

COATINGS FOR INCREASED CORROSION RESISTANCE OF ALUMINIUM-CLAD SPENT FUEL IN WET STORAGE

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ABSTRACT

Corrosion protection of spent RR fuel for long term wet storage was considered important, primarily from the safety standpoint and the use of conversion coatings was proposed in 2008. This paper presents the results of: (a) on-going field tests in which un-coated, boehmite, hydrotalcite (HTC) and cerium modified boehmite as well as HTC coated Al alloy coupons were exposed to the IEA-R1 reactor spent fuel basin for durations of up to 9 months; (b) HTC coating preparation at room temperature; (c) evaluation of corrosion resistance of aluminium alloy AA 1100 and AA 6061 specimens coated with different types of boehmite and HTC. In the field studies the HTC coated coupons were the most corrosion resistant. The cerium modified HTC coated specimens showed marked increase in pitting corrosion resistance, both in laboratory and the field tests, indicating its potential for use as a protective coating of spent Al-clad RR fuels.

1. Introduction

Most of the wet storage facilities for spent aluminium-clad research reactor (RR) fuel have water quality management programmes, to prevent and/or reduce degradation of the fuel cladding. Pitting corrosion has been identified as the main form of degradation that could cause 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 aluminium 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 aluminium 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 laboratory and field investigations carried out at IPEN in Brazil, revealed that cerium hydroxide coating increased the corrosion resistance of Al alloys [7,8]. 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 aluminium-nitrate-hydroxide hydrate and it forms on Al alloys immersed in an appropriate alkaline lithium salt solution [9]. Immersion of Al alloys in such solutions result 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 coating were prepared from solutions at 95 °C.

This paper presents the results of: (a) field studies in which uncoated, 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 6 and 9 months; (b) HTC coating preparation from different aqueous solutions; (c) evaluation of corrosion resistance of aluminium alloy AA 1100 and AA 6061 specimens coated with different types of boehmite and HTC.

2. Methods and materials

Aluminium alloys AA 1100 and AA 6061 (Table 1) were used in the laboratory and field tests. The field test procedure consisted of preparing Al alloy coupons, stacking the coupons in racks, immersion of the racks in the spent fuel section of the IEA-R1 research reactor in IPEN, Brazil, for 6 and 9 months, removal of the racks followed by disassembly and examination of the coupons [1].

Tab 1. Chemical composition of aluminium 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

Coupons 10 cm in diameter and 3 mm thick of the two alloys were treated by immersion in solutions and under conditions shown in table 2. The coupon stacking sequence in the racks from top to bottom consisted of untreated, HTC coated, boehmite coated, HTC-Ce coated and boehmite-Ce coated. The surface features of the uncoated and coated coupons exposed for 6 and 9 months were examined with an optical microscope.

Tab 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.

In the laboratory tests HTC coatings were deposited on AA 1100 and AA 6061 specimens from solutions 5, 6 and 7 of Table 2. The composition, morphology and extent of corrosion protection provided by these coatings to the substrate were determined. The electrochemical behaviour of uncoated and coated specimens was determined from anodic potentiodynamic polarization measurements 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. Some of the HTC coated specimens were further treated by immersion in solution 8 of Table 2 to incorporate cerium.

3.Results and discussion

3.1 Laboratory tests

The main features of the coatings formed from the different solutions are summarized in Table 3. 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 [9]. 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 ~2 μm .

Tab 3. Aluminium alloy surface features following treatment in different solutions. (vide table 2 for solution composition; RT – room temperature)

Alloy AA	Coating solution and conditions			Surface features
	Solution	$^{\circ}\text{C}$	Main anion	
1100	5	95	NO_3	HTC forms – well defined crystallites
6061	5	95	NO_3	HTC forms and Mg_2Si detected
1100	6	RT	CO_3	HTC forms and surface etched
6061	6	RT	CO_3	HTC and Mg_2Si detected
1100	7	95	$\text{NO}_3 + \text{S}_2\text{O}_8$	No HTC
6061	7	95	$\text{NO}_3 + \text{S}_2\text{O}_8$	No HTC, Mg_2Si detected
1100	5 + 8	RT + RT	$\text{CO}_3 + \text{CeO}_2$	HTC forms and surface etched
6061	5 + 8	RT + RT	$\text{CO}_3 + \text{CeO}_2$	HTC forms and surface etched.

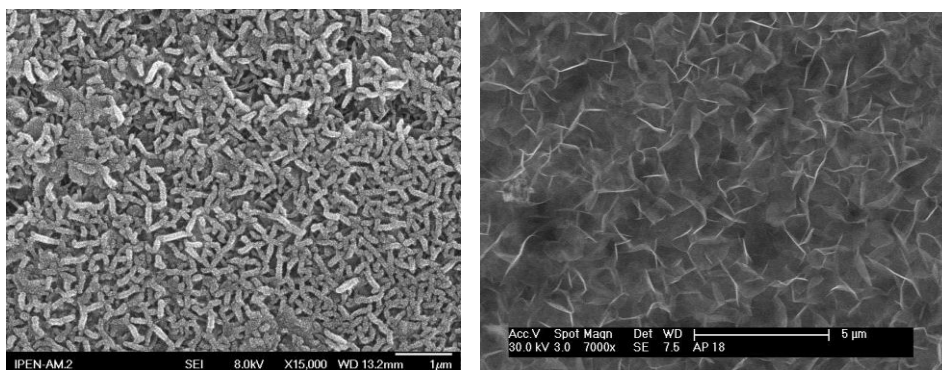


Fig 1. Micrographs of: (a) HTC on AA 6061 from NO_3 solution at 95°C
 (b) HTC on AA 1100 from CO_3 solution at RT + Ce impregnation

The electrochemical behaviour alloy AA 6061, with or without the coatings revealed differences in the anodic as well as the cathodic polarization curves. Table 4 summarizes the corrosion potential (E_{corr}), 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.

Tab 4. 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} (mA.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

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

The coupons were removed from the racks, rinsed, decontaminated, dried and examined visually and 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.

Tab 5. Surface features of coupons exposed to the IEA-R1 reactor spent fuel section.

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.

The main features of the coupons exposed for 6 and 9 months to IEA-R1 spent fuel basin is summarized in table 5. 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 to the spent fuel section of the IEA-R1 reactor, where as the untreated coupons revealed many pits of varying size.

4. 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 considered to be '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.

5. Conclusions

1. Hydrotalcite (HTC) coatings on AA 1100 and AA 6061 alloys were prepared from nitrate baths at 95 °C and carbonate baths at room temperature.
2. The cerium modified HTC and boehmite coatings increased markedly the pitting resistance of the two alloys.
3. 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.
4. 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.

6. References

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