

## Effect of surface preparation prior to cerium pre-treatment on the corrosion protection performance of aluminum composites

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### Abstract

The effect of surface preparation prior to cerium treatment on the corrosion protection of AA6061 T6–10% Al<sub>2</sub>O<sub>3</sub> in NaCl solution was investigated using electrochemical impedance spectroscopy and DC polarization techniques. A new surface preparation method consisted of pre-etching followed by oxide-thickening is proposed. Optical microscope and scanning electron microscopy showed a marked decrease in the number and depth of pits for the pre-etched as compared to the as-polished specimens. X-ray photoelectron spectroscopy revealed that pre-etching eliminated the active sites where the chloride ions can adsorb. Simultaneously, the adsorption of cerium ions is uniformly on the surface. The oxide-thickening step has a vital role in the protection mechanism. It was found that presence of a thick oxide layer completely changed the mechanism of protection.

### 1. Introduction

Chromate conversion coatings have been widely applied for corrosion protection of aluminum alloys due to their self-healing nature, ease of application, high electrical conductivity and high efficiency/cost ratio. Moreover, they provide the greatest level of under film corrosion resistance and facilitate the application of further finishing treatment [1]. However, use of chromates is restricted in a number of countries due to environmental considerations and health hazards.

Many attempts have been made to find alternatives to chromate such as manganese [2–5], molybdenum [6–10] and vanadium treatments [11–13]. Lanthanide compounds are also among the substances that have been investigated as an alternative to chromate. It is well known that lanthanide ions form insoluble hydroxides [14], which enable them to be used as cathodic inhibitors. Lanthanides have low toxicity and their ingestion or inhalation is not considered harmful to health [15]. For these reasons, it is reasonable to consider the development of corrosion protection methods using this family of compounds.

Among many lanthanide compounds, cerium was found to achieve the best corrosion inhibition. The degree of inhibition provided by CeCl<sub>3</sub> was similar to that obtained with chromate [16]. The passivation of aluminum and aluminum alloys, by cerium, in aqueous NaCl solution has been studied [17–20]. There are

many attempts depending on cerium treatments to enhance the behavior against corrosion of several aluminum alloys and composites. However, data reported to date suggest that conversion coatings based on cerium, have various disadvantages such as non-uniform distribution [16, 19–21]. In the first part of this work, Hamdy et al. [22, 23] studied the effect of cerium pre-treatments on the corrosion behavior of aluminum composites. Results showed that direct cerium pretreatment slightly improved the surface protection against localized corrosion. The degree of protection was found to be a function of treatment time. A long-time (30 days) was required to obtain significant protection against localized corrosion. However, even after long time of cerium treatment (30 days), it was not possible to obtain a highly protected passive layer because the adsorption of cerium at the material surface was not uniform and, hence, localized corrosion occurred. These observations are in agreement with the other data [16, 19, 20]. In this work, we will try to understand if, and to what extent, the mechanism of protection depends on the treatment time and the techniques to apply cerium at the material surface. This will include the effects of surface preparation prior to cerium application. Thus, the effect of pre-etching and oxide-thickening, on the corrosion protection performance of Al-composites in 3.5% NaCl aqueous solution will be studied using EIS and DC polarization techniques. Surface examination was performed by scanning

electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS).

## 2. Experimental

### 2.1. Materials

The tested material was aluminum metal matrix composite, AA6061 T6 alloy-10% Al<sub>2</sub>O<sub>3</sub> p (v/v), in the form of 60 × 30 mm pieces taken from sheet of 3 mm thick. The nominal composition of the Al matrix was (wt.%): 0.35 Cu; 0.95 Mg; 0.70 Fe; 0.50 Si; 0.15 Mn; 0.15 Cr; 0.25 Zn; 0.15 Ti; remainder Al.

### 2.2. Specimens preparation and solutions

Specimens were abraded to 800 finish with SiC grit papers, degreased in ethanol followed by acetone, washed with bi-distilled water, dried with dry air and treated under stagnant condition as follows:

- A solution of pure 3.5% NaCl (Blank).
- A solution of pure 1000 ppm CeCl<sub>3</sub> for 30 days (direct Ce treatment).
- Etched in 0.01 M KOH for 15 min followed by direct treatment in a solution of pure 1000 ppm CeCl<sub>3</sub> for 3 h (Etching + Ce 3 h).
- Immersion in boiling distilled water for 1 h followed by treatment in a solution of pure 1000 ppm CeCl<sub>3</sub> for 3 h (BW 1 h + Ce 3 h) and one day (BW 1 h + Ce 1 day), respectively.
- Etched in 0.01 M KOH for 15 min, immersed in boiling distilled water for 30 min, followed by treatment in a solution of pure 1000 ppm CeCl<sub>3</sub> for 3 h (Etching + BW 30 min + Ce 3 h).
- Etched in 0.01 M KOH for 15 min, immersed in boiling distilled water for 1 h followed by treatment in a solution of pure 1000 ppm CeCl<sub>3</sub> for 3 h (Etching + BW 1 h + Ce 3 h) and one day (Etching + BW 1 h + Ce 1 day), respectively.

The solutions were prepared from laboratory grade chemicals and double distilled water.

### 2.3. Methods

The corrosion behavior of the specimens was monitored using electrochemical impedance spectroscopy (EIS) and DC polarization techniques during immersion in 3.5% NaCl solution open to air and at room temperature for up to 60 days.

A three-electrode set-up described elsewhere [22] was used with impedance spectra being recorded at the corrosion potential  $E_{\text{corr}}$ . A saturated calomel electrode (SCE) was used as the reference electrode. It was coupled capacitively to a Pt wire to reduce the phase shift at high frequencies. EIS was performed between 0.01 Hz and 65 kHz frequency range using a frequency response analyzer (Autolab PGSTAT 30, The Netherlands). The amplitude of the sinusoidal voltage signal was 10 mV.

DC polarization tests of specimens previously immersed for 60 days in NaCl solution were made at a scan rate of 0.07 mV s<sup>-1</sup> in the applied potential range from -0.15 to 0.7 V<sub>SCE</sub> with respect to  $E_{\text{corr}}$  using an Autolab PGSTAT 30 galvanostat/potentiostat, The Netherlands. The exposed surface area was 2.54 cm<sup>2</sup>. All curves were normalized to 1 cm<sup>2</sup>.

Qualitative and quantitative analysis of the corrosion layers was made by XPS. A VG Escalab 210 XPS spectrometer, with a spherical sector analyzer and unmonochromatized Mg K<sub>α</sub> radiation (E = 1253.6 eV) as excitation source, Fisons Instruments, Uckfield, UK, was used. Spectra were obtained at a vacuum better than 10<sup>-8</sup> mbar with a detection angle perpendicular to the surface. Binding energies were determined with reference to Au 4f<sub>7/2</sub>, Ag 3d<sub>5/2</sub> and Cu 2p<sub>3/2</sub> and C 1s binding energy, 285.1 ± 0.1 eV, of hydrocarbon contamination, was used to compensate for charging effects. Qualitative analysis was made by deconvolving the spectra of the various elements with the Reduced Chi-squared method in order to obtain different peaks corresponding to the different species of each element. Quantitative analysis was made with the Schofield method.

SEM images were obtained using a SEM Model Stereoscan 250 MK3, Cambridge Instruments, UK. Electron microprobe analysis using energy dispersive spectrometry, EDS, was performed using an AN 10000 X-ray analyzer LZ-5 Link Analytical Limited, UK.

## 3. Results and discussions

In pure NaCl solution (without cerium addition), a thick layer of Al-oxide was formed. This layer increased the insulating power of the passive film in addition to hindering the ion diffusion through the surface. Unfortunately, this layer could not protect the surface completely against localized corrosion and hence, many pitted areas were observed [22].

Direct treatment of as-polished specimens in CeCl<sub>3</sub> (Direct Ce for 30 days) does not offer an acceptable resistance (Figure 1) even after very long time of treatment (30 days). XPS of the specimens directly treated in CeCl<sub>3</sub> revealed the presence of a small amount of cerium. Conversely, electron-probe microanalysis, EDS, did not detect the presence of cerium indicating that cerium constitutes a very thin film [24]. Moreover, Figure 2 shows non-uniform corrosion. This suggests that the adsorbed film was not distributed uniformly and the distribution depends on the substrate microstructure [20] resulting in localized corrosion [22].

Direct treatment of the pre-etched specimens in CeCl<sub>3</sub> (Etching + Ce treatment for 3 h) showed localized corrosion. The etching step inhibited many active surface sites, whereby the number of pitting areas decreased from about seven pits for the as-polished specimens to four pits. This can be explained by formation of a very thin film of cerium oxide adsorbed

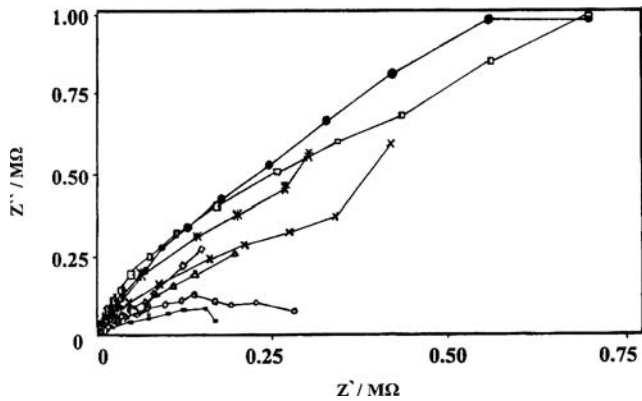


Fig. 1. Different cerium treated specimens after 30 days in NaCl. (■) As-polished (without cerium treatment) (●) BW 1 h + Ce 3 h, (□) Etching + BW 1 h + Ce 3 h, (○) Etching + BW 1 h + Ce 1 d, (X) Etching BW 30 min + Ce 1 h, (△) Direct Ce for 30 days, (◇) Etching + Ce 3 h and (○) BW + Ce 1 day.

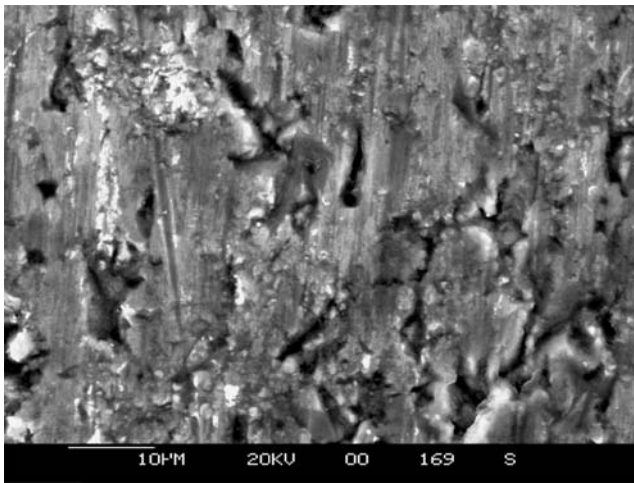


Fig. 2. SEM after immersion in  $\text{CeCl}_3$  for 30 days followed by 30 days in NaCl.

at the surface. Because the distribution of this film is not uniform, localized corrosion occurs.

Specimens of groups 4 (BW 1 h + Ce 3 h) and (BW 1 h + Ce 1 day) and group 6 (Etching + BW 1 h + Ce 3 h) and (Etching + BW 1 h + Ce 1 d), which were subjected to an oxide thickening step in boiling water for 1 h showed outstanding corrosion resistance. Thirty minutes of immersion in boiling water (group 5) was insufficient for the formation of a thick Al-oxide layer as indicated by a comparative low corrosion resistance. This confirms the vital role of the oxide-thickening process on the corrosion protection mechanism.

Immersion in boiling water results in the formation of a thick Al-oxide film [20–22, 25]. Cerium ions, probably incorporated into the pores of the oxide layer, seal the active sites on the metal surface. It seems that after 3 h of cerium treatment, all active sites were covered with cerium. Accordingly, the corrosion resistance is markedly improved after 30 days of immersion in NaCl (Figure 1). Conversely, the SEM of long-time cerium

pre-treatment (one day) showed intergranular corrosion (white zones) around the alumina particles after 30 days of immersion in NaCl (Figure 3). This may be attributed to the effect of chloride ions resulting from  $\text{CeCl}_3$  pre-treatment, which attack the active sites at the material surface initiating anodic/cathodic electrochemical cells and, hence, some of the alloying elements around the alumina particles can be dissolved causing intergranular and pitting corrosion. For this reason, increasing the treatment time (up to one day) in  $\text{CeCl}_3$  in groups 4 and 6 has an adverse effect on the corrosion resistance, especially for non-pickled specimens.

In contrast to the non-pickled specimens of the previous group which were treated for one day in  $\text{CeCl}_3$  and, showed severe intergranular and pitting corrosion, the specimens pre-etched, immersed in boiling water, and treated in  $\text{CeCl}_3$  for one day showed no sign of corrosion after 30 days immersion in NaCl. This confirms the important role of the pickling process, especially for long-time cerium pre-treatment, which inhibits the active surface sites and, hence, the chloride ions resulting from  $\text{CeCl}_3$  become ineffective. Another confirmation was obtained by EDS analyses, which revealed the presence of chloride ions in the non-pickled specimens, even before immersion in NaCl while the pickled ones showed no sign of chloride.

A comparison between the corrosion resistance of group 4 after 3 h in  $\text{CeCl}_3$  (non-etched) and group 5 and 6 (etched) after 60 days of immersion in NaCl indicates that:

- The specimens of group 5 which were treated in boiling water for 30 min showed a sharp decrease in resistance. The resistance is about one third of that observed for groups 4 and 6 (Figure 4) confirming the vital role of oxide-thickening process.
- The pickled specimens of group 6 show outstanding corrosion protection as compared to the non-pickled ones. SEM analyses of non-pickled specimens reveals micro-cracked zones, while the

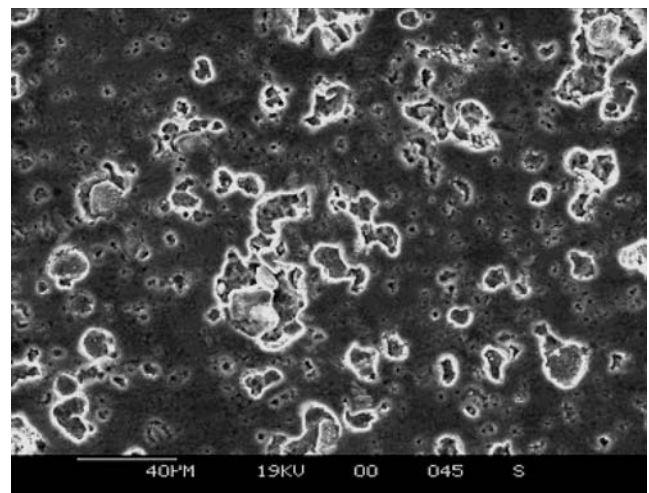


Fig. 3. SEM of specimen treated in boiling water for 1 h,  $\text{CeCl}_3$  for one day followed by 30 days in NaCl.

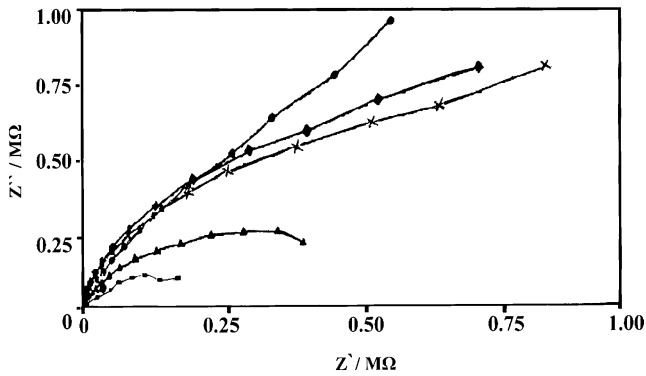


Fig. 4. Nyquist plots of Ce-treated specimens after 60 days of immersion in NaCl. (■) As-polished (without cerium treatment) (●) BW 1 h + Ce 3 h, (◆) Etching + BW 1 h + Ce 3 h, (X) Etching + BW 1 h + Ce 1 day, (▲) Etching BW 30 min + Ce 1 h.

pickled ones show no sign of cracking (Figures 5 and 6). Polarization tests (Figure 7) confirm this observation, where the presence of cerium im-

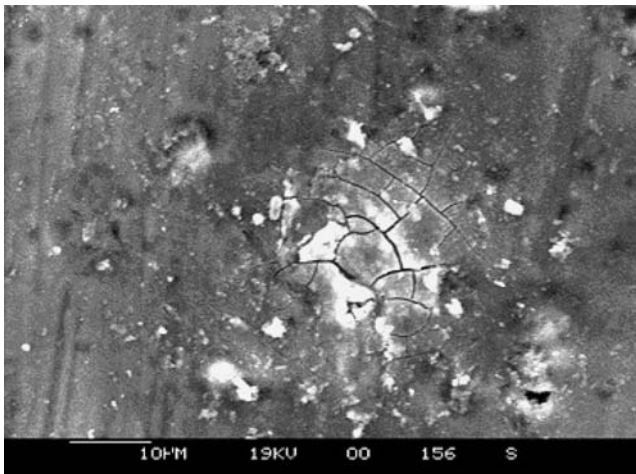


Fig. 5. SEM of specimen treated in boiling water for 1 h,  $\text{CeCl}_3$  for 3 h and then NaCl for 60 days.

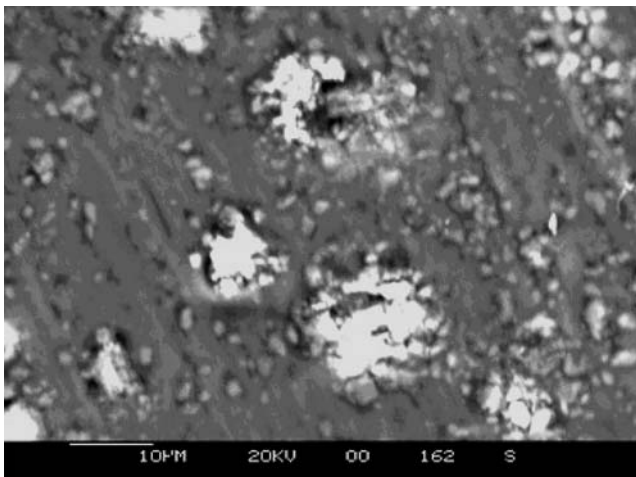


Fig. 6. SEM of specimen pickled, treated in boiling water for 1 h,  $\text{CeCl}_3$  for 3 h and then NaCl for 60 days.

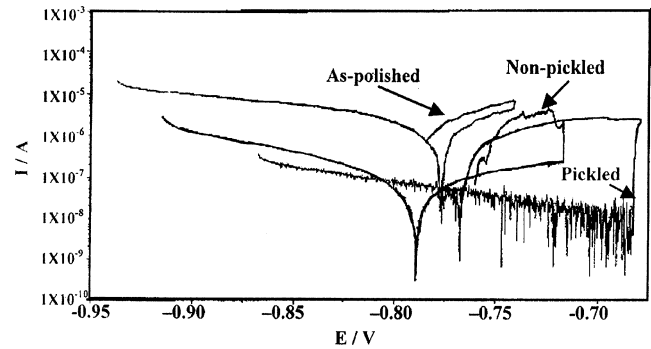


Fig. 7. Potentiodynamic curves of as-polished (without cerium treatment), non-pickled and pickled specimens after 60 days of immersion in NaCl.

proves the pitting resistance by increasing the perfect passivity domain, while the as-polished specimens show no perfect passivity domain. The pickled specimens show the highest resistance to pitting corrosion. The pitting potential,  $E_{\text{pit}}$ , of pickled specimens is 50 mV higher than for the non-pickled ones. The passive current is 10 times lower than for non-pickled specimens. Moreover, pickled specimens showed pitting auto-repair, while non-pickled ones did not show this behavior. This confirms the important role of the pickling step to offer a homogenous distribution of cerium over the material surface. The effect of pickling on the homogenous distribution of cerium is confirmed by SEM (Figures 8 and 9).

The percentage of chloride ions detected by XPS after 60 days immersion in NaCl for the pickled specimens is lower than that for non-pickled ones (Figure 10). This confirms the important role of pre-etching to inhibit the active sites, and thus retards Cl ion adsorption on the surface.

The amount of cerium ions detected by XPS was very small. However, the pickled specimens showed a relatively higher amount than the non-pickled ones. It was impossible to calculate this amount correctly due to the

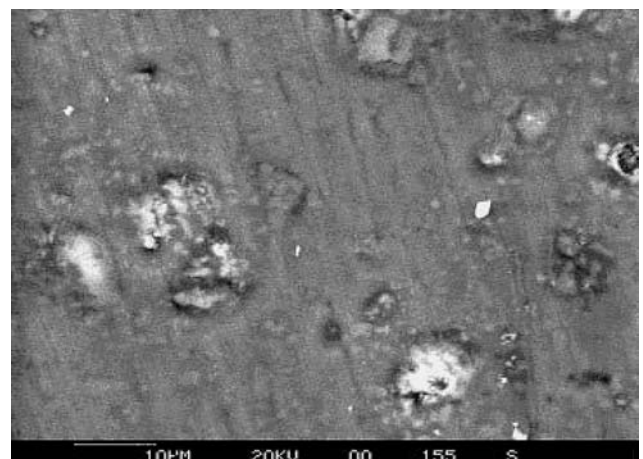


Fig. 8. Non-pickled cerium treated specimen before corrosion.

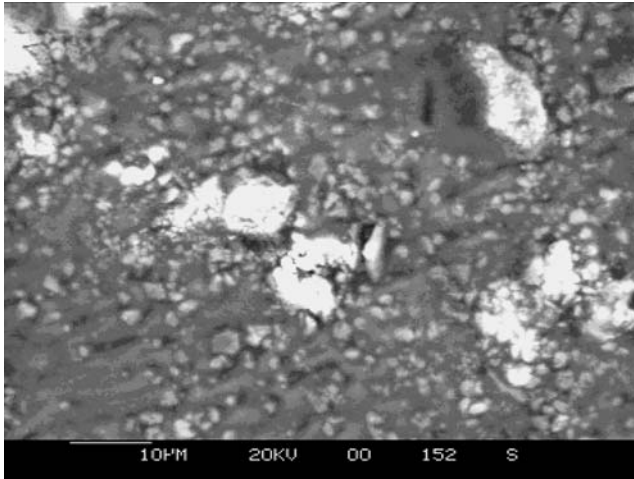


Fig. 9. Pickled cerium-treated specimen before corrosion.

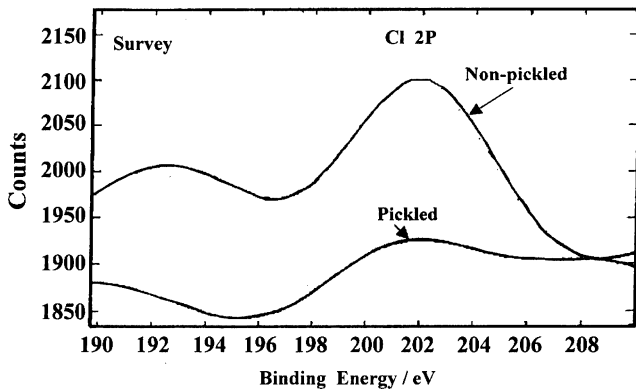


Fig. 10. XPS spectra illustrated the chloride ratios for pickled and non-pickled specimens after 60 days of immersion in NaCl.

low ratio between the signals for cerium and background (Figures 11 and 12). Cerium seems to be present simultaneously as Ce (III) and Ce (IV). The lower amount of cerium revealed by XPS and the absence of cerium in depth, as confirmed by EDS [25], clearly demonstrate that cerium is present only at the surface as a very thin film.

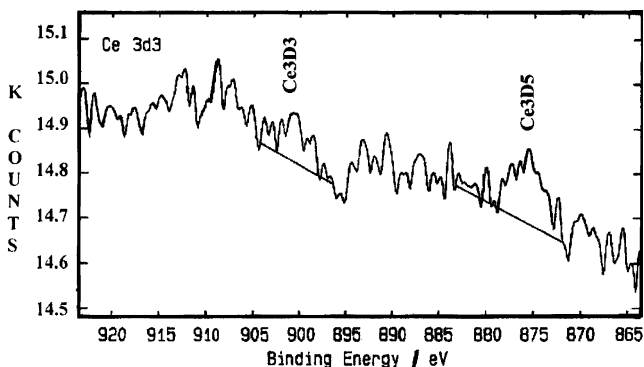


Fig. 11. Ce 3D spectra of the corrosion layer formed at the specimens immersed in boiling distilled water for 1 h followed by treatment in a solution of pure 1000 ppm  $\text{CeCl}_3$  for 3 h (BCe3h) after 60 days of immersion in NaCl.

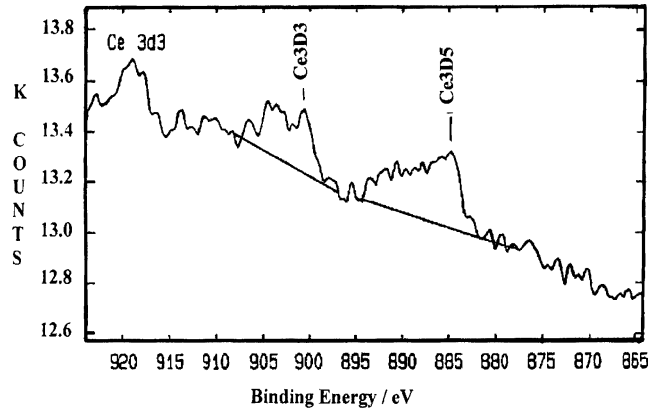


Fig. 12. Ce 3D spectra of the corrosion layer formed at the specimens etched in 0.01 M KOH for 15 min, immersed in boiling distilled water for 1 h followed by treatment in a solution of pure 1000 ppm  $\text{CeCl}_3$  for 3 h (KBCE3h) after 60 days of immersion in NaCl.

Beside its important role in inhibiting the active sites at the surface, pickling also helps to form a Si-rich surface layer. XPS (Figure 13) and EDS revealed a large amount of silicon for the pickled specimens. The most probable source of silicon is the matrix, where silicon is mainly concentrated at the interface between the matrix and alumina particles. Another source is the dissolution of silicon from glass during the pickling process by KOH [22, 23, 25].

Microscopic examination showed self-repair at the pitting zones in the case of the pickled specimens (Figure 6) confirming the results of polarization tests. This behavior can be attributed to the effect of silicon ions which play a role in pit repair.

#### 4. Conclusions

1. Direct treatment in cerium solution does not provide a good corrosion protection for aluminum composites because the adsorption of cerium over the surface was found to depend on the microstructure of the materials. So, localized corrosion is al-

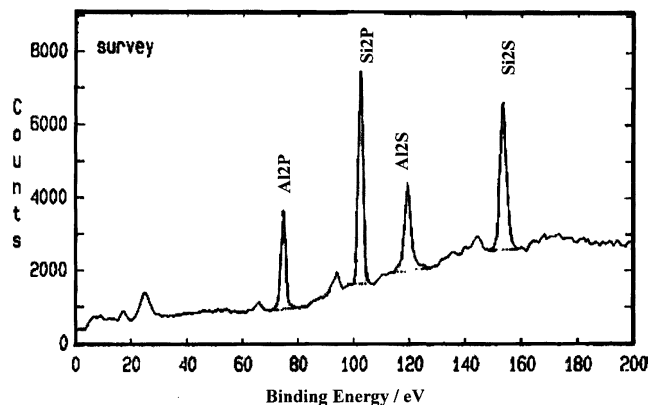


Fig. 13. XPS of the specimens pickled, boiling water for 1 h,  $\text{CeCl}_3$  for 3 h after 60 days in NaCl.

ways present after immersion in NaCl, even after long-time pretreatment (30 days) in cerium.

2. The level of protection strongly depends on the specimen preparation prior to cerium pre-treatment. In the case of direct cerium pre-treatment, the mechanism of corrosion inhibition depends on the non-uniform adsorption of cerium on the material surface, while in the case of the specimens pre-etched and oxide-thickened prior to cerium treatment, the mechanism is changed from simple adsorption to absorption of cerium within the pores of the thick Al-oxide layer.
3. Oxide-thickening plays a vital role in the corrosion protection of the aluminum composites.
4. Pickling plays an important role in inhibiting the active surface sites, rejecting the chloride ions from the surface and forming a Si-rich surface layers that assists pit repair. Moreover, pickling increases the ability of cerium to distribute uniformly over the material surface.

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#### References

1. M. Bethencourt, F.J. Botana, J.J. Calvino, M.M. Marcos and M.A. Rodriguez-Chacòn, *Corr. Sci.* **40** (1998) 1803.
2. J.W. Bibber, US Patent 4, 755, 224, Aug. 17, 1987.
3. J.W. Bibber, *Met. Finish.* **4** (1998) 28.
4. J.W. Bibber, 'The NACE International Annual Conference and Corrosion Show', CORROSION 95, Paper No. 392, 1995.
5. A.S. Hamdy and A.M. Beccaria, 'A chrome free pretreatment for aluminum composites', 9th European Conference on Application of Surface and Interface Analysis, ECASIA'01, 30 September–5 October, Avignon, France (2001).
6. M.A. Stranick, CORROSION 85, Paper No. 380 (NACE, Houston, TX, 1985).
7. K.M. El-Sobki, A.A. Ismail, S. Ashour, A.A. Khedr and L.A. Shalaby, *Corr. Prev. Control* **28** (1981) 7.
8. W.C. Moshier and G.D. Davis, *Corrosion* **46** (1990) 43.
9. B.A. Shaw, G.D. Davis, T.L. Fritz and K.A. Olver, *J. Electrochem. Soc.* **137** (1990) 359.
10. W.A. Badawy, F.M. Al-Kharafi and A.S. El-Azab, *Corr. Sci.* **41** (1999) 709.
11. A.J. Davenport, A.J. Aldykiewicz Jr, H.S. Isaacs, M.W. Kendigs and A.M. Mundy, Proceedings of the symposium on X-ray methods, in 'Corrosion and Interfacial Electrochemistry' (edited by The Electrochemical Society, Pennington, NJ, 1992) Vol. 92-I, p. 306.
12. R.L. Cook Jr. and S.R. Taylor, *Corrosion* **56** (2000) 321.
13. A.S. Hamdy and A.M. Beccaria, *Corr. Prev. Control* **48** (2001) 143.
14. N.N. Greenwood and A. Earnshaw, *Chemistry of Elements* (Pergamon press, Oxford, England, 1984), p. 1437.
15. T.J. Haley, *J. Pharm. Sci.* **54** (1965) 633.
16. B.R.W. Hinton, D.R. Arnott and N.E. Ryan, *Mater. Perform.* **8** (1987) 42.
17. B.R.W. Hinton, D.R. Arnott and N.E. Ryan, *Mater. Forum* **9** (1986) 162.
18. A. Hughes, B.R.W. Hinton, R. Taylor, M. Henderson, K. Nelson, L. Wilson and S.A. Nugent, International Patent application No. PCT/AU94/00539, International Patent No. WO95/08008.
19. S. Lin, H. Shih and F. Mansfeld, *Corr. Sci.* **33** (1992) 1331.
20. M. Dabalà, L. Armelao, A. Buchberger and L. Calliari, 2nd International Symposium on Aluminum Surface Science and Technology, UMIST, Manchester, England, 21–25 May (2000), Paper No. 97.
21. B.R.W. Hinton, D.R. Arnott and N.E. Ryan, *Mater. Aust.* **19** (1987) 18.
22. A.S. Hamdy, A.M. Beccaria and R. Spiniello, *Corr. Prev. Control* **48** (2001) 101.
23. A.S. Hamdy, A.M. Beccaria and P. Traverso, 'Corrosion protection of aluminum metal-matrix composites by cerium conversion coatings', 9th European Conference on Application of Surface and Interface Analysis, ECASIA'01, Avignon, France, 30 September–5 October (2001).
24. S. Music, *J. Radioanal. Nucl. Chem* **99** (1986) 161.
25. A.S. Hamdy, Ph.D. Dissertation, University of Cairo (2003).