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Corrosion Protection of Spent Aluminium-Clad Research Reactor Fuel during Long Term Wet Storage

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ABSTRACT

Protection of the aluminium cladding of spent research reactor (RR) fuels was proposed to prevent pitting corrosion during long term wet storage. This paper will present the effect of HTC (a lithium aluminium-nitrate-hydroxide hydrate that forms on Al alloy surfaces immersed in an appropriate alkaline lithium salt solution) coatings prepared from different baths on AA 6061 alloy surfaces pre-treated to simulate spent fuel surface features. The results of field studies in which dummy fuel elements, consisting of Al alloy plates coated with HTC from different baths (with or without post coating treatments), were immersed in the IEA-R1 reactor's spent fuel basin for 30 months and then evaluated, indicated that the cerium modified HTC coating imparted very high corrosion resistance. This paper will discuss the HTC corrosion protection mechanism and present a mock-up of the arrangement required to remotely handle and coat the dummy-fuel elements.

1 Introduction

Spent aluminum-clad fuels from research reactors (RRs) are stored in light water filled pools for decades. Despite water quality management programs at the fuel storage sites, pitting corrosion has been reported. This could lead to cladding failure, release of fissile material and radioactive contamination of the storage facilities. The pitting corrosion of the fuel cladding has been attributed to synergism in the effect of some basin water parameters on corrosion of aluminum 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] The shape of the RR fuel and the radioactivity of spent fuels preclude electrochemical surface treatments. Therefore chemical surface treatment to form a coating is the only option and the use of conversion

coatings to protect spent Al-clad RR fuel was proposed in 2007. 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 obtained from baths at 98 °C imparted marked improvements in pitting corrosion resistance. [12, 13] Studies were subsequently carried out to obtain HTC coatings from baths at lower temperatures (50 °C) followed by post-treatments and recently an all-room temperature (RT) process (which includes several chemical treatments to pre-treat, coat and post-treat) to obtain high quality HTC coated specimens was developed. Such a process is essential as it is up-gradable to coat and protect irradiated spent Al-clad MTR fuel elements. Further, RT-HTC coatings were also prepared on Al specimen surfaces that were pre-treated to simulate the surface of spent Al-clad MTR fuels. This paper presents: (a) the preparation and characterization of hydrotalcite coatings from different baths on AA 6061 alloy specimens given a variety of pre-treatments followed by post-coating treatments; (b) the corrosion behavior of the different HTC coated AA 6061 alloy specimens; (c) results of field studies in which uncoated and HTC coated AA 6061 alloy full size plates were exposed to the IEA-R1 reactor spent fuel basin for almost 2 years.

2. Methods and materials

In the first set of studies, aluminium alloy AA 6061 specimens (2 x 2 x 0.2 cm) for the laboratory tests and 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 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 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 RT-HTC	0.1M Li ₂ CO ₃ ; LiOH; Al; pH 12; 15min; R.T.
5	Form RT-HTC	0.1M Li ₂ CO ₃ ; LiOH; Al; 30% H ₂ O ₂ ; pH 12; 15min; R.T.
6	Form RT-HTC	0.1M Li ₂ CO ₃ ; LiOH; Al; 2.5 g/l K ₂ S ₂ O ₈ ; pH 12; 15min; R.T.
7	Form RT-HTC	0.1M Li ₂ CO ₃ ; LiOH; Al; 30% H ₂ O ₂ ; 2.5 g/l K ₂ S ₂ O ₈ pH 12; 15min; R.T.
8	Incorporate Ce in HTC	10 g/L Ce (NO ₃) ₃ ; 30% H ₂ O ₂ ; R.T.; 5 min.
9	Sealing	MgC ₄ H ₆ O ₄ ; 82 °C; 15 min.

- HT-high temperature; RT-room temperature

In the second set of studies also, AA 6061 specimens and plates, similar to those used in the first set of studies, were degreased, deoxidized, coated with HTC and post-treated to incorporate cerium, **all at room temperature**, as shown in Table 2. Some AA 6061 alloy specimens were also pre-treated to form boehmite (AlOOH) or a thick air formed layer of Al_2O_3 on the surface, as shown in Table 3, to simulate surfaces of spent fuels. These oxidized specimens were then pre-treated and coated with HTC, under conditions mentioned in Table 2. The coatings obtained from the three sets of studies were examined in a field emission scanning electron microscope. The corrosion behavior of uncoated and coated specimens was determined from laboratory tests that consisted of anodic polarization measurements in 0.01M NaCl solution. These 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.

Table 2. Solutions and conditions used to prepare HTC coatings on Al alloy AA 6061 at room temperature.

Solution	Purpose	Composition of solution and conditions
10	Degrease	1:10 Sulphonic acid based industrial degreaser; 3 min.
11	Deoxidize	10% HNO_3 ; 3 min.
4	Form RT-HTC	0.1M Li_2CO_3 ; LiOH; Al; pH 12; 15min;
9	Incorporate Ce in HTC	10 g/L $\text{Ce}(\text{NO}_3)_3$; 30% H_2O_2 ; 5 min.

- RT-room temperature

Table 3. Pre-treatments of AA 6061 specimens to simulate spent fuel surfaces.

Purpose	Conditions
Form boehmite	Deionized water; $\sim 100^\circ\text{C}$; 5 min.
Form thick dry oxide	Exposure in air for 1 hour at 100°C

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

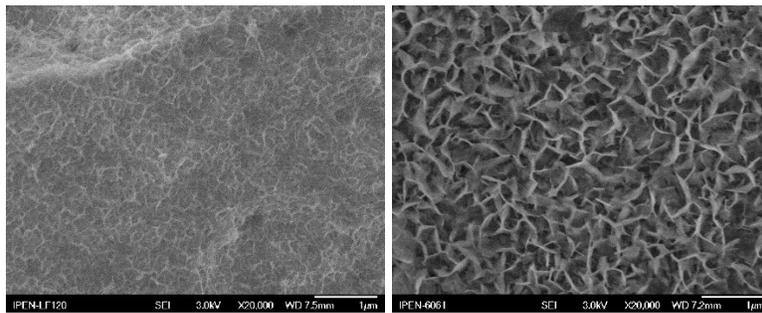


Figure 1: Photograph of plates assembled to form dummy fuel elements.

3. Results and discussion

3.1 The hydrotalcite coatings

The morphology of HTC formed from solutions 3 and 4 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 layer of amorphous or nanocrystalline lithium aluminate forms below the outer layer and this was confirmed from the broadening of the HTC x-ray diffraction peaks. [14]



(a)

(b)

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

The RT-HTC coating is thinner than the HT-HTC and the crystallites are quite small. In order to obtain RT-HTC with features similar to that of HT-HTC from a bath at room temperature, solutions 5, 6 and 7 were prepared with additions of H_2O_2 and/or $\text{K}_2\text{S}_2\text{O}_8$, as shown in Table 1. The coatings obtained from these baths are shown in Figure 3 and these reveal well-formed intersecting crystallites. Formation of this morphology is essential to incorporate cerium in the coating.

An all-room temperature process implies not only formation of HTC at room temperature but pre-treatment of the Al alloy surface and post-treatment of the HTC, all at room temperature. Towards this end, HTC formation was attempted on Al alloy AA 6061 surfaces that were degreased using an industrial sulphonic acid based degreaser and de-oxidation with nitric acid at room temperature. Figure 4 shows micrographs of RT-HTC formed on surfaces that were just degreased and just deoxidized at room temperature.

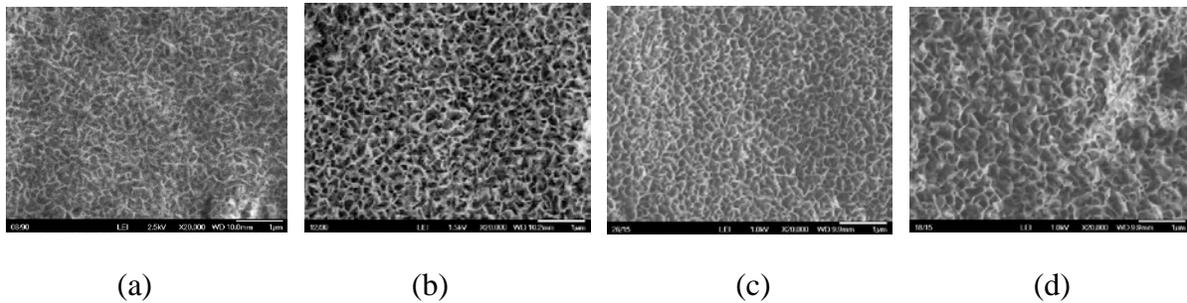


Figure 3. Scanning electron micrographs of RT-HTC coatings formed from solution 3 at room temperature: (a) without additions; (b) with H_2O_2 ; (c) with $\text{K}_2\text{S}_2\text{O}_8$; (d) with H_2O_2 and $\text{K}_2\text{S}_2\text{O}_8$.

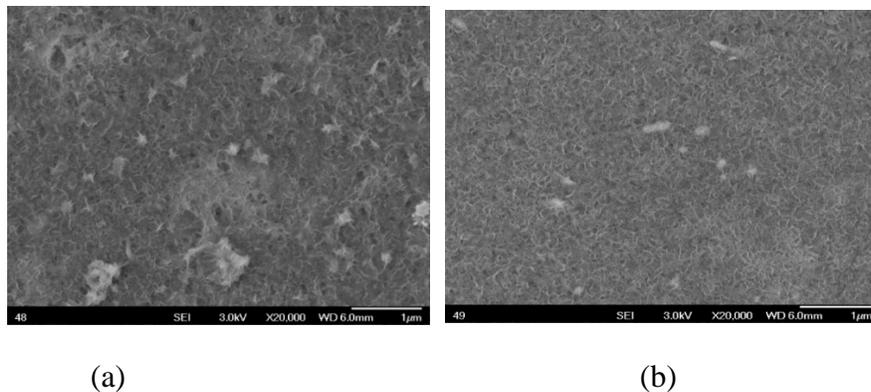


Figure 4. Scanning electron micrographs of RT-HTC on: (a) specimen degreased with a sulphonic acid based industrial degreasing agent; (b) specimen deoxidized with HNO_3 .

The formation of RT-HTC layer on surfaces that simulated the surface of a spent fuel was studied. The surfaces of Al-clad fuel that has been burnt in the RR core for years, if not decades, have a thick layer of the aluminium oxide boehmite or alumina, depending on the power of the

reactor and consequently, the temperature of the fuel surface as well as the surrounding primary coolant. In this study AA 6061 specimens were: (a) oxidized in a muffle furnace at 100 °C for 1 hour to form an alumina layer on the specimen surface; (b) exposed to boiling water for 1 hour to form boehmite on the surface. The specimens were then pre-treated, treated to form RT-HTC and post-treated, all at room temperature in solutions shown in Tables 2 and 3. Figure 5 shows micrographs of the surfaces of these specimens and reveals that RT-HTC forms on surfaces with both boehmite and alumina after pre-treatments.

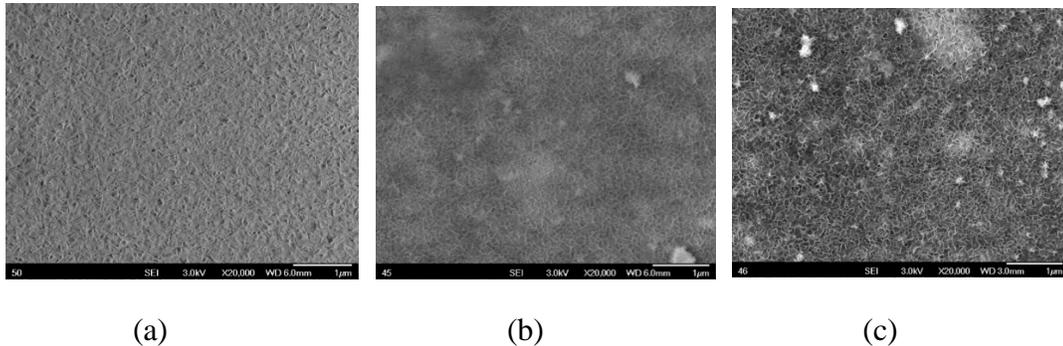


Figure 5. Scanning electron micrographs of RT-HTC on : (a) Specimen surface where boehmite was deliberately grown; (b) specimen surface where an alumina layer was deliberately grown following degreasing in sulphonic acid; (c) specimen surface where an alumina layer was deliberately grown following de-oxidation in nitric acid.

The results of electrochemical measurements carried out with HT-HTC and RT-HTC coated specimens in 0.01 M NaCl were reported earlier. [15] On the basis of the corrosion current densities, the main conclusions were: (a) specimens with any type of coating, with or without post treatments were more corrosion resistant than the uncoated specimens; (b) the incorporation of Ce in the HT-HTC or RT-HTC coating increased corrosion resistance; (c) sealing improved corrosion resistance of the HT-HTC coating whereas it decreased that of RT-HTC; (d) the duration of RT-HTC and HT-HTC formation or cerium incorporation in the HTC coatings had no significant effect on the electrochemical parameters.

Table 4. Surface features on untreated and treated AA 6061 plates exposed to the IEA-R1 reactor's spent fuel section for 8, 14 and 23 months.

Surface treatment	Plate surface features after				
	8 months		14 months		23 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.	<u>Many pits on both sides.</u> Surface stained dark all over.
Boehmite	No pits, surface very dark.	1 pit, surface very dark.	4 pits, stained.	6 pits, stained.	Two pits on one side. Stained uniformly on one side and in patches on the other. Zillions of extremely tiny spots with a dot in the middle.
Boehmite + Ce	No pits, surface white.	7 pits, dark stain in center.	No pits, Grey stain.	No pits, stained.	Plate quite bright, no stains. A very large number of dark spots but with no halo around them and about 10 pits with halos on one side of the plate.
Boehmite + Ce + sealed	No pits, surface oxide layer.	5 pits, dark stain in center	1 pit, surface stained.	4 pits, surface stained.	Bright on both sides and <u>no pits.</u>
HTC	No pits, dark surface.	No pits, dark surface.	<u>No pits,</u> very dark surface.	<u>No pits,</u> dark surface.	<u>Top 2/3rds stained dark grey and no pits.</u>
HTC + Ce	8 pits at lower end.	8 pits at lower end.	<u>No pits,</u> stained.	<u>No pits,</u> stained.	<u>Top 2/3rds stained light grey and no pits.</u>
HTC + Ce + sealed	No pits.	No pits.	<u>No pits.</u>	<u>No pits.</u>	<u>Bright plate, unstained. No pits.</u>

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

Figure 6 shows photographs of the uncoated and coated plates 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 boehmite coated and the uncoated plates. These plates however did not reveal pits. All these plates, exposed for 8, 14 and 23 months to the IEA-R1 reactor spent fuel basin were

examined visually and with an optical microscope. The main surface features of these plates are summarized in Table 4.



Figure 6. Photographs of full-size plate surfaces. (a) Boehmite coated and (b) HTC coated. The plates above the identification mark were exposed for 8 months and the plates below, for 14 months.

The uncoated plates exposed for 14 and 23 months were more stained than those exposed for 8 months. The boehmite coated plates, with or without cerium treatment and/or sealing, were stained to the same extent after 8, 14 and 23 months. The HTC coated plates exposed for 8, 14 and 23 months were heavily stained. The HTC + Ce coated plates did not reveal stains after 8 months but were slightly stained after 14 and 23 months. The plates that were HTC coated, cerium treated and sealed did not reveal any stains or pits after all three duration, 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, 16, 17] Progressive loss of the yellow color with time has been observed and attributed to the hydroxide transforming to oxide [18], 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 RT-HTC. In the context of eventually protecting spent Al-clad RR fuels during long term wet storage, the coating process for irradiated fuels would be facilitated if treatments are carried out at room temperature and to meet this requirement a set up as shown in Figure 7 was prepared and 3 dummy fuels were pre-treated and HTC coated. These dummy fuels were immersed in the IEA-R1 reactor's spent fuel section and will be removed for evaluation after 1, 2 and 3 years.



Figure 7. Setup to coat a dummy fuel element with HTC.

At present the extent to which RT-HTC imparts protection is lower than that imparted by HT-HTC and attempts are in progress to increase the RT-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 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 $\text{CeO}_2 \cdot 2\text{H}_2\text{O}$ allows the formation of $\text{Ce}(\text{OH})_2^{2+}$ 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 $\text{Ce}(\text{OH})_3$ and thus seal the layer. Basically, this involves release of Ce ions from the coating, transport of Ce 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. Another reason that can be attributed for the increased protection given by the HT-HTC + Ce compared with that given by RT-HTC + Ce is the availability of more cerium in the former, caused by treatment in a high temperature solution as opposed to treatment of RT-HTC coated specimen in a room temperature cerium solution.

5. Conclusions

1. HTC coatings increased the pitting corrosion resistance of the aluminium alloy.
2. Cerium incorporation in the HTC coating and sealing increased further the pitting corrosion resistance of the aluminium alloy.
3. An all-room temperature process was developed to coat aluminium alloy with HTC.

4. Aluminium alloy surfaces pre-treated to simulate the surface of a spent fuel were also HTC coated at room temperature.
5. Full size plates coated with HTC and exposed to the IEA-R1 reactor spent fuel section for almost two years did not reveal any pits, indicating marked potential for use of HTC as a protective coating on spent RR fuel during long term wet storage.
6. A set up to mock remote handling of spent radioactive RR fuel to pre-treat the Al surface, to coat with HTC and to post-treat the HTC coating was tested.

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