Electrochemical study of modified bis-[triethoxysilylpropyl] tetrasulfide silane films applied on the AZ31 Mg alloy

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Abstract

This work investigates the protective behaviour of bis-[triethoxysilylpropyl] tetrasulfide silane pre-treatments on the AZ31 Mg alloy. The silane solution was modified by the addition of cerium nitrate or lanthanum nitrate in order to introduce corrosion inhibition properties in the silane film. The corrosion behaviour of the pre-treated AZ31 magnesium alloy was studied during immersion in 0.005 M NaCl solution, using electrochemical impedance spectroscopy and the scanning vibrating electrode technique (SVET). The electrochemical experiments showed that the presence of cerium ions or lanthanum ions improve the protective behaviour of the silane film. The SVET experiments evidenced that the presence cerium in the silane film led to an important reduction of the corrosion activity.

The results demonstrate that either cerium ions or lanthanum ions can be used as additives to the silane solutions to improve the performance of the pre-treatments for the AZ31 magnesium alloy.

Keywords: Magnesium alloy AZ31; Silanes; SVET; Cerium; Corrosion

1. Introduction

The use of magnesium alloys for different applications has been increasing during the last years. The need of lighter materials for specific applications such as the electronic industry led to an increasing interest on the corrosion behaviour of Mg alloys. They are used in the production of cellular phones, notebooks and other electronic devices. The alloys are also used in the automotive and aeronautical industry, mainly in structural components.

The increasing interest on the use of Mg alloys is due to the fact that these alloys exhibit an attractive combination of low density, high strength, good damping capacity, castability and machinability. The AZ grades of Mg alloys contain aluminium and zinc. Zinc is effective to increase strength. Aluminium increases strength and corrosion resistance, but reduces castability and weldability.

Mg alloys show a surface film composed essentially of a mixture of MgO and Mg(OH)2, which provides reasonable corrosion protection in air, but becoming very unstable in aqueous or in high humidity environments. Thus, Mg alloys are generally used in environments with reduced aggressiveness because they are very sensitive to corrosion attack. To improve the lifetime of Mg alloys different chemical treatments and organic coatings are generally applied on their surface. In addition to improved durability, organic coatings also confer specific functionalities and aesthetic properties. For such purposes, adhesion of the coating to the bare substrate is an important issue for the durability of the coated material under service. Thus, the performance of coated Mg alloys is strongly dependent on the corrosion resistance and on the adhesion properties of the coating to the metallic substrate.

The corrosion resistance of Mg and its alloys can be enhanced by different procedures. Anodising [1–4] has proved to improve the corrosion resistance of the alloys under aggressive environments. Anodic oxidation produces an oxide film with good corrosion resistance and reasonable adhesion properties. The deposition of chemical conversion layers using modified permanganate solutions led to the formation of a nearly protective
uniform coating [5,6]. The use of cerium rich conversion films is also reported in literature [7,8]. It is generally accepted that cerium ions are effective corrosion inhibitors and that they constitute a promising alternative to the use of pre-treatments based on Cr (VI)-containing formulations. Brunelli et al. [7,8] reported that cerium conversion films increased the corrosion resistance of the Mg alloys because they enoble the corrosion potential and decrease both the anodic and cathodic currents. An acid pre-treatment prior film formation increased the corrosion performance of the Ce conversion films.

Literature [9] also reports that the corrosion performance of painted samples pre-treated with phosphate exceeds that of painted Cr conversion layers.

Conversion films lead to the formation of a protective barrier, which delays or inhibits corrosion onset. However, the adhesion properties of these layers are somewhat poor and often they fail. Thus, adhesion promoters have also been tested. Surface treatments based on organofunctional solutions became an attractive method to reduce the corrosion rate of metallic substrates and to enhance adhesion. Functional silanes [10] and self assembled monolayers [11] have been successfully tested as pre-treatments for Mg alloys. These pre-treatments provide corrosion protection in addition to surface functionality, improving the compatibility of the metallic substrate with the painting systems.

Silane based pre-treatments lead to the formation of a thin organic coating that provides corrosion protection because it acts as a physical barrier that delays the ingress of aggressive species towards the metallic substrate. The performance of the silane coatings can be improved through the addition of species with corrosion inhibition properties to the silane solutions used for the pre-treatments. Among the possible additives, cerium and lanthanum salts show promising properties, since they have proven to inhibit the corrosion processes on steel [12], galvanised steel [13,14] and aluminium and its alloys [15,16]. In previous works it was demonstrated that cerium can be used as dopant in hybrid sol–gel and multifunctional silane pre-treatments [17–21]. The presence of this additive improved the barrier properties of the pre-treatment layer and decreased the corrosion rate of galvanised steel and aluminium substrates.

In the present work bis-[triethoxysilylpropyl] tetrasulfide silane pre-treatments modified with cerium nitrate or with lanthanum nitrate were applied on the AZ31 Mg alloys. The samples were tested during immersion in 0.005 M NaCl, which is a very aggressive environment for the Mg alloys. The pre-treated samples were studied via electrochemical impedance spectroscopy (EIS) and via scanning vibrating electrode technique (SVET). The results showed that silane based pre-treatments provide corrosion protection of the AZ31 Mg alloy and that the presence of cerium or lanthanum induced a decrease of the corrosion rate of the substrate.

2. Experimental procedure

2.1. Materials and solutions

AZ31 Mg alloy was obtained from Goodfellow. The surface of the alloy was polished with SiC paper of grit 2400. All the substrates were ultrasonically cleaned using acetone. Following cleaning the panels were washed with deionised water (Millipore) and dried in air.

The bis-[triethoxysilylpropyl] tetrasulfide silane (BTESPT) was obtained from Sigma/Aldrich. The pre-treatment solution was prepared by dissolving 5% (v/v) of silane in a mixture of methanol (90%, v/v) and the aqueous solution 10⁻³ M of nitrate salt (5.0%, v/v). Two aqueous solutions of nitrate salts were used: Ce(NO₃)₃ or La(NO₃)₃. The final concentration of the rare earth cation in the silane solution was 5.0 × 10⁻⁵ M. The silane solution was stirred during 1 h and kept for 3 days before use.

The pre-treatment consisted in the immersion of the metallic coupons in the silane solution for 10 s. The excess of solution was removed by using air stream and then the panels were cured in a Memmert oven at 120 °C for 40 min.

2.2. Electrochemical measurements

The scanning vibrating electrode technique (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.

The EIS measurements were performed at room temperature in a Faraday cage, using a Gamry FAS1 Femtostat plus a PC4 controller board. A three-electrode electrochemical cell was used, consisting of the working electrode (3.15 cm² of exposed area), the saturated calomel electrode as reference and the platinum as counter electrode. The measuring frequency ranged from 5 × 10⁻⁵ Hz down to 5 × 10⁻³ Hz. All the experiments were performed at the corrosion potential.

Electrochemical experiments were performed during immersion in 0.005 M sodium chloride solution. Reproducibility was confirmed on a minimum of two identical samples per condition.

3. Results and discussion

3.1. Electrochemical study

The EIS plots obtained for the bare metal (no pre-treatment) during immersion in 0.005 M NaCl are presented in Fig. 1. Due to the high corrosion rate of the blank substrate in this aggressive solution the EIS spectra were taken only during the first 24 h of immersion. It can be observed that the impedance increased by about one order of magnitude during the immersion period.

The EIS results obtained for samples treated with the silane solutions are presented in Figs. 2–4. For the silane treated samples the EIS measurements were performed during 1 week. The comparison of the EIS spectra obtained in the different samples after 1 day of immersion is depicted in Fig. 5. The presence of the silane film increased the low frequency impedance by more than one order of magnitude comparatively to the blank sample. The addition of cerium to the silane film increased the impedance by two orders of magnitude.
Fig. 1. EIS bode plots obtained for the bare AZ31 Mg alloy during 1 day of immersion in 0.005 M NaCl.

For the blank sample, the EIS spectra (Fig. 1) revealed a well-defined time constant around 10 Hz and, another one, at lower frequencies (<0.1 Hz). The high and the low frequency time constants were attributed to the response of charge transfer controlled processes and mass diffusion-controlled reactions, respectively.

The EIS spectra obtained for the samples treated with the silane solution modified with cerium nitrate (Fig. 2) showed different shapes during immersion. During the first 2 days of immersion the spectra revealed the presence of a time constant at frequencies around 100 Hz, which was attributed to the silane film properties (i.e., capacitance and resistance) and another one at lower frequencies (10 Hz), in the same frequency range of that observed for the blank sample, which was attributed to charge transfer controlled processes at the metal/silane film interface. Latter on the shape of these spectra changed and became more identical to that obtained for the blank sample, which was attributed to charge transfer controlled processes at the interface metal/silane coating. The absence of the time constant characteristic of the silane coating was also

and, contrarily to the spectra obtained for the system containing cerium, the silane layer did not reveal a defined time constant in the high frequency range of the EIS spectra. From Fig. 5 it can be seen that the spectra obtained for the BTESPT treated sample are very close to those of the blank sample. The sample treated with BTESPT and La shows a broader phase angle, which seems to include two overlapped time constants in the same frequency range of those observed for the Ce-containing film. However, the response of the silane film could not be clearly distinguished. The shape of the EIS spectra suggests that the barrier effect of the silane film on the BTESPT and the BTESPT plus La pre-treated samples were not as marked as that observed for the cerium-containing films. Despite the presence of the silane layers there was a very fast electrolyte uptake and the silane coating capacitance and resistance could not be clearly separated from the response of the processes occurring at the interface metal/silane coating. The absence of the time constant characteristic of the silane coating was also
Fig. 3. EIS bode plots obtained for the AZ31 Mg alloy pre-treated with BTESPT and La(NO₃)₃ during 1 week of immersion in 0.005 M NaCl.

reported for galvanised steel substrates treated with aminosilanes [22].

Detailed interpretation of the EIS plots was performed by numerical simulation, using an equivalent circuit composed of two-time constants (Fig. 6). This equivalent circuit reasonably fits the experimental results as can be confirmed in Fig. 6b and c. This equivalent circuit included constant phase elements (CPEs) to simulate the capacitive response of the EIS spectra. The CPE is generally attributed to distributed surface reactivity, surface heterogeneity, roughness or fractal geometry, electrode porosity, and to current and potential distributions related with electrode geometry. The CPE is associated with an exponent (α) and it has been considered to represent a circuit parameter with limiting behaviour as an ideal capacitor if α = 1 and a resistor for α = 0 [23].

Fitting parameters for the blank sample are presented in Fig. 7 and for the silane treated samples are presented in Figs. 8 and 9. Fig. 7a depicts the evolution of the low frequency CPE and high frequency CPE for the blank sample. The high frequency CPE was nearly constant and around $4 \times 10^{-5}$ F/cm$^2$. Such values indicate that for the blank sample the high frequency time constant is due to charge transfer controlled reactions. The resistance associated with this time constant increased with time, from $6 \times 10^3$ to $7 \times 10^4 \Omega$ cm$^2$. This increase can be explained assuming that the corrosion products formed at the surface developed a protective layer. The following reactions occur when the Mg substrates are immersed in neutral NaCl solution:

- **Cathodic reactions:**
  
  \[
  \begin{align*}
  \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- & \rightarrow 4\text{OH}^- \\
  2\text{H}_2\text{O} + 2\text{e}^- & \rightarrow 2\text{OH}^- + \text{H}_2 \uparrow
  \end{align*}
  \]

- **Anodic reactions:**
  
  \[
  \begin{align*}
  \text{Mg} & \rightarrow \text{Mg}^{2+} + 2\text{e}^-
  \end{align*}
  \]
Consequently the following reaction also occurs:

\[ \text{Mg}^{2+} + 2\text{OH}^- \rightarrow \text{Mg(OH)}_2 \downarrow \]  

The precipitation of corrosion products led to the formation of a hydroxide layer, which thickens with time and progressively hinders the corrosion processes. According to literature [24] when the corrosion rate decreases, a balance may occur between the formation and dissolution of the Mg(OH)_2 layer, which reaches a constant thickness. However, this layer is porous and not fully protective, allowing the diffusion of charged species involved in the corrosion processes. The low frequency response is characterised by CPE values around \(1 \times 10^{-3} \text{F/cm}^2\), which are likely to be associated with mass transfer controlled processes.

For the blank sample, during the first hours of immersion, both the high frequency and low frequency resistances increased (Fig. 7b) reflecting the build-up of the corrosion products film. However, after about 5 h of immersion the low frequency resistance \(R_{LF}\) started to decrease, reflecting an increase of the conductivity of the corrosion products layer. Identical trends are reported in literature for anodised Mg alloys immersed in NaCl [25].

For the silane treated samples, the evolution of the high frequency parameters is depicted in Fig. 8. The BTESPT treated sample showed CPE values that increased with time (from \(7 \times 10^{-7}\) to \(3 \times 10^{-6} \text{F/cm}^2\)), being one order of magnitude lower than those observed for the blank sample. The high frequency CPE decreased even more in the presence of lanthanum or cerium. Comparatively to the BTESPT film (without additive) the presence of lanthanum or the presence of cerium decreased the CPE values for more than one order of magnitude. These trends suggest that the barrier layer created by the modified silane film presented a decreased number of conductive pathways comparatively to the non-modified BTESPT film. The high frequency resistance was above \(1 \times 10^6 \text{\Omega cm}^2\) for the BTESPT film with cerium and one order
of magnitude lower for the silane films without additive. For the BTESPT film-containing lanthanum the resistance values were lower than those of cerium and decreased with time, but did not reach the values observed for the film without additives. The increased resistances and decreased capacitances observed in the high frequency range of the EIS spectra for the silane pre-treated samples are mainly due to the presence of the silane film, which creates a protective barrier. This effect is more pronounced for the cerium or lanthanum modified films.

The lowest frequency processes observed for the silane treated samples are likely to be associated with the development of corrosion activity and growth of porous corrosion products. For the BTESPT sample, the low frequency CPE values (Fig. 9) increased from $8 \times 10^{-5}$ to $8 \times 10^{-4}$ F/cm$^2$ during the first hours of immersion, reflecting an increase of the active area and the presence of diffusion-controlled mechanisms as observed for the blank sample (Fig. 7). Fig. 9 also shows that the low frequency CPE increased with time, being lower for the modified films. For the Ce-containing film, the low frequency resistance was about two orders of magnitude above that of the non-modified film and kept constant with time, revealing that the corrosion rate was strongly reduced.

During the first 2 days of immersion, the low frequency resistance values for the La-modified film were identical to those obtained with cerium, but after that period they decreased. Nevertheless, they were always higher than those obtained for the BTESPT film.

The trends observed in Figs. 8 and 9, indicate that the modified films are more protective than the non-modified films and also indicate that cerium is the most effective additive in reducing the corrosion rate of the AZ31 substrate.

The EIS measurements provide information on the average response of the exposed surface. The localised electrochemical techniques, such as the scanning vibrating electrode technique (SVET) allow local electrochemical information to be obtained in the form of current density maps. These maps are very helpful to understand the effect of inhibitors on localised defects. Thus, it was decided to investigate the protective properties of the silane films with and without additives by using the scanning vibrating electrode technique (SVET).
To understand the performance of cerium or lanthanum ions as corrosion inhibitors, the pre-treated samples were immersed for a period of 24 h in the 0.005 M NaCl solution and after this period an artificial defect was made on the surface. This defect creates a preferential anodic site and therefore the corrosion inhibition properties of the additives can be studied.

For the BTESPT treated sample localised corrosion activity was noticed after 6 h of immersion (before defect). After 24 h of immersion a defect was created on the surface and a rise of the anodic activity could be observed (Fig. 10a and d). After more 24 h of immersion, the anodic currents decreased by about one order of magnitude (Fig. 10b and d).

A quantitative approach of the SVET results was performed by plotting the anodic and cathodic current densities measured over an horizontal line that crossed the defect (Fig. 10d). The anodic current densities measured after defect formation showed a sharp increase, reaching values around 70 μA/cm² after 1 h. About 2 h after defect formation the anodic currents started to decrease, approaching stable values around 10 μA/cm². The cathodic currents were around −10 μA/cm². The line scan shows that preferential magnesium oxidation occurs at the centre of the defect, whereas reduction reactions surround the defect. An interesting feature is that the cathodic current densities reached a maximum at a distance around 600–700 μm from the defect centre.

In addition to the artificial defect more anodic areas appeared on the defect vicinity, becoming larger with time (Fig. 10b and c). However, both the anodic and cathodic currents decreased due to the protective behaviour of the corrosion products produced, in good agreement with the previous EIS results.

The SVET maps obtained on the BTESPT films modified with lanthanum nitrate were similar to those of BTESPT. Corrosion activity was detected during the first 24 h of immersion (i.e., before defect formation). After defect formation significant corrosion activity was observed. At the defect the maximum anodic current density reached a maximum around 20 μA/cm² after few minutes and than decreased for longer immersion times. During a 72 h immersion period, other smaller anodic areas appeared on the surface, revealing that the corrosion inhibition properties of the lanthanum ions were not completely effective. Nevertheless, the anodic or the cathodic currents were always lower than those observed for the BTESPT film without additives.

The SVET results obtained on the Ce-modified film are presented in Fig. 11. During the first 24 h of immersion (i.e., before defect formation) no activity could be observed on the surface. After defect formation, a small anodic spot could be detected and the anodic currents reached values around 3 μA/cm² (Fig. 11a and e). These values were much lower than the values measured for the BTESPT film without additives. For longer immersion times the anodic and the cathodic activity vanished. This behaviour was observed until the end of the tests (72 h of immersion period) and illustrates that the corrosion activity was completely hindered (Fig. 11c–e). A random distribution of anodic and cathodic sites was detected across the line scan and the current densities were around zero.

The results obtained by the SVET technique can be explained by the following assumptions: the SVET technique measures cathodic or anodic currents, based on the local flow of cations and anions. Defect formation disrupted the protective silane film, exposing the metallic substrate that started to dissolve. The anodic currents are due to the oxidation of the magnesium and flow of magnesium ions produced during reaction (3). Simultaneously, the cathodic reactions release hydroxyl ions that increase the cathodic currents—reactions (1) and (2). The metallic cations (Mg²⁺) react with hydroxyl ions (OH⁻) leading to the formation of negatively charged complexes or precipitation of Mg(OH)₂ (reaction (4)). As previously observed in the EIS measurements the build-up of corrosion products seems to have a protective character. This mechanism explains the decrease of the anodic currents observed in the SVET results obtained on the BTESPT treated sample.

In the presence of cerium the anodic activity is much weaker as well as the cathodic activity. This means that the flux of anions and cations is strongly hindered and corrosion could not proceed.

The presence of cerium improves the barrier properties of the silane film as demonstrated by the EIS and introduces corrosion inhibition properties in the silane films as demonstrated...
by SVET and EIS. To understand this behaviour the overall silane system must be considered. When the silane solution is put in contact with the metallic substrate, the silanol groups (R–Si–OH) formed during hydrolysis of the silane molecules establish covalent bonds with the native surface hydroxides, according to the reactions depicted below:

- **Hydrolysis:**
  \[
  3R–Si(OR')_3 \rightarrow R–Si(OH)_3 + 3R'OH \quad (5)
  \]

- **Condensation/polymerisation:**

The assembling of the silane molecules creates a stable Si–O rich network, which grows leading to the formation of the barrier film. Additionally, the assembling of the silane film modifies the chemical composition of the metallic surface. Thus, the native oxide film, which is originally a mixture of MgO/Mg(OH)₂ can be converted into a Mg–O–Si interface, which anchors the barrier silane film. This barrier is hydrophobic and resistant to electrolyte uptake. The number of conductive pathways in this barrier defines the capacitance and the resistance of the silane film and therefore its protective character. The presence of additives, especially cerium increases the resistance and decreases the capacitance of the barrier film and therefore cerium enhances the barrier properties. The increased resistance and decreased capacitance suggests that the porosity and/or conductivity of the film decrease and that the thickness increases. Increased film thickness was found for sol–gel coatings doped with cerium [26].

Literature reports that Ce³⁺ ions [27–29] can be converted in Ce⁴⁺ ions in solution in the presence of oxygen. These ions can be incorporated in the silane film, substituting some of the Si atoms, leading to the formation of a modified Si–O–Ce network. Thus, a modified film as the one depicted in Fig. 12 is likely to be obtained. Identical assumption was proposed in literature [26].
to explain the improved corrosion behaviour of sol–gel coatings containing different amounts of cerium nitrate.

The formation of a defect in the silane film exposes the metallic substrate and originates localised anodic and cathodic activity. The increase of pH at the cathodic sites disrupts the siloxane network, releasing cerium ions. These become free to react with the hydroxyl ions (reactions (7) and (8)) and lead to the formation of very insoluble hydroxides, which precipitate in the cathodic sites that surround the defect, hindering corrosion activity as confirmed by SVET (Fig. 11):

\[
\text{Ce}^{3+} + 3\text{OH}^- \rightarrow \text{Ce(OH)}_3 \tag{7}
\]

\[
\text{Ce}^{4+} + 4\text{OH}^- \rightarrow \text{Ce(OH)}_4 \tag{8}
\]

The presence of Ce\(^{4+}\) and Ce\(^{3+}\) in the silane film was confirmed by XPS measurements performed on galvanised steel substrates pre-treated with the same silane, but doped with a higher concentration of cerium (1 × 10\(^{-2}\) M) [17].
On the other hand, when the silane film is immersed in the aggressive electrolyte there is deterioration of the outer layers of the film as reported in previous works [20–22]. This may cause leaching of cerium ions incorporated or trapped in the outer layers of the siloxane matrix to the vicinity of the anodic areas where they precipitate in the form of Ce(III) or Ce(IV) hydroxides, hindering the corrosion reactions. Leaching of cerium ions from silane films was also reported by van Ooij and co-workers [30].

The beneficial effect of lanthanum ions is not so marked as that of cerium. Although these ions are known to have corrosion inhibition properties too, in the AZ31 substrates they could not inhibit the corrosion process in the same extent as cerium. The effects on the barrier properties of the film are also poorest than those of cerium. The differences can be attributed to the different chemistry of cerium and lanthanum ions. Both rare-earth ions precipitate when the pH increases as it happens at the cathodic sites. Lanthanum ions form mainly La(III) hydroxides, whereas cerium is likely to form Ce(IV) and Ce(III) hydroxides and oxides. These species are more insoluble then the La(III) hydroxides and therefore they can be more effective in hindering the cathodic activity. Similar explanation has been proposed to understand the superior corrosion inhibition performance of cerium ions in AA2024 substrates immersed in NaCl solutions [31]. Nevertheless, the presence of lanthanum enhances the film properties and decreases the corrosion rate of the substrate, making it an interesting dopant to improve the protective properties of silane coatings.

4. Conclusions

Pre-treatments for the AZ31 Mg alloy using bis-[triethoxysilylpropyl] tetrasulfide silane solutions provide corrosion protection and can be considered a promising technical alternative to the use of chromates.

The addition of cerium nitrate or lanthanum nitrate to the silane solutions improved the barrier properties of the silane films and decreased the corrosion rate of the metallic substrate, comparatively to the non-modified silane film. The presence of cerium led to an important drop of the anodic and cathodic activity when defects are formed in the silane film. Cerium ions could inhibit the corrosion processes at the damaged areas, conferring corrosion inhibition properties to the barrier silane film.

Acknowledgement


References