



# Corrosion behavior study of AZ91 magnesium alloy coated with methyltriethoxysilane doped with cerium ions

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## ABSTRACT

The present work aims to investigate the corrosion behavior of AZ91 magnesium alloy treated with a 4% (v/v) methyltriethoxysilane (MTES) alcohol solution, with and without an alkaline pretreatment. The corrosion resistance was assessed by electrochemical impedance spectroscopy (EIS) and current densities were monitored by potentiodynamic polarization curves during immersion in a 0.1 M Na<sub>2</sub>SO<sub>4</sub> solution. Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) were used to perform a surface analysis. The electrochemical results showed an improvement of anticorrosion properties of AZ91. Furthermore, alkaline pretreatment enhances adhesion between silane film and substrate surface. This can be attributed to a surface enrichment in hydroxyl groups after the alkaline step, which increases formation of Si–O–Mg covalent bonds. The addition of Ce(NO<sub>3</sub>)<sub>3</sub> to the MTES bath was evaluated, and it was found that the electrochemical response depends on the cerium ions concentration used. It was shown that the addition of  $6.0 \times 10^{-5}$  M of Ce(NO<sub>3</sub>)<sub>3</sub> to a MTES bath improves corrosion resistance. Higher concentration of cerium ions lead to destabilizing the siloxane network, decreasing the efficiency of the silane coatings.

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## 1. Introduction

Magnesium alloys have interesting properties such as low density, high specific strength and hardness, which increase their use in microelectronic, automotive and aerospace industries [1,2]. Magnesium shows low density (1740 kg/m<sup>3</sup>) equivalent to 2/3 aluminum density, and typical magnesium alloys weigh about 35% less than aluminum alloy with the same hardness [3].

The magnesium–aluminum system has been the base of the most used magnesium alloys. Many of them contain from 8 to 9% aluminum content in weight, with low amounts of zinc. Among these, AZ91 series which have 1% zinc content, have been used in the automotive industry [2].

A serious limitation for a more widespread use of these alloys, AZ91 in particular, is their corrosion susceptibility. The standard electrode potential for magnesium is –2.375 V (NHE) [4], though in aqueous solution, it is –1.5 V due to formation of Mg(OH)<sub>2</sub>. In this way, many researchers have shown an interest in studying the corrosion behavior of magnesium alloys and developing protective methods [2].

Chromate layers give excellent anticorrosion properties to aluminum alloys and others, besides good adhesion properties. Nevertheless, this method has been abandoned due to the use of hexavalent chromium, which is carcinogenic. An environmentally friendly alternative is the use of sol–gel methods [5,6]. Organic–inorganic hybrid coatings have attracted the interest because they combine properties of ceramic and polymeric materials. The inorganic components increase resistance, durability and adhesion to metallic substrate. The organic components improve flexibility and compatibility with organic functionalities, as painting, for example [7].

The addition of a corrosion inhibitor to silane films can modify barrier properties of the layer, increasing its thickness and densification [8,9], consequently enhancing anticorrosive performance. Literature reports modification of silane films by rare earth salts addition [10,11], which confer good anticorrosion properties when used as isolated layers on aluminum alloys, galvanized steel and magnesium alloys [12–14]. Among rare earth salts, the most used are based on cerium. When cerium ion is introduced in the silane matrix, it increases film thickness and hydrophobicity, and confers good healing properties on defects formed by aggressive species [15]. van Ooij et al. [16] reported that cerium ions are mobile inside the film, and allow them to react with the products from cathodic sites, generating cerium oxides/hydroxides that heal the silane film defects. Tamborim et al. [17] reported that cerium is efficient when

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used as an independent layer, intercalated with silane layers over aluminum alloy.

This work aims to study the corrosion behavior of AZ91 alloy, pretreated with and without immersion in a NaOH solution, as well as treated with methyltriethoxysilane (MTES). The role of cerium ions used as inhibitor in the protective performance of the silane was also investigated.

## 2. Experimental

### 2.1. Magnesium AZ91 alloy pretreatment

Magnesium AZ91 alloy (nominal composition: 7–8% Al, 0.2–0.3% Mn; 0.5–0.6% Zn; <0.04% Si; <0.01% Cu; <0.02% Ni; <0.004% Fe) obtained by die casting process was used as substrate, and was submitted to two pretreatments.

The AZ91 panels were polished with silicon carbide paper up to grade #2000, degreased with ethyl alcohol, rinsed with distilled water and then dried under a hot air stream. This procedure was called pretreatment 1 ( $P_1$ ). Pretreatment 2 ( $P_2$ ) consisted of applying pretreatment 1 followed by the immersion of the substrates in a 1 M NaOH solution for 1 min, rinsed with distilled water and dried under a hot air stream (alkaline pretreatment).

### 2.2. Magnesium AZ91 alloy post-treatment

The AZ91 magnesium alloy substrates pretreated with the pretreatments  $P_1$  and  $P_2$  were post-treated with different silane precursors to obtain a silane film.

The silane films were obtained from a sol constituted by methyltriethoxysilane (MTES) (Sigma/Aldrich) (4%, v/v), methanol (90%, v/v) and distilled water (6%, v/v), with different  $\text{Ce}(\text{NO}_3)_3$  concentrations addition (0,  $1.0 \times 10^{-3}$  and  $6.0 \times 10^{-5}$  M). The MTES sol pH values determination was carried out using a glass electrode for nonaqueous solutions, which is supplied with LiCl 3M ethanolic solution. The pH sol values of MTES without  $\text{Ce}(\text{NO}_3)_3$  addition, MTES with  $1.0 \times 10^{-3}$  M  $\text{Ce}(\text{NO}_3)_3$  and MTES with  $6.0 \times 10^{-5}$  M  $\text{Ce}(\text{NO}_3)_3$  were respectively 4.16, 2.87 and 3.19.

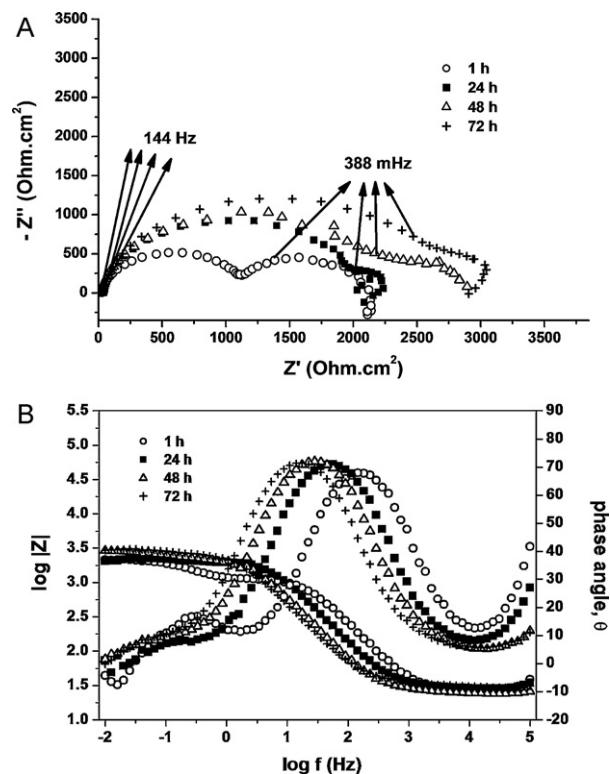
The mixture was stirred for 1 h at room temperature and aged for 3 days to ensure complete hydrolysis. The panels were immersed in this solution for 35 min and then cured in an oven at 130 °C for 40 min.

All the samples used in this work are summarized and described in Table 1.

**Table 1**  
Description of the samples.

Sample	Description
Pretreatment 1 ( $P_1$ )	AZ91 magnesium alloy cleaned with ethanol and rinsed with distilled water
Pretreatment 2—alkaline pretreatment ( $P_2$ )	AZ91 magnesium alloy cleaned with ethanol, rinsed with distilled water, immersed for 1 min in a NaOH solution and rinsed with distilled water again
Treatment 1 ( $T_1$ ) <sup>a</sup>	AZ91 magnesium alloy with $P_2$ followed by the treatment with a 4% MTES solution without addition of $\text{Ce}(\text{NO}_3)_3$
Treatment 2 ( $T_2$ )	AZ91 magnesium alloy with $P_2$ followed by the treatment with a 4% MTES solution with addition of $1.0 \times 10^{-3} \text{ mol L}^{-1} \text{ Ce}(\text{NO}_3)_3$
Treatment 3 ( $T_3$ )	AZ91 magnesium alloy with $P_2$ followed by the treatment with a 4% MTES solution with addition of $6.0 \times 10^{-5} \text{ mol L}^{-1} \text{ Ce}(\text{NO}_3)_3$

<sup>a</sup> AZ91 magnesium alloy with  $P_1$  followed by the treatment with a 4% MTES solution without addition of  $\text{Ce}(\text{NO}_3)_3$  was also tested, but it does not appear in the table, since all the comparisons done in the text refer to the treatment 1 applied after pretreatment 2.



**Fig. 1.** Evolution of the impedance diagrams with immersion time in a 0.1 M  $\text{Na}_2\text{SO}_4$  solution for AZ91 alloy after pretreatment 1: (a) Nyquist diagrams; (b) Bode diagrams ( $\theta$  versus  $\log f$  and  $\log |Z|$  versus  $\log f$ ).

### 2.3. Electrochemical and analytical techniques

The experimental apparatus used for the electrochemical investigation was a potentiostat (AUTOLAB PGSTAT 30) coupled to a frequency response analyzer (FRA 2) system. A three-electrode electrochemical cell arrangement was used, consisting of the AZ91 panel (with 1 cm<sup>2</sup> of exposed area) as working electrode, saturated calomel as reference electrode and Pt as counter electrode. All the electrochemical measurements were carried out in a naturally aerated 0.1 M  $\text{Na}_2\text{SO}_4$  (pH 6) solution at 25 °C. The electrochemical impedance spectroscopy (EIS) measurements were performed in potentiostatic mode at the open circuit potential (OCP). The amplitude of the perturbation signal was 10 mV, and the frequency range varied from  $10^5$  to  $10^{-3}$  Hz. The potentiodynamic polarizations were recorded at the scan rate of 5 mV/s after 1 h of immersion in a naturally aerated 0.1 M  $\text{Na}_2\text{SO}_4$  solution ranging from −1.9 V to −1.1 V. The microstructure and qualitative chemical composition of the MTES silane films were studied by scanning electron microscopy (SEM) coupled with energy dispersive spectroscopy (EDS) before and after immersion in a sulfate solution. The analyses were carried out using a Jeol JSM 5800 scanning microscope by secondary electrons using a beam with an acceleration of 20 keV. SEM analyses were also used to evaluate the silane film thickness, by cross section images. The images were analyzed with the Image J software to determine the film thickness.

## 3. Results and discussion

### 3.1. Electrochemical impedance spectroscopy (EIS)

#### 3.1.1. AZ91 magnesium alloy pretreated

Electrochemical impedance spectroscopy measurements for pretreated alloy after pretreatment 1 were performed and depicted in Fig. 1.

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