Self-Healing Hydrotalcite Coatings for Corrosion Protection of Aluminum-Clad Spent Nuclear Fuels During Long Term Wet Storage

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Abstract

Pitting corrosion of the aluminium cladding of spent nuclear fuels stored in light water pools has been observed. To prevent this, coating of the Al cladding with hydrotalcite (HTC) was proposed. The effect of processing parameters on microstructure and corrosion behavior of HTC coated AA 6061 specimens was studied. The HTC coating from the high temperature nitrate bath was homogeneous, thicker and consisted of well-defined intersecting platelets than that formed from the low temperature bath. Electrochemical polarization measurements carried out with HTC coated AA 6061 specimens in 0.01 M NaCl revealed that specimens coated with HTC from the nitrate bath and further treated in a cerium salt solution were most resistant to corrosion. Field tests in which un-coated and HTC coated AA 6061 alloy coupons as well as mock fuel plates were exposed to the IEA-R1 reactor's spent fuel basin for duration of up to two years further corroborated the higher corrosion resistance imparted by the high temperature HTC + Ce coating. The self-healing mechanism by which this coating protects the Al alloy is discussed.

Keywords: Hydrotalcite, coatings, corrosion, aluminum alloy.

Introduction

Spent aluminum-clad nuclear fuels from research reactors 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 the spent research

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reactor 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 nuclear 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 nuclear fuel was proposed. The results of preliminary investigations revealed that cerium hydroxide coatings increased the corrosion resistance of Al alloys. [7, 8] 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. [9-11]. Studies were carried out to obtain HTC coatings from baths at 98 °C and at 25 °C followed by post-treatments. This paper presents: (a) the preparation and characterization of hydrotalcite coatings from different baths on AA 6061 alloy specimens 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 6061alloy coupons as well as mock fuel plates were exposed to the IEA-R1 reactor spent fuel basin for almost 2 years.

Materials and methods

Aluminium alloy AA 6061 specimens (2 x 2 x 0.2 cm) for the laboratory tests and coupons (10 cm in diameter) 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 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_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; 25 °C
5	Form LT-HTC	0.1M Li_2CO_3; LiOH; Al; 30% H_2O_2; pH 12; 15 min; 25 °C
6	Form LT-HTC	0.1M Li_2CO_3; LiOH; Al; 2.5 g/l $K_2S_2O_8$; pH 12; 15 min; 25 °C
7	Form LT-HTC	0.1M Li_2CO_3; LiOH; Al; 30% H_2O_2; 2.5 g/l $K_2S_2O_8$ pH 12; 15 min; 25 °C.
8	Incorporate Ce in HTC	10 g/L Ce $(NO_3)_3$; 30% H_2O_2; 25 °C; 5 min.
9	Sealing	$MgC_4H_6O_4$; 82 °C; 15 min.

- HT-high temperature; LT- low temperature

The coatings obtained 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.

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; (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]


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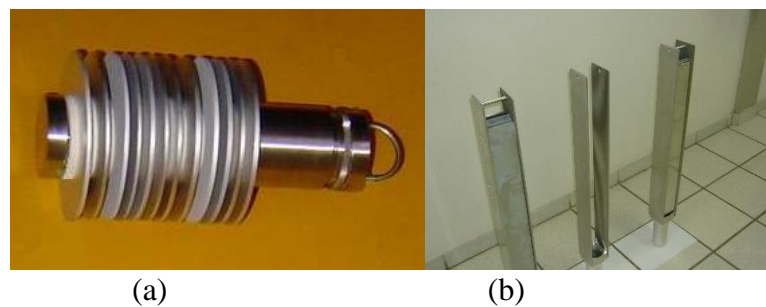
**Figure 1 - Photographs of: (a) coupons stacked in a rack; (b) plates assembled to form dummy fuel elements.**

Results and discussion

Morphology of 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 as shown in Figure 3. 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 broadening of the HTC x-ray diffraction peaks. [9]


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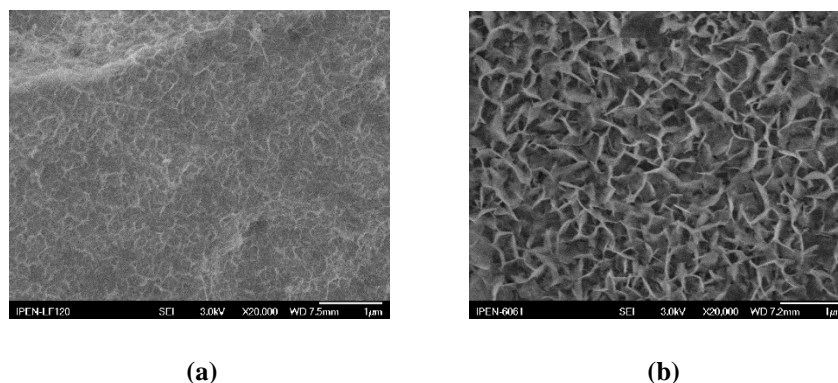
Figure 2 - Scanning electron micrographs of: (a) LT-HTC (b) HT-HTC

(a)   (b)
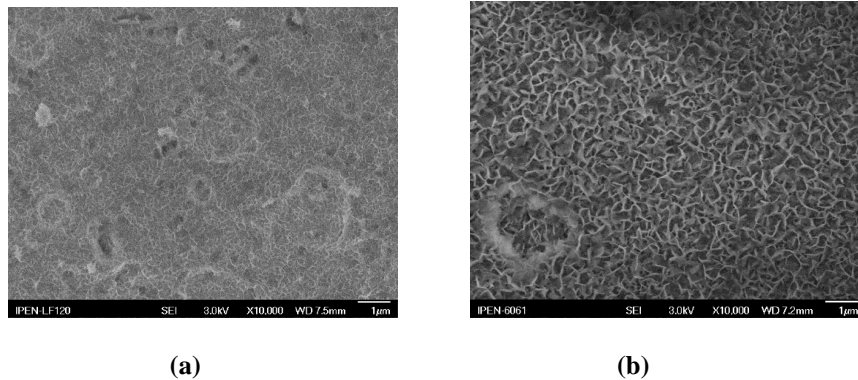
Figure 3 - Scanning electron micrographs revealing HTC formation within pits and crevices: (a) LT-HTC; (b) HT-HTC.

The LT-HTC coating is thinner than the HT-HTC and the crystallites are quite small. In order to obtain LT-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 $K_2S_2O_8$, as shown in Table 1. The coatings obtained from these baths are shown in Figure 4 and these reveal well-formed intersecting crystallites. Formation of this morphology is essential to incorporate an adequate amount of cerium in the coating.

(a)   (b)   (c)   (d)
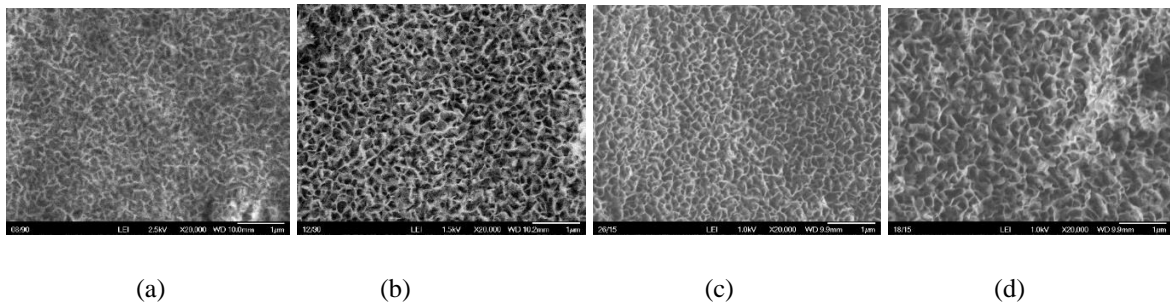
Figure 4 - Scanning electron micrographs of LT-HTC coatings formed from solution 3 at room temperature: (a) without additions; (b) with H_2O_2; (c) with $K_2S_2O_8$; (d) with H_2O_2 and $K_2S_2O_8$.

Corrosion behavior of HTC coated specimens

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) 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 2 - The corrosion potential E$_{corr}$ and corrosion current i$_{corr}$ as 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 (S7)	0.26	-0.69
LT-HTC	0.77	-0.62
LT-HTC + Ce (S 7)	0.71	-0.60
HT-HTC + sealed	0.13	-0.63
LT-HTC + sealed	0.99	-0.61

- S7 is solution 7 in Table 1.

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 3. 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. On the basis of these observations the full-size plates were coated with HT-HTC and not LT-HTC.

Table 3 - 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
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

All the 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.

The uncoated plates exposed for 14 and 23 months were more stained than those exposed for 8 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.

Table 4 - Surface features on untreated and treated AA 6061 plates exposed to the IEA-R1 reactor's spent fuel section for 8 and 14 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.	Many pits on both sides. Surface with dark stains
HTC	No pits, dark surface.	No pits, dark surface.	No pits, dark surface.	No pits, dark surface.	Top 2/3rds stained dark grey and no pits.
HTC + Ce	8 pits	8 pits	No pits, stained.	No pits, stained.	Top 2/3rds stained light grey and no pits.
HTC +Ce + sealed	No pits.	No pits.	No pits.	No pits.	Bright plate, unstained. No pits.

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. 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

heals the layer, stifling further corrosion. Another 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 low temperature cerium solution.

Conclusions

1. Hydrotalcite (HTC) coatings on aluminium alloy AA 6061 alloy were prepared from nitrate baths at 98 °C and carbonate baths at room temperature.
2. HTC coatings increased the pitting corrosion resistance of the aluminium alloy.
3. Cerium incorporation in the HTC coating and sealing increased further the pitting corrosion resistance of the aluminium alloy.
4. 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.

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