

## 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 sealing and corrosion resistance of the AA7475-T761 anodized aluminium alloy has been investigated in this study. The hydrothermal treatments tested are environmental compatible without chromium ions involved. Anodizing was carried out by a tartaric-sulphuric anodizing (TSA) process and this was followed by hydrothermal treatments for partial sealing, in various solutions. The effect of propyleneglycol (PRG) and/or cerium ions in the hydrothermal treatment solution was evaluated. Four treatment times were tested, specifically, 2.5, 5.0, 7.5 and 10 min. The corrosion resistance of the anodized and treated samples was evaluated by Electrochemical Impedance Spectroscopy (EIS) and the anodic layers formed were characterized by Scanning Electron Microscopy (SEM). The EIS results showed that the hydrothermal treatments in solutions with cerium ions resulted in similar impedances for periods of treatment from 5 to 10 min whereas in the solutions with PRG the impedance increased with time of treatment from 2.5 to 10 min showing a slower kinetics of anodic layer sealing. However, the fastest kinetics of sealing were associated to the treatments that combined two steps, one in PRG and other in cerium containing solutions with similar impedances obtained from 2.5 to 10 min of treatment. Surface evaluation by SEM showed that the porosities in the anodic layer were not sealed for the periods of hydrothermal treatments corresponding to 2.5 min. The presence of cerium in hydrothermal treatment had a beneficial effect on the stability of the anodic layer formed and provided a healing effect on the corroding sites.

### Introduction

The 2XXX and 7XXX aluminium alloys are often used in the aircraft industry due to their properties of high mechanical resistance, low density, formability and machinability [1]. The alloying elements of the 7XXX series of aluminium such as Zn, Cu, and Mg improve their mechanical properties but also reduces their localized corrosion resistance [2]. Consequently, it is necessary to protect their surfaces against corrosion by coatings to ensure a long lasting protection. In the aircraft industry, many parts made of aluminium alloys are anodized to improve their corrosion resistance[1]. Anodizing promotes the growth of an anodic layer of aluminum oxide on aluminium alloys and its characteristics depend on the composition of the anodizing bath [3]. Sulfuric and chromic acids are often used as electrolytes for anodizing, and the chromic type that it contains Cr (VI) is the most used in acid baths for anodizing of aluminium alloys used in the aircraft industry due to its effectiveness [4,5].

Due to the harmful properties of Cr (VI), specifically its carcinogenic and toxic characteristics, the restrictions to its use has largely increased in the last years. Thus, many alternatives of

chromium free processes have been tested, such as baths composed of inorganic acids or mixtures of organic and inorganic acids. One of the European aircraft industry is already using an organic/inorganic acid bath in a process called tartaric-sulfuric acid anodizing (TSA) [6]. The TSA anodizing process is environmentally friendly, once it does not generate toxic residues. It also promotes increased corrosion resistance and better paint adhesion of the anodic layer formed on aluminium alloys compared to those formed in chromic baths [7]. After anodizing, the anodic layer formed on aluminum alloys is either sealed or painted. The sealing process is a post-treatment to decrease the porosity of the anodic layers carried out hydrothermally (in boiling water) or in cold solutions, particularly in solutions with potassium dichromate [1,8]. Chromium free sealing treatments are also of great interest and research has been carried out to find potential replacements for these type of treatments. Among the possibilities, some works have been carried out testing cerium compounds; hydrocarbon molecules and treatments with silane [1,9]. However, until now effective chromium free treatments for the surface of aluminium alloys with similar efficiency to those that use hexavalent chromium has not yet been found. The aim of this work is to investigate the effect of chromium free hydrothermal treatments on the corrosion resistance of TSA anodized AA7475-T761 alloy. It is important to highlight that was not the intention of this work to fully seal the porosities of the anodic layer but evaluate the evolution of the sealing process and the effect of incorporation of species in the porosities of the anodic layer on the corrosion resistance of the anodized aluminium alloy surface.

## Experimental

In this study, the AA7475-T761 alloy was investigated as substrate for anodizing and post-treatments. Samples of this alloy were degreased in acetone and subsequently anodized in TSA bath. After TSA anodizing, post-treatments were carried out by immersion in solutions at their boiling temperature (hydrothermal treatments). Three solutions were used in the hydrothermal post-treatments: a solution with 50 mM of  $\text{CeNO}_3$ , a solution with 7 wt. % of propylene glycol (PRG) and a two step treatment, where the samples were firstly immersed in the 50 mM of  $\text{CeNO}_3$  and then immersed in the solution with PRG. The effect of hydrothermal treatment time on the corrosion resistance of the anodic layer obtained by TSA anodizing was investigated by using the following periods of treatment: 2.5, 5.0, 7.5 and 10 minutes. The corrosion resistance of the samples was evaluated by electrochemical impedance spectroscopy measurements performed using an amplitude signal of 20 mV in the frequency range from  $10^5$  to  $10^{-1}$  Hz. The area exposed to the electrolyte ( $0.5 \text{ mol L}^{-1}$  NaCl) was  $3.73 \text{ cm}^2$ . The electrolyte was naturally aerated and at  $(22 \pm 2) ^\circ\text{C}$ . TSA anodized samples without hydrothermal treatments were also tested for comparison reasons. Scanning electron microscopy (SEM) images were obtained using a Auanta FEG 200 microscope by FEI.

## Results and discussion

### Electrochemical impedance spectroscopy (EIS)

Fig. 1 shows the effect of hydrothermal treatment time in solution with PRG for the TSA anodized AA7475 samples exposed for 6 h to  $0.5 \text{ mol L}^{-1}$  NaCl solution. The results show that the impedance tends to increase with time of treatment despite of the small decrease observed from 2.5 to 5 min of treatment. For the samples treated for 2.5 and 5 min, a second time constant is suggested at low frequencies as a shoulder in the Bode diagrams. Two time constants are clearly indicated for periods of treatment corresponding to 7.5 and 10 min. These results indicates that sealing or growth of the  $\text{AlOOH}$  gel on the pores wall of the  $\text{Al}_2\text{O}_3$  anodic layer occurs gradually with time of immersion in the PRG solution and periods longer than 5 min are necessary to reveal the two time constants.

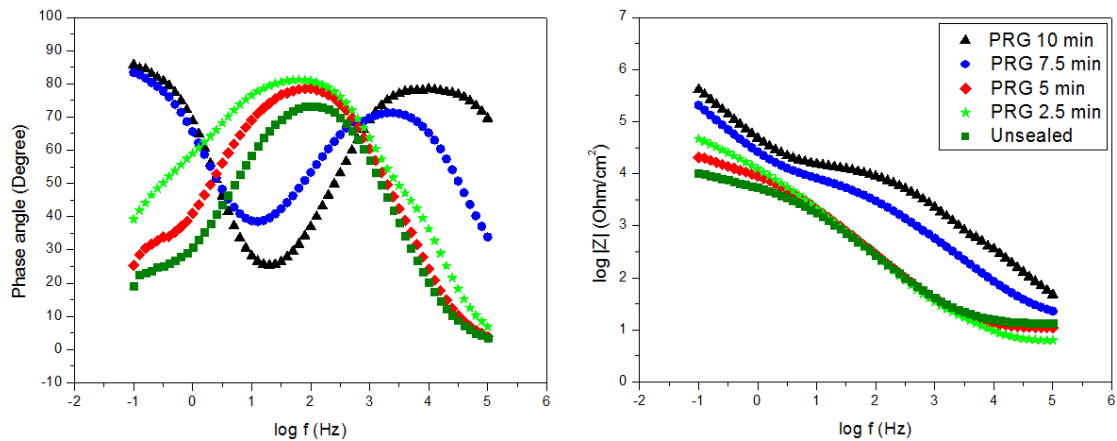


Fig. 1: EIS diagrams for AA7475-T761 anodized and then exposed for various periods to hydrothermal treatments in PRG containing solution after immersion for 6 h in 0.5 mol L<sup>-1</sup> NaCl solution.

Fig. 2 compares the EIS results as Bode diagrams for the AA7475 anodized and then exposed to hydrothermal treatments for different times in solution with cerium after 6 h of immersion in 0.5 mol L<sup>-1</sup> NaCl solution. The effect of the hydrothermal treatment is clearly noticed even for the shortest period of treatment (2.5 min). At least two time constants are indicated for all samples with hydrothermal treatments showing that the sealing of the anodic layer occurs very rapidly in the cerium nitrate containing solution under the conditions of hydrothermal treatments adopted in this study. These results suggest that cerium nitrate interacts with the exposed surface at the anodic layer during the hydrothermal treatment resulting in a surface of increased corrosion resistance. It is proposed that the presence of cerium during the hydrothermal treatment acts during the sealing process mainly at the base of the pores resulting in precipitation of cerium hydroxide that helps sealing, evenly, the porosities at the defective sites in the anodic layer [10]. It is well known that cerium ions precipitates as insoluble hydroxides on the cathodic sites surrounding the anodic ones corresponding to exposed metallic substrate at sites of defects in the film [11]. These precipitates promote an obstruction effect, limiting the transport of electrons to the surface and consequently decreasing the rate of oxygen reduction reactions [12,13]. The oxides/hydroxides of cerium are formed preferably where are located the intermetallic particles containing copper, eliminating the local cathodes. In addition to increased corrosion resistance, the cerium also provides excellent adhesion to the paint [13,14].

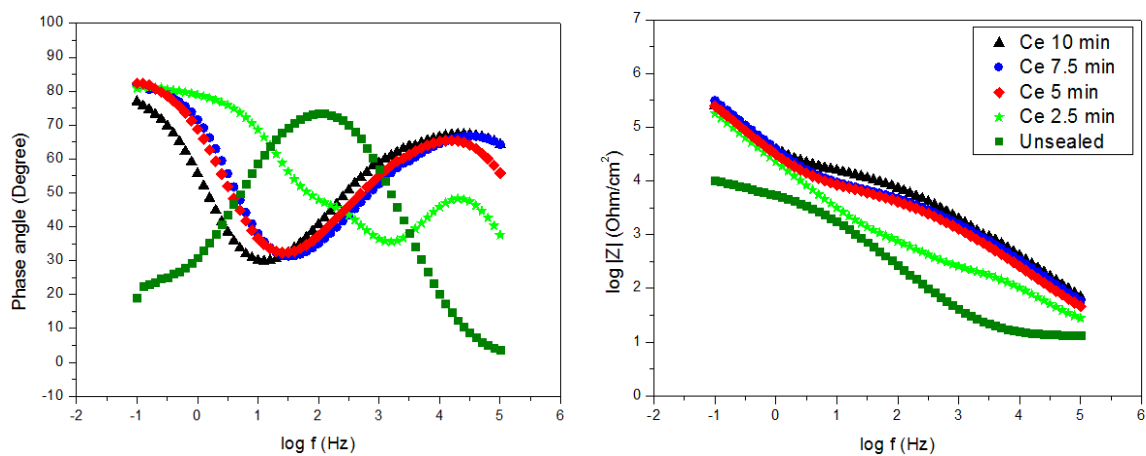


Fig. 2: EIS diagrams for AA7475-T761 anodized and then exposed for various periods to hydrothermal treatments in cerium containing solution after immersion for 6 h in 0.5 mol.L<sup>-1</sup> NaCl solution.

The effect of combination of two sequential treatments, firstly in the cerium nitrate containing solution in the sequence in the PRG solution on the electrochemical behavior of the anodized

AA7475 alloy is shown in Fig. 3. The Bode diagrams show that for the combined treatment even low periods of treatment largely increased the impedances of the anodized alloy. The beneficial effect of the treatment in cerium nitrate solution has been already indicated in Fig. 1. These results show that an additional step in PRG solution favored the growth of the pseudo bohemite  $\text{AlOOH}$  inside the pores. The results show two clearly defined time constants for all periods of treatment but the Bode phase angle diagrams suggest more capacitive results at low frequencies associated to the samples treated for 7.5 min. The PRG is an organic compound with hydroxyl groups (OH). The two step treatments, Ce + PRG, was highly effective in the sealing process, providing high protection by combining the beneficial effects of cerium in the solution and the effects of PRG probably acting by forming a hybrid organic-inorganic layer that increasing the impedance of the porous layer of the anodic film. The presence of Ce in oxide layer is found either as  $\text{Ce}_2\text{O}_3$  and/or  $\text{Ce}(\text{OH})_3$ . The formation of  $\text{Ce}(\text{OH})_2^{2+}$  ions in the anodic film is possible. These ions might migrate to defects and when in contact with the substrate might be reduced to  $\text{Ce}^{3+}$  and precipitates as  $\text{Ce}(\text{OH})_3$ , allowing the sealing of the layer [15,16].

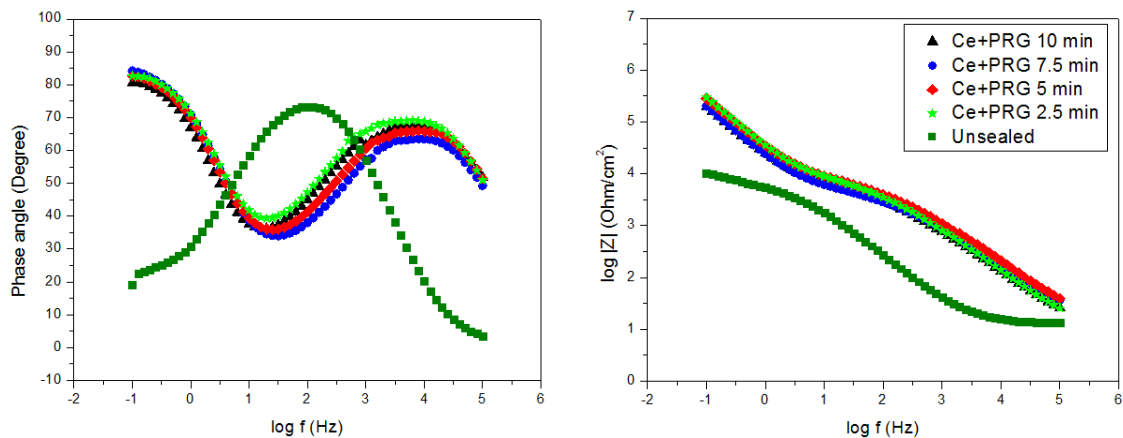


Fig. 3: EIS diagrams for AA7475-T761 anodized and exposed to a two step hydrothermal treatment with a first step in cerium nitrate solution and a second step in PRG containing solution. Results obtained in  $0.5 \text{ mol.L}^{-1}$  NaCl solution after 6 h of exposure to the solution.

### Characterization of the anodized surface either with or without hydrothermal treatments

Surface observation of the TSA anodized AA7475-T761 alloy was carried out by scanning electron microscopy (SEM), and the micrographs of the surfaces are shown in Fig.4. (a) without hydrothermal treatment or with the hydrothermal treatments in (b) PRG solution, (c) solution with cerium nitrate, and (d) composed of two steps treatments, firstly in solution with cerium nitrate and then in PRG solution. Cross section observation of the anodized alloy showed that the anodic layer formed was homogenous and uniform, with an average thickness of  $(3.74 \pm 0.05) \mu\text{m}$ .

The morphology of the surface after hydrothermal treatments carried out for 10 min that it is dependent of the type of treatment solution used. On all hydrothermally treated surfaces a structure typical of bohemite or pseudoboehmite is indicated with a morphology of needles. For the treatment in PRG solution this structure does not cover the whole surface and part of it is coated by a smooth film showing the lower trend of this treatment to form bohemite responsible for sealing the anodic film, as it was indicated by the EIS results. For the treatment in cerium nitrate solution, the boehmite structure is evident, but also present some white areas as petals that are rich in cerium (results obtained of EDS), as can be seen in Fig. 4 (c).

This result shows that the precipitation of cerium compounds occurs during the sealing treatment and helps in sealing the anodic film. Similar morphology but with larger concentration of cerium rich precipitates were associated to the treatment in two steps (Fig. 4 (d)).

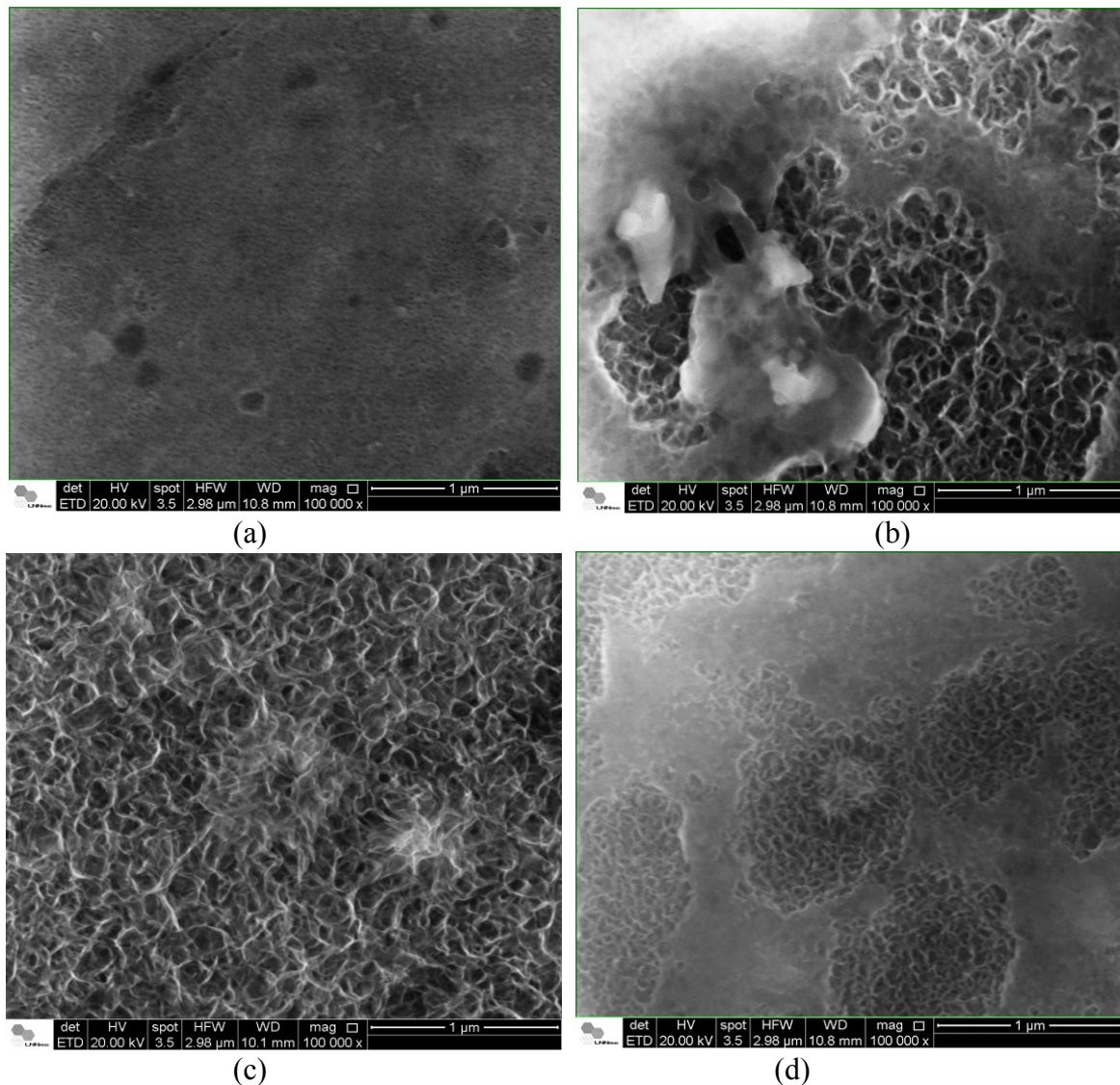


Fig. 4: Micrographs obtained by SEM of TSA anodized AA7475-T761 alloy (a) without hydrothermal treatment, or with hydrothermal treatment (b) in PRG solution for 10 min (c) in cerium nitrate solution for 10 min and (d) hydrothermal treatment in two steps, firstly in cerium nitrate solution for 5 min and then in PRG solution for 5 min.

## Conclusions

The results of this work showed the beneficial effect of a hydrothermal treatment in cerium nitrated solution on the corrosion resistance of the TSA anodized AA7475-T761. This treatment increased the stability of the anodic layer formed and provided a healing effect on the corroding sites. A faster kinetics of pores sealing seemingly occurred during hydrothermal treatments involving cerium compounds.

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**References**

- [1] V.R. Capelossi, M. Poelmanc, I. Reclouxa, R.P.B. Hernandez,; H.G. de Melo, M.G. Oliveira, Corrosion protection of clad 2024 aluminum alloy anodized intartaric-sulfuric acid bath and protected with hybrid sol–gel coating, *Electrochimica Acta*. 124 (2014) 69–79.
- [2] K. Dejun, W. Jinchun, Salt spray corrosion and electrochemical corrosion properties of anodic oxide film on 7475 aluminum alloy, *Journal of Alloys and Compounds*. 632 (2015) 286–290.
- [3] V. Moutarlier, M.P. Gigandet, B. Normand, J. Pagetti, EIS characterisation of anodic films formed on 2024 aluminium alloy, in sulphuric acid containing molybdate or permanganate species, *Corrosion Science*. 47 (2005) 937-951.
- [4] G. Boisier, N. Pébère, C. Druetz, M. Villatte, S. Suel, FESEM and EIS Study of Sealed AA2024 T3 Anodized in Sulfuric Acid Electrolytes: Influence of Tartaric Acid, *Journal of The Electrochemical Society*. 155 (2008) C521-C529.
- [5] F.M. Reis, H.G. de Melo, I. Costa, EIS investigation on Al 5052 alloy surface preparation for self-assembling monolayer, *Electrochimica Acta*. 51 (2006) 1780-1788.
- [6] M.A. Arenas, A. Conde, J.J. de Damborenea, Effect of acid traces on hydrothermal sealing of anodising layers on 2024 aluminium alloy, *Electrochimica Acta*. 55 (2010) 8704–8708.
- [7] M. García-Rubio, P. Ocón, M. Curioni, G.E. Thompson, P. Skeldon, A. Lavía, I. García, Degradation of the corrosion resistance of anodic oxide films through immersion in the anodising electrolyte, *Corrosion Science*. 52 (2010) 2219–2227.
- [8] X. Zhao, Y. Zuo, J. Zhao, J. Xiong, Y. Tang, A study on the self-sealing process of anodic films on aluminum by EIS, *Surface & Coatings Technology*. 200 (2006) 6846-6853.
- [9] L.E.M. Palomino, V.I. Aoki, H.G. de Melo, Microstrutural and electrochemical characterization of Ce conversion layers formed on Al alloy 2024-t3 covered with Cu-rich smut, *Electrochimica Acta*. 51 (2006) 5943-5953.
- [10] M. Dabalà, L. Armelao, A. Buchberger, I. Calliari, Cerium-based conversion layers on aluminum alloys, *Applied Surface Science*. 172 (2001) 312-322.
- [11] P. Campestrini, H. Terryn, A. Hovestad, J.H.W. de Wit, Formation of a cerium-based conversion coating on AA2024: relationship with the microstructure, *Surface and Coatings Technology*. 176 (2004) 365-381.
- [12] M. van Soestbergen, S.J.F. Erich, H.P. Huinink, O.C.G. Adan, Inhibition of pH fronts in corrosion cells due to the formation of cerium hydroxide, *Electrochimica Acta*. 110 (2013) 491–500.
- [13] F. Mansfeld, C.B. Breslin, A. Pardo, F.J. Pérez, Surface modification of stainless steels: green technology for corrosion protection, *Surface and Coatings Technology*. 90 (1997) 224-228.
- [14] F. Mansfeld, Use of Rare Earth Metal Salt Solutions for Corrosion Protection of Aluminum Alloys and Mild Steel. 36 (2000) 1063-1071.
- [15] R.G. Buchheit, S.B. Mamidipally, P. Schmutz, H. Guan, Active corrosion protection in Ce-modified hydrotalcite conversion coatings, *Corrosion*. 58 (2002), 3-14.
- [16] A. Decroly, J.P. Petitjean, Study of the deposition of cerium oxide by conversion on to aluminium alloys, *Surface and Coatings Technology*. 194 (1) (2005) 1-9.