

Hydrothermal surface treatments with Cerium and Glycol molecules on the AA 2024-T3 clad alloy

Wagner Izaltino Alves dos Santos^{1a}, Isolda Costa^{1b}, Célia Regina Tomachuk^{2c*}

¹ IPEN/CNEN, Av. Prof. Lineu Prestes, 2242, 05508-000, São Paulo, SP, Brazil

² Escola de Eng. Lorena - USP, Estr. Municipal do Campinho s/n, 12602-810, Lorena, SP, Brazil

^a wagner_quimica@hotmail.com, ^{b*} celiatomachuk@usp.br, ^c icosta@ipen.br

Keywords: AA2024-T3 Clad, Surface treatments, chromium hexavalent, SAM, Cerium treatment

Abstract. New treatments for replacement of chromate require lower toxicity and corrosion protection. This study aims to investigate the influence of the combination of a Ce conversion coating (CCCe) with glycol molecules on the corrosion resistance of the AA2024-T3 clad (AA1230). The corrosion resistance of surface treated and untreated samples was evaluated by electrochemical techniques (electrochemical impedance spectroscopy, polarization tests and open circuit potential). These tests were complemented by salt spray tests to accelerate the corrosive effects of weathering. The surfaces were analyzed after corrosion tests by scanning electron microscopy with X-ray energy dispersive detector (SEM - EDX). The results of the CCCe samples in combination with glycol were compared with that of the surface with chromate layer and the results showed that the CCCe treatment is a candidate for replacement of chromating with the advantage that it does not generate toxic residues. The self-healing capacity of the new treatment tested was indicated by the increased formation of corrosion products deposition on top of Fe rich intermetallis in the AA1230 clad with time of exposure to the electrolyte.

Introduction

Conversion coatings based on hexavalent chromium have been widely used for promoting corrosion protection and paint adhesion to aluminum and its alloys in aerospace applications [1,2]. However, solutions with Cr⁶⁺ compounds have toxic effects and due to environmental restrictions, the use of this type of treatment is increasingly being banished. Much research has been carried out for the development of environmentally friendly surface treatments to replace the Cr⁶⁺ containing types, but to date no surface treatment has yet been found that can satisfactorily replace yellow chromates [1-9]. Consequently, there has been an upsurge of interest in the corrosion prevention of aluminum alloys using various types of surface treatments such as those based on Self-Assembling Molecules (SAMs) [1,10-13]. Moreover, there is large number of other alternative coatings in development for corrosion protection, as described in the literature [3-13]. The hydrothermals treatments of aluminum alloys produce surface films of oxihydroxides (pseudoboehmite and boehmite). These last products are formed together with Al₂O₃ and Al(OH)₃ when aluminum is immersed in boiling water and it is believed that its structure is composed of AlO(OH) of double chains (HO-Al(-O-)₂Al-OH where the pseudoboehmites form hydrogen bonds between the OH-ions and the oxygen through the water [13]. This kind of film has been used with the aim of increasing the corrosion resistance of anodized aluminum surfaces [14], but a layer by itself provides fair corrosion resistance to the aluminum surface [11].

Cerium conversion layers have been investigated since the 80's as corrosion protection coatings for aluminum alloys and it has been proposed that the cerium conversion layers present self-healing properties similar to that of hexavalent chromium [15-23]. According to Decoly [18] and Palomino

[19], this property is associated to gradual release of Ce^{3+}/Ce^{4+} that migrate to the defects. It is proposed that the self-healing effects of the cerium conversion layers occur due to alkalization of the cathodic areas, favoring the precipitation of $Ce(OH)_3$, and, consequently controlling the cathodic reaction [21, 23]. Li et. al. [22] investigated the corrosion resistance of anodized films doped with cerium salts on aluminum and showed that doping with these ions resulted in more compact, thicker and harder surface films.

The aim of this study is to evaluate various surface treatments for corrosion protection of commercially pure aluminum (AA2024-T3 Clad) that do not generate toxic residues to the environment, as potential alternative for replacement of hexavalent chromium conversion coating.

Experimental

The material used as substrate for surface treatments was AA2024-T3 Clad (AA1230). Samples of the AA2024-T3 Clad had their surfaces initially prepared by grinding with SiC emery paper up to #400. All AA2024-T3 Clad samples was exposed to a degreasing (ST133® – 3 min/40°C and ST181-B® – 1 min/40°C) and etching (ST495-B® – 3 min/40°C). After surface preparation, the following treatments were carried out: (i) chromating with hexavalent chromium (CrVI) ions, (ii) chromating with trivalent chromium (CrIII) ions, (iii) bohemitization by immersion for 20 min in boiling water, (iv) bohemitization by immersion for 20 min in boiling water followed by immersion in a solution with alkane diphosphonate molecules (SAM) for 3 h, (v) immersion in a boiling solution with Ce ions for 20 min, (vi) immersion in a boiling solution with Ce ions for 20 min followed by a treatment that consisted in immersion in a solution with glycol molecules for 20 min.

The corrosion resistance of the surface treated samples was evaluated monitoring the open circuit potential (OCP) as a function of time, electrochemical impedance spectroscopy (EIS), anodic polarization tests. The solution used as electrolyte was 10^{-2} mol/L NaCl solution. In the EIS tests the samples were immersed by 3 days. A three electrode experimental setup was adopted for the electrochemical tests with a Pt wire and an Ag/AgCl electrode, used as counter and reference electrodes, respectively. The area exposed to the electrolyte corresponded to 3.14 cm^2 (Gamry EIS 300 - Gamry model PCI/300 - Echem Analyser 135 software). EIS data was obtained daily from 1 until 3 days of immersion in the electrolyte, in a frequency range from 10 kHz to 10 mHz, with a perturbation signal of 10 mV and an acquisition rate of 10 points/decade. Anodic polarization curves were obtained from -20 mV vs OCP until 1300 mV vs Ag/AgCl with a scan rate of 1 mVs^{-1} . Prior to immersion and after polarization tests, the surface was analyzed by Scanning Electron Microscopy (SEM), using a Philips SEM 515 microscope.

Results and discussion

Figure 1 shows the open circuit potential (OCP) variation with time after 24 h of immersion in 10^{-2} mol/L NaCl solution. The results suggest pitting corrosion associated to the surface treatment here called bohemite. The growth of a porous oxide film during this treatment and the use of a chloride based electrolyte must explain this behaviour. These results also indicate a deleterious effect of chloride ions reaching the metallic AA2024-T3 clad (AA1230) substrate during the 24 h of immersion. In fact, the monitoring of OCP as a function of time showed unstable values after about 3 h of immersion (results not shown here).

In order to improve the protective properties of the surface, a post-treatment after bohemitization was carried out that consisted of immersion of the samples in solutions with self-assembling molecules (SAM). This treatment (Bohemite+ SAM) produced a more stable surface, indicated by the more steady potentials seen in Fig. 1, likely due to partial blockage of the porosities in the surface layer by the SAM molecules. A beneficial effect of the SAM treatment on AA2024-T3 samples after bohemitization treatment has been previously reported in literature [10-14].

Despite the decreased pitting susceptibility due to the combination of bohemitization and SAM treatment, the OCP potentials that were close to the pitting potential indicates a high susceptibility of the surface with this treatment to localized corrosion. Other types of surface treatments, mainly two types associated to treatment with Ce ions were tested and compared with chromating, either with CrVI or CrIII. Much lower OCP values were associated to the other surface treatments tested.

The much inferior OCP values suggest polarization of the cathodic reaction caused by the presence of the surface layer. It is believed that all these treatments protect the substrate by formation of oxide/hydroxides, mainly at cathodic areas surrounding the active sites. Results that support this hypothesis will be presented subsequently.

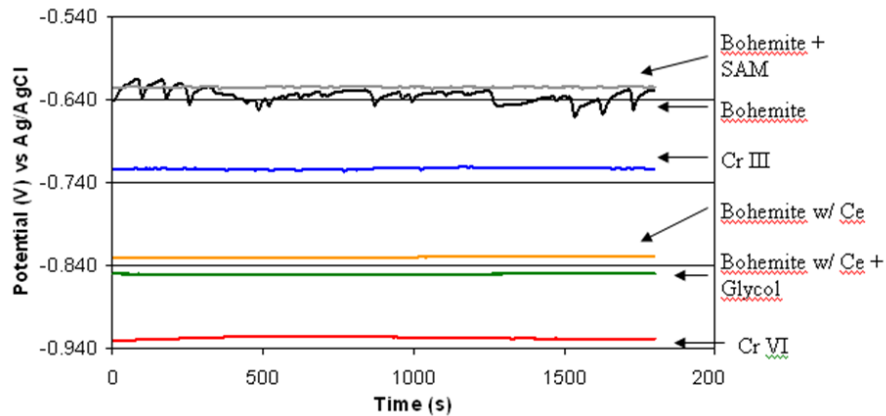


Fig. 1 Open circuit potential variation with time after 24 h of immersion in 10^{-2} mol/L NaCl solution for AA2024-T3 clad (AA1230) samples with various surface treatments.

The polarization curves shown in Fig. 2, for all the treatments tested show high current densities associated to the chromating treatments, either with CrVI or CrIII, both showing that the breakdown of the passive film occurred at low overpotentials. Corrosion resistance improvement was provided by the bohemitization treatment and the additional step of SAM treatment had a small protective effect at low overpotentials (until approximately 0V). The polarization results showed that the combination of bohemitization with Ce ions significantly improved the corrosion resistance of the surface of the clad material as indicated by OCP measurements. The addition of another step of treatment with glycol after bohemitization with cerium ions, however, resulted in a surface with the highest pitting resistance among the tested ones.

The lower current densities associated to the bohemite and bohemite+SAM treatments comparatively to the CrIII and CrVI treatments, after film breakdown, is due to the higher resistivity of the thicker oxide film that remains on the surface despite of polarization and pitting corrosion. Lower corrosion currents comparatively to the other treatments were associated to the treatment in solution with Ce ions. For the bohemite+Ce treatment, the film breakdown occurred at potentials of approximately 0.2 V, showing its superiority in comparison to the treatments without Ce. The addition of the further step of treatment with glycol, however, had a large contribution to the corrosion resistance of the surface with much lower current densities in the whole range of polarization and increased pitting potentials at potential of approximately 0.7 V. These observations were supported by EIS data as shown in Fig. 3. This Figure clearly shows much higher impedances after 24 h of immersion for the treatments with Ce comparatively to the others. The effect of the two treatments with Ce was evaluated by monitoring the EIS as a function of time of immersion and the results are presented in Fig.4 (a) and (b), for the Bohemite+Ce and Bohemite+Ce+glycol, respectively.

The results show that the impedance largely increased with time of immersion for the two types of treatments with Ce, suggesting the formation of protective corrosion products at the surface

indicating self-healing properties associated to Ce containing surface films. Surface observation prior and after 3 days of exposure to the NaCl solution showed a large increase in the proportion of area covered by white precipitates, as Fig. 5 shows. EDX analysis on the white areas showed that Ce was the main component of the precipitates, mainly Ce oxide/hydroxide. The precipitation of $\text{Ce}(\text{OH})_3$ products is favored at the cathodic sites as the pH increases at the interface in result of the corrosion processes. The precipitation of these products hinders the access of the corrosive species to the metallic substrate and, consequently, increases the corrosion resistance at the active sites at the substrate.

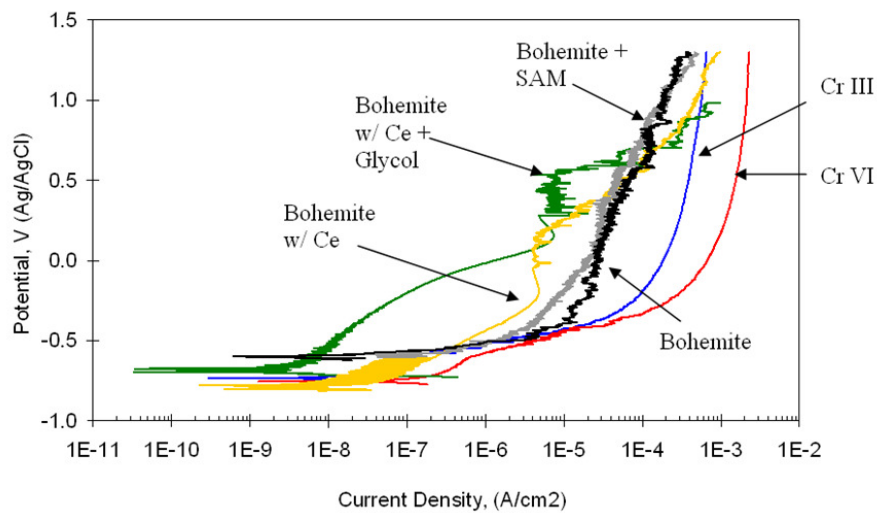


Fig. 2 Anodic polarization curves of AA2024-T3 clad (AA1230) for the various surface treatments tested after 24 h of immersion in 10^{-2} mol/L NaCl solution.

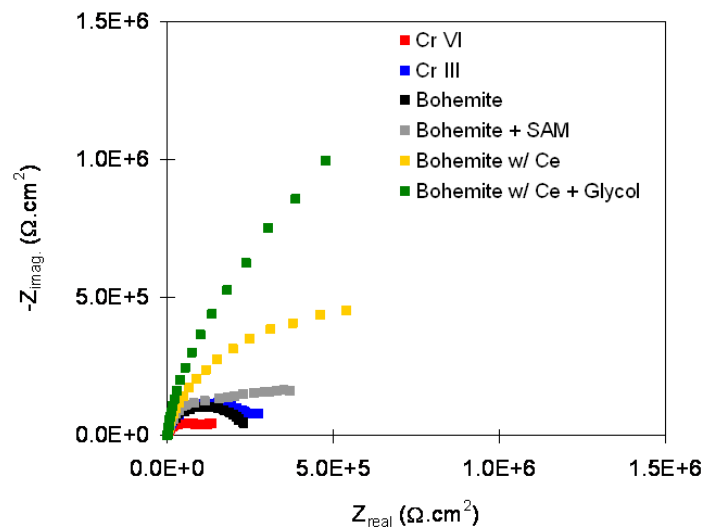


Fig. 3 Nyquist diagrams for the clad material of AA2024 T3 clad (AA1230) samples with the various surface treatments tested after 24 h of immersion in 10^{-2} mol/L NaCl solution.

Rosero-Navarro et. al. [23] found corrosion inhibition associated to a hybrid coating doped with Ce and related it to $\text{Ce}(\text{OH})_3$ precipitation that also resulted in increased impedance with time. Palomino et. al. [9,] investigated a cerium conversion coating and associated the increase in impedance with pores blockage.

Precipitation of Ce corrosion products, most likely $\text{Ce}(\text{OH})_3$, occurs mainly at the cathodic sites and it acts by a barrier mechanism hindering the access of corrosion species to the metallic

substrate. The precipitates support the hypothesis of active sites blockage leading to increased corrosion resistance.

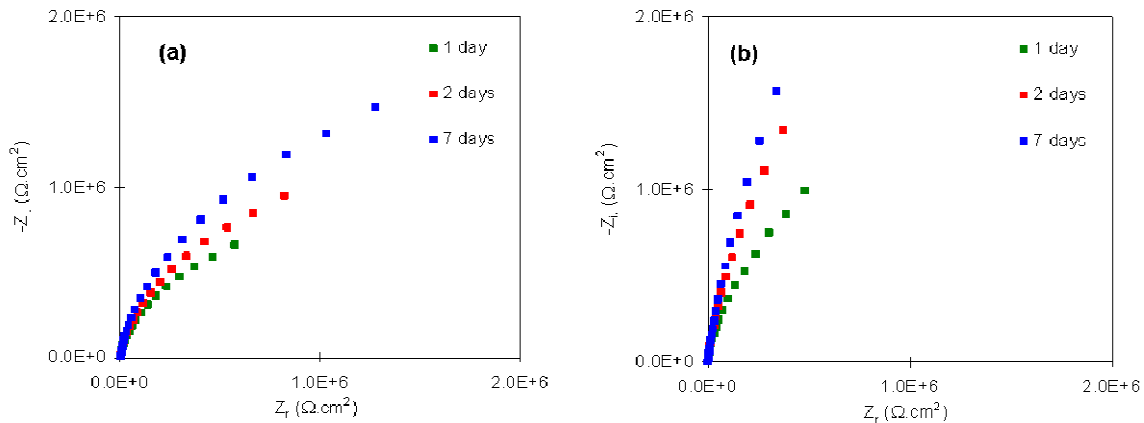


Fig. 4 (a) Evolution of Nyquist diagrams as a function of time of exposure to NaCl solution for the AA1230 clad surface with treatments (a) bohemite with Ce and (b) bohemite with Ce + glycol.

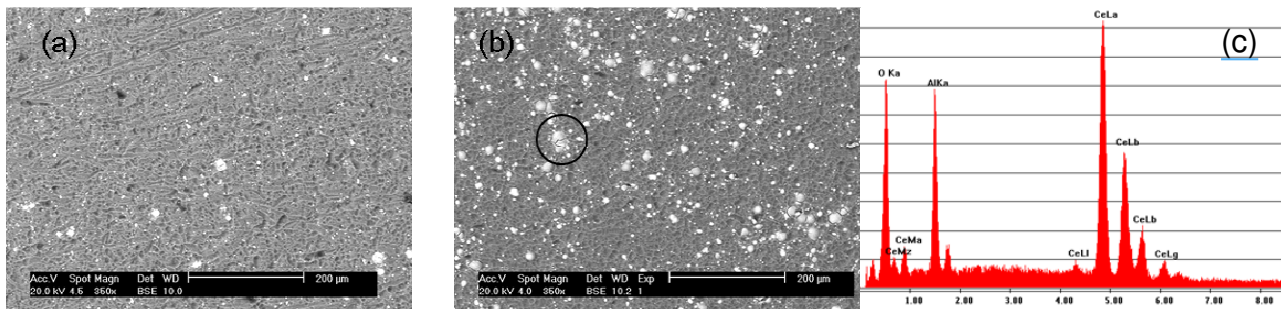


Fig. 5 SEM micrographs of the clad surface (AA1230) after treatment corresponding to bohemitization with Ce (a) prior and (b) after 3 days in NaCl solution, (c) EDS at the circled area.

Conclusions

The results of the present study showed that surface treatments corresponding to bohemitization with Ce ions provide high corrosion resistance to the clad material of the AA2024-T3 alloy (AA1230). They also indicated that treatments with Ce ions could be a proper alternative to replace the chromating passivation ones. The electrochemical results evidenced the importance of increasingly blockage of the active sites in the surface film for prolonged protection.

Acknowledgments

The authors acknowledge CNPq (Proc. N^o 400781/2013-1) and FAPESP (Process 2015/09952-0) for the financial support.

References

- [1] G.S. Frankel, R.L. McCreery, Inhibition of Al alloy corrosion by chromates, *The Electrochem. Soc. Interface*. 10 (2001) 34-38.
- [2] P. Campestrini, S. Böhm, T. Scram, H. Terryn, J.H.W. de Wit, Study of the formation of chromate conversion coatings on Alclad 2024 aluminum alloy using spectroscopic ellipsometry, *Thin Solid Film*. 410 (2002) 76-85.
- [3] W. Trabelsi, P. Cecilio, M.G.S. Ferreira, M.F. Montemor, Electrochemical assessment of the self-healing properties of Ce-doped silane solutions for pre-treatment of galvanised steel substrates, *Prog. Org. Coat.* 54 (2005) 276-284.

- [4] [A.R. Mendoza, F. Corvo, Outdoor and indoor atmospheric corrosion of non-ferrous metals, *Corr. Sci.* 42 \(2000\) 1123-1147.](#)
- [5] [W. Funke, The role of adhesion in corrosion protection by organic coatings, *Jour. Oil Col. Chem. Ass.* 68 \(1985\) 229-232.](#)
- [6] [R. Grilli, M.A. Baker, J.E. Castle, B. Dunn, J.F. Watts, Corrosion behaviour of a 2219 aluminium alloy treated with a chromate conversion coating exposed to a 3.5% NaCl solution, *Corr. Sci.* 53 \(2011\) 1214-1223.](#)
- [7] [A.M. Pereira, G. Pimenta, B.D. Dunn, A Comparison of Alodine 1200 with chromium-free conversion coatings, *ESA STM-276* \(2008\) 1-61.](#)
- [8] [V. Gentil, *Corrosão, Liv. Téc. e Cie. Editora, RJ, 1996.*](#)
- [9] [L.E.M. Palomino, P.H. Suegama, I.V. Aoki, M.F. Montemor, H.G. Melo, Electrochemical study of modified non-functional bis-silane layers on Al alloy 2024-T3, *Corr. Sci.* 50 \(2008\) 1258-1266.](#)
- [10] [F.M. Reis, H.G. de Melo, I. Costa, EIS investigation on Al 5052 alloy surface preparation for self-assembling monolayer, *Electrochem. Acta*, 51 \(2006\) 1780-1788.](#)
- [11] [W.A.S. Izaltino, S.L. Assis, S. de Souza, D.S. Yoshikawa, I. Costa, Self assembling molecules as corrosion inhibitors for the 1050 aluminium alloy, *EUROCORR* \(2009\), France.](#)
- [12] [S. de Souza, D.S. Yoshikawa, S.L. Assis, W.A.S. Izaltino, I. Costa, Efeito de moléculas auto-organizáveis na resistência à corrosão da liga AA2024-T3, *Tec. Met. Mat. Min.* 6 \(2010\) 130-135.](#)
- [13] [S. de Souza, D.S. Yoshikawa, W.A.S. Izaltino, S.L. Assis, I. Costa, Self-assembling molecules as corrosion inhibitors for 1050 aluminum, *Surf. Coat. Tech.* 204 \(2010\) 3238-3242.](#)
- [14] [R.S. Alwitt, *The aluminum water system. Ed. JW Diggie, New York, 1972, 169-254.*](#)
- [15] [A. Baltat-Bazia, N. Celati, M. Keddou, H. Takenouti, R. Wiert, Electrochemical impedance spectroscopy and electron microscopies applied to the structure of anodic oxide layers on pure aluminium, *Material Sci. Forum*, 111 \(1992\) 359-368.](#)
- [16] [B.R.W. Hinton, D.R. Arnot, N.E. Ryan, Cerium conversion coatings for the corrosion protection of aluminum, *Met. Forum.* 9 \(1986\) 162-173.](#)
- [17] [R.G. Buchheit, S.B. Mamidipally, P. Schmutz, H. Guan, Active corrosion protection in Ce-modified hydrotalcite conversion coatings. *Corrosion.* 58 \(2002\) 3-14.](#)
- [18] [A. Decroly, J.P. Petitjean, Study of the deposition of cerium oxide by conversion on to aluminum alloys, *Surf. Coat. Tech.* 194 \(2005\) 1-9.](#)
- [19] [L.E.M. Palomino, P.H. Suegama, I.V. Aoki, Z. Pászti, H.G. de Melo, Investigation of the corrosion behaviour of a bilayer cerium silane pre-treatment on Al 2024-T3 in 0.1 M NaCl, *Electrochemical Acta* 52 \(2007\) 7496-7505.](#)
- [20] [F.M. Seon, Rare-earths for materials corrosion protection, *Jour. Less Comm. Met.* 148 \(1989\) 73-78.](#)
- [21] [Q.Z. Li, Y. Zuo, J.M. Zhao, Y.M. Tang, X.H. Zhao, J.P. Xiong, Corrosion behaviors of Ce- and Nd-modified anodic films on aluminum, *Anti-Corr. Meth. Mat.* 57 \(2010\) 238-243.](#)
- [22] [N.C. Rosero-Navarro, S.A. Pellice, A. Durán, S. Ceré, M. Aparicio, Corrosion protection of aluminium alloy AA2024 with cerium doped methacrylate-silica coatings, *Jour. Sol-Gel Sci. Tech.* 52 \(2010\) 31-34.](#)
- [23] [S.J. Hinder, R. Grilli, R. Rustame, W.I.A. Santos, M.A. Baker, I. Costa, A surface analytical investigation of cerium-based conversion coatings deposited onto an AA2024-T3 aluminium alloy cladding layer, *Surf. Int. Anal.* 46, \(2014\) 735-739.](#)