Effect of cerium (III) on the corrosion protection properties of the film formed on the AA2524-T3 alloy by hydrothermal treatments

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Abstract

Many industries use chromium-based anodizing processes with a subsequent sealing post-treatment containing hexavalent chromium ions to protect Al alloys. However, this method of protection causes large environmental and health related problems. This has encouraged the search for new surface treatments for metals with the requirements of effective protection against corrosion and generation of non-toxic residues to the environment. Recent studies are pointing towards chromium free anodizing processes, specifically the tartaric-sulfuric acid (TSA) one, as a viable alternative. Besides, sealing treatments of the Al anodic layer in chromate solutions are another source of toxic residues and their replacement for environmentally friendly alternatives are also of great interest. Surface treatments with cerium ions are being largely studied for the corrosion protection of Al alloys due to their good anticorrosion properties associated to the lack of toxic residues generated. In this investigation, a hydrothermal treatment in aqueous solution with cerium ions has been proposed as a post-treatment for TSA anodizing, and its effects on the AA2524-T3 alloy corrosion resistance investigated. This alloy presents a chemical composition similar to the AA2024 but with lower and more controlled amounts of alloying elements. The sealing treatment was carried out by immersion in aqueous solutions with cerium ions at the boiling temperature. The effect of Ce on the characteristics of the surface film formed, such as morphology and corrosion resistance, was investigated by SEM and electrochemical impedance spectroscopy. The results were compared to those of sealing in boiling water. The results showed that the sealing treatment in solution with Ce(III) ions presented a less stable behavior than the sealing with only boiling water. However, the results of the EIS experiments showed recovery of the protective properties of the system, indicating that some self-healing properties must be imparted to the system.

Keywords: AA2524-T3; TSA; Ce(III) ions; sol-gel, sealing treatment

Introduction

Chromating is the main type of chemical conversion treatment used in the aerospace industry. The coating formed by this treatment presents the required corrosion resistance due to its self-healing properties [1-3]. However, this method of protection causes large environmental and health related problems due to the toxic residues generated, mainly hexavalent chromium compounds [2-3].

Recent studies recommend chromium free anodizing processes, specifically the tartaric-sulfuric anodizing (TSA), as a viable alternative [4]. The requirements for the new treatments are effective protection against corrosion and reduction of toxicity of the generated waste. Depending on their application, anodized alloys need to be sealed and this might be carried out in boiling water or in hexavalent chromium containing solution.

For replacement of sealing treatments with hexavalent chromium based additives, surface treatments with cerium ions are being studied. The corrosion protection of sealed aluminum alloys in chromium free solutions and the potential for replacement of chromating treatments is under evaluation based on their environmentally friendly properties. Inoue *et al.* studied the incorporation of cerium ions into the surface layer formed by hydrothermal treatments on the AA2524 alloy. Besides, the effect of polyethylene glycol on the protective properties of the layer formed was also investigated [5].

Sol–gel coatings have also been extensively studied as potential pre-treatments not associated to toxic residues for aluminum alloys surface preparation prior to paint. It has been demonstrated an efficient alternative for replacement of the chromate technology [6].

In this study, samples of AA2524 alloy were anodized in a tartaric-sulfuric acid bath, hydrothermal sealed in a solution with Ce^{+3} ions and then coated with sol-gel. The effect of Ce^{+3} ions on the corrosion resistance of the AA2524 alloy was investigated by SEM and electrochemical impedance spectroscopy (EIS).

Experimental

The AA2524 alloy was 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 of the AA2524 alloy with dimensions of 4.5 cm x 5.0 cm x 0.105 cm were degreased by sonication in acetone for 10 min. Surface preparation was carried out 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 then 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 anodizing, some samples were immediately rinsed with distilled water and partially sealed for 10 min by hydrothermal treatment in boiling deionized water (BW) without or with the addition of 50 mM of Ce^{+3} ions. After the sealing treatment, all samples were coated with a hybrid organic–inorganic sol–gel layer using a KSV Nima dip-coater for 2 min with withdrawal speed fixed at 100 mm.min^{-1} and afterwards cured at 150 ºC for 1 h in a furnace.

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.

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 immersion test was carried out until 1008 h, corresponding to 6 weeks.

Scanning electron microscopy characterization was performed in a Field Emission Gun Microscope FEI Quanta 650. Despite the sol-gel coating, AA2524 samples were not coated with conductive materials for the investigation.

Results and Discussion

EIS data of the TSA anodized sample, sealed for 10 min in boiling water (BW) and then coated with a hybrid sol-gel AA2524 were obtained up to 6 weeks of test. In all diagrams presented in Fig. 1a, at least two time constants are indicated since the beginning of the exposure period. The Bode phase diagrams were very similar up to 1 week on immersion. Between 1 and 2 weeks, the peak of the phase angle at higher frequencies decreases, and the time constant at lower frequencies is displaced to increasingly higher frequencies and becomes more capacitive. However, the impedances did not show many changes during the entire test, Fig 1b. These results suggest electrolyte penetration through the outer layer of the protective system (HF phase angle diminution) but the corrosion products and probably the increasing hydration of the external part of the anodic layer (boehmite layer) protects the metallic substrate. This latter evaluation is supported by the increasing low frequency phase angle with immersion time and also by the fact that impedance modulus hardly changes during the whole test period.

Fig 2 presents scanning electron (SEM) micrographs of samples similar to those presented in Fig 1 in the as-prepared condition and after 6 weeks immersion tests. Fig 2a shows a cross-section view of the former sample. This micrograph indicates that the sol-gel coating integrates with the boehmite layer. The top view, Fig 2b, shows white particles coated by the sol-gel. Corrosion products are seen around corroded areas, after 6 weeks of test in a 0.1 mol.L^{-1} NaCl solution, Fig 2c.

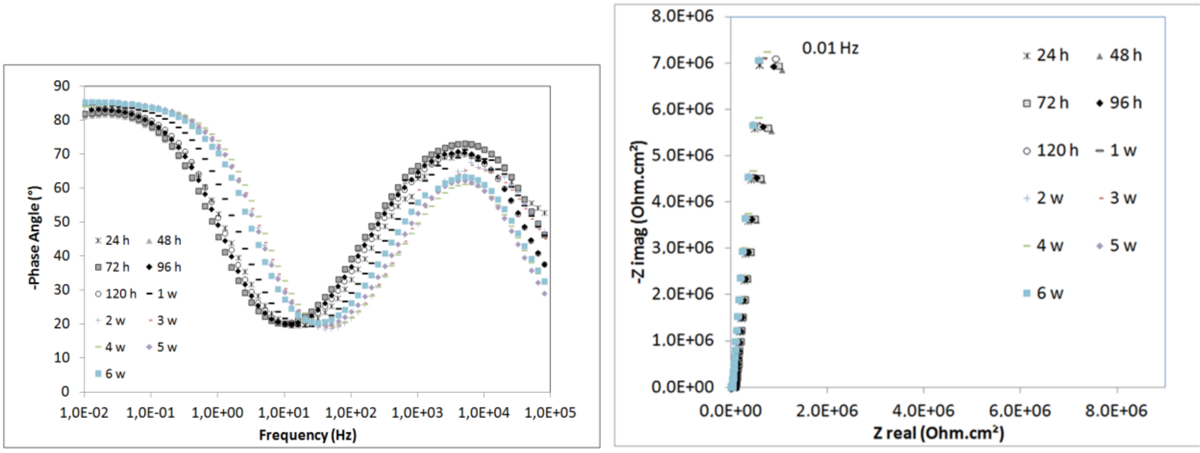

Figure 1: EIS diagrams for the AA2524 TSA anodized alloy (10 V) sealed for 10 min in boiling water and then coated with sol-gel. Immersion up to 6 weeks in a 0.1 mol.L^{-1} NaCl solution. a) Bode phase angle and b) Nyquist diagrams .

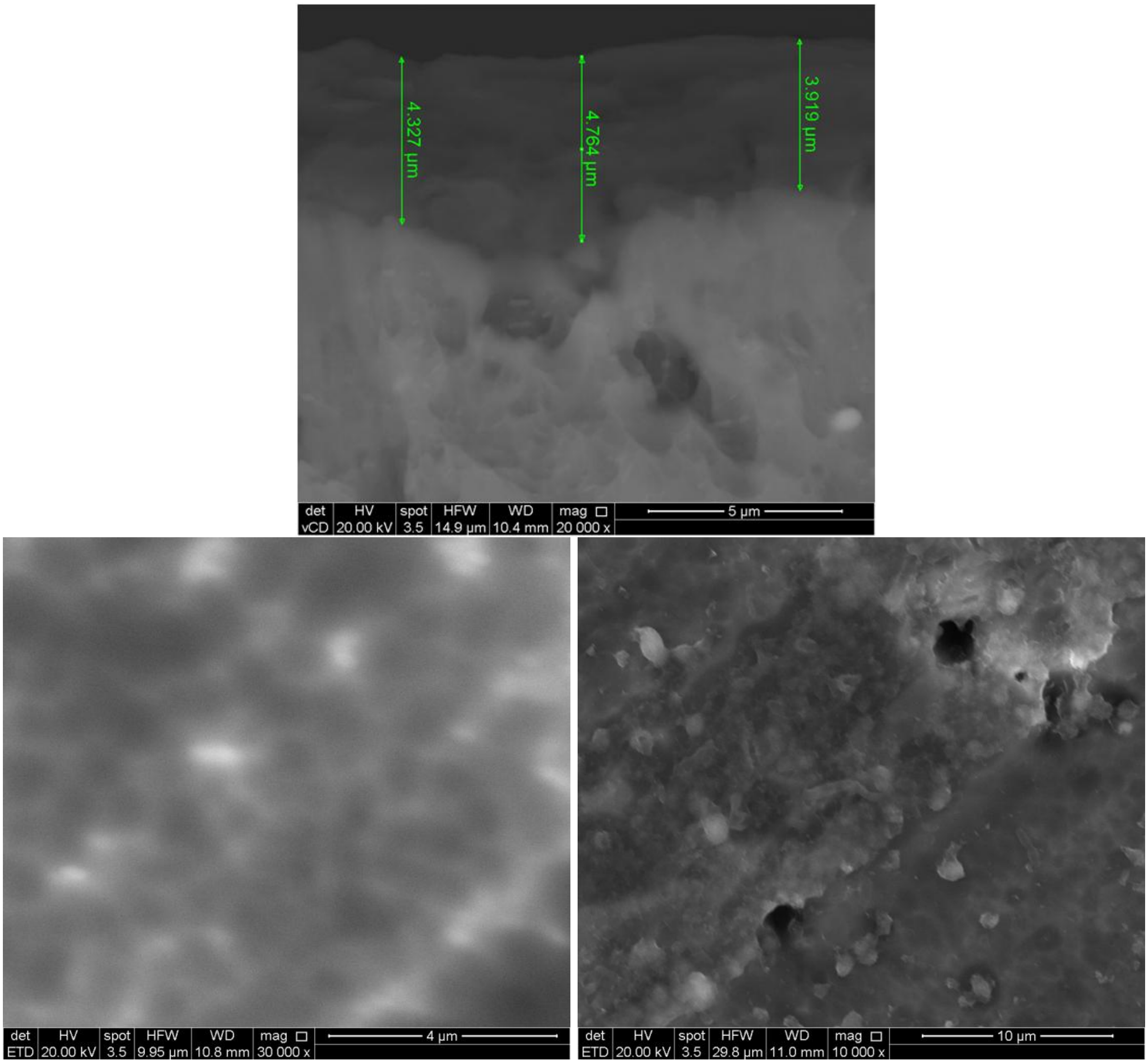

Figure 2: SEM micrographs of AA2524 TSA anodized 10 V + sealed in water (10 min BW) + coated with sol-gel. a) cross-section (BSE detector), b) top view prior to immersion and c) top view after 6 weeks immersion in 0.1 mol.L^{-1} NaCl solution.

The impedance diagrams of Fig. 1 were fitted with the electrical equivalent circuit (EEC) presented in Fig. 3. C_{pw} represents the capacitive response of the pore walls. The $CPE_{sg}//R_{sg}$ pair is attributed to the response of the sol-gel coating integrated with the boehmite and C_b is assigned to the response of the barrier layer. The use of a pure capacitor to describe the pore walls (C_{pw}) and the barrier layer (C_b) suggests that these systems are fairly homogeneous and free of defects. 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.

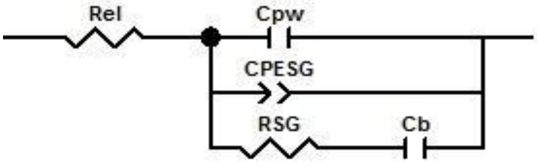

Figure 3: Electrical equivalent circuit (EEC) used to fit the EIS data of the AA2524 alloy TSA anodized, sealed for 10 min in boiling water and then coated with a hybrid sol-gel.

Table 1 shows the fitted parameters values for the EIS diagrams of the AA2524 TSA anodized at 10 V sealed for 10 min in boiling water and then coated with a hybrid sol-gel. The exponents for the n_{SG} of the samples varies from 0.60 to 0.70. For sealed anodized Al, values close to 0.5 have been frequently reported by the literature for the CPE exponent associated with the sealed porous layer [7-9]. This has been ascribed to the porous nature of the sealed pore that would be better represented by a transmission-line type EEC [9]. C_b remains relatively stable during the whole test period. On the other hand, CPE_{SG} gradually increased and R_{SG} decreased with immersion time, indicating the hybrid coating degradation, confirming the qualitative analysis of the Bode phase angle diagrams previously presented.

Table 1 - Fitted parameters values for the EIS results for the AA2524 TSA anodized (10 V) alloy + 10 min BW + sol-gel.

Immersion Time	**CPE_{SG} ($F.cm^{-2}.s^{(n-1)}$)**	**n_{SG}**	**C_b ($F.cm^{-2}$)**	**R_{SG} ($\Omega.cm^2$)**
1day	2.11E-07	0.60	1.57E-06	2.07E+05
2 d	2.38E-07	0.62	1.64E-06	9.92E+04
3 d	2.19E-07	0.63	1.66E-06	9.97E+04
4 d	2.32E-07	0.63	1.65E-06	8.41E+04
5 d	2.30E-07	0.63	1.65E-06	7.57E+04
1week	2.53E-07	0.64	1.65E-06	4.63E+04
2 w	2.65E-07	0.66	1.66E-06	2.22E+04
3 w	2.78E-07	0.66	1.64E-06	2.17E+04
4 w	2.62E-07	0.69	1.59E-06	2.01E+04
5 w	2.67E-07	0.68	1.62E-06	2.38E+04
6 w	2.65E-07	0.69	1.62E-06	2.31E+04

EIS diagrams of the TSA anodized AA2524 alloy, sealed for 10 min in boiling water solution with Ce^{+3} ions and then coated with the hybrid sol-gel were also obtained up to 6 weeks, Fig 4. Similar to the samples sealed in boiling water, Fig 1, all Bode phase angle diagrams presented two time constants, Fig 4a, however, for this sample the low frequency one is more well-defined. The impedance decreased during the first week of immersion in the solution solution, until a minimum was reached, indicating corrosion of the metallic substrate and degradation of the anodic layer. However, from 1 week onwards the impedance gradually increased approaching the impedances obtained for 24 h of exposure to the corrosive environment. These results suggest a healing process associated to the sealing treatment in presence of Ce^{+3} ions. Surface observation by SEM after immersion tests support the healing process hypothesis, Figure 5. It is seen that despite the indication of localized attack at some points, the surface around these areas did not show significant amounts of corrosion products (Fig 5(b)).

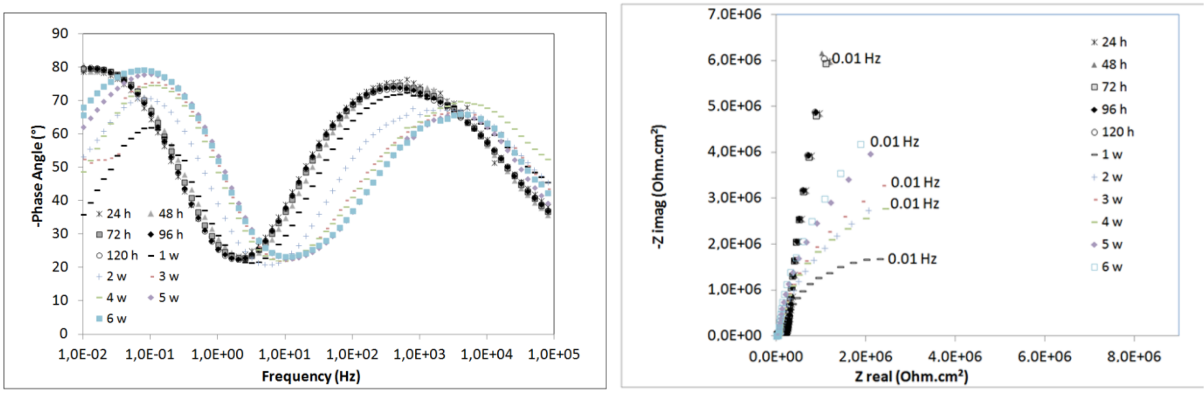

Figure 4: EIS diagrams for the AA2524 TSA anodized alloy (10 V) sealed for 10 min in solution with Ce^{+3} ions and then coated with sol-gel. Immersion up to 6 weeks in a 0.1 $mol.L^{-1}$ NaCl solution. a) Bode phase angle and b) Nyquist diagrams.

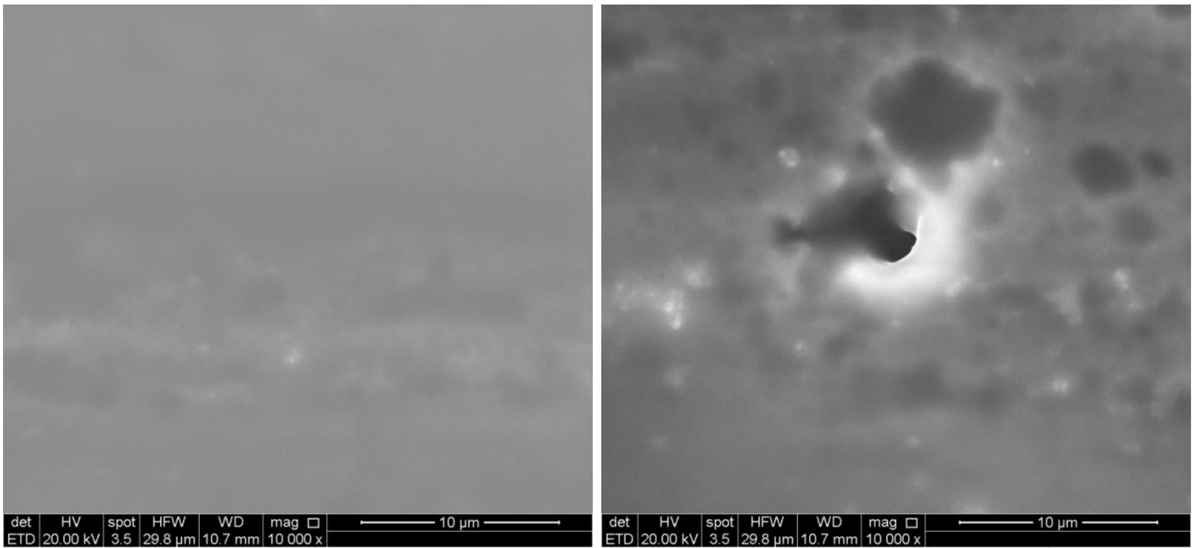

Figure 5: SEM micrographs of the AA2524 TSA anodized at 10 V, sealed in Ce^{+3} solution for 10 min and then sol-gel coated (a) prior to immersion and (b) after 6 weeks of immersion in 0.1 $mol.L^{-1}$ NaCl solution.

The impedance data shown in Fig 4 were fitted with the EEC model presented in Fig. 6, which includes the resistive response of the barrier layer (R_b).

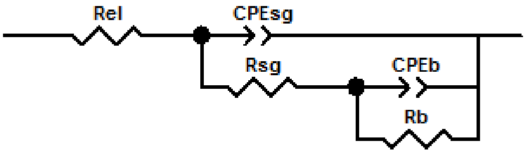

Figure 6: Electrical equivalent circuit used to fit the EIS data of the AA2524 alloy TSA anodized, sealed for 10 min in boiling Ce^{+3} *solution and then coated with a hybrid sol-gel.*

Table 2 shows the values of the fitted parameters for the EIS diagrams of Fig 4. It can be seen that the exponents for n_{SG} varied along the test period from 0.78 to 0.84. Besides, CPE_{SG} gradually increased indicating degradation of this layer likely due to ionic species and water penetration, even though thinning of the sol-gel cannot be ruled out. On the other hand, R_{SG} remained relatively constant up to 5 days of test and then continuously decreased with immersion time, suggesting easier conductive pathways due to the deterioration of the integrated sol-gel-boehmite layer. CPE_b remained stable. For R_b, the values slightly increases until 120 h of test, as verified for R_{SG}, pointing to an improvement of the protective properties of this layer. However, after one week, R_b dropped by nearly one order of magnitude indicating that aggressive species has reached the barrier layer with the onset of the corrosive process. Nevertheless, for longer test periods, R_b showed an increasing trend until the end of the test.

The results reported in the last part of the previous paragraph indicate that, although they do not avoid the degradation of the sol-gel coating, Ce^{3+} ions addition to the hydrothermal sealing bath adds on the recovering of the barrier layer properties, pointing to a possible active corrosion protection. This might be related to the recognized inhibitive properties of such ions towards Al corrosion [10,11] and must be explored by our group in the future with other anodizing formulations and procedures. On the other hand, the comparison of the fitted values for CPE_{SG} and R_{SG} for both hydrothermal sealing treatments (Tables 1 and 2) indicates that the addition of Ce(III) ions does not hinder the protective properties of the integrated sol-gel-boehmite protective layer.

Table 2 - Fitted parameters values for the EIS diagrams of the AA 2524 TSA anodized 10 V + 10 min Ce^{+3} *+ sol-gel.*

Immersion time	**CPE_{SG} ($F.cm^{-2}.s^{(n-1)}$)**	**n_{SG}**	**CPE_b ($F.cm^{-2}.s^{(n-1)}$)**	**n_b**	**R_{SG} ($\Omega.cm^2$)**	**R_b ($\Omega.cm^2$)**
1day	1.25E-07	0.84	2.12E-06	0.98	2.83E+05	4.02E+07
2 d	1.28E-07	0.84	2.14E-06	0.98	2.76E+05	4.02E+07
3 d	1.32E-07	0.83	2.15E-06	0.98	2.49E+05	4.33E+07
4 d	1.33E-07	0.83	2.15E-06	0.98	2.71E+05	4.59E+07
5 d	1.35E-07	0.83	2.15E-06	0.99	2.72E+05	4.81E+07
1week	1.49E-07	0.82	2.34E-06	0.92	1.56E+05	3.68E+06
2 w	1.74E-07	0.79	2.56E-06	0.92	8.60E+04	6.63E+06
3 w	1.92E-07	0.78	2.29E-06	0.94	5.48E+04	8.09E+06
4 w	1.61E-07	0.79	2.35E-06	0.93	5.65E+04	6.61E+06
5 w	1.73E-07	0.78	2.36E-06	0.93	4.45E+04	1.31E+07
6 w	1.85E-07	0.78	2.39E-06	0.93	3.75E+04	1.66E+07

Conclusions

In the present work the effectiveness of Ce(III) ions addition to an hydrothermal sealing treatment applied to 10 V TSA anodized AA2524 samples towards the anticorrosion properties of the anodized layer was investigated and tested against boiling water sealed samples. As an additional procedure, a hybrid sol-gel layer further protected both samples.

The EIS response has shown that the samples sealed in the bath containing Ce(III) ions present a less stable behavior, particularly in the first week of immersion in the 0.1 mol L^{-1} NaCl solution, when a great decrease of impedance was verified. However, for longer test periods, EIS diagrams clearly show a recovery of the system protective properties, indicating that active protection might be imparted to the system. EEC fitting of the EIS data also indicate that the addition of Ce(III) ions to the hydrothermal sealing bath does not hinder the protective properties of the integrated sol-gel-boehmite protective layer.

The results obtained in this work were promising and further strategies using Ce(III) ions for anticorrosion protection of anodized Al alloys must be adopted by our group in the future.

Acknowledgments

Authors acknowledge CAPES and CNPq (Proc. 4007810/2013-1) for the financial support to this work. Dr. Maysa Terada is grateful for the grant awarded (Proc. 1536157), MSc. Hellen Costenaro and Dr. Fernanda Martins Queiroz. The authors are also thankful to LNNano/CNPEM for scanning electron microscopy characterization.

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