Analytical characterization of silane films modified with cerium activated nanoparticles and its relation with the corrosion protection of galvanised steel substrates

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Abstract

Galvanised steel substrates were pre-treated in bis-1,2-[triethoxysilylpropyl]tetrasulphide silane solutions containing SiO\textsubscript{2} or CeO\textsubscript{2} nanoparticles activated with cerium ions. The surface composition was investigated by infrared spectroscopy. The film thickness was determined by scanning electron microscopy. The results showed that the barrier properties of silane films modified with nanoparticles depend upon the concentration of nanoparticles. The results also showed that the silane film thickness increases when the nanoparticles are activated with cerium ions. The anti-corrosion behaviour of the cerium activated nanoparticles was also investigated at the microscale level, in artificial induced defects, using the scanning vibrating electrode technique (SVET). The substrates treated with the silane coating modified with CeO\textsubscript{2} nanoparticles revealed improved corrosion behaviour comparatively to the coatings modified with SiO\textsubscript{2} nanoparticles. X-ray photoelectron spectroscopy and Auger electron spectroscopy experiments carried out on the defects after immersion in NaCl solutions revealed the presence of a surface film containing zinc corrosion products and cerium/ceria compounds.

Keywords: Silanes; Corrosion; SVET; SiO\textsubscript{2}; CeO\textsubscript{2}; Nanoparticles

1. Introduction

The modification of surface films like sol–gel or silane films used for corrosion protection of metallic substrates is an emerging field with potential impact on the steel industry. Among the possible methodologies to modify these surface films, the addition of nanoparticles has been successfully investigated \cite{1–10}. The nanoparticles can be synthesised in the films, as reported for sol–gel coatings \cite{1–3} or they can be added to the pre-treatment solutions \cite{4}. The corrosion resistance of Mg alloys pre-treated with sol–gel coatings containing ZrO\textsubscript{2} and CeO\textsubscript{2} nanoparticles was investigated and it was reported that the CeO\textsubscript{2} component provides enhanced corrosion protection, while ZrO\textsubscript{2} imparts corrosion as well as wear resistance \cite{5}. Van Ooij and co-workers \cite{6} showed that silane films could be thickened and strengthened by loading them with silica particles. That work \cite{6} demonstrates that SiO\textsubscript{2} particles improve corrosion resistance by entering a reaction that produces stable silicates. The results also report that the silane films, when heavily loaded with silica, develop a porous structure, which promotes electrolyte uptake and premature film delamination. The addition of SiO\textsubscript{2} nanoparticles to silane films electrodeposited on aluminium substrates revealed improved corrosion resistance and “critical contents” have been proposed \cite{7}.

A literature survey revealed that the CeO\textsubscript{2} nanoparticles are used in many different fields. However no works could be found reporting the use of these nanoparticles as fillers for silane films. Therefore, the present research work reports and discusses the protective behaviour of silane films loaded with CeO\textsubscript{2} nanoparticles (average diameter 10–20 nm) or SiO\textsubscript{2} (average diameter 30–40 nm). The work also presents an innovative approach in which the nanoparticles are activated with cerium ions in order to improve the corrosion resistance of galvanised steel substrates. The work reports the analytical and morphological characterisation of silane films modified with the nanoparticles and relates these features with the corrosion resistance of pre-treated galvanised steel substrates.
The results obtained in the present work show that the protective behaviour depends upon the concentration of nanoparticles and that the activation of the nanoparticles with cerium ions leads to the formation of thicker and more protective silane films. In the presence of localised defects, the CeO₂-filled films present better anti-corrosion performance when compared to the SiO₂-filled ones.

2. Experimental procedure

2.1. Pre-treatment

The silica nanoparticles (diameter of 30–40 nm) were obtained from Degussa (Aerosil®) and the ceria nanoparticles (diameter of 10–20 nm) were obtained from Sigma–Aldrich. The purity of the nanoparticles was ≥99.8% for SiO₂ and ≥99.9% for CeO₂. The nanoparticles were ultrasonically dispersed in aqueous solutions of cerium nitrate and this aqueous dispersion was then used for the preparation of the silane solution. Dispersions of the same nanoparticles but without cerium ions were also prepared. The final concentration of nanoparticles in the silane solution was 100 ppm, 250 ppm or 500 ppm. The concentration of cerium ions in the solutions used for activation of the nanoparticles was also 250 ppm of Ce³⁺.

The bis-[triethoxysilylpropyl] tetrasulfide silane (Sigma–Aldrich) solution was prepared by dissolving 5% (vol/vol) of silane in a mixture of methanol (90% v/v) and the aqueous dispersion of nanoparticles. The silane solution was stirred for 1 h and was kept for few days before use.

The substrate was galvanised steel (10 μm zinc layer without post-annealing). The metallic coupons were degreased in acetone and then immersed in a solution of alkaline cleaner.
Novomax®) for 4–5 min at 50 °C for cleaning and degreasing. After this the coupons were washed with bi-distilled water, dried in air and dipped in the modified silane solution for 10 s. The coupons were cured in the oven at 120 °C for 40 min.

2.2. Electrochemical techniques

The EIS measurements were carried out using a Gamry FAS1 Femtostat with a PC4 Controller Board at room temperature, in a Faraday cage, at the open circuit potential. 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 was used. The measuring frequency ranged from 10⁵ 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.

The SVET measurements were performed using the Applicable Electronics equipment, controlled by the ASET program (Sciencewares). The vibrating electrode was made of platinum–iridium covered with polymer, leaving only an uncovered tip with a diameter of 40–50 μm. The distance of the tip to the surface was kept at 200 μm, as previously optimised. The scanned area was 0.2 cm × 0.2 cm. To evaluate the corrosion inhibition performance of the modified silane film, a scratch was made on the surface using an edge knife. The dimensions of the scratch were approximately 0.5–0.6 mm length by 0.1 mm wide. The zinc surface was exposed in the scratch. The silane treated galvanised steel coupons were immersed in the aggressive solution (0.005 M NaCl) and measurements were taken periodically.

The potentiodynamic polarization curves were performed using a RADIOMETER-VOLTALAB PGZ 100 apparatus. The scan rate was 1 mV/s in the anodic direction, starting from the open circuit potential after different stabilisation times. An electrochemical cell consisting of three-electrodes as the one described for the EIS measurements was used.

2.3. Analytical techniques

AES and XPS analyses were carried out using a 310 F Micro-lab (Thermo Electron, former VG Scientific). XPS spectra were taken in CAE mode (30 eV), using an Mg (non-monochromated) anode. The spot of the X-ray beam was around 0.3 cm × 0.3 cm. Auger spectra were obtained using a 10 keV and ~40 nA primary electron beam.

The FTIR experiments were performed using a Nicolet 5700 Fourier Transform Infrared spectrometer from Thermo Electron.

Scanning electron microscopy was performed using a Hitachi Model S-2400 Microscope with a 25 keV electron beam.

3. Results and discussion

Fig. 1 depicts the electrochemical impedance results obtained on the silane films filled with 100, 250 and 500 ppm of CeO₂ or SiO₂ nanoparticles after 24 h of immersion in 0.005 M NaCl. The impedance spectra show a capacitive response in the high frequency range and a resistive response in the low frequency range.

Fig. 3. SEM images obtained on the modified silane films. (a) Film modified with SiO₂, (b) film modified with SiO₂ activated with cerium ions, (c) film modified with CeO₂ and (d) film modified with CeO₂ activated with cerium ions.
range, followed by an inductive behaviour at the lowest frequency values.

The low frequency impedance values depend upon the type and concentration of nanoparticles. For the films modified with 100 and 250 ppm of CeO$_2$ the low frequency resistance values are identical ($\sim 10\, \text{MΩ cm}^{-2}$), but there is a strong drop, of about two orders of magnitude, for the films modified with 500 ppm of CeO$_2$. The impedance values approach those of the blank silane film.

The films modified with SiO$_2$ show an identical trend. However, the highest impedance values ($\sim 5\, \text{MΩ cm}^{-2}$) are observed for the films containing 250 ppm of SiO$_2$ and the lowest ones for the films with 500 ppm of SiO$_2$. The EIS results suggest that the amount of nanoparticles has an important impact on the barrier properties of the silane films. The lowest contents result in better barrier properties, whereas the increase of the amount of nanoparticles has a negative impact on the barrier properties. This trend has been noticed in literature [6,7] and has been attributed to the fact that nanoparticles are likely to agglomerate and to create large defects in the coating, promoting the uptake of the aggressive solution and therefore corrosion activity.

Following these results it was decided to investigate the films modified with 250 ppm of CeO$_2$ or SiO$_2$ nanoparticles and the films modified with the same amount of nanoparticles, but previously activated with cerium ions. After 24 h of immersion, in the same electrolyte solution, the EIS spectra show that the activation of the nanoparticles with cerium ions results in higher impedance values; the effect being more marked for the CeO$_2$ activated nanoparticles (Fig. 2). The activation of CeO$_2$ with cerium ions increased the low frequency values from $10\, \text{MΩ cm}^{-2}$ (as observed in Fig. 1) to values above $100\, \text{MΩ cm}^{-2}$ (Fig. 2).

The EIS results show that the activation of the nanoparticles with cerium ions enhances the protective properties of the modified silane films. These effects can be result of increased film thickness and/or reduced porosity.

The thickness of the silane films was determined by scanning electron microscopy—Fig. 3. The films filled with SiO$_2$ present a thickness around 3 $\mu$m that increases about twice for the films filled with SiO$_2$ nanoparticles activated with cerium ions. The films filled with CeO$_2$ reveal thicknesses around 2.7–2.8 $\mu$m that increase to values around 5.5 $\mu$m in the presence of cerium ions. All the modified films are thicker than the blank silane film, which showed thicknesses below 1 $\mu$m.

The SEM results show that the improved barrier properties observed in the EIS measurements for the films containing the activated nanoparticles can be a consequence of the increased film thickness. On the other hand, the presence of cerium ions also promotes the formation of reactive silanol groups in the silane molecules, leading to a higher degree of cross-linking, higher silicon content and therefore more homogeneous films with better barrier properties as reported in a previous work [8]. In this way the total impedance can increase by one (or more) order of magnitude.

The composition of the silane films modified with 250 ppm of nanoparticles was investigated by FTIR. Fig. 4 depicts the FTIR results obtained on the different samples after subtraction of the spectra characteristic of the blank silane film. This procedure evidences the differences between the modified silane films and the blank film. Some characteristic bands can be observed in the spectra [9,10]: the band around 3400 cm$^{-1}$ is due to stretching of OH in the Si–OH groups. The band at approximately 1000 cm$^{-1}$ was assigned to Si–O–Si. At slightly higher wave numbers there are several bands that correspond to the presence...
of Si–(CH\textsubscript{2})\textit{n} and O–CH\textsubscript{2}CH\textsubscript{3} groups. The spectra obtained for the films modified with CeO\textsubscript{2} (Fig. 4a and b) reveal the presence of two features at 516 and 450 cm\textsuperscript{-1} that are likely to be due to the presence of Ce–O bonds \cite{11} as expected. However, these bands are also present in the films containing SiO\textsubscript{2} nanoparticles activated with cerium ions (Fig. 4d), suggesting that the cerium ions can be bond on the surface of the SiO\textsubscript{2} nanoparticles and/or inserted in the siloxane network.

The investigation of the corrosion inhibition properties of the films modified with the nanoparticles was investigated with the scanning vibrating electrode technique (SVET). This is an electrochemical mapping technique that resolves and quantifies localised corrosion. It has been used to investigate pitting and corrosion phenomena like, corrosion at cut edges and zinc dissolution \cite{12–14}. SVET measurements use a vibrating microtip electrode that is mechanically scanned at a fixed distance from the corroding surface and that do not perturb the local activity.

In this work, the SVET technique was used to investigate the corrosion activity starting at scratches artificially formed on the surface of the modified films. The formation of an artificial scratch before immersion of the pre-treated coupons in the aggressive electrolyte ensures that corrosion activity starts at the same time in all the samples and ensures identical geometry and dimensions for the defects. In this way, the results are comparable and the corrosion ability performance of the different fillers can be clearly distinguished.

SVET maps were obtained periodically during immersion in 0.005 M NaCl, as depicted in Fig. 5. The maps show development of anodic activity over the scratch. The remaining surface behaves as cathodic. The highest anodic current densities were observed for the SiO\textsubscript{2}-filled films. After 3 h of immersion these films already revealed an enlargement of the scratched area and some delamination of the silane film. These effects were clearly delayed in the presence of SiO\textsubscript{2} nanoparticles activated with cerium ions—Fig. 5b.

From the SVET maps, the values of the anodic (positive) and cathodic (negative) currents were determined along a line, crossing the defect perpendicularly to it. Figs. 6 and 7 depict the current plots obtained on the scratched samples. In the abscissas axis, the zero value corresponds to the centre of the defect. The plots obtained for the scratched film filled with SiO\textsubscript{2}—Fig. 6(a) reveal increasing anodic current densities around the defect. After 8 h of immersion the SVET scans show strong anodic activity and, after that, the scratched area could not be distinguished with accuracy due to deterioration of the coating. However, for the films modified with SiO\textsubscript{2} activated with cerium ions, although important anodic activity, the currents are lower and accurate results could be taken during a 24 h

![Fig. 5. SVET map obtained on the films modified with SiO\textsubscript{2} after 3 h of immersion in 0.005 M NaCl. The scanned area is 0.2 cm × 0.2 cm and the current units are µA/cm\textsuperscript{2}.](image-url)
immersion period. During this period, the SVET maps obtained on the films modified with cerium activated SiO₂ reveal anodic current densities that are about one half of the values measured for the systems containing SiO₂ only. The SVET results suggest that there is practically no corrosion inhibition in the SiO₂-filled films; however, the corrosion processes and film delamination are delayed when the silica nanoparticles are activated with cerium ions.

The CeO₂-filled films reveal a distinct behaviour—Fig. 7. For the system filled with CeO₂ both anodic and cathodic currents are very low, suggesting that corrosion activity was very weak. This trend was observed during a 72 h immersion period for the films modified with CeO₂ only and for more than 120 h (5 days) for the films modified with the CeO₂ nanoparticles activated with cerium ions. The SVET maps show that in the presence of identical defects in the surface film, the anodic and the cathodic activities are strongly reduced in the presence of CeO₂ nanoparticles. The more protective behaviour of the films modified with CeO₂ was also confirmed by potentiodynamic polarisation (Fig. 8). After 6 h of immersion the results show a strong polarisation of the anodic reaction for the systems filled with CeO₂ nanoparticles activated with cerium ions. These films also reveal anodic current densities that are much lower, than those of the films loaded with SiO₂, in good agreement with the SVET measurements. Furthermore, the anodic branch reveals the presence of an incipient passivation plateau, which suggests the presence of a more protective surface film. This plateau could not be observed in the reference film and in the SiO₂-filled films. The results suggest that the addition of CeO₂ and the activation of the nanoparticles with cerium ions provide polarisation of the anodic reactions and formation of more protective surface films.

The composition of the scratched surface was investigated via Auger electron spectroscopy. Figs. 9 and 10 depict the AES results obtained along a line that crossed the defect, perpendicularly to it, on the samples modified with CeO₂ and SiO₂ cerium ions activated nanoparticles, respectively. Spectra were taken after 6 h of immersion. Outside the defect the Auger spectra reveal the presence of carbon, silicon sulphur and oxygen. In the defect, the spectra reveal the presence of zinc, oxygen cerium and traces of chloride. The amount of cerium is very low; however it seems to be slightly higher in the films containing CeO₂ activated with cerium ions. This result suggests that the CeO₂ nanoparticles are also present in the oxide layer that forms on the exposed surface.

XPS measurements were taken over the scratched surface after the same immersion period. The spectra for the Ce 3d
region are depicted in Fig. 11. The spectrum is more defined for the CeO$_2$-filled film and it is possible to detect two forms of cerium: Ce$^{3+}$ and Ce$^{4+}$. The presence of Ce$^{4+}$ is confirmed by the satellite peak that appears at approximately 918 eV. The peak characteristic of Ce$^{4+}$ is mainly due to the presence of nanoparticles, whereas that of Ce$^{3+}$ accounts for cerium species, resulting from the precipitation of cerium (III) ions. These features could not be detected in the SiO$_2$-filled films activated with the nanoparticles because of the low signal to background ratio.

The analytical results revealed the presence of cerium species on the surface film that growth on the exposed zinc surface. The electrochemical results showed that the presence of CeO$_2$
nanoparticles and the addition of cerium ions are highly effective in the inhibition of the corrosion processes starting at defects.

Literature [15] reports that different species like Zn$^{2+}$, ZnCl$^+$, Zn(OH)$^+$, ZnO and Zn$_3$(OH)$_8$Cl$_2$ contribute to the stability of the protective layer of corrosion products formed during zinc corrosion. The presence of cerium ions, that are leached out from the surface of the nanoparticles or from the silane film results in the formation of protective cerium oxides/hydroxides, which provide extra corrosion protection. The improved behaviour observed for the scratched films filled with CeO$_2$ nanoparticles can also be explained based on the fact that CeO$_2$ nanoparticles easily incorporate other species, like ions, by forming charge-compensating defects on the oxygen sub-lattice [16, 17]. Therefore, the CeO$_2$ nanoparticles can complex the species that promote the loss of passivation, like chlorides. Additionally they may contribute to stabilise the passive film through the formation of stable ceria-based oxides as proposed in a previous work [18]. Therefore, the improved corrosion resistance can be explained assuming: (i) a more stable and protective film of corrosion products formed on the exposed surface and/or (ii) a lower amount of free chlorides, available for disruption of this protective film.

The SiO$_2$ nanoparticles are not as effective as the CeO$_2$ ones; however, the corrosion resistance could be improved with previous activation with cerium ions. The poorest corrosion results obtained for films filled with SiO$_2$ are probably due to the low stability of SiO$_2$ under increased alkaline conditions as those generated at the cathodic sites. The SiO$_2$ nanoparticles decompose in alkaline pH leading to the formation of an expansive gel that accelerates silane film degradation and delamination. This behaviour contrasts with that of CeO$_2$ that is very stable in alkaline conditions. When the silane network degrades, the CeO$_2$ nanoparticles are leached out and precipitate together with the zinc corrosion products, producing a more stable and protective layer of corrosion products.

4. Conclusions

The modification of bis-1,2-[triethoxysilylpropyl]tetrasulphide silane solutions with SiO$_2$ or CeO$_2$ nanoparticles results in improved barrier properties. However, the concentration of nanoparticles plays an important role in the silane film performance. An excess of nanoparticles leads to poorer barrier properties.

The activation of the nanoparticles with cerium ions reinforces the barrier properties of the silane films and imparts corrosion inhibition ability.

The addition of CeO$_2$ nanoparticles delays corrosion activity and film delamination and generates an important polarisation of the anodic reactions. These effects are enhanced when these nanoparticles are activated with cerium ions. Cerium(III) and cerium(IV) species were detected together with the corrosion products layer formed on the scratched surface.

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