

## EFFECT OF PREPARATION TECHNIQUE ON THE EXTENT OF CORROSION PROTECTION OF AA 6061 ALLOY BY HYDROTALCITE COATINGS

S. M Fernandes, O. V. Correa, J.A. Souza, L. V.Ramanathan,  
Instituto de Pesquisas Energéticas e Nucleares, Av. Prof. Lineu Prestes 2242,  
Cidade Universitária, 05508-000 São Paulo. [lalgudi@ipen.br](mailto:lalgudi@ipen.br)

R. A. Antunes,  
CECS, Federal University of ABC, 09210-170, Santo André, SP.

M. C. de Oliveira  
Eletrocell Ind. Com. Equip. Ltda, CIETEC, 05508-000 São Paulo.

### ABSTRACT

*Aluminium alloy AA 6061 is widely used to clad research reactor (RR) fuel. Spent fuels of this type have exhibited pitting corrosion during wet storage. The use of conversion coatings is being considered to protect these fuels during storage and boehmite as well as hydrotalcite (HTC) coatings were proposed. This paper presents the effects of preparation techniques of hydrotalcite coatings on aqueous corrosion of AA 6061 alloy. To this effect, different baths and post-coating treatments were used. HTC coating process variables such as temperature, duration of treatment and the duration of cerium modification on HTC morphology and electrochemical polarization behavior of HTC coated AA 6061 alloy in NaCl were determined. Laboratory and field test results revealed that specimens or plates coated with HTC from a high temperature bath followed by cerium modification were the most resistant to pitting corrosion.*

**Keywords:** corrosion, coating, hydrotalcite, aluminium.

### INTRODUCTION

Pitting corrosion of the aluminium cladding of spent research reactor fuel during wet storage is the main form of degradation and it could eventually lead to release of fissile material into storage facilities. (1, 2) Preliminary laboratory and field investigations carried out at IPEN in Brazil revealed that cerium hydroxide

coatings increased the corrosion resistance of Al alloys. (3) These investigations were extended to include boehmite and hydrotalcite (HTC), coatings on Al alloy surfaces. HTC is lithium aluminium-nitrate-hydroxide hydrate and it forms on Al alloys immersed in an appropriate alkaline lithium salt solution. (4-6) The HTC coating imparted marked improvements in pitting corrosion resistance. (7) Further studies were carried out recently to obtain HTC coatings from baths at different temperatures followed by post-treatments.

This paper presents: (a) the preparation of hydrotalcite coatings from different baths followed by post-coating treatments; (b) the effect of HTC coating process variables such as temperature, duration of treatment and the duration of cerium modification on HTC morphology and electrochemical polarization behavior of HTC coated AA 6061 alloy in NaCl, (d) results of field tests in which un-coated and HTC coated AA 6061 plates were exposed to the IEA-R1 reactor spent fuel basin for 8 months.

## **MATERIALS AND METHODS**

Aluminium alloy AA 6061 specimens and plates, for the laboratory and the field tests respectively, were treated to coat their surfaces with HTC by immersion in solutions and under conditions shown in Table 1. Boehmite coated specimens and coupons were prepared and tested for comparison with HTC.

The laboratory tests consisted in determination of the electrochemical behaviour of uncoated and coated specimens. In this test, anodic potentiodynamic polarization measurements were carried out with a standard 3-electrode arrangement in 0.01 M NaCl, using a saturated calomel reference electrode and a platinum counter electrode. The potential was scanned from - 0.3 V to + 0.5 V at 0.167 mV/s. In these tests, aluminium alloy AA 6061 specimens 10 mm x 10 mm were treated in solutions shown in Table 1 to form coatings of either boehmite, HTC at 98 °C (referred to as HT-HTC) and HTC at room temperature (referred to as LT-HTC). Specimens coated with boehmite, HT-HTC and LT-HTC were also treated in Ce containing solutions 4 and 7 to incorporate Ce in the coatings. The effect of duration of treatment in the Ce solutions was also examined.

**Table 1 - Solutions and conditions used to prepare coatings on Al alloys.**

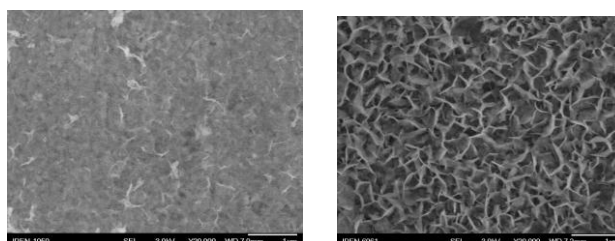
Solution	Purpose	Composition of solution and conditions
1	Degrease	25 g/L Na <sub>2</sub> SiO <sub>3</sub> ; 25 g/L Na <sub>2</sub> CO <sub>3</sub> ; 65 °C; 2 min.
2	Deoxidize	10% HNO <sub>3</sub> ; 3% NaBrO <sub>3</sub> ; 55 °C; 3 min.
3	Form boehmite	Deionized water; 97-100 °C; 5 min.
4	Incorporate Ce in boehmite	0.1% CeCl <sub>3</sub> ; 97 °C; pH 4; 5 min.
5	Form HTC – HT	6.9g/L LiNO <sub>3</sub> ; 28.3 g/L KNO <sub>3</sub> ; 2.4 g/L LiOH; 0.06 g/L NaAlO <sub>2</sub> ; 98 °C; pH 12; 10 min.
6	Form HTC – LT	0.1M Li <sub>2</sub> CO <sub>3</sub> ; LiOH; Al; pH 12; 15 min; R.T.
7	Incorporate Ce in HTC	10 g/L Ce (NO <sub>3</sub> ) <sub>3</sub> ; 30% H <sub>2</sub> O <sub>2</sub> ; R.T.; 5 min.
8	Sealing	MgC <sub>4</sub> H <sub>6</sub> O <sub>4</sub> ; 82 °C; 15 min.

The field test procedure consisted of preparing and coating plates (624 mm x 70 mm), preparing a dummy fuel element with these plates, immersion of this element with the plates oriented vertically in the spent fuel section of the IEA-R1 research reactor in IPEN for 8 months. This was followed by removal of the element, rinsing, decontamination, disassembly and examination of the plate surfaces both visually and with an optical microscope. (1)

## RESULTS AND DISCUSSION

### Laboratory tests

The coatings obtained from solutions 5 and 6 were identified by x-ray diffraction analysis as HTC and their morphologies are shown in Figure 1. (7)



**Figure 1 - Scanning electron micrographs of: (a) LT-HTC (b) HT-HTC**

The surfaces revealed intersecting blade like HTC crystallites that formed a layer across the surface. Typical coating thickness after 10 minutes of immersion was  $\sim 2 \mu\text{m}$ .

**Table 2 - The corrosion potential  $E_{\text{corr}}$ , corrosion current  $I_{\text{corr}}$  and breakdown potentials  $E_b$  of AA 6061 in 0.01 M NaCl.**

Specimen	$I_{\text{corr}} (\mu\text{A}\cdot\text{cm}^{-2})$	$E_{\text{corr}} (\text{V})$	$E_b (\text{V})$
Uncoated	6.120	-1.23	-0.59
Boehmite coated	0.327	-0.54	-
Boehmite + Ce (S4)	1.749	-0.59	-
Boehmite + Ce (S7)	1.694	-0.58	-
HT-HTC	0.972	-0.90	-0.59
HT-HTC + Ce (S7)	0.085	-0.69	-0.56
LT-HTC	0.141	-0.62	-
LT-HTC + Ce (S 7)	0.284	-0.60	-
HT-HTC + sealed	0.134	-0.63	-
LT-HTC + sealed	0.998	-0.61	-

The anodic polarization curves of the different specimens in 0.01 M NaCl solution at room temperature were plotted and data extracted from these curves are in Table 2. It is evident that specimens with any type of coating, with or without post treatments were more corrosion resistant as indicated by the shift in their open circuit potentials (OCP) to more anodic values. Even though the untreated specimen (RC-0) revealed a distinct passive region, the OCP of the coated specimens were close to the breakaway (pitting potential) of RC-0. The HT-HTC coated specimen's OCP was more cathodic (-0.9 V) but incorporation of Ce in this coating increased its OCP. The corrosion current densities of the coated specimens were significantly lower than that of the uncoated specimen indicating marked increase in protection rendered by the coatings. The corrosion behavior of boehmite coating deteriorated with incorporation of Ce, due in part to partial corrosion of the boehmite coating during the Ce treatment and formation of discontinuities. The incorporation of Ce in the HT-HTC coating reduced drastically its corrosion current density whereas in LT-HTC, it

increased slightly. Sealing improved corrosion of the HT-HTC more than that of LT-HTC.

The corrosion current density of specimens coated with HT-HTC and further treated to incorporate Ce did not vary significantly with increase in duration of treatment in S4. However the corrosion current density of specimens coated with LT-HTC and further treated in S7 to incorporate showed a decrease with increase in time of treatment in S7. Overall the corrosion current density of the cerium modified HT-HTC coated specimens was significantly lower compared with specimens that were coated with cerium modified LT-HTC.

### Plates exposed to IEA-R1 reactor spent fuel section.

Examination of the plates after exposure to the IEA-R1 reactor spent fuel section was done visually and with an optical microscope. The main features of the plate surfaces are summarized in Table 3.

**Table 3. Surface features on untreated and treated AA 6061 plates exposed to the IEA-R1 reactor's spent fuel section for 8 months.**

Surface treatment	Plate surface features	
	Side - A	Side - B
Untreated	11 pits surface dark.	5 pits, surface dark.
Boehmite	Surface very dark.	1 pit, surface very dark .
Boehmite + cerium treated	No pits, surface white.	7 pits, dark stain in the middle.
Boehmite + cerium treated + sealed	No pits, oxide layer on surface.	5 pits in the middle within a dark stain.
HT-HTC	<b>No pits</b> , drying stains.	<b>No pits</b> , drying stains.
HT-HTC + cerium treated	8 pits at lower end and stained.	8 pits at lower end and stained.
HT-HTC + cerium treated + sealed	<b>No pits</b> , slightly stained.	<b>No pits</b> , slightly stained.

The laboratory and field tests have indicated the marked increase in corrosion resistance of Al alloys coated with HT-HTC. The corrosion resistance was

further enhanced by modifying the boehmite coating with cerium dioxide. Sealing of the coatings in magnesium acetate improved the pitting corrosion resistance of LT-HTC coated specimens and coupons. In the context of eventually protecting Al-clad spent RR fuels during long term wet storage, the coating process for irradiated fuels would be facilitated if treatments were to be carried out at room temperature. However, at present, the extent to which LT-HTC imparts protection is lower than that imparted by HT-HTC. Attempts are in progress to increase the LT-HTC layer thickness to increase its protection efficiency. Nonetheless, protecting spent fuel with HTC coatings modified with cerium is the obvious choice. The HTC layer imparts pitting corrosion protection by acting as a physical barrier between the solution and the surface. The mechanism by which the cerium modified HTC imparts protection is considered to be 'active corrosion protection', analogous to chromium coatings. This involves release of Ce ions from the coating, transport of these ions through the solution and its action at defect sites to stifle corrosion. It has been speculated that if a  $Ce^{4+}$  bearing inorganic coating contacts a solution, soluble  $Ce^{4+}$  is released into the solution. When these ions encounter reducing conditions, like those associated with exposed bare metal at coating defects, it reduces to  $Ce^{3+}$ , which forms an insoluble hydroxide and precipitates. The precipitated cerium hydroxide at the defect then stifles further corrosion.

## CONCLUSIONS

1. HT-HTC formed from the nitrate bath increased pitting resistance more than LT-HTC formed from the carbonate bath.
2. The corrosion resistance of HT-HTC coated specimens did not increase with increase in duration of cerium treatment.
3. Sealing of LT-HTC coatings increased pitting corrosion resistance.
4. HT-HTC coated plates exposed to the spent fuel section for 8 months did not reveal any pits, indicating its potential for use as a protective coating on spent RR fuel.

## REFERENCES

1. IAEA – International Atomic Energy Agency, Technical Report Series 418, **Corrosion of research reactor aluminium-clad spent fuel in water**. 2003.
2. RAMANATHAN, L.V.; HADDAD, R.; ADELFIANG, P.; RITCHIE, I., Corrosion of Spent Aluminium-clad Research Reactor Fuel – Synergism in the Role of Storage Basin Water Parameters, **Proceedings of 12<sup>th</sup> International topical meeting on Research Reactor Fuel Management (RRFM)**, Hamburg, Germany, 2008.
3. FERNANDES, S.M.C.; CORREA, O.V.; SOUZA, J.A.; RAMANATHAN, L.V. Lanthanide based conversion coatings for long term wet storage of aluminium-clad spent fuel, **Proceedings of 14<sup>th</sup> International topical meeting on Research Reactor Fuel Management (RRFM)**, Marrakech, Morocco, 2010.
4. BUCHHEIT, R.G.; BODE, M.D.; SONER, G.E., Corrosion-resistant chromate-free talc coatings for aluminum, **Corrosion**, v. 50, n. 3, p. 205, 1994.
5. DREWIEN, C.A.; EATOUGH, M.O.; TALLANT, T.R.; HILLS, C.R.; BUCHHEIT, R.G., Lithium-aluminum-carbonate-hydroxide hydrate coatings on aluminum alloys: Composition, structure, and processing bath chemistry, **Journal of Materials Research**, v. 11, p. 1507, 1996.
6. ZHANG, W.; BUCHHEIT, R.G. Hydrotalcite coating formation on Al-Cu-Mg alloys from oxidizing bath chemistries, **Corrosion**, v.58, n. 7, p. 591, 2002.
7. FERNANDES, S.M.C.; CORREA, O.V.; SOUZA, J.A.; ANTUNES, R.A.; OLIVEIRA, M.C.L.; RAMANATHAN, L.V., Conversion coatings to protect Al-clad spent fuel in wet storage, Transactions of European Research Reactor Conference, Saint Petersburg, Russian Federation, 2013.