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Corrosion Protection of AA2524-T3 Anodized in Tartaric-Sulfuric Acid Bath and Protected with Hybrid Sol-Gel Coating

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Abstract. 2xxx Al alloys are particularly sensitive to localized corrosion in chloride environments and in order to maintain their integrity, minimize maintenance needs and repairs, and to maximize component life, protective treatments are required.

Anodizing is an electrochemical process based on the growth of the Al oxide layer by applying anodic potentials. One of the alternatives is tartaric/sulphuric acid (TSA) anodizing, which is environmentally compliant and provides corrosion resistance properties, compatible with the requirements of the aerospace industry with appropriate paint adhesion.

In this study, AA2524-T3 specimens were anodized in a tartaric-sulfuric acid bath (TSA) and subsequently protected by application of a hybrid sol–gel coating. The sol–gel coating was prepared using a solution with high water content (58 %v/v) and obtained by the hydrolysis and condensation of tetraethoxysilane (TEOS) and 3-glycidoxypropyltrimethoxysilane (GPTMS). The corrosion resistance evaluation of both unsealed and coated samples was carried out in a sodium chloride solution by EIS as a function of immersion time. The results were also fitted using electrical equivalent circuits.

Introduction

The AA2524-T3 alloy is a relatively new aluminium alloy (formerly C188-T3) developed as a fuselage skin replacement for AA2024-T3 and is currently used in the Boeing 777 aircraft [1,2]. This aluminum alloy presents high damage-tolerance and excellent fatigue properties [1]. However, this alloy also presents a large amount of secondary phase particles and this is the main reason for their high susceptibility to localized corrosion, such as pitting corrosion and stress corrosion cracking [3].

In order to avoid localized corrosion, usually the aircraft parts are coated with organic coatings avoiding their exposure to the corrosive environment. Prior to organic coating application, the aluminum alloy is anodized. Many industries still use anodizing processes with hexavalent chromium, but its use causes large environmental and health related problems [4-5]. Recent studies are pointing towards chromium free anodizing processes, specifically the tartaric-sulphuric anodizing (TSA), as a viable alternative.

Sol–gel coatings have been extensively studied as potential surface paint pre-treatments for aluminum alloys in replacement of environmentally harmful treatments and they have demonstrated efficient alternatives to the chromate technology [6]. Siloxanes based coatings applied by the sol–gel process have very good chemical stability and provide an effective protection for metallic substrates [7].

The aim of this work is to investigate the corrosion resistance of TSA anodized AA2524 alloy coated with a hybrid organic-inorganic sol–gel layer with the purpose of improving the corrosion resistance while maintaining the future compatibility with organic coatings.

Experimental

The AA2524 alloy specimens were kindly supplied by EMBRAER S.A. The chemical composition of the alloy is 4.07 wt.% Cu, 1.66 wt.% Mg, 0.60 wt.% Mn, 0.10 wt.% Zn, 0.11 wt.% Fe, 0.03 wt.% Ti, 0.01 wt.% Si and 0.02 wt.% others.

Prior to anodizing, specimens with dimensions of 4.5 cm x 5.0 cm x 0.105 cm were degreased by sonication in acetone for 10 min. The surface treatment was performed by dipping the samples in an alkaline etching solution: NaOH (40 $g.L^{-1}$) at 40 ºC for 30 s and in a chromate-free commercial acid dismutting bath (Turco® Smuttgo-Henkel) at room temperature for 15 s. Between each step of surface preparation the specimens were thoroughly washed with distilled water.

Samples were anodized in a tartaric-sulfuric acid bath (TSA) (40 $g.L^{-1}$ H_2SO_4 and 80 $g.L^{-1}$ $C_4H_6O_6$) at 10 V for 20 min at 37 ºC. After the anodizing step, some samples were immediately rinsed with distilled water and hydrothermally sealed in boiling deionized water for 5 min and then coated with a hybrid organic–inorganic sol–gel layer using a KSV Nima dip-coater for 2 min with withdrawal speed fixed of 100 $mm.min^{-1}$ and afterwards cured at 150 ºC for 1 h in a furnace. Others were coated with sol-gel using the same process.Unsealed samples were also tested for comparison.

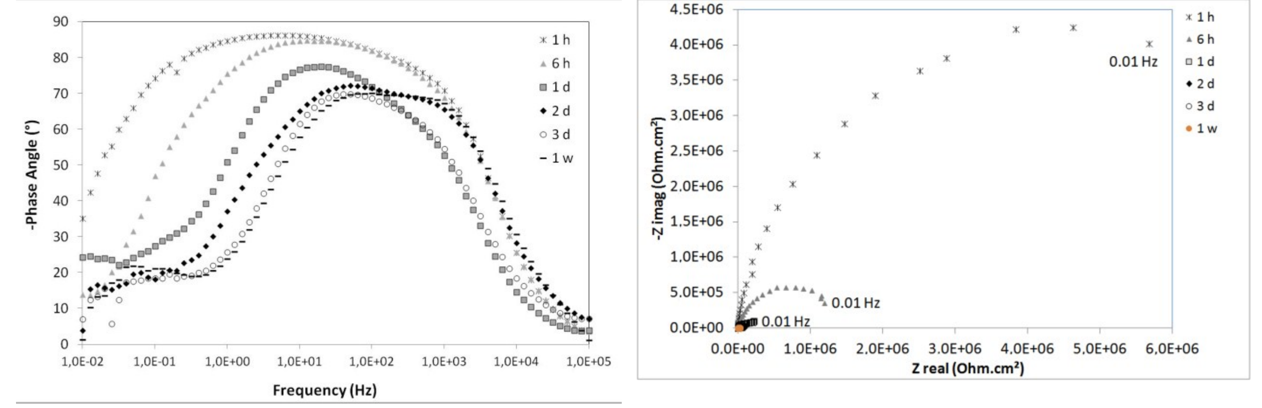
The sol–gel solution was prepared by addition of tetraethoxysilane (TEOS) (20 % v/v) and 3-glycidyloxypropyl-trimethoxysilane (GPTMS) (10 % v/v) in a mixture of ethanol (10 % v/v) and distilled water (58 %v/v). The pH was adjusted with acetic acid in a continuously stirred sol-gel solution to 2.3-2.5. All chemicals were of analytical grade and used as received.

For the EIS tests, three different types of samples were tested: (1) anodized and not sealed, (2) anodized, sealed and coated with sol-gel, (3) anodized and coated with sol-gel. A Gamry PCI4/300 potentiostat-frequency response analyzer system was used. EIS was carried out in a classical three electrodes arrangement using 3.80 cm^2 area of the specimen as working electrode, Ag/AgCl (+0.207 V vs. SHE) as reference electrode and a platinum plate as counter electrode. EIS measurements were taken at different immersion times at room temperature, in a naturally aerated 0.1 $mol.L^{-1}$ NaCl solution, over a frequency range from 10^5 to 10^{-2} Hz with 10 points per decade using an ac signal amplitude of 20 mV (rms). The monitoring of the electrochemical behavior during immerison test was carried out until 1008 h, corresponding to 6 weeks.

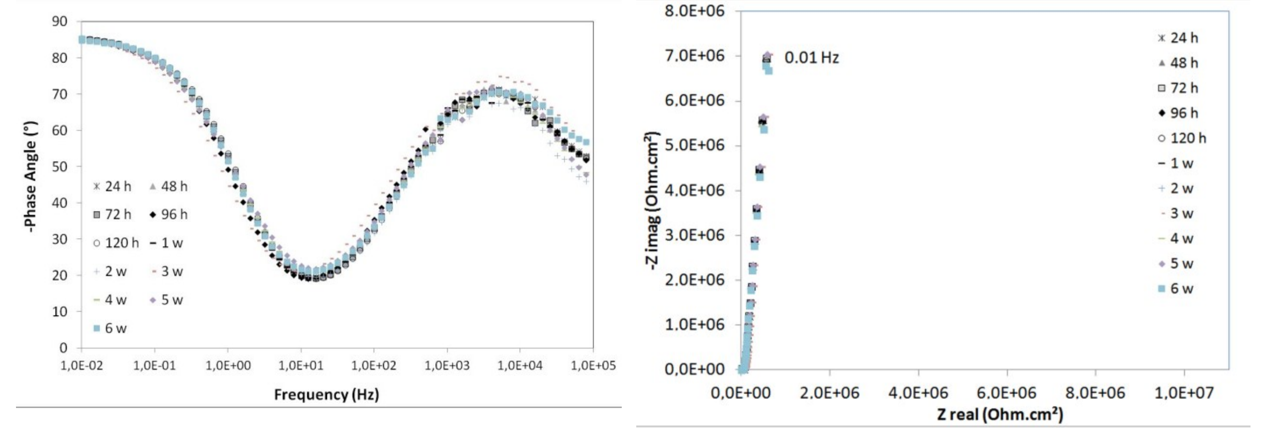
Results and Discussion

EIS data of the unsealed TSA anodized AA2524 were obtained up to 168 h. However, after 72 h, the surfaces of this type of sample were completely corroded. Overall, the impedance decreased more than two orders of magnitude during the test period showing a very poor corrosion resistance of such surfaces.

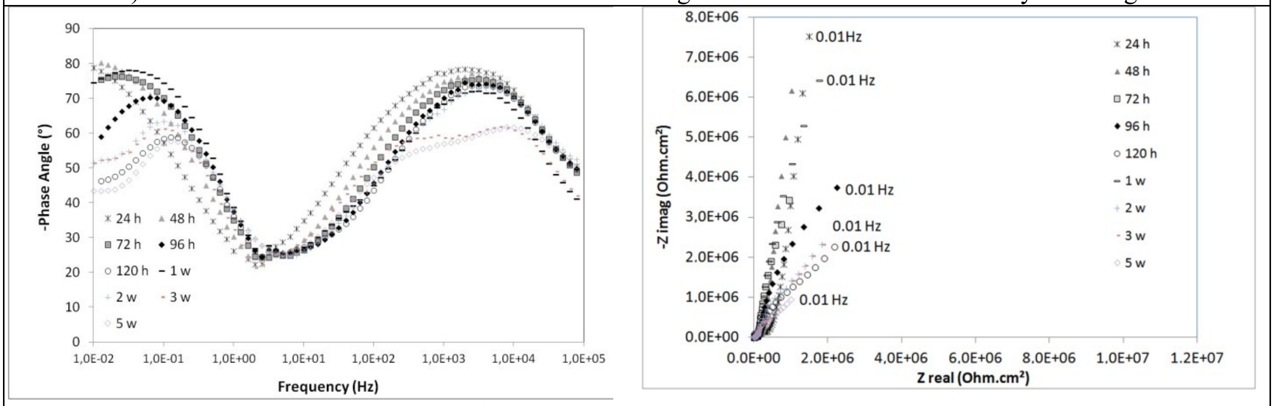
For all surface conditions whose EIS data are represented in Fig. 1, two time constants are indicated since the beginning of the exposure period, the impedance largely decreased in the first hours of exposures to the electrolyte due to the incorporation of electrolyte in the pores of the anodic layer. Electrical equivalent circuits (EEC) were proposed for various periods of immersion, as shown in Fig. 2, to fit the EIS responses of Fig. 1. For the EECs proposed, R_{el} represents the electrolyte resistance; CPE_b is the constant phase element representing the properties of the barrier layer; R_b is the pore resistance of the barrier layer; CPE_{dl} and R_{ct} are ascribed, respectively, to the double layer capacity and the charge transfer resistance; and CPE_{corr} and R_{corr} accounts for corrosion reactions taking place at the surface of a highly deteriorated electrode.



a) unsealed TSA anodized AA2524

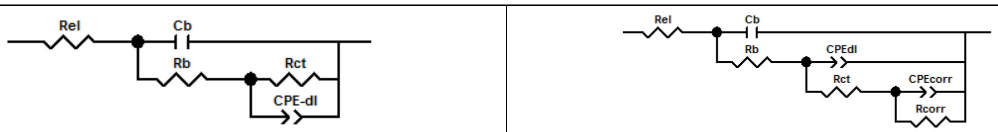


b) TSA anodized AA2524 sealed for 5 min in boiling water and then coated with a hybrid sol-gel



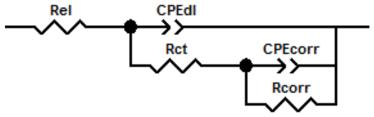
c) TSA anodized AA2524 coated with a hybrid sol-gel

Fig. 1 – Bode phase angle and Nyquist diagrams for TSA anodized AA2524 at different exposure periods to 0.1 mol.l^{-1} NaCl solution



1 h, 6 h – 10 V unsealed

24 h, 72 h – 10 V unsealed



1 week - 10 V unsealed

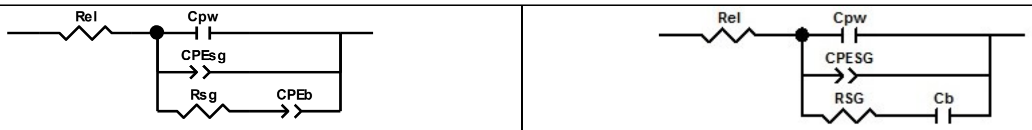
Fig. 2 – Electrical equivalent circuit used to fit the EIS data of the unsealed TSA anodized AA2524 sample from 1 h to 168 h (1 week) of immersion in 0.1 mol.L^{-1} NaCl solution

Table 1 shows the fittings parameters for the EIS diagrams of the unsealed AA 2524 anodized samples. The C_b values are in order of $\mu F.cm^{-2}$ until 72 h of immersion. R_b values decreased with time from 1 to 6 h and then from 24 to 72 h indicating the degradation of the barrier layer with immersion time. R_{ct} and R_{corr} decreases with time of immersion, due to the corrosion process. The same explanation can be atributted to the increase of CPE_{dl} and $CPE_{corr.}$

Table 1 – Fitted parameters values for the EIS diagrams of the unsealed AA 2524 TSA anodized at 10 V

Immersion time	C_b ($\mu F.cm^{-2}$)	CPE_{dl} ($\mu F.cm^{-2}.s^{(n-1)}$)	n_{dl}	CPE_{corr} ($F.cm^{-2}.s^{(n-1)}$)	n_{corr}	R_b ($Ohm.cm^2$)	R_{ct} ($Ohm.cm^2$)	R_{corr} ($Ohm.cm^2$)
1 h	0.57	0.48	0.88			1210.3	8.70E+06	
6 h	0.58	0.76	0.85			472.64	1.22E+06	
24 h	0.61	1.44	0.86	1.79E-05	0.79	704.20	1.27E+05	1.73E+05
72 h	0.06	3.26	0.83	8.86E-05	0.83	35.29	3.15E+04	3.11E+04
1 w		7.35	0.84	2.03E-04	0.77		1.14E+04	1.96E+04

The impedance diagrams of Figs 1b and 1c were fitted with the EEC presented in Fig. 3. C_{pw} represents the capacitive response of the pore walls. In both EEC $CPE_{sg}//R_{sg}$ is attributed to the response of the pores filled with the sol gel coating and C_b and CPE_b is assigned to the response of the barrier layer. R_b could not be estimated once the time constant of this process is below the lowest frequency used in this experiment, and only few points were available for its definition. The EEC considers that the sol-gel coating penetrates the whole pore; therefore, aggressive species can only reach the barrier layer through conductive pathways established along the whole coating thickness.



a) coated with a hybrid sol-gel from 24 h to 2 weeks

b) coated with a hybrid sol-gel from 3 to 5 weeks and coated with the hybrid sol-gel and sealed for 5 min in boiling water and then coated with a hybrid sol-gel from 24 h to 6 weeks

Figure 3 – Electrical equivalent circuits used to fit the EIS data of the AA2524 alloy TSA anodized and coated with a hybrid sol-gel

Tables 2 and 3 show the fitted parameters values for the EIS diagrams of the AA 2524 TSA anodized at 10 V and coated with the hybrid sol-gel or sealed for 5 min in boiling water and then coated with a hybrid sol-gel, respectively.

Table 2 – Fitted parameters values for the EIS diagrams of the AA 2524 TSA anodized at 10 V and coated with the hybrid sol-gel

Immersion time	**CPE_{SG} ($\mu F.cm^{-2}.s^{(n-1)}$)**	**n_{SG}**	**CPE_b ($\mu F.cm^{-2}.s^{(n-1)}$)**	**n_b**	**R_{SG} ($\Omega.cm^2$)**
1day	0.11	0.69	1.20	0.84	4.24E+05
2 d	0.15	0.70	1.61	0.87	2.10E+05
3 d	0.30	0.68	2.71	0.86	8.75E+04
4 d	0.48	0.55	1.32	0.91	1.48E+05
5 d	0.97	0.45	0.92	0.96	2.13E+05
1 week	0.28	0.64	1.41	0.91	1.35E+05
2 w	0.97	0.47	1.30	0.99	1.76E+05
3 w	2.54	0.51	3.20	1	1.10E+05
5 w	2.19	0.47	1.65	1	1.51E+05

Table 3 – Fitted parameters values for the EIS diagrams of the AA 2524 TSA anodized at 10 V, sealed for 5 min in boiling water and then coated with a hybrid sol-gel

Immersion time	**CPE_{SG} ($\mu F.cm^{-2}.s^{(n-1)}$)**	**n_{SG}**	**C_b ($\mu F.cm^{-2}$)**	**R_{SG} ($\Omega.cm^2$)**
1day	0.27	0.62	1.62	7.29E+04
2 d	0.25	0.63	1.64	7.34E+04
3 d	0.25	0.63	1.66	7.03E+04
4 d	0.25	0.63	1.67	6.73E+04
5 d	0.26	0.63	1.67	6.70E+04
1week	0.25	0.62	1.67	7.51E+04
2 w	0.26	0.63	1.70	6.51E+04
3 w	0.26	0.60	1.60	1.08E+05
4w	0.29	0.61	1.64	7.38E+04
5w	0.30	0.61	1.52	7.60E+04
6 w	0.29	0.63	1.72	6.94E+04

The exponents for the n_{SG} of the samples anodized and coated with a hybrid sol-gel, either after hydrothermal sealing or not, varies from 0.45 to 0.70, indicating the main contribution of diffusive processes, also found by Capelossi *et al.* [8] in their EIS investigation of the corrosion behaviour of TSA anodized Alclad 2024-T3 aluminium alloy coated with a sol-gel layer.

The resistances of the hybrid sol-gel layer, R_{SG}, decrease for the TSA anodized samples at 10 V and coated with the hybrid sol-gel until 3 days of immersion. However, they remain relatively stable, for the samples sealed for 5 min in boiling water and then coated with a hybrid sol-gel, even after 6 weeks of immersion in a 0.1 mol.L^{-1} NaCl solution, indicating that the electrolyte hardly penetrates through the coating.

For the sample coated with a hybrid sol-gel, CPE_{SG} gradually increases with immersion time pointing either to water uptake or to a thinning of the hybrid coating. This value remains stable for the samples sealed for 5 min in boiling water and then coated with a hybrid sol-gel, even after 6 weeks of electrochemical tests.

Finally, C_b for the samples sealed for 5 min in boiling water and then coated with a hybrid sol-gel, remained fairly constant during the whole experiment, indicating that the layer properties did not change. For the sample coated with a hybrid sol-gel, n_b values were closer to one with time of immersion, showing that CPE_b behave almost like an ideal capacitor.

Conclusion

The results of the present study showed the beneficial effects of the use of a hybrid TEOS-GPTMS sol-gel on the corrosion resistance of the TSA anodized AA2524 alloy. Despite of the increase corrosion resistance of the AA2523 anodic layer provided by the sol-gel coating, the results showed that a hydrothermal treatment for short periods (5 min) in order to avoid the complete sealing of the pores, increased the stability of the surface anodic layer prolonging its protection properties for long periods of exposure to 0.1 mol.L^{-1} NaCl solution.

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