On the effects of hydrothermal treatments on the corrosion resistance of the TSA anodized AA7475-T761 alloy

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Abstract. The effect of hydrothermal treatment time on the sealing and corrosion resistance of the anodized AA7475-T761 aluminium alloy has been investigated in this study. The treatments tested are environmental compatible and has not chromium ions involved. Anodizing was carried out by tartaric-sulphuric anodizing (TSA) and this was followed by hydrothermal treatments for partial sealing, either with or without propyleneglycol (PRG) and/or cerium ions. Four different treatment times were tested, specifically, 2.5, 5.0, 7.5 and 10 min. The corrosion resistance of the treated samples was evaluated by Electrochemical Impedance Spectroscopy (EIS) and the anodic layers formed by anodizing and hydrothermal treatments were characterized by Scanning Electron Microscopy (SEM). The EIS results indicated that the best corrosion resistance was related to the treatments that combined hydrothermal treatments in boiling water with PRG for 10 minutes or boiling water with PRG and cerium ions for 5 min. The SEM images for the samples showed the formation of a homogeneous anodic layer and the thickness is approximately 3 μm. It was noticed that the porosities were not completed sealed by the treatments tested and this was on purpose in order to allow coating adhesion to the anodic layer.

Introduction

The 2XXX and 7XXX alluminium alloys are often used in the aircraft industry due to high mechanical resistance coupled low density and easily forming and machining [1]. The 7XXX alluminium alloys have in their compositions some alloying elements such as Zn, Cu, Mg and Cr which improve their mechanical properties but that cause a reduction in corrosion resistance due to the presence of intermetallics in the microstructure, presenting good resistance only mildly aggressive environments [2]. Therefore it is necessary to employ coatings to ensure their protection in long time. These protectives coatings avoid direct contact of the electrochemical matrix with the environmental delaying the corrosive process. In the aircraft industry the alluminium alloys are anodized to improve its protection against corrosion [1]. The anodizing increases the anticorrosive properties of the Al alloy, being a process in which there is growing a layer of aluminum oxide on the alloy due to the application of an anodic potential on the sample immersed in an electrolyte [3]. The sulfuric acid and chromic acid are often used as electrolytes for the anodizing, being the chromium it contains Cr (VI), the most used in acid baths for anodizing of alluminion alloys in the aircraft industry due to its excellent application and effectiveness characteristics [4,5].

However the Cr (VI) is carcinogenic and highly toxic to the environment and to human health and because of that the hexavalent chromium has suffered limitations and prohibitions against their

use. Thus, many alternatives have been tested, such as baths compounds of inorganic acids or mixtures of organic and inorganic acids. Among the studies, European aircraft industry is already using an organic/inorganic acid bath in a process called tartaric-sulfuric acid anodizing (TSA) [6]. The TSA is environmentally friendly and promotes an increase in the corrosion resistance of aluminum alloys and in addition to providing adhesion to paint if comparable to chromic bath [7]. In the aircraft industry, after the anodized process the aluminum alloys are sealed or painted. The sealing process is a post-treatment that decreases the porosity of the anodic layer which the pores may be sealed hydrothermally (boiling water) or various cold sealing solutions, in particularly, solutions with potassium dichromate [1,8]. So, finding substitutes for chromium has become even more necessary, being the interest of research centers and governments. Among the possibilities, the main alternatives for replacing the chromium in the anodizing process of aluminum alloys, include the use of conversion coatings based on oxides and hydroxides of rare earth elements, particularly cerium compounds; hydrocarbon molecules and treatments with silane [1,9]. Then, the aim of this work is study the post-treatment of TSA that can replace the cromium (VI) treatment.

Experimental

In this study was employed the AA7475-T761 aluminium alloy. The aluminium alloys samples were degreased in acetone and after that to submitted a various surface treatments and subsequently it was anodized in TSA bath. To determine the effect of post-treatment with the environmental coatings, three different surface hydrothermal post-treatments were undertaken as below: Ce (III) ions, propylene glycol (PRG) and Ce (III) ions followed by propylene glycol. All the treatments involved immersion of the sample in boiling water for 2.5, 5.0, 7.5 and 10 minutes. The treatments requiring a further step involved immersion in water with relevant additive for 2.5, 5.0, 7.5 and 10 minutes. To evaluate the corrosion performance of the treatments were carried the electrochemical measurements. Electrochemical impedance measurements were performed using signal amplitude of 20 mV and frequency range from 10^5 to 10^{-2} Hz. The immersed area was 3.73 cm^2. The impedance measurements were performed after different immersion times in a 0.5 $mol.L^{-1}$ NaCl naturally aerated solution at room temperature. Unsealed AA7475 aluminium alloy was used as a control. The Quanta FEG 200 microscope by FEI was utilized to obtain the scanning electron microscopy (SEM) images.

Results and discussion

Electrochemical impedance spectroscopy (EIS)

EIS measurements for the various treatments were carried after immersion for 6 h in a 0.5 mol L^{-1} NaCl solution at room temperature. The results are presented in Figures 1, 2 and 3. In these figures, the effect of all treatments time tested on the corrosion resistance is compared. In the Bode diagram, Fig.1, it can be observed the presence of two time constants in all sealing conditions in solution containing Ce (III) ions. It is evident the increase of impedance modulus value in approximately two orders of magnitude between the samples sealed in Ce (III) solution and the sample unsealed. This occurs due to the Ce (III) salts cause the formation and precipitation of insoluble oxides and/or hydroxides on the cathodic sites on the surface of the substrate surface. These precipitates promote an obstruction effect, limiting the transport of electrons to the surface and consequently decreasing the rate of oxygen reduction reactions [10].

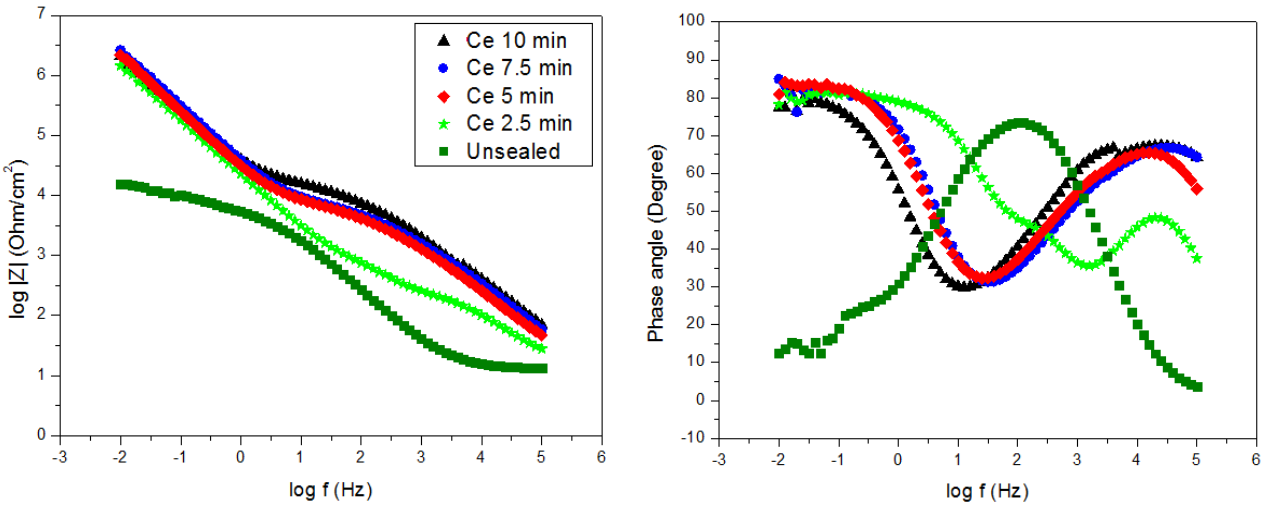


Fig.1: EIS diagrams for AA7475-T761 anodized and hydrotermal post treated with Ce (III) ions in different times.

The sealed samples in solution with propylene glycol (PRG) for 2.5 min and 5 min exhibit, Fig.2, a single constant of time extended, i.e., time was very short for there to be sealing the pores, having occurring only a small formation of aluminum hydroxide gel on the pore walls [11]. The results for samples sealed at 7.5 min and 10 min are superior to the others in which can identify the presence of two constants of time well defined. In these samples, possibly exist within the pores, precipitates that originate in the formation process of the pseudo-boemita, starting the sealing of the pores of the outer layer.

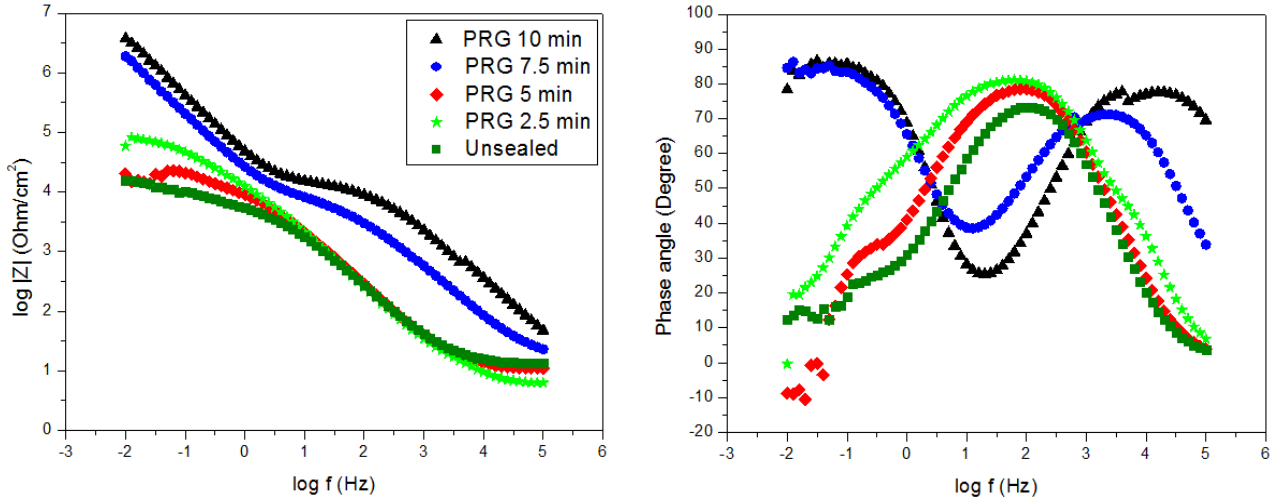


Fig.2: EIS diagrams for AA7475-T761 anodized and hydrotermal post treated with PRG in different times.

In the Bode diagram, Fig.3, can observe the presence of two time constants well defined for the sealeds samples in Ce (III) solution + PRG solution, in which the sealing process occured efficiently, providing certain obstruction of the pores and, consequently, increased impedance. The PRG is an organic compound with hydroxyl groups (OH) and when in contact with cerium, reacts and produces oxides/hydroxides of cerium which act as inhibitor. Thus, the presence of Ce in oxide layer is found as precipitates of Ce_2O_3 e/ou $Ce(OH)_3$, where the solubility of Ce makes possible the formation of $Ce(OH)_2^{2+}$ ions, which migrate to the defects, and when in contact with the substrate is reduced a Ce^{3+} and precipitates as $Ce(OH)_3$, allowing the sealing of the layer [12,13]. Thus, the hydrothermal sealing in solution containing Ce (III) ions and, subsequently, solution containing PRG, tends to generate films more homogeneous than in other sealing options considered.

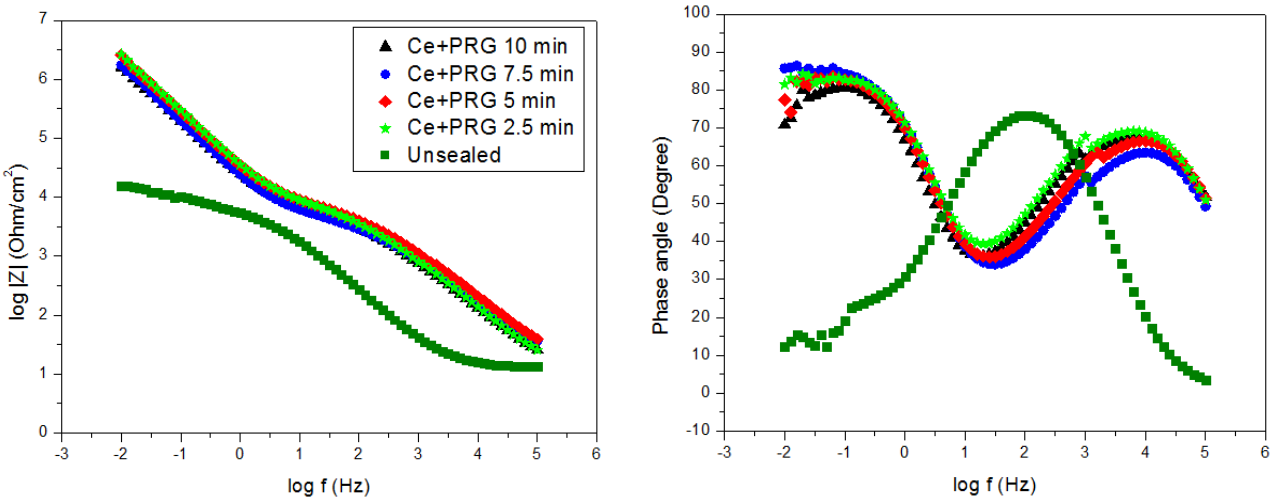
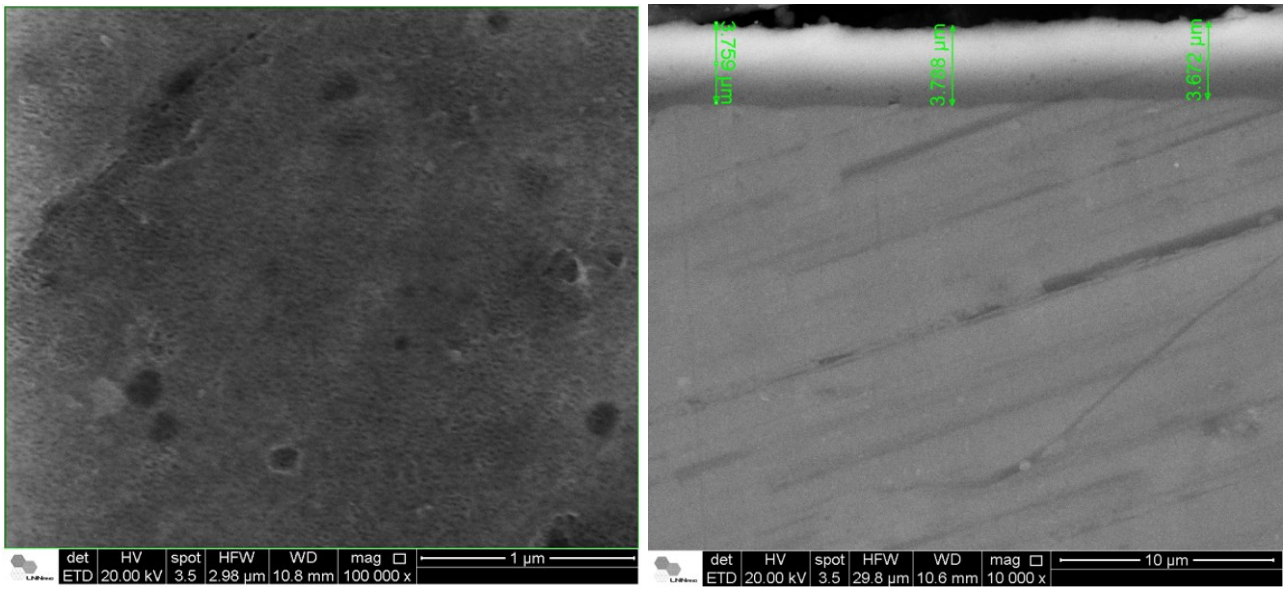


Fig.3: EIS diagrams for AA7475-T761 anodized and hydrotermal post treated with Ce (III) ions + PRG in different times.

Morphological characterization

When the alloy AA7475-T761 goes through the process of tartaric-sulfuric anodized, occurs the formation of a porous layer oxide, whose nanosized pores are homogeneously distributed, Fig.4 (a). Analyzing transversely a sample anodized and unsealed, Fig.4 (b), is observed that the anodized layer formed on AA7475-T761 alloy in TSA, is characterized by being homogenous and uniform, with an average thickness of 3,74 μm and with standard deviation of 0.049.



(a) (b)

Fig.4: Micrographs obtained by SEM of sample AA 7475-T761 unsealed, being (a) top image of the surface and (b) image of the cross section.

When the alloy AA7475-T761 anodized is sealed hidrothermically in solution with Ce (III) ions for 10 min, in solution with PRG for 10 min and in solution Ce (III) + solution with PRG for 5 min, is observed a partial sealing of the pores and the existence of a petals layer, characteristic of formation of boemita, as shown in the micrographs (Fig.5). Analyzing the Fig.5, is observed that each sealing process provides different characteristics to the surface of the samples, being according to the EIS diagrams, where the greater impedance is due to pore sealing process. Another uniqueness that is observed is the presence of regions rich in Ce, located mainly in the heterogeneities of the surface, Fig.5 (a) and (c).

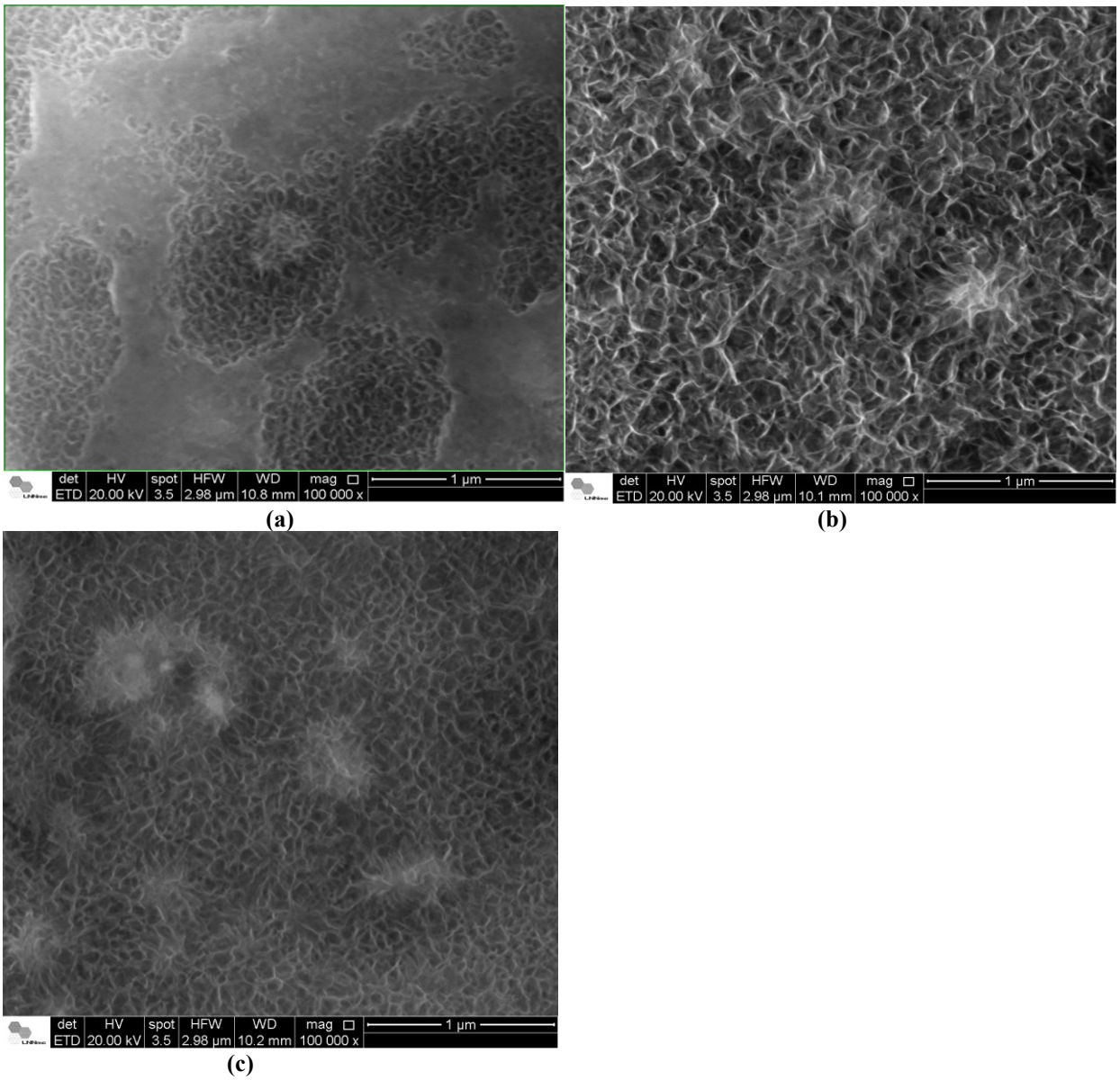


Figura 5: Micrographs of top obtained by SEM of the samples AA7475-T761 anodized and sealed in (a) Ce (III) solution for 10 min (b) propylene glycol solution for 10 min (c) Ce (III) solution + propylene glycol solution for 5 min.

Conclusions

The EIS results indicated that the best corrosion resistance was related to the treatments that combined hydrothermal treatments in boiling water with Ce (III) for 10 min, in boiling water with PRG for 10 minutes or boiling water with PRG and cerium ions for 5 min. The SEM images for the samples showed the formation of a homogeneous anodic layer and the average thickness is 3,74 µm. It was noticed that the porosities were not completed sealed by the treatments tested and this was on purpose in order to allow coating adhesion to the anodic layer. Thus, by the fact of providing a significant gain in resistance to corrosion process, anodization in tartaric-sulfuric acid bath followed by hydrothermal sealing in solution containing Ce (III) ions and/or PRG is shown as a promising alternative and environmentally friendly to replacement of chromic sealing, thereby allowing the total elimination of the chrome in conversion coating process of the alloy AA7475-T761.

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