Coatings for Safe Long Term Wet Storage of Spent Al-clad Research Reactor Fuels

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Abstract. Pitting corrosion of the aluminium cladding of spent research reactor (RR) fuels in wet storage has been observed and the use of conversion coatings to protect the cladding was proposed. A coating prepared by conventional chemical processing as opposed to electrochemical processing is the only option due to constraints related to the shape of the fuel and its high radioactivity. Hence, hydrotalcite (HTC) and boehmite were considered. This paper presents: (a) preparation of hydrotalcite (HTC) coatings from different baths followed by post-coating treatments; (b) corrosion behavior of HTC coated AA 6061 alloy; (c) results of field studies in which uncoated and HTC 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 extended periods. The laboratory and field tests revealed marked improvements in the corrosion resistance of HTC coated specimens, coupons and plates. The mechanism of corrosion protection is presented.

Key Words: Hydrotalcite coating, aluminium cladding, pitting corrosion, spent research reactor fuel.

1. Introduction

Worldwide, spent aluminum-clad fuels from research reactors (RRs) are stored for decades in light water filled pools or basins. Despite water quality management programs at the fuel storage sites, pitting corrosion of the cladding has been reported, which could lead to cladding failure and radioactive contamination of the storage facilities. This type of corrosion of the aluminium cladding is due to synergism in the effect of certain basin water parameters on corrosion. [1, 2] Hence, corrosion protection of the Al cladding of spent RR fuel was considered important 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] The complex shape and extent of radioactivity of spent RR fuels precludes electrochemical surface treatments. Thus chemical surface treatments to form a conversion coating is the only option. Results of preliminary laboratory and field investigations revealed that cerium hydroxide coatings increased the corrosion resistance of Al alloys. [7] 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. [8-10] The HTC coating imparted marked improvements in pitting corrosion resistance. [11] 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 HTC coatings from different baths followed by post-coating treatments; (b) the effect of duration of both HTC formation and cerium treatment on corrosion behavior of HTC coated AA 6061 alloy in NaCl; (c) results of field studies in which uncoated, HTC coated AA 6061alloy coupons and full size plates were exposed to the IEA-R1 reactor spent fuel basin for different duration.

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 HTC, with or without incorporation of cerium in the coating, by immersion in solutions and under conditions shown in Table I.

TABLE I: SOLUTIONS AND CONDITIONS USED TO PREPARE HTC COATINGS ON AA 6061.

Solution	**Purpose**	**Composition of solution and conditions**
1	Degrease	25 g/L Na_2SiO_3; 25 g/L Na_2CO_3; 65 °C; 2 min.
2	Deoxidize	10% HNO_3; 3% $NaBrO_3$; 55 °C; 3 min.
3	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.
4	Form LT-HTC	0.1M Li_2CO_3; LiOH; Al; pH 12; 15 min; R.T.
5	Incorporate Ce in HTC	10 g/L Ce $(NO_3)_{3;}$ 30% $H_2O_{2;}$ R.T.; 5 min.
6	Sealing	$MgC_4H_6O_4$; 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 both HTC formation and cerium treatment was also examined.

(a) *(b)*

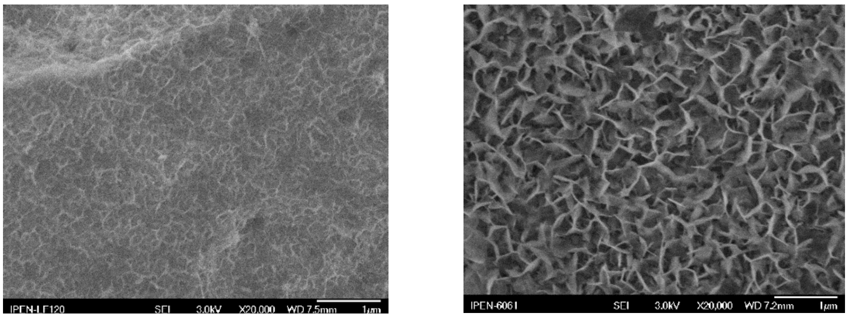
FIG. 1. Photographs of: (a) coupons stacked in a rack; (b) plates assembled to form dummy fuel elements.

The field test procedure consisted of: (a) preparing uncoated and coated coupons and plates; (b) stacking of the coupons in racks (Fig. 1 a); (c) assembling the plates to form a full size dummy fuel element (Fig. 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; (e) removal of the racks or dummy fuel elements, rinsing and decontamination; (f) disassembly and examination of the coupons and plates with an optical microscope. [1]

3. Results and discussion

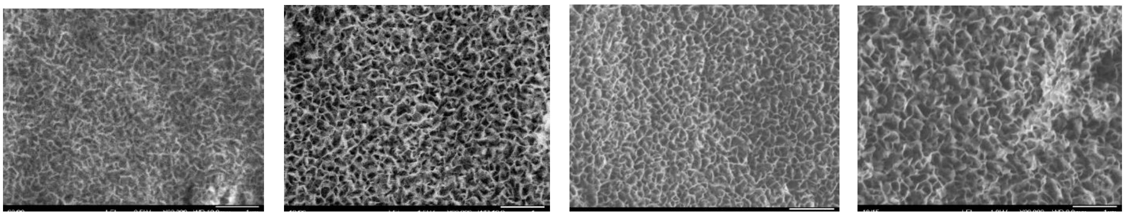
3.1. The HTC coatings

The morphology of LT-HTC and HT-HTC, formed from solutions 3 and 4 are shown in Fig. 2. The surfaces revealed intersecting blade like HTC crystallites that formed a layer across the surface. The LT-HTC coating is thinner and the crystallite, quite small. In order to obtain HTC with features similar to that of HT-HTC from a bath at room temperature, solution 3 was prepared with additions of H_2O_2 and/or $K_2S_2O_8$. The coatings obtained from these baths are shown in Fig.3 and these reveal well-formed intersecting crystallites. Formation of this morphology is essential to incorporate cerium in the coating. Typical HT-HTC coating thickness after 10 minutes of immersion was ~2 µm. A layer of amorphous or nanocrystalline lithium aluminate forms below the outer layer and this was confirmed from the broadened x-ray diffraction peaks. [8]



(a) (b)

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



(a) (b) (c) (d)

FIG. 3. Scanning electron micrographs of HTC coatings formed from solution 3 at room temperature: (a) without additions; (b) with H_2O_2; (c) with $K_2S_2O_8$; (c) with H_2O_2 and $K_2S_2O_8$.

3.2. Laboratory tests

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 II. It is evident that the HTC coated specimens, with or without post treatments were more corrosion resistant as indicated by the shift in their open circuit potentials (OCP) or E_{corr} to more anodic values. The corrosion current densities i_{corr} of the coated specimens were significantly lower than that of the uncoated specimen indicating marked increase in protection rendered by the coatings. The incorporation of Ce in the HT-HTC or LT-HTC coating reduced its i_{corr}. Sealing improved corrosion resistance of the HT-HTC coating whereas it decreased that of LT-HTC.

TABLE II: THE CORROSION POTENTIAL E_{corr} AND CORROSION CURRENT i_{corr} DETERMINED FROM THE ELECTROCHEMICAL POLARIZATION CURVES.

Specimen	**i_{corr} (μA.cm^{-2})**	**E_{corr} (V)**
Uncoated	1.56	-1.23
HT-HTC	0.35	-0.90
HT-HTC + Ce	0.26	-0.69
LT-HTC	0.77	-0.62
LT-HTC + Ce	0.71	-0.60
HT-HTC + sealed	0.13	-0.63
LT-HTC + sealed	0.99	-0.61

TABLE III: EFFECT OF DURATION OF HT-HTC FORMATION ON ELECTROCHEMICAL PARAMETERS OF UNCOATED AND COATED AA 6061 IN 0.01 M NaCl.

Specimen condition	**i_{corr} (μA.cm^{-2})**	**E_{corr} (V)**
Untreated	1.56	-0.79
HT-HTC (20’)	0.35	-0.58
HT-HTC (30’)	0.78	-0.57
HT-HTC (60’)	0.93	-0.58

TABLE IV: EFFECT OF DURATION OF LT-HTC FORMATION ON ELECTROCHEMICAL PARAMETERS OF UNCOATED AND COATED AA 6061 IN 0.01 M NaCl.

Specimen condition	**i_{corr} (μA.cm^{-2})**	**E_{corr} (V)**
Untreated	1.56	-0.79
LT-HTC (20’)	0.77	-0.59
LT-HTC (30’)	0.46	-0.59
LT-HTC (60’)	0.72	-0.60

The effect of duration of treatment in the solutions to form LT-HTC and HT-HTC on electrochemical parameters revealed that the E_{corr} remained unchanged but the I_{corr} increased slightly with increase in duration of HT-HTC treatment and without any significant change in the duration of LT-HTC treatment, as shown in Tables III and IV.

TABLE V: EFFECT OF DUARTION OF CERIUM TREATMENT ON ELECTROCHEMICAL PARAMETERS OF HTC COATED SPECIMENS.

Surface condition	**i_{corr} (μA.cm^{-2})**	**E_{corr} (V)**
HT-HTC + Ce (5 min.)	0.26	-0.60
HT-HTC + Ce (10 min)	0.12	-0.59
HT-HTC + Ce (15 min)	0.37	-0.59
LT-HTC + Ce (5 min)	0.96	-0.58
LT-HTC + Ce (10 min)	0.78	-0.56
LT-HTC + Ce (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 as shown in Table V. However i_{corr} of specimens coated with LT-HTC and further treated to incorporate Ce showed a decrease with increase in time of treatment. 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.

3.3. Coupons and plates 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 VI. 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. Therefore, the full-size plates were coated with only HT-HTC.

TABLE VI: COUPON SURFACE FEATURES COMPARED WITH 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
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

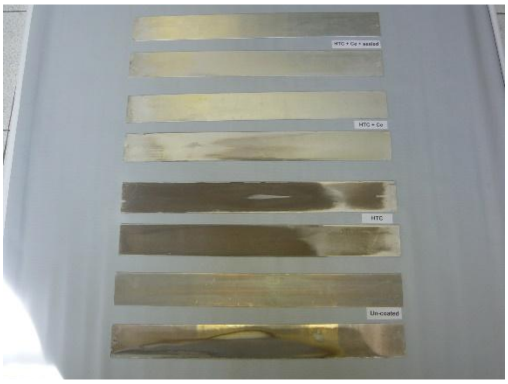


FIG. 4. Photograph of surfaces of full-size uncoated and HTC coated plates. The plates above the identification mark were exposed for 8 months and the plates below, for 14 months.

Fig. 4 shows a photograph of the uncoated and coated plates that were exposed to the IEA-R1 reactor spent fuel section. The plates stained to different extent, depending on the duration of exposure and the nature of surface treatment. The HTC coated plates were stained very dark compared with the uncoated plates. These plates however did not reveal pits. All these plates were examined visually and with an optical microscope and the main surface features are summarized in Table VII.

TABLE VII: SURFACE FEATURES ON UNTREATED AND TREATED AA 6061 PLATES EXPOSED TO THE IEA-R1 SPENT FUEL SECTION.

Surface treatment	**Plate surface features**			
	After 8 months		**After 14 months**	
	Side - A	Side - B	Side - A	Side - B
Untreated	11 pits surface dark.	5 pits, surface dark.	10 pits, surface dark.	No pits, surface dark.
HTC	**No pits**, dark surface.	**No pits**, dark surface.	**No pits**, very dark surface.	**No pits**, dark surface.
HTC + Ce	8 pits at lower end.	8 pits at lower end.	**No pits**, stained.	**No pits**, stained.
HTC + Ce + sealed	**No pits**.	**No pits**.	**No pits**.	**No pits**.

The uncoated plate exposed for 14 months was more stained than that exposed for 8 months. The HTC coated plates exposed for 8 and 14 months were heavily stained. The HTC + Ce coated plates did not reveal stains after 8 months but were slightly stained after 14 months. The plates that were HTC coated, cerium treated and sealed did not reveal any stains or pits after 8 and 14 months, indicating marked increase in the corrosion resistance imparted by the HTC coating followed by cerium incorporation and sealing.

4. General discussion

The laboratory and field tests have indicated a marked increase in corrosion resistance of Al alloys coated with HT-HTC. The corrosion resistance was further enhanced by cerium incorporation in the coating. Cerium was chosen to enhance corrosion protection as it is the only rare earth (besides europium) that can involve a change in oxidation state and form a water insoluble hydroxide/oxide on Al. The faint yellow coating obtained upon immersion of the HTC coated plate in the cerium solution is constituted of an insoluble cerium hydroxide/oxide. [3, 12, 13] Progressive loss of the yellow color with time has been observed and attributed to the hydroxide transforming to oxide [14], or surface degradation of the surface peroxide containing species. Sealing of the coatings with magnesium acetate improved the pitting corrosion resistance of specimens coated with HT and LT-HTC. The HTC layer imparts pitting corrosion protection by acting as a physical barrier between the solution and the surface. The higher corrosion resistance of the Al surface with cerium in the HTC coating could be also attributed to coarsening of the HTC crystallites during cerium treatment at 98 °C and also during the long term exposure to the spent fuel basin, which is akin to a hydrothermal treatment. The mechanism by which the cerium in the HTC imparts protection is considered to be ‘active corrosion protection’, analogous to chromium coatings. According to this mechanism, the lower solubility of $CeO_2.2H_2O$ allows the formation of $Ce(OH)_2^{2+}$ ions in solution which then diffuse to defects in the coating that have exposed bare metal. When in contact with the bare metal, these ions reduce to Ce^{3+} and precipitate as $Ce(OH)_3$ and thus seal the layer. A reason that can be attributed for the increased protection given by the HT-HTC + Ce compared with that given by LT-HTC + Ce is the availability of more cerium in the former, caused by treatment in a high temperature solution as opposed to treatment of LT-HTC coated specimen in a room temperature cerium solution. In the context of eventually protecting spent Al-clad RR fuels during long term wet storage, the coating process for irradiated fuels could be simplified if it could be carried out at room temperature. Since the extent to which LT-HTC imparts protection is lower than that imparted by HT-HTC attempts are on-going to prepare and characterize thick room temperature HTC coatings.

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 coating increased pitting resistance of the alloy.
4. The corrosion resistance of HT-HTC coated specimens did not increase with increase in duration of HTC formation or 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 periods of up to 14 months 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.

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