

# Corrosion Protection of the Clad on AA2024-T3 by Cerium Based Conversion Coatings

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## Introduction

Aluminum alloys are largely used due to their low density and good mechanical properties. Besides, the naturally formed oxide layer during aluminum exposure to the environment provides fair corrosion protection at low aggressive environments. However, the passivating oxide film formed does not present corrosion resistance in chloride containing environments, and surface treatments are necessary to protect the aluminum alloys surfaces. The surface treatments based on hexavalent chromium (Cr VI) are the most effective and have been used for many years with aluminum alloys used in the aeronautic industry due to their self-healing properties. However, due to the generation of toxic residues associated to these treatments, they are increasingly being prohibited. This has led to much research in search for alternative treatments that are environmentally friendly, mainly in the last decades [1-3]. The new treatments must also provide high corrosion resistance to the aluminum substrate. Research work has been carried out using surface treatments based on trivalent chromium, cerium conversion layers [1], silane based coatings [2] and treatments involving nanotechnology [3]. The cerium conversion treatments for corrosion protection of aluminum alloys have been evaluated since the 80's. The results have showed that the immersion of aluminum in cerium containing solutions promotes the formation of a surface film that increases the corrosion resistance of the aluminum substrate. These results also indicated that the Ce conversion coating might present active protection properties similar to the self-healing characteristics presented by the hexavalent chromium conversion films, showing potential to replace these chromium conversion coatings. The regeneration properties indicated by the Ce conversion coating seems to be related to the  $\text{Ce}(\text{OH})_3$  precipitation at the cathodic areas due to a pH increase. This precipitation results in polarization of the cathodic reaction and, consequently, decreases the corrosion reaction kinetics. Preliminary studies involving immersion of the aluminum AA1050 in boiling solution with Ce ions showed excellent corrosion protection of the substrate. However, the fairly high temperatures involved in this treatment prompted the continuation of this research in search for more efficient process conditions for the surface treatment. The aim of the present study is to evaluate the effect of colloidal silica and other organic compound addition into the Ce ions containing solution in order to allow temperature decrease and solution stabilization for the Ce conversion layer formation.

## Experimental

The substrate used in this investigation for surface treatments was the clad on the AA2024-T3 alloy. Samples of this material were cut, degreased by immersion in a  $40 \text{ g L}^{-1}$  low alkalinity degreasing solution for 3 minutes at  $(40 \pm 2) \text{ }^\circ\text{C}$ , followed by immersion in a 7% (vol.) high alkalinity solution at  $(40 \pm 2) \text{ }^\circ\text{C}$  for 3 minutes. After degreasing, the samples were deoxidised in an acid solution with  $120 \text{ g L}^{-1}$  of a deoxidizer, during 3 minutes at  $(40 \pm 2) \text{ }^\circ\text{C}$ , rinsed with deionized water and dried under a hot air stream. Subsequently, the surface samples were exposed to either of the following treatments: (1) immersion in a solution with Ce ions (CCCe); (2) chromating in a solution with hexavalent chromium ions (Cr VI); and (3) immersion in a solution with Ce ions and colloidal silica (CCCe-Si). The corrosion resistance of the surface treated samples was evaluated by electrochemical impedance spectroscopy (EIS) and polarization methods as a function of immersion time in a 100 mM

NaCl solution. The EIS data were obtained after 24h, 48h and 72h of immersion. The surface of the treated samples was observed prior and after immersion tests by scanning electron microscopy (SEM). The EIS data were obtained at the OCP using a *Gamry EIS 300* frequency response analyser coupled to a *Gamry PCI/300* potentiostat controlled by the *Echem Analyser 135* software, in the frequency range from 10 kHz to 10 mHz, with a 10 mV amplitude perturbation signal at an acquisition rate of 10 points per decade.

## Results

EIS and polarization results obtained for the AA 2024-T3 clad samples with the three types of surface treatments tested at 24h of immersion in 100 mM NaCl solution are shown in Fig. 1(a) and (b). The results show a clear distinction of the impedances associated with the three types of surface treatments tested. The Ce conversion treatment without colloidal silica largely increased the impedance of the clad on the AA 2024-T3 alloy comparatively to the hexavalent chromating type. However, the addition of colloidal silica to the surface treatment solution led to further increase in the surface impedance. These results might be explained by a *bohemite-like* layer on the surface of the aluminum alloy impregnated with Ce ions. This results in precipitation of corrosion products at the cathodic sites during corrosion. The effect of the silica on the surface layer increasing its impedance was clear being related to the incorporation of silica into the surface layer. The literature has already reported the beneficial effects of silica incorporation on the corrosion resistance of various types of surface layer [2]. The polarization curves shown in Fig. 1 (b) supported the EIS results showing that the treatments with Ce, particularly that with colloidal silica, decreased the corrosion currents of the clad surface, proving the beneficial effects of these treatments. A micrograph of the treated surface and EDS spectra of the matrix and of a white precipitate indicated by arrow, are shown in Fig. 2. The EDS spectrum corresponding to the white precipitate shows high Ce and Si peaks, showing Si incorporation into the surface film. Besides, the clear Fe peak suggests that the precipitation of a Ce containing product is associated to Fe rich particles at the clad on AA2024-T3 alloy. In fact, many Fe rich precipitates were identified on the clad surface as shown in Fig.3, and these were associated with corrosion initiation. It is believed that after corrosion initiation,  $\text{Ce}(\text{OH})_3$  precipitates at the cathodic sites of the galvanic cells hindering further corrosion. It is proposed that silica incorporation in the film surface increases the film barrier effect and consequently the impedance showing the beneficial effect of silica on the corrosion resistance of the surface layer.

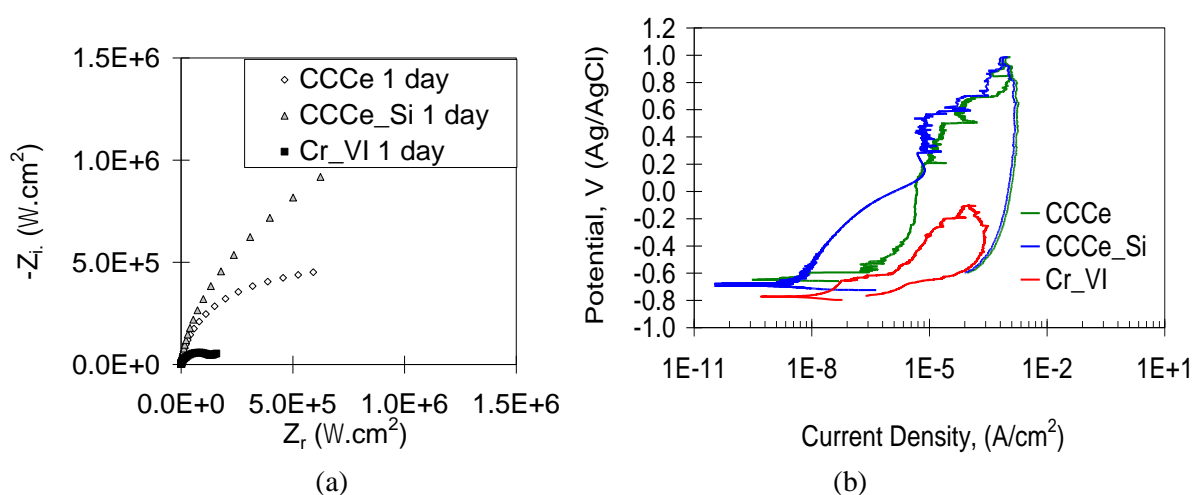


Figure 1. (a) Nyquist diagrams of the clad on AA2024-T3 samples with the various surface treatments tested after 24h of immersion in 100 mM NaCl solution. (b) Polarization curves for 24h immersion.

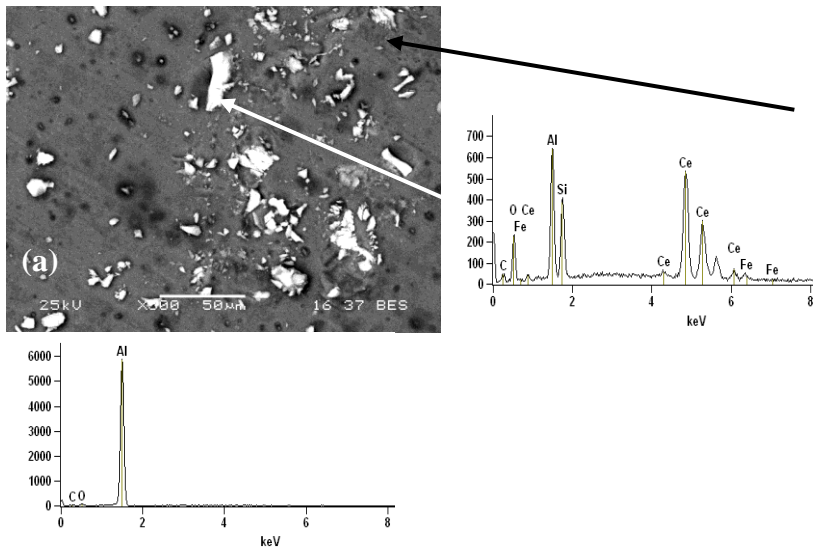


Figure 2. (a) SEM micrograph of AA2024-T3 clad after surface treatment with Ce and colloidal silica (CCCe\_Si) solution, (b) EDS spectra of the white area and matrix indicated by arrows.

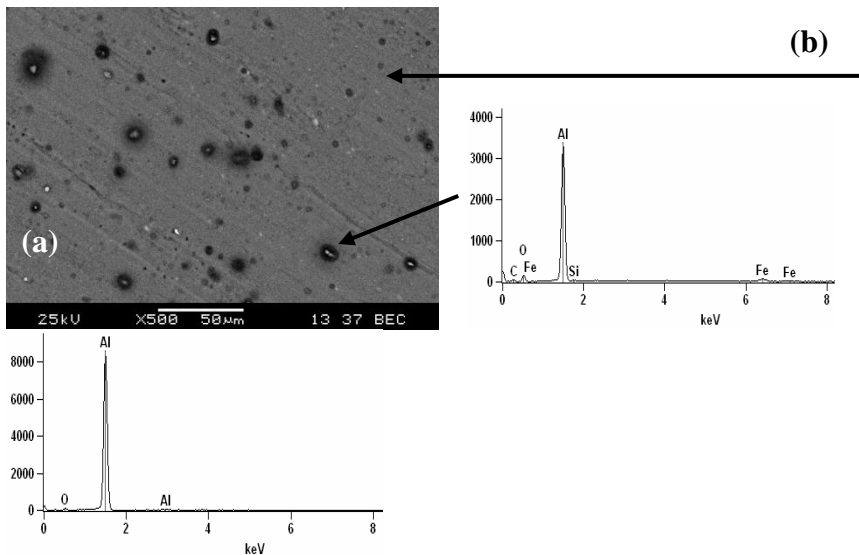


Figure 3. (a) SEM micrograph of treated clad on AA2024-T3 with Ce and colloidal silica (CCCe\_Si) solution after immersion in 100 mM NaCl solution, (b) EDS spectra of the area indicated by arrow.

## Conclusions

The surface treatments of the aluminum alloy in Ce containing solutions led to increased surface impedances comparatively to chromating with hexavalent chromium ions. The addition of colloidal silica into the solution with Ce, increased further the impedance and the results showed that Si was incorporated in the surface film, increasing the barrier effect of the film between the corrosive environment and the substrate. Both treatments tested in this study showed potentialities for replacement of the hexavalent chromating type

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## References

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