Corrosion Behavior of AA2024 Coated with Phosphonate-containing VTMS/TEOS

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Introduction

Sol-gel processing has been reported as one of most the promising methods to replace chromate conversion coatings [1]. Sol-gel films exhibit good adherence to metallic surfaces due to bonds formed between the metallic surface and silanol groups, metalo-siloxane bonds and behave as a physical barrier delaying the entry of aggressive agents toward the substrate [1]. The silica network generated is porous and can contain low crosslink density moieties, thus the corrosion protection is reduced. To improve the performance of sol-gel coatings the functionality silanes with long carbon chains and bi-silanes [2] have been investigated, nevertheless they are very expensive for routine technological applications. On the other hand, ours previous works appointed that the incorporation of phosphonic acids in the TEOS matrix result in a pronounced improvement in the corrosion protection of AA 2024 alloy [3,4]. It is well known that the silica network derived from TEOS has hydrophilic characteristics. Thus, in this work the vinyltrimethoxysilane which has hydrophobic characteristics was combined with TEOS. The principal objectives of this work are: First, using mixtures of VTMS and TEOS, evaluate the influence of VTMS/TEOS concentration ratio on the corrosion behavior of AA2024 alloy. Second, to evaluate the protective effect of 1,2-diaminoethanetetrakis methylenephosphonic acid (EDTPO) addition in the VTMS/TEOS sol-gel matrix.

Experimental

Pretreatment and coating deposition

The AA2024-T3 samples before immersion onto silanization baths were polished with silicon carbide paper up to 1200 and submitted to 5 minutes of immersion in the 0.05 mol L^{-1} acetic acid solution, washed with distilled water and dried under a hot air stream [4]. The deposition bath was prepared by mixing 90% v/v ethanol (Nuclear, 99.5%) and 6% deionized water (18.3 MΩ cm) with different proportions (v/v) of tetraethylorthosilicate (TEOS) (Merck, 98%,) and vinyltrimethoxysilane (VTMS) (Aldrich, 97%). The amount of VTMS/TEOS used were 1/3% v/v, 2/2% v/v, 3/1% v/v, 1/4% v/v and the coating obtained were denoted as 1V, 2V, 3V and 4V, respectively. The deposition bath with incorporation of phosphonic acid was prepared by dissolving EDTPO in the deionized water, corresponding to 6% v/v in a mixture with 3% v/v VTES, 1% v/v TEOS and 90% v/v ethanol. The concentration tested in the baths was 3.75×10^{-5} mol L^{-1} EDTPO. The films produced were denoted 3VE5. The baths were stirred for 1 h at room temperature and then stored for 3 days prior to use. Immediately, to pretreatment the samples were immersed in a sol–gel system for 30 min and cured in an oven at 110 °C for 1 h.

Measurements

Electrochemical Impedance Spectroscopy: The electrochemical measurements were performed using an AUTOLAB PGSTAT 30/FRA 2 system. A three-electrode electrochemical cell arrangement was used, consisting of the AA2024-T3 panel with 1 cm^2 of exposed area (working electrode), a saturated calomel electrode (SCE) (reference electrode), to which all the potentials were referred, and a Pt mesh (counter electrode). EIS measurements were performed in the potentiostatic mode at the open circuit potential (OCP). The amplitude of the EIS perturbation signal was 10 mV, and the studied frequency ranged from 10^5 to 10^{-2} Hz. The experiments were carried out at 25 °C and 0.05 mol L^{-1} NaCl solution was employed.

Results and Discussion

Assessment of ratio VTMS/TEOS

Figure 1 shows the evolution of the EIS spectra with immersion time for aluminum alloy AA2024-T3 coated with 1V, 2V, 3V and 4V in a 0.05 mol L^{-1} NaCl solution.

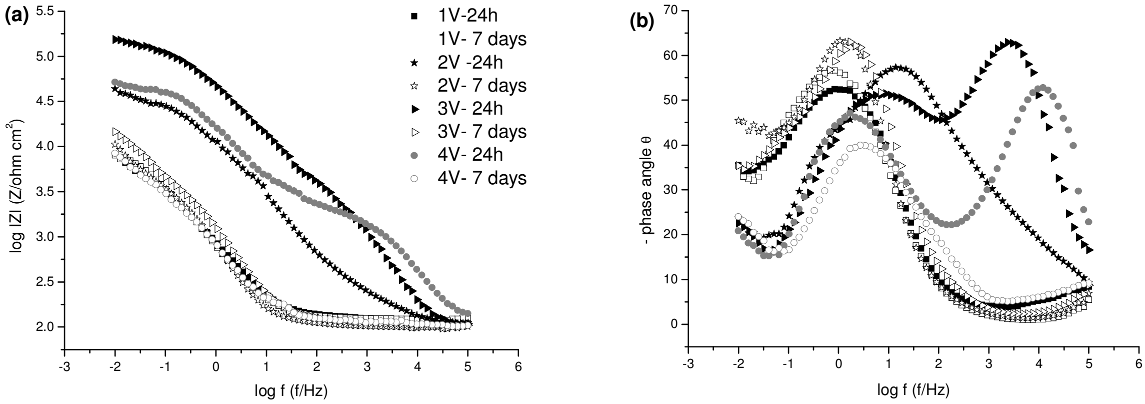

Figure 1: Bode plots for the AA2024-T3 alloy coated with 1V, 2V, 3V and 4V films ((a) log |Z| plots and (b) phase angle (θ) plots as a function of log f) after 24 hand 7 days immersed in 0.05 mol L^{-1} NaCl.

After 24h of exposition in chloride solution the samples 3V and 4V show one time constant at high frequency (10^4 Hz), with a phase angle of approximately -63 and -53°, respectively, associated to the silane layer. After 48h the value of phase angle decreases to -50 and 35°, respectively and disappears after 7 days of immersion, which can be related with the degradation of the film. A second time constant is observed at 8.75 and 2.72 Hz for 3V and 4V, respectively and a third constant time is detected at 51.3 mHz for both data sets. The medium frequency time constant has been associated to interfacial layer silane/metal and the low frequency time constant to the corrosion process. For the 2V sample, after 24h, time constants at the high and medium frequencies were overlapped, around 15.8 Hz and at low frequency (c.a. 51 mHz) appears the time constant related to corrosion phenomena. After 48h occurs a narrowing of phase angle curve and the time constant at high frequency is not detected. The decrease of VTMS concentration up to 1% results in a maximum phase angle close to - 52° at medium frequency. Moreover the time constant at high frequency is not detected, suggesting that the film formed is more hydrophilic, being not efficient to prevent the uptake of the electrolyte. The highest values of impedance modulus in all immersion time studied are achieved with 3V panels. The EIS analysis evidence the improvement of corrosion performance with increase of the VTES concentration from 1V to 3V. It is expected that the vinyl groups disrupt the integrity of the hydroxylated surface, i.e., occurs a decrease of superficial SiOH groups in the formed silica network [5], thus the more hydrophobic films were obtained leading to better barrier proprieties.

Assessment of EDTPO concentration

Functionalized silanes bearing phosphonic acid groups have been used for the coverage of metals [6], the efficacy of these films for corrosion protection being evidenced. The EDTPO addition to VTMS/TEOS films was tested as a way to obtain a cooperative effect in order to improve the protective characteristics of the coating. The inhibitive efficiency of phosphonic acids is strongly dependent on its concentration in the silane bath [3,4]. Based on the above results the concentration of 3% VTMS and 1% TEOS was chosen to prepare films with incorporation of EDTPO. The optimal concentration of EDTPO within the silane matrix was

3.75× 10^{-5} mol L^{-1} determined from EIS measurements (not given here). Figure 2 depicts the EIS spectra of the alloy coated with 3V and 3VE5. After 24 h of immersion, two time constants were detected with an increased in the overall impedance, in the presence of phosphonic acid, suggesting an improved corrosion protection for this electrode. A new relaxation process at lower frequencies appears after 48 h of immersion followed by a decrease of the impedance modulus which was associated with the onset of corrosion activity at the alloy surface. However, the EIS spectra of 3VE5 undergo small variations from the 2rd to the 7th day of immersion, remaining the impedance modulus around 10$^{5.5}$, indicating that the corrosion protection is maintained even with prolonged immersion time. The SEM and EDX data (not given here) show that the lines of metallic substrate are not visible in 3VE5 films images and the general spectrum exhibits an intense peak of Si and a tiny peak of Al indicating that this coating covers almost entirely the alloy surface.

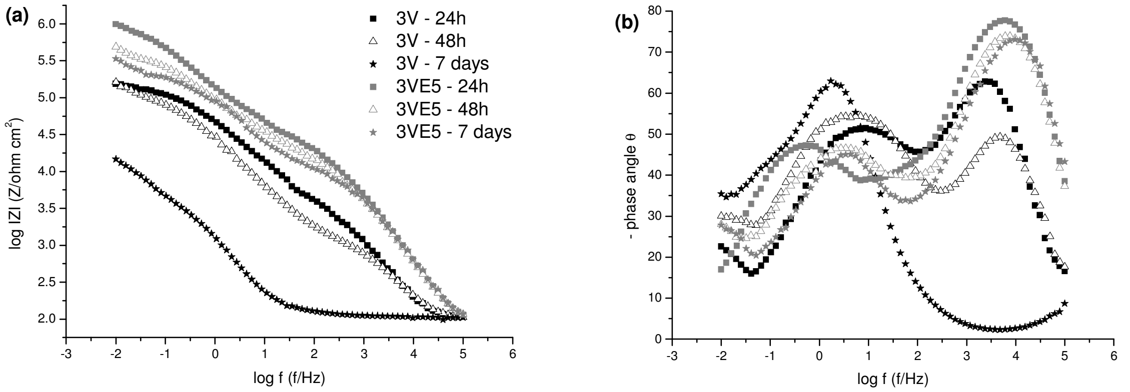

Figure 2: Bode plots for the AA2024-T3 alloy coated with 1V, 2V, 3V and 4V films ((a) log |Z| plots and (b) phase angle (θ) plots as a function of log f) of the AA2024 coated with 3V and 3VE5 after 24h, 48h, 7 days of immersion in 0.05 mol L^{-1}NaCl.

Conclusions

The corrosion behavior of AA2024 alloy coated with different ratio of VTMS/TEOS films was investigated. Increasing the concentration of VTMS entails the decrease of hydroxyl groups on the film surface and the EIS analysis appointed that the highest protection was achieved when the ratio VTMS/TEOS was 3/1. With the incorporation of EDTPO onto the matrix VTMS/TEOS the corrosion performance was improved, being the impedance modulus after 7days higher than that of non-modified matrix after 24h of immersion. The last results can be explained by the strong interaction between phosphonic group and aluminum substrate.

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