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**Protective Coatings for Long Term Wet Storage of Spent
Aluminum-Clad Research Reactor Fuel**

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ABSTRACT

Pitting corrosion of the aluminium cladding of spent research reactor (RR) fuels in wet storage has been reported and attributed to synergistic influence of certain water parameters. Hence, use of conversion coatings to protect spent Al-clad RR fuel during long term wet storage was proposed. This paper presents: (a) preparation of boehmite and hydrotalcite (HTC) coatings from different baths followed by post-coating treatments; (b) corrosion behavior of coated AA 6061 alloy; (c) results of field studies in which uncoated and coated AA 6061 alloy coupons and plates, the latter assembled as a dummy fuel element, were exposed to the IEA-R1 reactor spent fuel basin for 8 months. The laboratory tests revealed marked increase in corrosion resistance of HTC coated specimens. In field tests the HTC coated coupons and plates did not reveal any pits. The mechanism of corrosion protection is presented.

1. 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 some form of corrosion protection of spent

RR fuel was considered imperative for safe long term wet storage. Conversion coatings are widely used to control the corrosion of a variety of metallic materials in many industries and rare earth compounds have been used to inhibit aqueous corrosion of aluminium alloys. [3] Chemical treatments have been proposed to form rare earth based conversion coatings on Al alloys. [4-6] 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 and characterization of hydrotalcite coatings from different baths followed by post-coating treatments; (b) the effect of HTC coating process temperature and duration of cerium incorporation in the coatings on corrosion behavior of HTC coated AA 6061 alloy in NaCl; (c) results of field studies in which uncoated, boehmite and HTC coated AA 6061 alloy coupons and full size plates were exposed to the IEA-R1 reactor spent fuel basin for up to a year.

2. Methods and materials

Aluminium alloy AA 6061 specimens (2 x 2 x 0.2 cm) for the laboratory tests and coupons (10 cm in diameter and 0.3 cm thick) as well as plates (62.4 cm x 7.0 cm) for the field tests were treated to coat their surfaces with either boehmite or HTC, with or without incorporation of cerium in the coating, by immersion in solutions and under conditions shown in Table 1.

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 HT-HTC	6.9g/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 LT-HTC	0.1M 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.

- HT-high temperature; LT-low temperature

The coatings were examined in a field emission scanning electron microscope. The corrosion behavior of uncoated and coated specimens was determined from laboratory tests. In these tests, anodic potentiodynamic polarization measurements were carried out with a conventional 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. The effect of duration of treatment in the Ce solutions was also examined.

The field test procedure consisted of: (a) preparing uncoated and coated coupons and plates; (b) stacking of the coupons in racks (Figure 1 a); (c) assembling the plates to form a full size dummy fuel element (Figure 1 b); (d) immersion of the racks and the dummy fuel elements in the spent fuel section of the IEA-R1 reactor in IPEN, Brazil, for different duration (Figure 1 c); (e) removal of the racks or dummy fuel elements (Figure 1d), rinsing and decontamination; (f) disassembly and examination of the coupons and plates (Figure 1 e and f) with an optical microscope. [1]

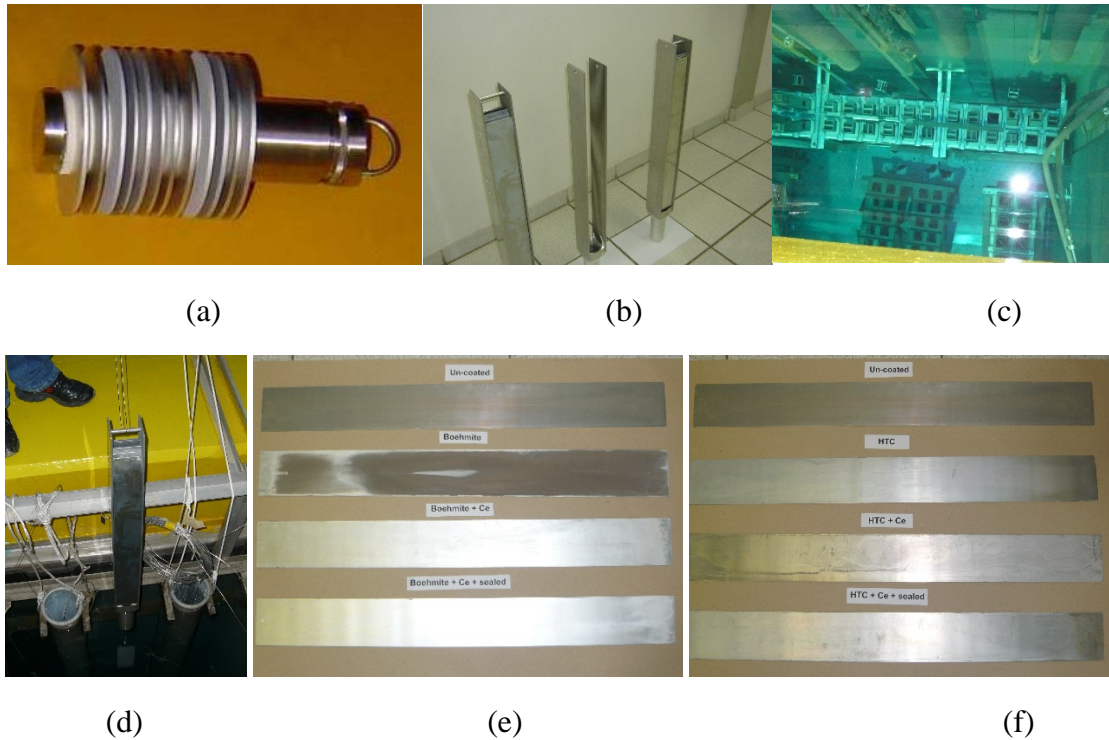


Figure 1. Photographs of: (a) coupons stacked in a rack; (b) plates assembled to form a dummy fuel element; (c) dummy fuel elements immersed in the spent fuel section of the IEA-R1 reactor; (d) a dummy fuel element being removed after 8 months of immersion; (e) uncoated and boehmite coated plates after 8 months of immersion; (f) uncoated and HTC coated plates after 8 months of immersion.

3. Results and discussion

3.1. Laboratory tests

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 HT-HTC coating thickness after 10 minutes of immersion was $\sim 2 \mu\text{m}$. A dense layer of amorphous or nanocrystalline lithium aluminate forms below the outer layer. (9)

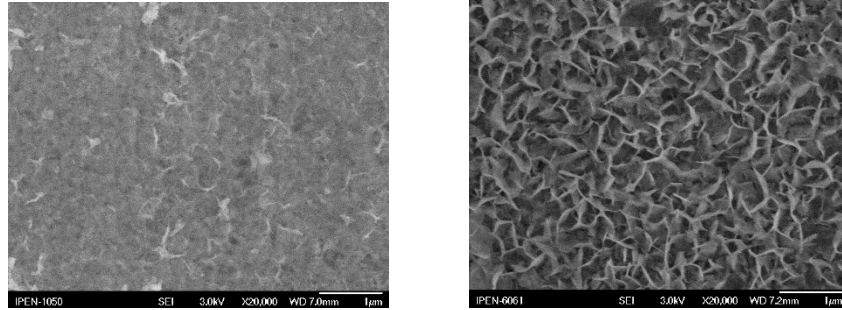


Figure 2. Scanning electron micrographs of: (a) LT-HTC (b) HT-HTC

Table 2. The corrosion potential E_{corr} , corrosion current I_{corr} and breakdown potentials E_b , as determined from the electrochemical polarization curves.

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	-

- **S4 and S7 are solutions 4 and 7 in Table 1.**

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 as shown in Table 3. However I_{corr} of specimens coated with LT-HTC and further treated in S7 to incorporate Ce showed a decrease with increase in time of treatment in S7. Overall the I_{corr} of the cerium incorporated HT-HTC coated specimens was significantly lower, compared with specimens that

were coated with cerium incorporated LT-HTC.

Table 3. The corrosion potential E_{corr} and corrosion current density I_{corr} as determined from the electrochemical polarization curves of specimens coated with cerium incorporated HT-HTC and LT-HTC as a function of duration of treatment in cerium containing solutions S4 and S7 of 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

3.2. 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 4. 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 4. 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

3.3. Full size 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 are summarized in Table 5.

Table 5. 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 center.
Boehmite + cerium treated + sealed	No pits, surface oxide layer.	5 pits, dark stain in center
HTC	No pits , drying stains.	No pits , drying stains.
HTC + cerium treated	8 pits at lower end and stained.	8 pits at lower end and stained.
HTC + cerium treated + sealed	No pits , slightly stained.	No pits , slightly stained.

4. 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 incorporating cerium in the coating. 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 cerium incorporated HTC coatings 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 containing 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 Ce³⁺, which forms an insoluble hydroxide and precipitates. The precipitated cerium hydroxide at the defect then stifles further corrosion.

5. Conclusions

1. Hydrotalcite (HTC) coatings on AA 6061 alloy were prepared from nitrate baths at 98 °C and carbonate baths at room temperature.
2. HT-HTC coating increased pitting resistance of the alloy more than LT-HTC coating
3. Cerium incorporation in the HT-HTC and boehmite coating increased pitting resistance of the alloy.
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 of the alloy.
6. Coupons and full size plates coated with HT-HTC and exposed to the IEA-R1 reactor spent fuel section for 5 and 8 months respectively did not reveal any pits, indicating marked potential for use of HT-HTC as a protective coating on spent RR fuel during long term wet storage.

6. References

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