Revestimentos a base de TEOS/ácido fosfônico como tratamento anticorrosivo para a liga AA2024-T3

TEOS/Phosphonic acid based coatings as anticorrosive treatment for AA2024-T3 alloy

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RESUMO

O objetivo deste estudo foi investigar o comportamento corrosivo da liga de alumínio AA2024-T3 tratada com filmes obtidos pela combinação de tetraetilortossilicato (TEOS) com ODPA (ácido octadecilfosfônico) em solução de NaCl 0,05 mol L^{-1}. As razões volumétricas de TEOS/etanol/água utilizadas foram 4:90:6 e 4:80:16, e os filmes formados foram denotados como 90TEOS e 80TEOS respectivamente. A adição de ácido fosfônico nos filmes TEOS foi testada como uma maneira de se obter um efeito cooperativo, a fim de melhorar as características de proteção do revestimento. Análises de espectroscopia de impedância electroquímica (EIE) e polarização potenciodinâmica mostraram que os filmes 90TEOS na presença de ODPA apresentaram um maior módulo de impedância após 168 horas de imersão em solução de cloreto. Os resultados obtidos indicam que os filmes obtidos apenas com TEOS não fornecem uma proteção adequada contra a corrosão, evidenciando a existência de sinergismo entre o ácido fosfônico e TEOS. Essa melhora foi relacionada à maior hidrofobicidade dos revestimentos.

Palavras chaves: Liga de Alumínio, Silano, Ácido fosfônico, EIE.

ABSTRACT

The aim of this study was to investigate the corrosion behavior of aluminum alloy AA2024-T3 substrates treated with self-assembled films obtained by combining tetraethylorthosilicate (TEOS) with ODPA (octadecylphosphonic acid)in a 0.05 mol L-1 NaCl solution. The volumetric ratios of TEOS/ethanol/water used were 4:90:6 and 4:80:16, and the corresponding films formed were denoted as 90TEOS and 80TEOS, respectively. The addition of phosphonic acid to TEOS films was tested as a way to obtain a cooperative effect in order to improve the protective characteristics of the coating. Electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization data showed that the 90 TEOS films in the presence of ODPA had the highest impedance modulus after 168h of immersion in chloride solution. The results obtained indicate that undoped sol-gel coatings do not provide adequate protection against corrosion, evidenced by the existence of synergism between phosphonic acid and TEOS, improving the hydrophobicity of the films.

Keywords: Aluminum alloy, silane, phosphonic acid, EIS.

1. INTRODUCION

The aluminum alloy AA 2024-T3 is widely used as a fuselage skin and structural material in the aeronautics industry. However, this alloy has a high susceptibility to chemical attack and pitting corrosion, which is generally associated with the distribution and electrochemical properties of intermetallic compounds (IMCs) [1, 2]. In recent years, metal pre-treatments based on the formation of silane films have been developed to improve the corrosion resistance of metal substrates and the adhesion between metals and painted organic coatings [3, 4, 5].

Silanes are classified as self-assembling molecules (SAMs), representing an environmentally-friendly alternative to the classic protection systems based on chromates. A surface pre-treatment using SAM acts as a barrier preventing the corrosion of the metal [3, 5, 6]. However, this procedure confers a passive corrosion protection which can be damaged by aggressive species reaching the metallic substrate, leading to corrosion. The protection against active corrosion obtained in the presence of an inhibiting component in this pre-treatment allows the corrosion rate to be minimized, preventing the degradation of the metal. Thus, a synergistic effect is obtained by using a silane layer modified with an inhibitor [7, 8, 9, 10]

Recent studies have been carried out with the use of silanes in combination with inhibitors[11], bilayer systems where a silane coating precedes the epoxy paint [12] and epoxy coating systems which are modified with silanes [13].

The formation of SAMs on the aluminum substrate occurs when these compounds react spontaneously with Al_2O_3, producing a more hydrophobic layer on the metal surface [6, 14, 15]. Films based on TEOS/DTMS electrodeposited on AA2024-T3 alloy in the presence of cerium nitrate were studied by Zhang *et. al* [16]. Through the water contact angle analysis, the authors observed angles near to 160º indicating the formation of superhydrofobic surfaces, which remains unchanged with the introduction of cerium. EIS analysis showed good results for the films in the presence of cerium salt. Recent studies in the literature involving inhibitors incorporation to TEOS films showed satisfactory results, improving anticorrosive properties [17, 18].

A comparative study of self-assembly monofunctional aliphatic molecules (phosphonic acids, thiols and carboxylic acid) on magnetron-sputtered aluminum was performed by Liakos et al[19]. The greater ability of the phosphonic acid head group was demonstrated, suggesting that greater coverage and order are attained with phosphonic acid. In recent studies, Dalmoro et al. investigated the effect of TEOS (tetraethoxyorthosilicate) modified with two phosphonic acids, ATMP (aminotrimethylenephosphonic acid) and EDTPO (1,2-diaminoethanetetrakis methylenephosphonic acid), on the corrosion behavior of the aluminum alloy AA 2024-T3, and demonstrated the enhanced protection obtained with EDTPO [20, 21].

It is well known that undoped TEOS films show high hydrophilicity and are not efficient for corrosion protection, requiring the addition of inhibitors. Octadecylphosphonic acid (ODPA) is an organic molecule which consists of a head phosphonic acid group that can chemically bond to the metal surface and a nonpolar portion that consists of an 18-member carbon chain. ODPA has been used for the formation of superhydrophobic surfaces and very good results have been reported [22, 23]. In this study, the corrosion protection of AA 2024 modified with self-assembled films obtained by combining TEOS with ODPA (octadecylphosphonic acid) in a 0.05 mol L^{-1} NaCl solution was investigated.

The films were prepared using solutions with different water contents. The volumetric ratios of TEOS/ethanol/water used were 4/90/6 and 4/80/16 and the corresponding films formed were denoted as 90TEOS and 80TEOS, respectively The corrosion behavior of ODPA-modified TEOS films was evaluated through electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization tests complemented by FT-IR spectroscopy data. The wetting behavior was examined by contact angle measurements.

2. MATERIALS AND METHODS

The bare alloy samples were previously polished followed by immersion in 0.05 mol L^{-1} acetic acid solution for 5 min, and then washed with distilled water and dried under a hot air stream[20]. The silanizing bath was prepared by mixing tetraethoxysilicate (TEOS, Sigma/ Aldrich), ethanol (Nuclear) and deionized water (18.3 MΩ cm^2) in 4:90:6 (v/v) ratio and 4:80:16 (v/v) ratio. The silanizing bath with the inhibitor was prepared by dissolving different amounts of ODPA (octadecylphosphonic acid) in water corresponding to 6% v/v in a 4% v/v TEOS and 90 %v/v ethanol and 16% v/v in a 4% v/v TEOS and 80 %v/v ethanol ,denoted as 90TEOS and 80 TEOS, respectively . Two concentration of phosphonic acid were tested in the baths: 5×10^{-5} and 5×10^{-4} mol.L^{-1} ODPA and the coatings were denoted as TEOS/ ODPA **10^{-5}** and TEOS/ ODPA **10^{-4}**, respectively. The mixtures were stirred for 1 h at room temperature and kept for 3 days before use. It was employed polarization methods and electrochemical impedance spectroscopy, complemented by water contact angle (WCA) and FT-IR measurements. EIS were performed using an AUTOLAB PGSTAT 30/FRA 2 system. The working electrode was a AA2024-T3 panel with 1 cm^2 of exposed area, a saturated calomel electrode (SCE) as reference electrode, to which all of the potentials are referred, and a Pt mesh as a counter electrode. EIS measurements were performed in the potentiostatic mode at OCP. The amplitude of the EIS perturbation signal was 10 mV, and the studied frequency range was 10^5 to 10^{-2} Hz. Experiments were performed at 25 °C, and a 0.05 mol L^{-1} NaCl solution was employed.

The analysis of surface hydrophobicity was done by contact angle measurements in water. The measurements were performed on a digital microscope Digital Blue brand, QXs model with the aid of Surf Tens software. The FT-IR analysis were performed with a Schimadzu spectrometer, model IR-Prestige-21. Spectra were collected by depositing the TEOS films on zinc selenate windows in a range of $4000 – 400$ cm^{-1}.

3. RESULTS AND DISCUSSION

Figure 1 shows the EIS plots for the bare alloy and for the alloy treated with 90TEOS and 80TEOS after immersion in NaCl for 24h and 168h. The bare alloy and 90TEOS show similar plots, indicating that no beneficial effect was obtained. On increasing the exposure time up to 168 h the overall impedance decreased for the bare alloy and 90TEOS, followed by a slight decrease in the phase angle. The Bode spectra show a distinct behavior for the sample 80TEOS which, after 24h, presented two maximum phase angles close to -35°, indicating that the film formed is very defective, leading to electrolyte uptake. After 168 h, a third time constant appears at lower frequencies, indicating the development of corrosion activity.
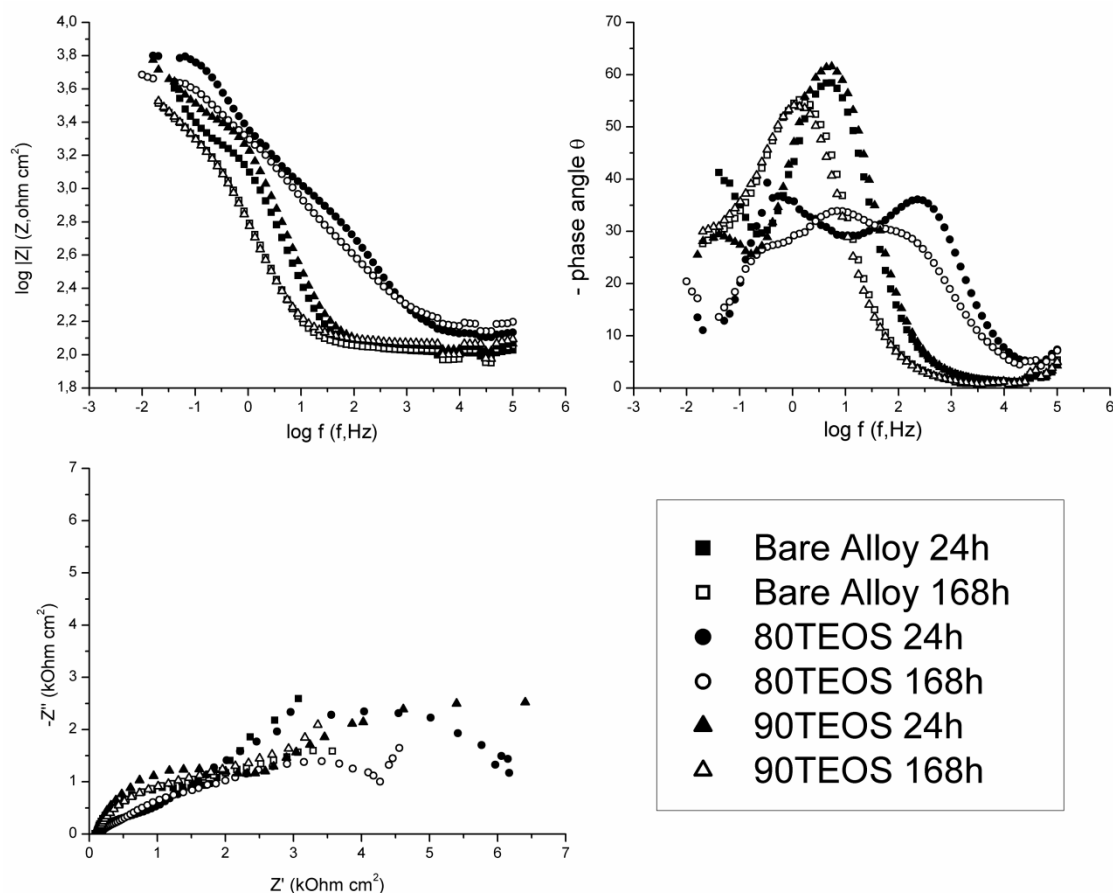

Figure 1: Effect of water content on EIS plots for AA2024 aluminum alloy in 0.05 mol/L NaCl at the open circuit potential after 24h and 168h of exposure.

The increased stability of the film produced with higher ethanol content (90TEOS) can be explained by the morphology of the films formed. According to Balbyshev and collaborators[24], when the mole ratio between water and alkoxide, denoted as R (R = moles water/mole alkoxide), is approximately equal to 4 the formation of linear structures capable of forming thicker films is favored, when R is close to 10 the formation of circular siloxane chains gives rise to porous structures and when R is around to 20 a particulate three-dimensional structure is formed. The excess water accelerates the hydrolysis reactions and condensation reactions slow down, since water is produced under these conditions, resulting in a greater number of monomers being hydrolyzed before significant condensation reactions occur. Thus, the condensation of al-

most completely hydrolyzed species favors the establishment of cyclic or branched siloxane bonds and the growth of particulate structures. Films obtained from 90TEOS have R values near to 4 while films obtained from 80TEOS have R values near to 12.

Figure 2 shows the FT-IR spectra for 90TEOS and 80TEOS. The strong band at 3356 cm-1 was attributed to the stretching of water and silanol O-H groups. The absorption at between 2974cm-1 and 2889 cm-1 is attributed to the asymmetric and symmetric C-H stretching vibrations of the ethoxy groups present in TEOS. The band at 1156cm-1 is associated with the C—H rocking mode of SiOCH2CH3 (δ rocking). At 1089 cm-1 and 1049 cm-1 the presence of two peaks can be observed, which are attributed to the asymmetric stretching (γas) of Si-O(Si-O-Si). Finally, the bending mode of Si-OH can be observed at 881 cm-1 (δ) [25, 26].

Table 1 compares the γas/δ and δ/δ rocking values for the coatings obtained using different ethanol:water ratios. As can be seen in Table 1, on increasing the water content the SIOH/SICH2CH3 ratio increases and the SIOSI/SIOH ratio decreases, since hydrolysis is facilitated by the presence of water in the silanization bath.
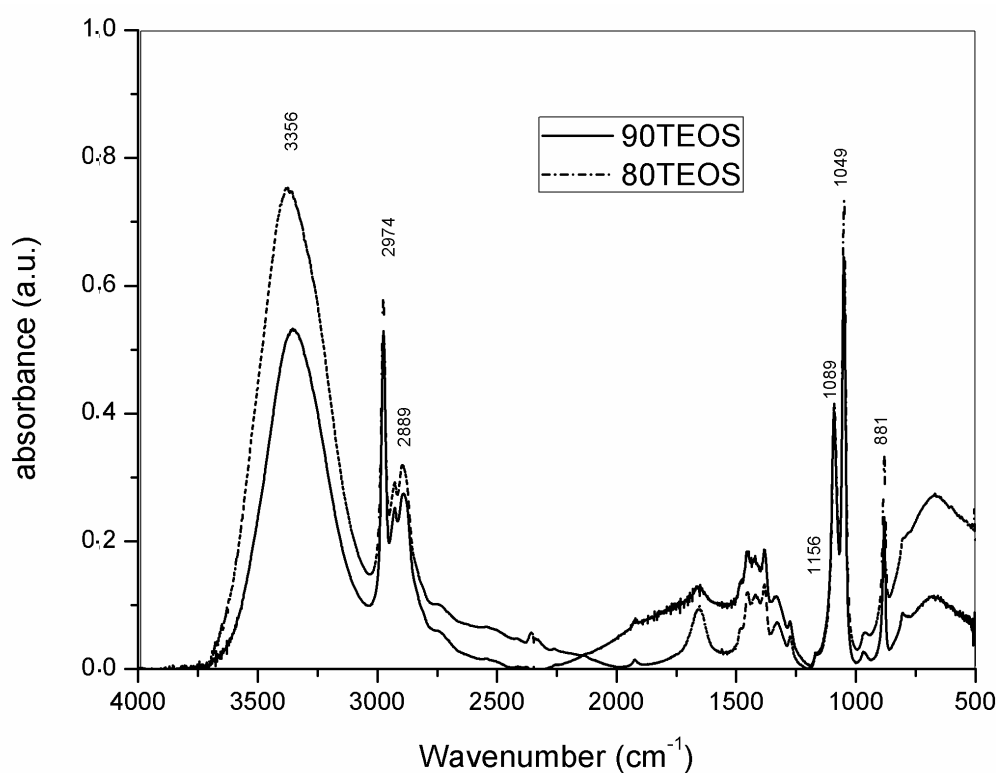

Figure 2: FT-IR spectra for 90TEOS and 80TEOS after 72h of hydrolysis.

Table 1: Ratio between the peak heights of the infrared bands obtained after 72h of hydrolysis of 90TEOS and 80TEOS.

	$\gamma SiOSi/\delta SiOH$	$\delta SiOH/\delta_{rocking} SiCH_2CH_3$
90TEOS	2.34	9.93
80TEOS	2.21	14.15

The addition of ODPA to TEOS films was tested in order to provide protective features. The EIS spectra were obtained for 90TEOS and 80TEOS and for the films with the incorporation of $5x10^{-5}$ and $5x10^{-4}$ mol L^{-1} of ODPA, after immersion in 0.05 mol L^{-1} NaCl for 24, 48 and 168 h. In the case of 80TEOS, the addition of 10^{-5} ODPA increased the impedance modulus for all immersion times tested (Figure 3).
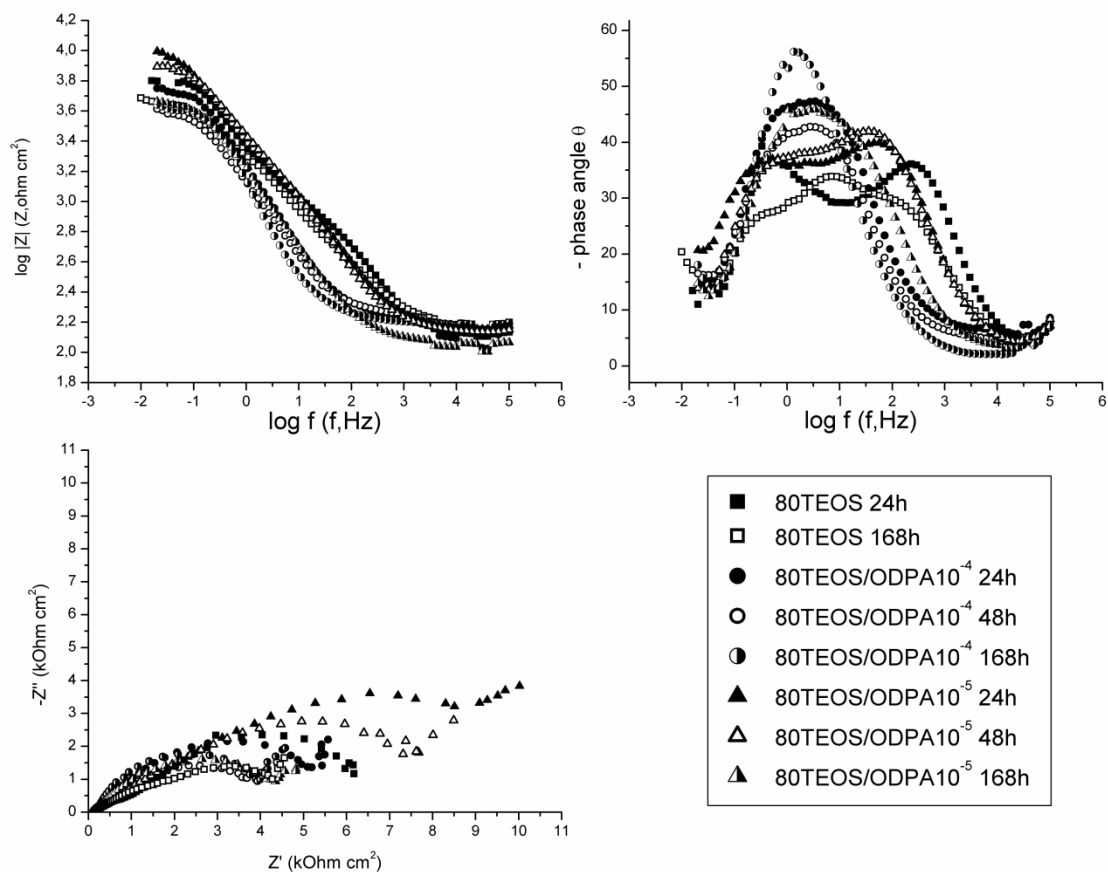
Figure 3: Effect of ODPA addition on EIS plots for 80TEOS in 0.05 mol/L NaCl at the open circuit potential after 24h, 48h and 168h of exposure.

In the case of 90TEOS, after 24h and 48h of immersion the highest protection was obtained with 10^{-4} mol L^{-1} of ODPA. However, on increasing the exposure time to 7 days the protective action of the lowest ODPA concentration gave the best response (Figure 3 b). The 90TEOS film with the addition of 5.00×10^{-5} mol L^{-1} ODPA presented the best performance considering all samples tested. Felhösi et al. [14] reported that a certain threshold concentration of phosphonate is necessary to ensure sufficient inhibition, this behavior being related to the surfactant nature of the phosphonic molecules. It has also been reported by Dalmoro et al. [21] that a high inhibitor concentration can hinder the synergistic effect of silane and phosphonic, affecting the degree of organization of the sol-gel network. Reports in the literature highlight the close relationship between the inhibitor concentration and the network stability, where a high content of inhibitor may lead to the formation of a fragile sol–gel layer with poor barrier properties [8,14,21,27].
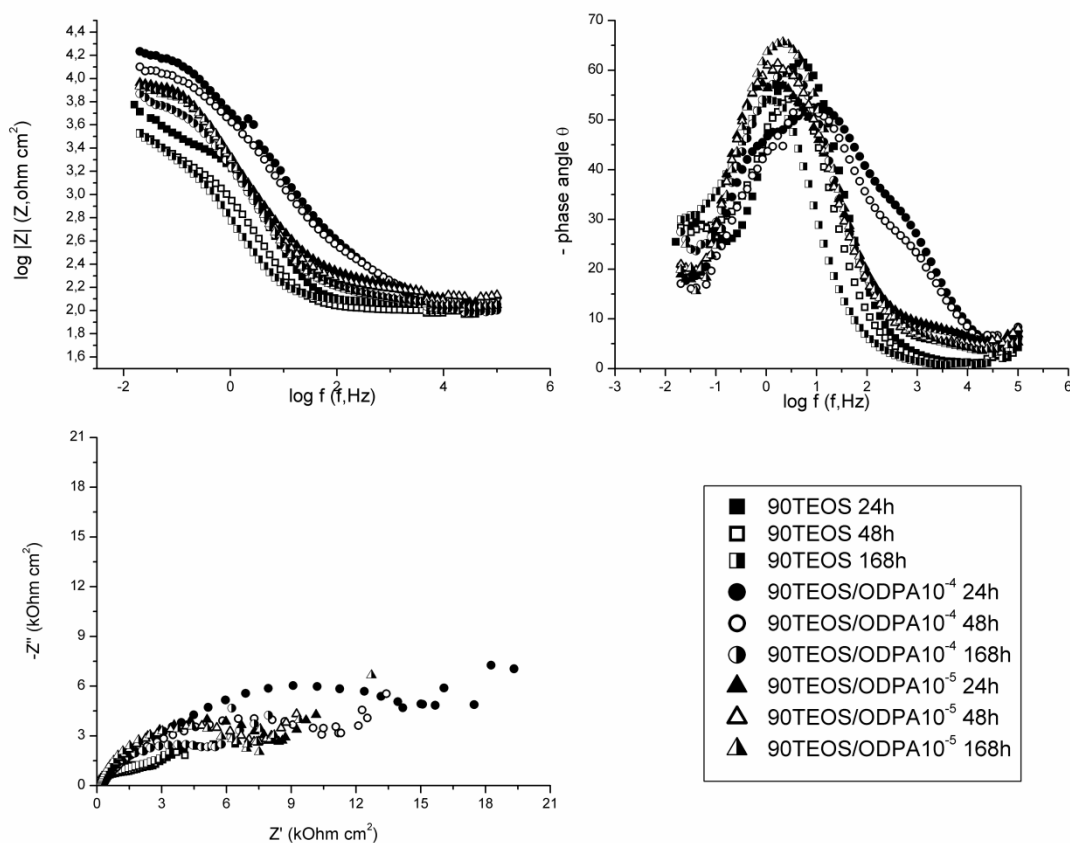
Figure 4: Effect of ODPA addition on EIS plots for 90TEOS in 0.05 mol/L NaCl at the open circuit potential after 24h, 48h and 168h of exposure.

The evolution of the EIS spectra with immersion time (24 and 168 h) in a 0.05 mol L^{-1} NaCl solution at 25°C, for AA2024-T3 coated with 90TEOS and 90TEOS/ODPA10^{-5} was analyzed using an equivalent circuit. It can be seen that for 90TEOS the overall resistance decreased with time, which may be related to the onset of corrosion. In the case of the 90TEOS/ODPA10^{-5} sample the overall impedance values remain more stable and the maximum phase angle is close to −70°, suggesting that it is less porous and more protective than other samples. The experimental data were analyzed using an equivalent circuit (EC) with three time constants, given by Rs(CPE$_{HF}$[R$_{HF}$(CPE$_{LF}$[R$_{LF}$ W)], where R$_s$ is the ohmic resistance between the working and the reference electrode. For the bare alloy the time constant at high frequency (R$_{HF}$ and CPE$_{HF}$) was associated with the internal oxide layer and that at lower frequency (R$_{LF}$ and CPE$_{LF}$) was related to the external porous oxide layer. The capacitance associated with the internal oxide layer and external porous layer was replaced by a constant phase element (CPE) that describes a non-ideal capacitor when the phase angle is different from −90°. The CPE impedance is attributed to the distributed surface reactivity, surface heterogeneity, roughness of the current and potential distribution, which in turn are related to the electrode geometry and the electrode porosity. A diffusional Warburg impedance (W) was included to account for the diffusion through the metal oxide layer on the bare alloy [28].

For the alloy treated with silanes , the time constant at higher frequencies (R$_{HF}$ and CPE$_{HF}$) was related to the silane film resistance and capacitance and that at lower frequencies (R$_{LF}$ and CPE$_{LF}$) to the resistance and capacitance of the interfacial layer. This interfacial layer is formed through the interaction of the Al OH groups with Si OH groups, forming Al-O-Si covalent bonds [27, 29]. The third time constant (W) in the lowest frequency range describes the electrochemical activity occurring inside the defects formed in the interfacial layers.

The fitting quality was assessed based on the error percentage associated with each circuit component, showing errors of less than 5%. The simulated parameters are given in Table 2.

Table 2: Parameters of the silica films 90TEOS and 90TEOS/ODPA 10^{-5} after 24h and 168h of immersion in 0.05 mol·L^{-1} NaCl obtained from the fitting of the experimental impedance spectra with the equivalent circuit.

	BARE ALLOY		90TEOS		90TEOS/ODPA 10^{-5}	
	24h	168h	24h	168h	24h	168h
Rs ($\Omega \cdot cm^2$)	101.2	101.0	109.1	109.5	126.6	110.4
R_{HF} ($\Omega \cdot cm^2$)	21.6	8.64	12.8	11.7	58.2	41.8
CPE_{HF} ($\mu F \cdot cm^{-2} s^{n-1}$)	41.2	37.2	13.8	78.6	5.52	19.4
n_{HF}	0.91	0.77	0.78	0.76	0.84	0.82
R_{LF} ($k\Omega \cdot cm^2$)	1.19	2.07	2.25	1.97	9.55	8.93
CPE_{LF} ($\mu F \cdot cm^{-2} \cdot s^{n-1}$)	38.1	64.2	24.8	72.2	67.5	17.8
n_{LF}	0.86	0.79	0.90	0.84	0,83	0.86
W ($k\Omega \cdot cm^2 \cdot s^{1/2}$)	1.41	0.58	1.17	0.71	0.69	0.64

On increasing the immersion time R_{HF} decreases and CPE_{HF} increases for all samples, reflecting the film degradation, this effect being more pronounced for films without ODPA added. For the bare alloy and the TEOS film similar R_{LF} and CPE_{LF} values were observed for longer exposure times, which could be related to the onset of corrosion activity. The highly hydrophilic character of the TEOS film does not provide the alloy with effective protection [30]. The addition of ODPA allows the formation of a less porous and more protective film during immersion, as observed from the increased   overall resistance and lower capacitance as compared to the 90TEOS samples. A previous study based on experimental analysis (FTIR and XPS) and theoretical calculations demonstrated that phosphonic groups can act as adhesion promoters for silane deposition on an aluminum surface, creating a more homogeneous and thinner coating. Conversely, according to the authors, in the absence of phosphonic molecules an irregular film was formed. Moreover, XPS results verified that the silanol groups are mainly located on the outside of the hybrid organic−inorganic film, whereas phosphorus and siloxane rings are found close to the metal surface [31].

The polarization curves for the bare alloy, 90TEOS and 90TEOS/ODPA10^{-5} are shown in Figure 5. It can be seen that the E_{corr} shifts toward more positive values for the sample treated with 90TEOS/ODPA10^{-5} even though the i_{corr} values remained within the same order of magnitude (around 10^{-7} A cm^{-2}). The curves indicate that in the absence of ODPA the dissolution processes occur earlier.
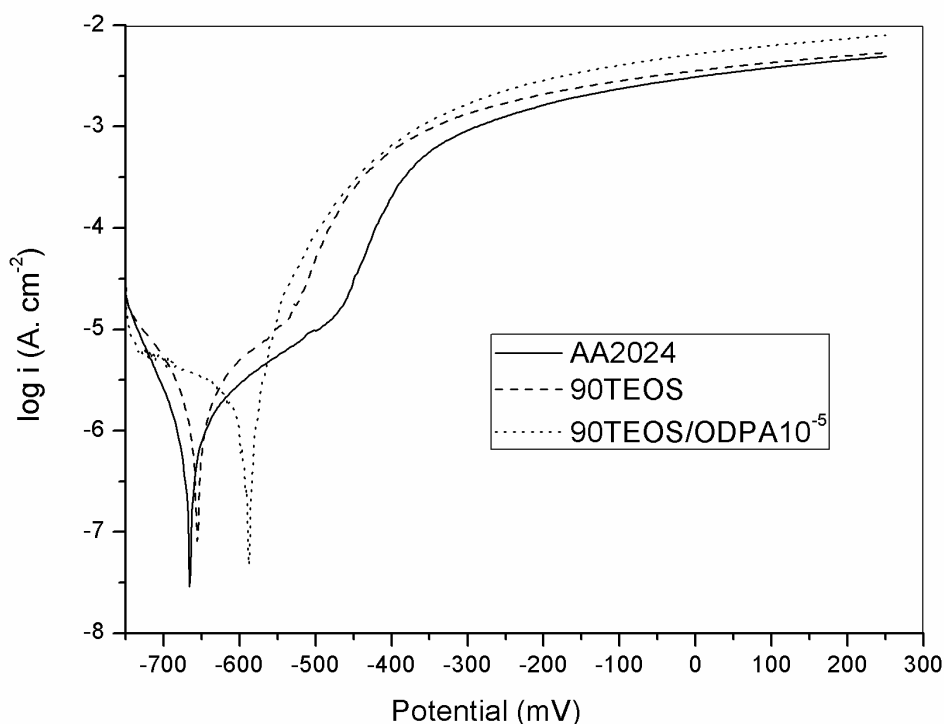
Figure 5: Polarization curves of AA2024 aluminum alloy, 90TEOS and 90TEOS/ODPA after 1h of exposure in 0.05 mol/L NaCl.

The values for the contact angle (WCA) obtained for the samples coated with non-modified TEOS and with TEOS containing ODPA are presented in Table 3. A higher WCA is associated with better film hydrophobicity and therefore greater resistant to aqueous solution uptake. This feature was related to the presence of a long apolar carbon chain in the phosphonic acid structure [32].

Table 3: Contact angle values obtained on samples coated with TEOS and TEOS/ODPA.

SAMPLE	CONTACT ANGLE (°)
Bare alloy	63.2 ± 1.6
90TEOS	70.2 ± 1.5
90TEOS/ODPA10^{-5}	97.6 ± 1.9
80TEOS	71.4 ± 0.1
80TEOS/ODPA10^{-5}	100.9 ± 0.5

4. CONCLUSIONS

Modified TEOS films with the incorporation of the phosphonic acid ODPA were successfully prepared, thus effectively overcoming the typical limitations of TEOS films and providing a protective effect against the corrosion of the AA 2024 alloy. FTIR data showed that on increasing the water content the ratio between $SIOH/SICH_2CH_3$ increases and the ratio between $SIOSI/SIOH$ decreases, since hydrolysis is facilitated by the presence of water in the silanization bath. The EIS analysis indicated an improvement in the corrosion performance when phosphonic acid is added to films with 90% of water content at the optimal concentration $(5x10^{-5}$ mol.L^{-1}). The incorporation of ODPA into TEOS film showed a positive effect on the barrier properties of the sample due to the presence of a long carbon chain. The water contact angles showed that the addition of phosphonic acid enhances the hydrophobicity.

5. ACKNOWLEDGMENTS

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