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Hydrotalcite and Boehmite coatings for increased protection of Aluminum clad spent nuclear fuel

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Abstract

It is essential to increase the corrosion resistance of Al-clad research reactor (RR) spent fuels during long term wet storage. Laboratory and field tests were carried out to evaluate the pitting corrosion resistance of rare earth containing conversion coatings on Al alloys, AA 1100 and AA 6061, used as cladding of RR fuel plates. These investigations were extended to include boehmite and hydrotalcite (HTC) coatings on Al alloy surfaces. Characterization of the coatings was done with the aid of SEM/FEG/EDS and x-ray diffraction analysis. The electrochemical behavior of uncoated and coated specimens was determined in 0.1 M NaCl. Field tests were carried out in which uncoated, lanthanide-based conversion coated, boehmite coated, cerium modified boehmite coated, HTC coated and cerium modified HTC coated Al alloy coupons were exposed to the IEA-R1 reactor spent fuel basin for varying periods and then their corrosion resistance evaluated. Most of the coatings increased the pitting corrosion resistance of the two alloys and among the coatings, the cerium modified HTC coating was the most efficient.

Keywords: Hydrotalcite, boehmite, coating, aluminum, rare earth.

Introduction

Most of the wet storage facilities for spent aluminum-clad research reactor (RR) fuel have water quality management programs, to prevent and/or reduce degradation of the fuel cladding. Pitting corrosion has been identified as the main form of degradation leading to cladding failure and release of fissile material, contaminating thereby the storage facilities. It has been shown that maintenance of water parameters within specified limits does not prevent pitting corrosion of the fuel cladding, due to synergism between many basin water parameters that affect corrosion of aluminum and its alloys (1,2). Hence, it was considered imperative that some form of corrosion protection be given to stored spent RR fuel. Use of conversion coatings is a well established corrosion control technique and it has been extensively used in many industries to control the corrosion of various metals. In recent years, rare earth compounds have been used in corrosion protection systems for aluminum alloys (3). Having observed the formation of cerium hydroxide films on Al alloys immersed in solutions containing cerium compounds as inhibitors, other 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 assemblies was proposed in 2007 and the results of preliminary

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laboratory and field investigations carried out at IPEN in Brazil, revealed that cerium hydroxide coating increased the corrosion resistance of Al alloys (7). The investigations were subsequently extended to include boehmite, hydrotalcite (HTC), cerium modified boehmite and cerium modified HTC coatings on Al alloy surfaces. Inclusion of cerium modified boehmite coatings was motivated by the fact that this type of Al hydroxide covers the surface of spent RR fuel. HTC is lithium aluminum-nitrate-hydroxide hydrate and it forms on Al alloys immersed in an appropriate alkaline lithium salt solution (8-10). Immersion of Al alloys in this solution results in formation of a polycrystalline barrier film composed mainly of HTC like compounds. Further studies were carried out recently to obtain HTC coatings at room temperature, as opposed to the previous set of studies where HTC coatings were prepared from solutions at 95 °C.

This paper presents the results of: (a) HTC coating preparation from different aqueous solutions; (b) evaluation of corrosion resistance of aluminum alloy AA 1100 and AA 6061 specimens coated with different types of boehmite and HTC; (c) field studies in which uncoated, lanthanide-based conversion coated, boehmite coated, HTC coated, cerium modified boehmite and cerium modified HTC coated Al alloy coupons were exposed to the IEA-R1 reactor spent fuel basin for up to a year.

Methodology

Aluminum alloys AA 1100 and AA 6061 with chemical composition shown in Table 1 were used in all the tests. In the laboratory tests, AA 1100 and AA 6061 specimens 2 cm x 2 cm x 0.2 cm were pretreated in solutions 1 and 2 of Table 2 and then boehmite or HTC coated from solutions 5, 6 and 7.

Table 1 - Chemical composition of aluminum alloys (wt%)

Alloy	Cu	Mg	Mn	Si	Fe	Ti	Zn	Cr
AA 1100	0.16	<0.1	0.05	0.16	0.48	0.005	0.03	0.005
AA 6061	0.25	0.94	0.12	0.65	0.24	0.04	0.03	0.04

Table 2 - 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	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 HTC	0.1M Li ₂ CO ₃ ; LiOH; Al; pH 12; 15 min; R.T.
7	Form HTC	6.9g/L LiNO ₃ ; 28.3 g/L KNO ₃ ; 2.4 g/L LiOH; 2.5 g/L K ₂ S ₂ O ₈ ; 0.06 g/L NaAlO ₂ ; 98 °C; pH 12; 10 min.
8	Incorporate Ce in HTC	10 g/L Ce (NO ₃) ₃ ; 30% H ₂ O ₂ ; R.T.; 5 min.

The boehmite and HTC coatings on some specimens of the two alloys were further modified by treatment in solutions 4 and 8 respectively. The composition of these coatings was determined by x-ray diffraction analysis and the morphology examined in a scanning electron microscope coupled to an energy dispersive spectrometer. The extent of corrosion protection provided by these coatings to the substrate was determined from anodic potentiodynamic polarization measurements. These measurements were carried out with a standard 3-electrode arrangement in 0.1 M NaCl, using a saturated calomel reference electrode. The motivation for these tests was to obtain a HTC coating at room temperature, mainly to facilitate the process to coat spent fuels.

The field tests consisted of preparing Al alloy coupons, stacking of these coupons in racks, immersion of the racks in the spent fuel section of the IEA-R1 research reactor in IPEN, Brazil, for periods of up to a year, removal of the racks and examination of the coupons. This procedure was used in the IAEA coordinated CRP on “Corrosion of Research Reactor Aluminium Clad Spent Fuel in Water” (1). Two sets of field tests were carried out. In the first set of tests, circular coupons 10 cm in diameter and 3 mm thick of the two alloys were pretreated in solution 1 of Table 3 and then coated with oxides of cerium, lanthanum, praseodymium and an oxide concentrate of cerium from solution 2 in Table 3 that was altered according to the required rare earth ion (7). The coupon stacking sequence in the racks from top to bottom consisted of as-received; oxidized; cerium oxide coated; cerium oxide concentrate coated; praseodymium oxide coated; lanthanum oxide coated. Some coupons were oxidized at 300° C in air for 4 h to form a surface oxide layer to simulate spent fuel plate surfaces. The racks were removed from the reactor after 2 and 12 months and examined in an optical microscope. In the second set of field tests identical coupons were used and were coated with boehmite and HTC using solutions in Table 2 after appropriate pretreatments, also shown in the same table. The coupon stacking sequence in the rack for the second set of tests was untreated, HTC coated, boehmite coated, HTC-Ce coated and boehmite-Ce coated. These coupons were exposed for 6 and 9 months and then their surfaces were examined with an optical microscope.

Table 3 - Composition of solutions and treatment conditions

Treatment conditions	Solution	
	1	2
Composition	0.5 M H ₂ SO ₄ 1.28 M HNO ₃ 0.05 M Ce(SO ₄) ₂ 0.04 M HF 0.1 M (NH ₄) ₂ SO ₄ 1 litre	0.035 M CeCl ₃ 0.12 M H ₂ O ₂ 1mM Cu (glycinate) 1 mM Ti(O ₂) ²⁺ 1 litre pH 2.0
Temperature (°C)	35	45
Duration (minutes)	10	5

Results and discussion

The laboratory tests

The main features of the coatings formed from the different solutions of Table 2 are summarized in Table 4. The coatings were identified by x-ray diffraction analysis. The surfaces treated in the nitrate, carbonate and carbonate + cerium solutions revealed intersecting blade or rod like HTC crystallites that formed a continuous layer across the surface. The coatings formed inside pits and recesses that developed during pre-treatment of the substrate. Scanning electron micrographs of HTC coatings on the Al alloys from the nitrate and carbonate solutions are shown in Fig. 1. Below the outer layer a dense layer of amorphous or nanocrystalline lithium aluminate forms (10). The coating thickness varied with the substrate alloy, bath composition, age of the bath and immersion time. Typical coating thickness after 10 minutes of immersion was $\sim 2 \mu\text{m}$.

Table 4 - Aluminum alloy surface features following treatment in different solutions.
(see Table 2 for solution composition; RT – room temperature)

Alloy AA	Coating solution and conditions			Surface features
	Solution	°C	Main anion	
1100	5	95	NO ₃	HTC forms – well defined crystallites
6061	5	95	NO ₃	HTC forms and Mg ₂ Si detected
1100	6	RT	CO ₃	HTC forms and surface etched
6061	6	RT	CO ₃	HTC and Mg ₂ Si detected
1100	7	95	NO ₃ + S ₂ O ₈	No HTC
6061	7	95	NO ₃ + S ₂ O ₈	No HTC, Mg ₂ Si detected
1100	5 + 8	RT + RT	CO ₃ + CeO ₂	HTC forms and surface etched
6061	5 + 8	RT + RT	CO ₃ + CeO ₂	HTC forms and surface etched.

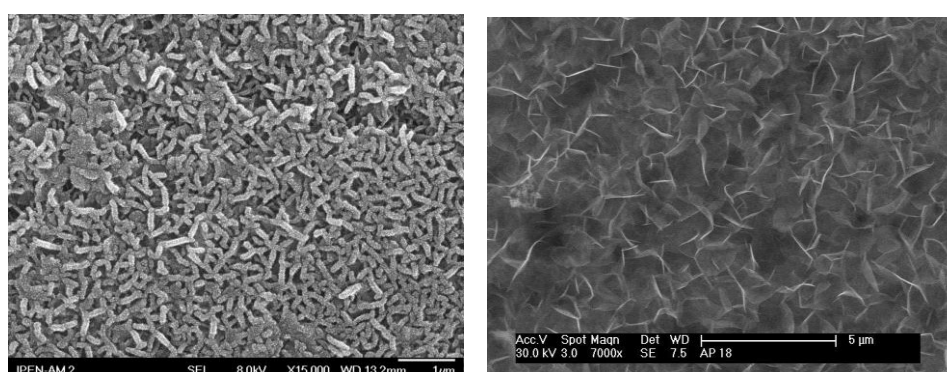


Figure 1 - Micrographs of: (a) HTC on AA 6061 from NO₃ solution at 95 °C
(b) HTC on AA 1100 from CO₃ solution at RT + Ce impregnation

The electrochemical behavior alloy AA 6061, with or without the coatings revealed differences in the anodic as well as the cathodic sides of the anodically determined polarization curves. Table 5 summarizes the corrosion potential (E_{corr}) that was determined

after 60 minutes, the pitting potential (E_{pit}) and the corrosion current densities (i_{corr}) of the AA 6061 specimens with the different coatings. The E_{pit} of the untreated specimen was very close to its E_{corr} signifying active corrosion and with boehmite coating, the E_{pit} increased to -650 mV. Cerium modified boehmite increased E_{pit} even more to -600 mV, indicating increased pitting corrosion resistance upon introduction of Ce. A HTC layer on the alloy surface resulted in an even more marked increase in the pitting resistance by increasing the E_{pit} from -750 to -580 mV. This increase in pitting resistance of the alloy with a HTC coat was further enhanced by modifying the HTC with Ce. The E_{pit} increased significantly to -420 mV. The cathodic current density of the AA 6061 specimen in 0.1 M NaCl decreased by an order of magnitude upon coating it with either boehmite or HTC. The difference in the i_{corr} between the boehmite coated and the HTC coated specimens was slight with no marked change even with the introduction of Ce into the coating. The open circuit or corrosion potential E_{corr} of AA 6061 increased to almost the same extent with formation of boehmite or HTC. Modification of either coating with Ce increased E_{corr} to again the same extent.

Table 5 - Corrosion current (i_{corr}), corrosion potential (E_{corr}) and pitting potential (E_{pit}) of alloy AA 6061 in 0.1M NaCl

Surface condition	i_{corr} (A.cm ⁻²)	E_{corr} (mV vs SCE)	E_{pit} (mV vs SCE)
None	1.5×10^{-6}	- 760	- 750
Boehmite	2.0×10^{-7}	- 711	- 650
Boehmite + Ce	3.5×10^{-7}	- 754	- 600
HTC	3.5×10^{-7}	- 718	- 580
HTC + Ce	4.0×10^{-7}	- 764	- 420

The field tests - coupons exposed to IEA-R1 reactor spent fuel section.

The coupons from the different racks were dismantled, rinsed, decontaminated, dried and examined visually and with an optical microscope. The top surfaces of all coupons revealed more pits compared to the bottom facing surface of the same coupon, indicating the influence of settled solids on the top surfaces. Table 6 summarizes the main features observed on the top surfaces of the different coupons from the first set of tests. Overall, the coupons exposed for 12 months were significantly darker, either brown or black, indicating formation of a thicker surface oxide, compared to corresponding coupons exposed for 2 months. A study of the surface features of the different coupons revealed that in general after 12 months of exposure to the spent fuel section of the IEA-R1 reactor, the CeO₂ coated coupons were the most resistant to pitting corrosion. The coupons coated with La₂O₃ and Pr₂O₃ were heavily pitted after just 2 months of exposure. Even though preliminary laboratory tests indicated improved corrosion resistance of La₂O₃ and Pr₂O₃ coated specimens, to the same extent as CeO₂ coated specimens, long term field tests have shown otherwise (10). This could be attributed to formation of only soluble Pr and La hydroxides on the coupon surface, and inability therefore to provide 'active corrosion protection', like that provided by cerium coated coupons.

Table 6 - Surface features of uncoated and lanthanide coated AA 1100 and AA 6061 coupons exposed for 2 and 12 months to the IEA-R1 reactor spent fuel section.

Alloy	Treatment	Surface features after exposure to IEA-R1 spent fuel basin for	
		2 months	12 months
AA 1050	None	Dull, no pits	Dark, stained, some pits
	+ CeO ₂	<i>Yellow bright, no pits</i>	<i>Mostly bright, no pits</i>
	+ La ₂ O ₃	Bright, many pits	Dark, many pits
	Oxidized	Dull, no pits	Dark, few pits
	Oxidized + CeO ₂	<i>Yellow bright, no pits</i>	<i>Dark, few pits</i>
	Oxidized + CeO ₂ conc	Bright, few pits	Dark, many pits
	Oxidized + La ₂ O ₃	Bright, many pits	Brown, many pits
	Oxidized + Pr ₂ O ₃	Bright, many pits	Dark, many pits
AA 6061	None	Dull, no pits	Dark brown, many pits
	+ CeO ₂	<i>Yellow, no pits</i>	<i>Very dark, very few pits</i>
	+ CeO ₂ conc	Light brown, few pits	Dark surface, many pits
	+ La ₂ O ₃	Dull, many pits	Dark surface, many pits
	Oxidized	Almost bright, no pits	Dark, some pits
	Oxidized + CeO ₂	<i>Semi bright, no pits</i>	<i>Dark, few pits</i>
	Oxidized + La ₂ O ₃	Semi-bright, many pits	Dark, many pits
	Oxidized + Pr ₂ O ₃	Semi-bright, many pits	Dark, many more pits

The surface features of the coupons from the second set of field tests are shown in Table 7. It is evident that the boehmite and HTC coated coupons of the two alloys revealed no pits on either side after 9 months of exposure, whereas the untreated coupons revealed many pits of varying size.

Table 7 - Surface features of coupons of the second set exposed to the IEA-R1 reactor spent fuel section for 6 and 9 months.

Alloy	Coating	Surface features after exposure for	
		6 months	9 months
AA 1100	None	Dark, many pits	Dark; Many pits
	HTC	Few stains, no pits.	Few stains, no pits.
	Boehmite	Bright, no pits.	Bright, no pits
	HTC + CeO ₂	Few stains, no pits,	Few stains, no pits.
	Boehmite + CeO ₂	Bright, no pits.	Bright, no pits.
AA 6061	None	Dark, few pits.	Very dark, few pits.
	HTC	Dark, stained, no pits.	Dark, stained, no pits.
	Boehmite	No pits.	No pits.
	HTC + CeO ₂	No pits.	No pits.
	Boehmite + CeO ₂	No pits.	No pits.

General discussion

The laboratory and field tests have indicated the marked increase in corrosion resistance of Al alloys coated with boehmite and HTC. The corrosion resistance was further enhanced by modifying the two types of coatings with cerium dioxide. 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. In this context, protecting 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 by 'active corrosion protection', analogous to chromium coatings. 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 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.

Conclusions

1. Laboratory tests revealed that the pitting corrosion resistance of AA 6061 alloy increased when it was coated with boehmite. Impregnation of the boehmite with Ce increased further the pitting corrosion resistance. Further, the pitting corrosion resistance of HTC coated AA 6061 specimens was higher than those coated with boehmite. Cerium modification of the HTC coating aided pitting corrosion resistance.
2. The first set of field tests revealed that among the 3 rare earths, the CeO₂ coated coupons were the most resistant to pitting corrosion after 12 months of exposure to the spent fuel section of the IEA-R1 reactor.
3. Hydrotalcite (HTC) coatings on AA 1100 and AA 6061 alloys could be prepared from nitrate baths at 95 °C and carbonate baths at room temperature.
4. The cerium modified HTC and boehmite coatings increased markedly the pitting resistance of the two alloys.
5. Coupons of the two types of alloys coated with boehmite and HTC when exposed to the IEA-R1 reactor spent fuel section for 9 months did not reveal any pits whereas the uncoated coupons of the two alloys revealed many pits.
6. Coating HTC on Al alloys from carbonate baths at room temperature followed by cerium modification from a nitrate bath, also at room temperature, is a simple process that can be tailored and scaled-up to protect radioactive spent Al-clad RR fuel assemblies for long term wet storage.

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