates pretreated with bis-silanes has been reported in literature [8,9,12,14,18]. The high-frequency time constant has been attributed to the response of an external silane layer, and the low-frequency time constant has been correlated with the presence of an “interfacial inorganic layer.” Corrosion is normally attributed to a third relaxation process, occurring in a very low frequency range. The EIS spectra for BTSE plus SiO$_2$ (Fig. 1) show a behaviour very close to that previously described. Thus, the high-frequency time constant can be attributed to the presence of an outer silane layer, whereas the process observed at lower frequencies can be correlated with an “oxide-type” film existing at the interface silane film/substrate. During the first 3 days of immersion, the shape and values of the phase angle in the high-frequency range are nearly constant, suggesting that the resistance and capacitance of the outermost silane layer are nearly constant. However, in the low-frequency region, there is a clear modification characterized by an increase of the resistance. This behaviour shows that the inner layer of the film seems to become slightly more protective with time.

![Anodic polarization curves for HDG substrates pretreated with bis-silanes with and without SiO$_2$ addition. The plot for HDG is also included.](image)

**Fig. 4.** Anodic polarization curves for HDG substrates pretreated with bis-silanes with and without SiO$_2$ addition. The plot for HDG is also included.

![SVET scans for the BTSE plus SiO$_2$ pretreated samples. (A) After 1 day of immersion; (B) after 5 days of immersion. Scan area, 1×1 mm.](image)

**Fig. 5.** SVET scans for the BTSE plus SiO$_2$ pretreated samples. (A) After 1 day of immersion; (B) after 5 days of immersion. Scan area, 1×1 mm.
Concerning BTESPT plus SiO$_2$, the time constant observed in Fig. 2 may be associated with the presence of only one layer or with the presence of two layers, which are characterized by relaxation phenomena presenting identical time constants. With increasing immersion time, the phase angle shifts towards higher frequencies, and later on, only one relaxation process is present.

Figs. 3 and 4 depict the potentiodynamic polarization curves obtained for the different systems. All the pretreatments led to a decrease of the cathodic currents comparatively to the untreated HDG (Fig. 3). The most important decrease is observed for the pretreatment with BTSE and SiO$_2$. The presence of SiO$_2$ has no effect on the cathodic polarization of the BTESPT pretreated substrates. The anodic branch (Fig. 4) shows a decrease of the anodic currents for all the different pretreatments. Literature [8,9,12,13] generally reports that the reduction of the anodic and of the cathodic currents are due to a physical barrier effect resulting from the presence of the silane coating that reduces the active area. The results depicted in Figs. 3 and 4 show that the silane pretreatment increases the polarization of the anodic and cathodic reactions in consequence of the increase of the ohmic drop on the surface.

Figs. 5–7 depict the current maps obtained by SVET measurements. After 1 day of immersion, the surface of the substrate pretreated with BTSE and SiO$_2$ (Fig. 5A) shows very low currents, suggesting reduced activity on the surface. After 5 days (Fig. 5B), there is evident surface activity, and two anodic areas were detected in good agreement with the impedance changes observed in the EIS spectra. For the substrate pretreated with BTESPT and SiO$_2$, identical behaviour was observed (Figs. 6A and B). For the untreated substrate, anodic activity was observed after only 1 h of immersion (Fig. 7). The SVET measurements show that the anodic activity develops in localised areas of the pretreated substrate and suggests that some sites of the film are “weaker” (thinner or presenting defects) and, thus, more prone to electrolyte uptake and localised corrosion onset. Furthermore, the SVET results indicate that the substrates pretreated with silane films modified with SiO$_2$ are much more resistant against corrosion development than the untreated substrates.

3.2. Analytical characterization

The chemical characterization and the in-depth distribution of the different elements present in the surface film for the specimens pretreated with silane solutions containing silica were assessed by Auger depth profiling. Prior immersion, the Auger depth profiles obtained on substrate pretreated with BTSE and SiO$_2$ (Fig. 8) reveal the presence of a film composed by carbon, silicon and oxygen deposited on the top of the native zinc surface. The amounts of silicon and oxygen are identical, being around 20–25%. After 4 days of immersion (Fig. 9), there is a marked decrease of the carbon content, and the amount of silicon and oxygen increases together with that of zinc. The silicon content is now around two times higher than the content determined prior immersion and passes through a maximum near the film/substrate interface. This evolu-
tion accounts for the presence of a Si-rich zone present in the inner layers of the surface film. The thickness of the BTSE films modified with silica also increases, comparatively to the films without silica addition. This statement is based on the evolution of the silicon profile. For the films without silica addition, silicon was removed after approximately 500 s of sputtering [18], whereas for the films modified with silica, the sputtering time necessary for silicon removal is about 1000 s.

For the substrates pretreated with BTESPT modified with SiO$_2$, the AES depth profiles obtained prior immersion reveal the presence of the same elements observed for BTSE and also the presence of sulphur. The most interesting feature of the depth profiles obtained on the BTESPT coatings is the fact that sulphur extends over a depth larger than that of silicon. This behaviour was addressed and discussed in previous works [14,19,20]. After 4 days of immersion, the Auger depth profiles revealed a surface film with very low content of silicon.

Figs. 10 and 11 depict the Si2p photoelectron spectra for the samples pretreated with BTSE and BTESPT modified with SiO$_2$, respectively. The Zn2p$_{3/2}$ spectra are also included in Figs. 10 and 11. The spectra obtained for each pretreatment were taken after different immersion times and reveal some important changes. For the films formed with BTSE modified with SiO$_2$, there is a decrease on the intensity of the Si2p spectra together with an increase on the intensity of the Zn2p$_{3/2}$ spectra. Simultaneously, the Si2p peaks shift from 103.2 eV towards lower binding energies (102.2 eV), revealing an important contribution of Si–O bonds. The highest binding energy value may be attributed to the presence of residual ester groups in the silane film, whereas the lowest values indicate formation of Si–O–Si bonds [18].

Concerning the substrate pretreated with BTESPT modified with SiO$_2$, the XPS results (Fig. 11) obtained

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**Fig. 8.** AES depth profiles obtained on the sample pretreated with BTSE plus SiO$_2$ prior immersion in the NaCl solution.

**Fig. 9.** AES depth profiles obtained on the sample pretreated with BTSE plus SiO$_2$ after 4 days of immersion in the NaCl solution.

**Fig. 10.** Si2p and Zn2p$_{3/2}$ photoelectron spectra obtained on HDG surfaces pretreated with BTSE plus SiO$_2$ after different immersion times.

**Fig. 11.** Si2p and Zn2p$_{3/2}$ photoelectron spectra obtained on HDG surfaces pretreated with BTESPT plus SiO$_2$ after different immersion times.
prior immersion and after 24 h of immersion reveal the presence of a film rich in silicon, oxygen and sulphur. After 4 days of immersion, the amount of silicon is very low, revealing strong deterioration of the silane film. Simultaneously, the amount of zinc and oxygen strongly increases, revealing corrosion onset. Traces of chloride were also detected on the surface.

The S2p photoelectron spectrum shows that sulphur is present in the film (Fig. 12). During immersion in the aggressive solution, the intensity of the S2p spectrum decreases, but after 4 days of immersion, some sulphur is still present on the surface. The presence of sulphur and the reduced contents of silicon suggest that sulphur bonds with the zinc substrate. It has been reported [2,3] that the sulphur groups existing in the BTESPT molecules may bind with substrates that have affinity for sulphur, such as zinc or copper. Previous works [20] report that BTESPT films without cure evidence S2p photoelectron spectra with increasing FWHM and slightly decreased binding energy, comparatively to the cured films. These changes were attributed to an interaction between sulphur and zinc, since zinc was detected during the analysis. The results depicted in Fig. 12 account for an identical behaviour. Thus, it seems that sulphur reacts with the native zinc substrate, leading to the formation of zinc–sulphur species, which remain on the surface even after the deterioration of the outer silane film.

The changes on the morphology of the pretreated surface were evaluated by AFM. The AFM images were obtained on polished zinc samples to avoid the large roughness characteristic of galvanized steel. Fig. 13 presents the morphology of polished zinc specimens coated with the different silanes prior immersion. The surface of the films formed with BTSE and BTESPT modified with SiO2 shows the presence of some particles with dimensions around 1–2 μm, which correspond to the silica particles in good agreement with the product content. The AFM scans suggest that the silica particles seem to form agglomerates. This may be due to a faster sedimentation process, resulting from the relatively high diameter and density of the silica particles. The silane films modified with silica and formed on polished surfaces seem to be thicker than the silane films without silica addition. This statement is based on the fact
that the morphology of the polished substrates could be observed in the AFM scans obtained on the films without silica addition, contrasting with the scans obtained on the films modified with silica, where the morphology of the substrate is more difficult to observe. This behaviour is in good agreement with the Auger depth profiles, which reveal that the BTSE plus SiO2 films (Figs. 8 and 9) seem to be thicker than the BTSE films without silica [18]. Gallardo et al. [21] also found an increase of the coating thickness for silica-based sol-gel coatings due to the addition of glass microparticles. The modified silane films also seem to be relatively uniform except in the zones where the SiO2 particles aggregate.

Fig. 14 presents the evolution of the surface morphology of the polished zinc specimens pretreated with BTSE plus SiO2 and BTSE solutions prior immersion and after 24 h of immersion in diluted NaCl solution. The AFM scans obtained after 24 h of immersion (Fig. 14A) show that the
surface presents an “oxide-type” structure. The topography profile accounts for a small increase of the surface roughness. This may be due to deterioration of the outer carbon-rich layers in good agreement with the AES measurements, which showed a decrease of the carbon content after immersion in the NaCl solution.

The topography of the zinc substrates coated with BTSE (without silica) is presented on the Fig. 14B. After 24 h of immersion, the surface of the BTSE film presents higher roughness, when compared to the film modified with silica (Fig. 14A). The topography profile shows that the roughness increases by more than one order of magnitude in the absence of SiO2.

The changes on the surface roughness for the BTESPT films were identical to that observed for the BTSE films. However, for BTESPT, the differences between the SiO2-containing films and the SiO2-free films were not so evident as those observed for the BTSE films.

4. Discussion

The pretreatments based on BTESPT solutions modified with SiO2 have been investigated in what concerns corrosion protection of aluminium alloys [15]. However, the use of such pretreatments aiming at corrosion protection of coil-coated galvanized steel has not been reported. Literature [12] suggests that pretreatments based on BTESPT are more effective for corrosion protection of aluminium alloys than for protection of galvanized steel. The effect was attributed to insufficient wetting of the native zinc oxide and consequently to the formation of a film presenting defects. However, previous results [18–20] showed that pretreatments based on BTESPT and BTSE solutions could improve the corrosion resistance of galvanized steel panels either painted or nonpainted. Furthermore, painted samples pretreated with BTESPT presented higher corrosion resistance than painted panels pretreated with Cr(VI)-based solutions [19,20]. These previous results suggest that BTESPT and BTSE can be used as alternative pretreatments for corrosion protection of galvanized steel.

Literature [2,5,12,13,16] reports that the corrosion protection provided by the silane coatings arises from the formation of a barrier film, which hinders the access of aggressive species to the metallic substrate. The improved corrosion protection of aluminium alloys (AA 2024) pretreated with BTESPT was also correlated with the possible formation of a sulphide film at the silane metal interface [2] or with the formation of an interfacial layer underneath an external silane-rich layer [8]. This interfacial layer seems to result from the formation of metal–silicon–oxygen (oxane) bonds. In some cases, the formation of a silicate conversion layer is also postulated [2,15]. All these assumptions led to the development of a number of models, especially for aluminium alloys, but none of them is fully proved.

It was shown [15] that the addition of controlled amounts of silica can reinforce and strength the bis-sulphur silane films, especially the interfacial layer. It is also claimed that the increasing amount of silica particles improves film strength. The role of SiO2 on bis-sulphur silane films was discussed for aluminium alloys [15], and it is suggested that small amounts of SiO2 can be converted into SiO32−, leading to the formation of an inhibiting silicate layer at the silane film/aluminium oxide interface. This silicate-containing layer improves corrosion protection of the substrate. However, the same work [15] also reports that the corrosion performance is dependent on the amount of silica. The excess of SiO2 can facilitate water uptake through the pores of the surface film, causing its premature deterioration. Nevertheless, the addition of controlled amounts of silica to bis-sulphur silanes films seems to increase corrosion resistance of the AA 2024 substrates. Results concerning the behaviour of SiO2-modified silane pretreatments on the corrosion behaviour of hot dip galvanized steel are nonexistent in spite of the importance of effective pretreatments for delaying “white staining” of zinc. Thus, the aim of the present work is to highlight the electrochemical behaviour and the chemical composition of the films formed on HDG substrates pretreated with bis-silane films modified with SiO2. Moreover, the work aims at understanding the role of the addition of SiO2 to the silane film and its early deterioration during immersion in NaCl solutions.

The results obtained in the present work show that the addition of 50 ppm of silica enhances the corrosion protection provided by the silane films. The presence of silica in the silane coating increases the impedance of the pretreated substrates comparatively to the films without silica addition. For BTESPT plus SiO2, after 24 h of immersion, the impedance values are about one order of magnitude above those of the substrate pretreated with BTESPT without SiO2 solutions. For BTSE, this difference is not so marked; however, with time, the impedance increases, and after 3 days, it attains values closer to those observed for BTESPT plus SiO2. During the first 3 days of immersion, the total impedance of the substrates pretreated with BTSE plus SiO2 increased, suggesting that some reactions occur within the film, helping to enhance corrosion protection.

During the first stages of immersion, the protection obtained with BTESPT modified with SiO2 seems to be more effective than that obtained with the BTSE modified films. However, according to the SVET and EIS results, the BTESPT plus SiO2 film looses its protective character faster than the BTSE modified film.

The increased corrosion protection observed for the pretreatments modified with silica during the 1st days of immersion can result from increased film thickness and/or decreased porosity due to incorporation of silica. The increased film thickness in the presence of SiO2 was stated by AES and AFM.

The XPS results reveal that the intensity of the Si2p, O1s and C1s photoionisation spectra decreases for both silanes
The addition of SiO2 particles reinforces the corrosion protection of the silane films. The improved protection may arise from a combination of decreased coating porosity, increased film thickness and reinforcement of the inner layers of the film. This combination results in a more protective and durable barrier film.

5. Conclusions

Bis-silane films modified with particles of SiO2 are effective pretreatments for corrosion protection of galvanized steel substrates. The addition of silica particles improves corrosion protection due to the formation of a thicker silane film and/or enhanced barrier properties provided by the inner layers of the silane film.

During the early stages of immersion, the films formed with bis-[triethoxysilylpropyl] tetrasulfide and silica are more protective than the films formed with bis-1,2-[triethoxysilyl]ethane and silica. Later on, this behaviour is modified, and the bis-sulphur silane becomes less protective. The long-term protection provided by the BTSE films results from the presence of a Si-rich oxide layer rather than the outer organic-rich layers.

The presence of sulphur in the films formed with bis-[triethoxysilylpropyl] tetrasulfide and its affinity for zinc seems to create a competition between sulphur and silicon during the formation of the first monolayers of the silane film. Sulphur can occupy a number of sites on the substrate, leading to stable bonds with the native zinc surface. This results in a decrease on the number of sites available for bonds between silanol and the metal. After long immersion times, sulphur remains on the surface, whereas silicon is released. Nevertheless, during the initial stages of immersion, the bis-[triethoxysilylpropyl] tetrasulfide films confer improved corrosion protection of the pretreated substrates.

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