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Corrosion behavior of hydrotalcite coated AA 6061 alloy

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Abstract

Pitting corrosion of the aluminium cladding of spent research reactor (RR) fuel during wet storage is the main form of degradation and this could eventually lead to release of fissile material and contamination of storage facilities. Hence, the use of conversion coatings to protect spent Al-clad RR fuel during long term storage was proposed. Preliminary laboratory and field investigations carried out at IPEN in São Paulo, Brazil, revealed that cerium hydroxide coatings increased the corrosion resistance of Al alloys. These investigations were extended to include boehmite, hydrotalcite (HTC), cerium modified boehmite and cerium modified HTC coatings on Al alloy surfaces. This paper presents: (a) the preparation of hydrotalcite coatings from different baths followed by post-coating treatments; (b) the results of x-ray diffraction analysis and scanning electron microscopic studies of the HTC coatings; (c) 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 uncoated and HTC coated AA 6061 coupons were exposed to the IEA-R1 reactor spent fuel basin for up to 5 months. The laboratory test specimens as well as the field test coupons coated with HTC from a high temperature bath followed by cerium modification were the most resistant to pitting.

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. It has been shown that synergism in basin water parameters affect pitting corrosion of aluminium and its alloys. (1,2) Hence, it was considered imperative that some form of corrosion protection be given to spent RR fuel for long term safe wet storage. Conversion coatings are widely used to control corrosion of a variety of alloys in many industries and rare earth compounds have been used to inhibit aqueous corrosion of

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aluminium alloys. (3) Chemical treatments have been also proposed to form rare earth based conversion coatings on Al alloys. (4-6) The use of conversion coatings to protect spent Al-clad RR fuel was proposed in 2007 and the results of preliminary laboratory and field investigations carried out at IPEN in Brazil revealed that cerium hydroxide coatings increased the corrosion resistance of Al alloys. (7,8) These investigations were extended to include boehmite, hydrotalcite (HTC), cerium modified boehmite and cerium modified 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. (9-11) The HTC coating imparted marked improvements in pitting corrosion resistance. (12,13) 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 results of x-ray diffraction analysis and scanning electron microscopic studies of the HTC coatings; (c) 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 coupons were exposed to the IEA-R1 reactor spent fuel basin for up to 5 months.

Materials and methods

Aluminium alloy AA 6061 specimens and coupons, for the laboratory and the field tests respectively, were treated to coat their surfaces with either boehmite or 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.

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

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 mol/L 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 incorporated Ce in the coatings. The effect of duration of treatment in the Ce solutions was also examined. Table 2 identifies the specimens used in the electrochemical tests.

Table 2 - Identification of the laboratory test specimens

Specimen identification	Surface coated with and post treatment
RC-0	Uncoated
RC-1	Boehmite
RC-2	Boehmite + Ce (solution 4)
RC-3	Boehmite + Ce (solution 7)
RC-4	HTC – HT
RC-5	HTC – HT + Ce (solution 7)
RC-6	HTC – LT
RC-7	HTC – LT + Ce (solution 7)
RC-8	HTC – HT + sealed
RC-9	HTC – LT + sealed

The field test procedure consisted of preparing coupons 10 cm in diameter and 3 mm thick, stacking of the coupons in racks, immersion of the racks in the spent fuel section of the IEA-R1 research reactor in IPEN, Brazil, for 3 and 5 months, removal of the racks, disassembly and examination of the coupons with an optical microscope coupled to an image analyzer. (1)

Results and discussion

Laboratory tests

In preliminary tests, Al alloy specimens were immersed in solutions 5 and 6 (Table 1) followed by examination of the coating in a scanning electron microscope and identification of the coatings by x-ray diffraction (XRD) analysis. Figure 1 shows the XRD spectra of the coatings obtained from solution 5 at 98 °C (Figure 1a) and solution 6 at RT (Figure 1b). (13) The spectra revealed the formation of HTC. The morphology of HTC formed from solutions 5 and 6 are shown in Figure 2. The surfaces revealed intersecting blade like HTC crystallites that formed a layer across the surface. The coatings also formed inside the pits and recesses that resulted during pre-treatment of the substrate. Typical coating thickness after 10 min of immersion was ~2 µm. Below the outer layer a dense layer of amorphous or nanocrystalline lithium aluminate forms. (9)

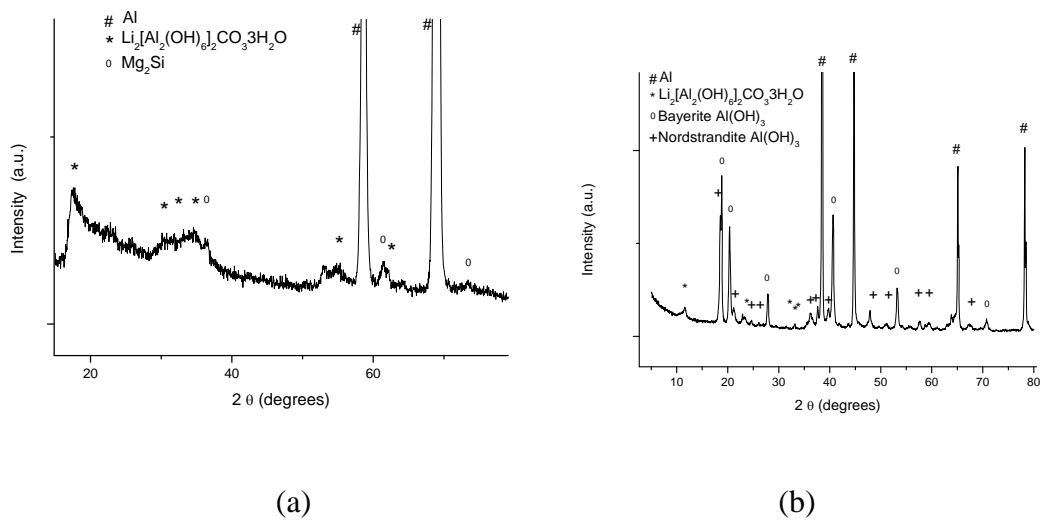


Figure 1 - X-ray diffraction spectra: (a) AA 6061 surface (Cr-K α); (b) AA 1050 powder (Cu-K α), indicating formation of hydrotalcite ($\text{Li}_2[\text{Al}_2(\text{OH})_6]_2\text{CO}_3 \cdot 3\text{H}_2\text{O}$).

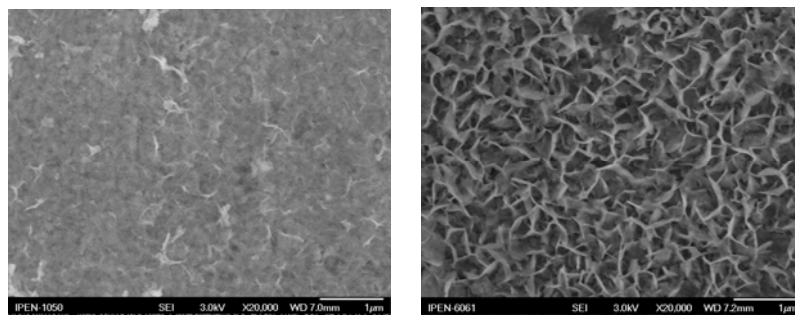


Figure 2 - Scanning electron micrographs of: (a) LT-HTC (b) HT-HTC

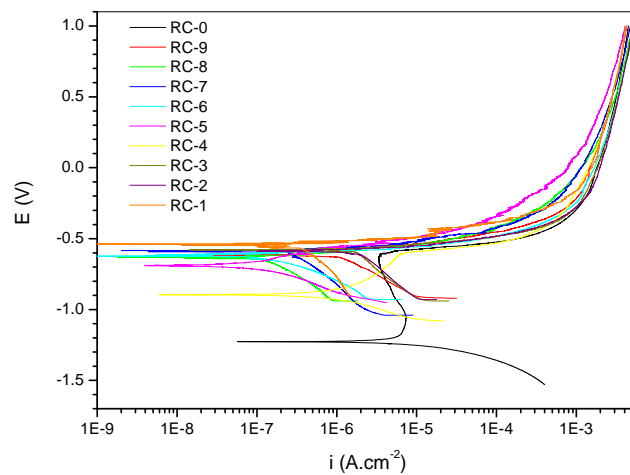


Figure 3: Polarization curves of uncoated and coated AA 6061 specimens in 0.01 mol/L NaCl at room temperature and at scan rate of 0.1 mV/s.

Table 3 - The corrosion potential E_{corr} , corrosion current i_{corr} and breakdown potentials E_b , as determined from the electrochemical polarization measurements. (Breakdown potential was determined only for curves in Figure 3 that showed breakdown of passivity). S4 and S7 are solutions 4 and 7 in Table 1

Specimen	i_{corr} ($\mu\text{A}\cdot\text{cm}^{-2}$)	E_{corr} (V)	E_b (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 are shown in Figure 3 and data extracted from these curves are in Table 3. 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.

Table 4 - The corrosion potential E_{corr} and corrosion current density i_{corr} as determined from the electrochemical polarization measurements of specimens coated with cerium modified HT-HTC and LT-HTC as a function of duration of treatment in the cerium containing solutions . (S4 and S7 are solutions 4 and 7 in Table 1.)

Surface condition	i_{corr} ($\mu\text{A}\cdot\text{cm}^{-2}$)	E_{corr} (V)
HT-HTC + Ce (S4 - 5 min.)	0.26	-0.60
HT-HTC + Ce (S4 - 10 min)	0.12	-0.59
HT-HTC + Ce (S4 - 15 min)	0.37	-0.59
LT-HTC + Ce (S7 - 5 min)	0.96	-0.58
LT-HTC + Ce (S7 - 10 min)	0.78	-0.56
LT-HTC + Ce (S7 - 15 min)	0.71	-0.58

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.

Coupons exposed to IEA-R1 reactor spent fuel section.

Examination of the coupons after exposure to the spent fuel section was done with an optical microscope. The top surface of the untreated coupons revealed more pits compared to the bottom facing surface of the same coupon, indicating the influence of settled solids on the top surfaces.

The main features of the coupons exposed for 3 and 5 months to IEA-R1 spent fuel basin, compared with those prior to exposure are summarized in Table 5. After 3 months of exposure, the LT-HTC coated coupon revealed no pits but after 5 months it revealed pits even with post treatments. The HT-HTC coated coupons did not reveal any pits even after 5 months exposure.

Table 5 - Coupon surface features compared to those observed prior to exposure to the IEA-R1 research reactor spent fuel section

Coating	Surface features after exposure for	
	3 months	5 months
None	Many pits	Stained + one pit
Boehmite	No difference	Many tiny pits
Boehmite + Ce	No difference	Few pits
HT-HTC	No difference	No difference
HT-HTC + Ce	No difference	No difference
HT-HTC + sealed	No difference	No difference
HT-HTC + Ce + sealed	No difference	No difference
LT-HTC	No difference	Dark + some pits
LT-HTC + Ce	No difference	Dark + some pits
LT-HTC + sealed	No difference	Very dark + one pit
LT-HTC + Ce + sealed	No difference	Very dark + two pits

General discussion

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 Ce⁴⁺ bearing inorganic coating contacts a solution, soluble Ce⁴⁺ 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. Hydrotalcite (HTC) coatings on AA 6061 alloy were prepared from nitrate baths at 98 °C and carbonate baths at room temperature.
2. HTC formed from the nitrate bath increased pitting resistance more than HTC formed from the carbonate bath.
3. Cerium modification of the boehmite coatings increased pitting resistance.
4. The corrosion resistance of HT-HTC coated specimens did not increase with increase in duration of cerium treatment.
5. Sealing of LT-HTC coatings increased pitting corrosion resistance.
6. Coupons coated with HT-HTC and exposed to the IEA-R1 reactor spent fuel section for 5 months did not reveal any pits, indicating its potential for use as a protective coating on spent RR fuel.

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