

Silane-Based Hybrid Coatings for the Corrosion Protection of AA 2024-T3 Alloy

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ABSTRACT: In order to contribute to the corrosion protection of aluminum alloys, silane-based hybrid coatings have been widely studied in the aerospace industry for their good adhesion to aluminum substrates, compatibility with organic paintings and to protect the underlying material, in addition to being much less toxic than the commonly used chromatization process. In this work, hybrid and inorganic sol-gel coatings were evaluated as corrosion inhibitor films for AA2024-T3 alloy. The films were characterized by linear polarization resistance (LPR) and scanning electron microscopy (SEM), which indicated that these coatings provide a lower tendency for the substrate corrosion.

KEYWORDS: Sol-gel; Coating; Corrosion resistance; Aluminum alloy.

INTRODUCTION

Aluminum and its alloys are among the most widely used metallic materials. In the aerospace and automotive sectors, their presence is justified by some of their properties, such as lightness, high fracture toughness, high fatigue performance, high moldability, increased damage tolerance and durability (Santos Junior *et al.* 2016). However, though aluminum itself has good corrosion resistance, determined by the presence of a natural oxide layer formed on its surface, aluminum alloys show improved mechanical properties, determined by the presence of alloying elements that precipitate in the form of intermetallics and cause localized corrosion. This problem shows up as a consequence of the electrochemical activity difference between the intermetallic precipitate and the aluminum matrix, which is especially high in the case of copper-containing aluminum alloys (Zhang *et al.* 2017). For these materials, the exceptional, but toxic and carcinogenic, chromatization process has been banned and a potential substitute is the hybrid silane-based coatings obtained from sol-gel process, since it provides good adhesion to aluminum and less environmental damages, with improved corrosion inhibition (Osborne, 2001). Thus, the application of inorganic and hybrid systems obtained by the sol-gel process as corrosion protection coatings for aluminum alloy 2024-T3 is the focus of this study.

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METHODOLOGY

AA2024 substrates were used in the form of discs, with $\phi = 35$ mm diameter and 2 mm thickness. Prior to coating deposition, the substrate surfaces were polished with alumina suspension ($0.3 \mu\text{m}$), applied manually over a disc-shaped polishing cloth ($\phi = 200$ mm) to minimize the natural and passive oxide layer, followed by degreasing with ketone-soaked cotton, according to SSPC-SP1 (2000) and drying at room atmosphere for 10 min.

The inorganic sol-gel system was prepared using tetraethoxysilane (TEOS), ethanol, HNO_3 , and H_2O , in a molar ratio of 0.27:0.59:0.05:0.46, respectively. For the hybrid compositions, the same parameters were maintained and both precursors, (3-glycidoxy)propyl-trimethoxysilane (GPTMS) and (3-trimethoxysilyl)propyl-methacrylate (TMSPM), were added at a 1:1 molar ratio relative to TEOS. The mixtures were kept for 30 min under an ultrasonic tip action (Hielscher UP 200S, 60 % amplitude, and 0.5 Hz frequency). The whole process was carried out at a temperature of 10°C , maintained by a thermostatic bath (JULABO GmbH - ME v.2).

The deposition of freshly prepared sol-gel coatings was performed with the aid of a dip coater, with immersion/emersion velocity of $1 \text{ mm}\cdot\text{s}^{-1}$ and 5 s of rest inside the solution. After the deposition, the substrates were kept under room atmosphere for 24 h to ensure the complete sol-gel reactions (hydrolysis and condensation) and the solvent evaporation. The linear polarization resistance test was performed using a potentiostat Autolab PGSTAT30, in an electrolytic cell arranged with three electrodes: a reference electrode (Ag/AgCl, saturated), a working electrode (sol-gel coated and uncoated substrate) and a counter electrode (platinum spiral). The potential window applied was -0.9 to 0.9 (Vref) with a scan rate of $0.001 \text{ V}\cdot\text{s}^{-1}$. The exposed area evaluated was 0.39 cm^2 . The electrolyte was a naturally aerated $0.1 \text{ mol}\cdot\text{L}^{-1}$ of NaCl solution at room temperature. For the morphological characterization of the films and substrate, the Scanning Electron Microscope – SEM Tescan Vegan 3 was used.

RESULTS AND DISCUSSION

The curves shown in Fig. 1 refer to the linear polarization resistance analysis of uncoated substrates and sol-gel coated substrates, specified as inorganic (TEOS), TEOS/TMSPM hybrid and TEOS/GPTMS hybrid.

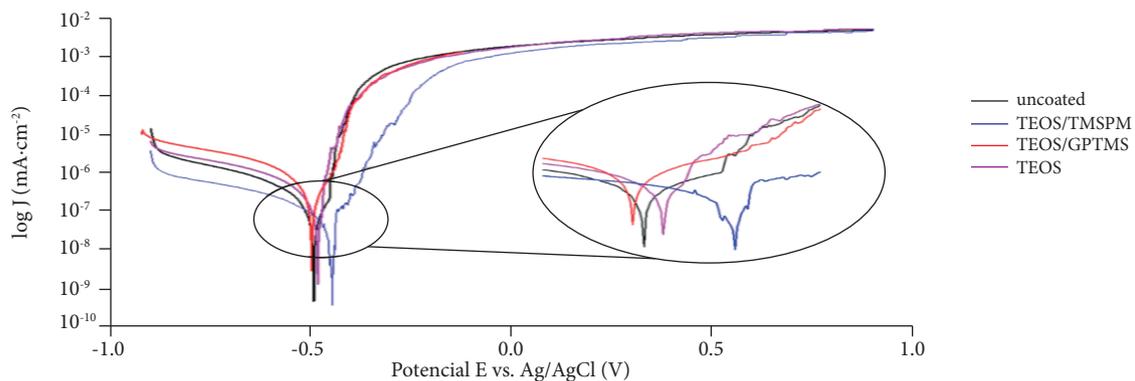


Figure 1. Polarization curves of the uncoated AA2024 substrate and sol-gel coated AA2024 substrate/TEOS, TEOS/TMSPM and TEOS/GPTMS.

By the Tafel extrapolation method applied to the polarization curves of Fig. 1, the corrosion or pitting potential and current density values, E_{corr} and J_{corr} respectively, were obtained for each sample, as shown in Table 1.

The corrosion potential represents the thermodynamic tendency of a material to undergo a corrosion process. The more negative the potential, the greater the tendency to corrosion. On the other hand, more positive potential indicates the lower tendency to corrosion.

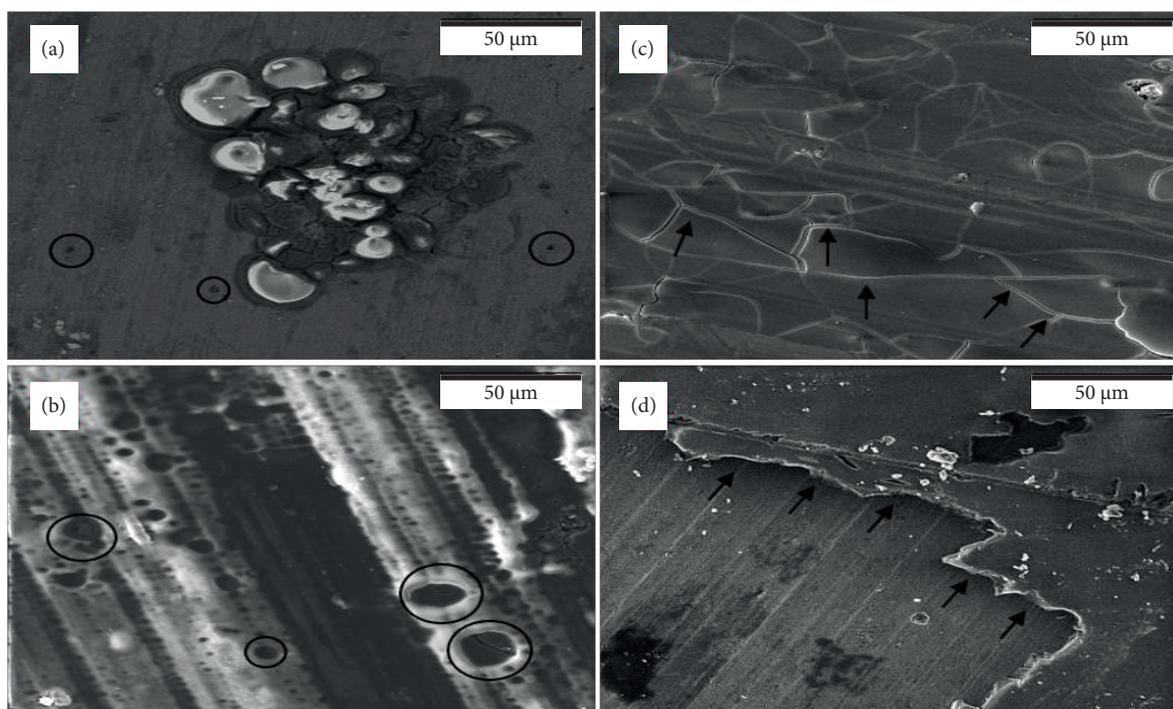
Table 1. Electrochemical parameters of uncoated AA 2024 substrate and coated AA 2024 substrate with different sol-gel systems.

AA 2024 Substrate	E_{corr} (V)	J_{corr} (mA/cm ²)
Uncoated	-0.52	2.51×10^{-7}
TEOS sol-gel coated	-0.50	2.39×10^{-7}
TEOS/TMSPM sol-gel coated	-0.44	4.07×10^{-8}
TEOS/GPTMS sol-gel coated	-0.47	2.29×10^{-7}
Standard deviation (σ)	0.03	9.98×10^{-8}

The current density represents the kinetic tendency for oxidation-reduction reactions to occur, thus the increase in the current density increases the charge exchange between the electrodes, favoring corrosion. Thus, it is observed by the polarization curves (Fig. 1) and by the E_{corr} and J_{corr} values (Table 1) that the hybrid coatings have higher efficiency than the inorganic ones in the protection of AA2024 alloy against corrosion, especially the hybrid TEOS/TMSPM coating, which presented the less negative corrosion potential and the lower current density. Figure 2 shows the morphology of the coatings after the electrochemical assay.

It is possible to observe in the micrographs (Fig. 2) whitish regions present in the uncoated substrate (Figure 2a) that indicates the presence of S phase (Al-Cu-Mg) intermetallic precipitate and the presence of darker spots that indicate the appearance of pitting corrosion (Buchheit *et al.* 1997), pointed by the circles. The inhomogeneous aspect of the inorganic film (Fig. 2b) is observed by the presence of cracks, indicated by arrows, which enables the contact between electrolyte/substrate and can lead to filiform corrosion points (Gentil 2011). The darker rounded regions observed on the TEOS/TMSPM coating (Fig. 2c), indicated by circles, resemble the presence of pores (Zajicová *et al.* 2011). Finally, the TEOS/GPTMS coating (Fig. 2d) shows a step between the coated and poorly coated regions, pointed by the arrows.

Though the films presented some defects, none of the coated substrates showed precipitates or pitting corrosion during the electrochemical evaluation, which indicates that the coating adhered to the metal surface protecting it from the medium.

**Figure 2.** SEM micrographs of the substrate, after linear polarization assay: (a) uncoated; (b) coated with TEOS sol-gel; (c) coated with TEOS/TMSPM sol-gel and (d) coated with TEOS/GPTMS sol-gel.

CONCLUSION

By the linear polarization results, the inorganic sol-gel coating contributes insignificantly to both the corrosion potential of the substrate and to its current density, which is attributed to the presence of cracks in the film. On the other hand, the corrosion potentials for the hybrid coatings shifted to more positive values with respect to the uncoated substrate, disfavoring the spontaneity of the oxidative process. The contribution of the TEOS/TMSPM hybrid coating to the noblest potential and the decrease in current density disfavours both the oxidative thermodynamic and kinetic processes. In addition, the hybrid films were more homogeneous than the inorganic one, although none of them showed any indication of corrosion.

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