CONVERSION COATINGS TO PROTECT Al-CLAD SPENT FUEL IN WET STORAGE

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ABSTRACT

Protection of spent research reactor (RR) fuel with conversion coatings was proposed in 2007 and laboratory as well as field studies carried out. Preliminary results revealed increased pitting corrosion resistance of cerium oxide coated aluminium alloys AA 1050 and AA 6061, used as RR fuel plate cladding. Further development of conversion coatings for Al alloys was carried out and this paper presents: (a) the preparation and characterization of hydrotalcite coatings from different baths followed by post-coating treatments; (b) results of laboratory immersion tests and electrochemical measurements in NaCl solutions; (c) results of field tests in which un-coated, boehmite coated, high temperature hydrotalcite (HTC – HT) coated, low temperature hydrotalcite (HTC – LT) coated and cerium modified boehmite / hydrotalcite coated AA 1050 and AA 6061 coupons were exposed to the IEA-R1 reactor spent fuel basin for up to 5 months. The immersion and polarization measurements revealed that specimens coated with HTC – HT and modified with Ce were the most resistant to pitting. The field tests further confirmed that coupons that were HTC – HT coated and modified with cerium did not reveal any pits after 5 months of exposure to the spent fuel basin.

1. Introduction

Pitting corrosion of the aluminium cladding has been identified as the main form of degradation that could cause failure and release of fissile material into storage facilities. One of the main conclusions of three IAEA coordinated research projects on corrosion of spent research reactor (RR) fuel in storage facilities was due to synergism in basin water parameters that affected pitting corrosion of aluminium and its alloys. [1,2] Hence, it was considered imperative that some form of corrosion protection be given to spent RR fuel in storage. Conversion coatings have been extensively used in many industries to control the corrosion of various metals. Rare earth compounds have been used to inhibit aqueous corrosion of aluminium alloys [3]. Chemical treatments have been also 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. [9-11] The results of the extended investigations revealed that HTC imparted marked improvements in pitting corrosion resistance. [12] Further studies were carried out recently to obtain HTC coatings from baths at different temperatures followed by post-treatments.

This paper presents the results of: (a) HTC and boehmite coating preparation and post treatments; (b) immersion tests in which pitting behavior of coated specimens was evaluated in NaCl solutions; (c) electrochemical measurements on uncoated and coated specimens in NaCl solutions; (d) field tests in which uncoated and coated (with boehmite; HTC; cerium modified boehmite; cerium modified HTC; cerium modified and sealed boehmite/HTC) Al alloy coupons were exposed to the IEA-R1 reactor spent fuel basin for 3 and 6 months.

2. Methods and materials

Aluminium alloys AA 1050 (commercially pure aluminium) and AA 6061 were used in the laboratory and field tests. The aluminium alloy specimens and coupons for the laboratory and the field tests respectively were treated to coat their surfaces with either boehmite or hydrotalcite (HTC) by immersion in solutions and under conditions shown in tab.1. Two types of laboratory tests were carried out. In the first, specimens 10mmx10mm of AA 6061 with or without coatings were immersed in 0.01 M and 0.1 M NaCl for 5, 10, 15 and 30 days and their surfaces examined after rinsing and drying.

Tab 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 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 – HT	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 – LT	0.1M Li_2CO_3; LiOH; Al; pH 12; 15 min; R.T.
7	Incorporate Ce in HTC	10 g/L Ce $(NO_3)_3$; 30% H_2O_2; R.T.; 5 min.
8	Sealing	$MgC_4H_6O_4$; 82 °C; 15 min.

Tab. 2. Identification of the laboratory test specimens

Specimen identification	Surface coated with and post treatment
RC-0	Uncoated
RC-1	Boehmite
RC-2	Boehmite + Ce (solution 4)
RC-3	Boehmite + Ce (solution 7)
RC-4	HTC – HT
RC-5	HTC – HT + Ce (solution 7)
RC-6	HTC – LT
RC-7	HTC – LT + Ce (solution 7)
RC-8	HTC – HT + sealed
RC-9	HTC – LT + sealed

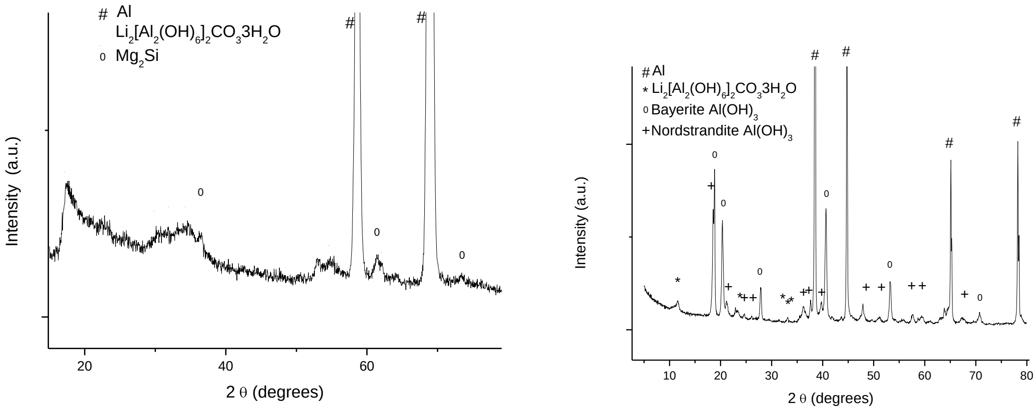
The second laboratory test consisted in determining the electrochemical behaviour of uncoated and coated specimens. In this test, anodic potentiodynamic polarization measurements were carried out with a standard 3-electrode arrangement in 0.01 M NaCl, using a saturated calomel reference electrode and a platinum counter electrode. The potential was scanned from - 0.3 V to +1.0 V at 0.1 mV/s. Tab. 2 shows the i.d. of specimens used in the electrochemical tests.

The field test procedure consisted of preparing Al alloy coupons 10 cm in diameter and 3 mm thick, stacking of the coupons in racks, immersion of the racks in the spent fuel section of the IEA-R1 research reactor in IPEN, Brazil, for 3 and 6 months, removal of the racks followed by disassembly and examination of the coupons with an optical microscope coupled to an image analyzer [1].

3.Results and discussion

3.1 Laboratory tests

Preliminary tests were carried out in which specimens of the alloys were immersed in two types of lithium salt solutions (solutions 5 and 6 in Tab. 1). The surfaces of these specimens were examined in a scanning electron microscope and the coatings formed identified by x-ray diffraction analysis. Fig.1 shows the x-ray diffraction spectra of the surfaces of AA 6061 treated in solution 5 at 98 °C (Fig.1a) and on AA 1050 treated in solution 6 at RT (Fig.1b). The spectra revealed the formation of hydrotalcite. The thickness of the coating formed from solution 5 was adequate to detect HTC using grazing angle diffraction. However, to detect the coating formed from solution 6, which was very thin, AA 1050 powder was treated under identical conditions and studied by XRD and results of this analysis, shown in Fig 1b, also revealed the formation of HTC. The morphology of HTC formed from solutions 5 and 6 are shown in figure 2. The surfaces revealed intersecting blade like HTC crystallites that formed a continuous layer across the surface. The coatings formed inside the pits and recesses that developed during pre-treatment of the substrate. Typical coating thickness after 10 minutes of immersion was ~2 µm. 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.



(a)

(b)

Fig. 1. X-ray diffraction spectra: (a) AA 6061 surface (Cr-Kα); (b) AA 1050 powder (Cu-Kα), indicating formation of hydrotalcite ($Li_2[Al_2(OH)_6]_2CO_3$ $3H_2O$).

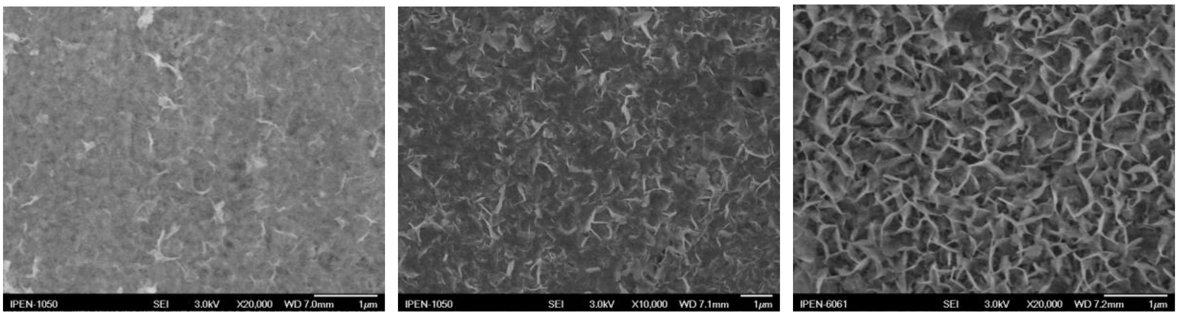


Fig 2. Scanning electron micrographs of: (a) HTC – LT on AA 1050;
(b) HTC – HT on AA 1050; (c) HTC – HT on AA 6061.

The immersion test results are summarized in Tab. 3. The objective of this test was to determine the extent to which the different coatings are resistant to extremely aggressive environment. The two NaCl solutions, in terms of its chloride ion concentration, compared to that in normal spent fuel basin water, are 4 and 5 orders of magnitude higher. All the coatings revealed some pits after 15 days exposure to the more aggressive solution. Overall, it is evident that HTC – HT, formed from the high temperature bath, was more protective than boehmite or HTC – LT (from the room temperature bath). Modification of the HTC – HT with Ce further increased protective properties.

Tab. 3. Results of tests in which AA 6061 specimens were immersed in 0.01 M and 0.1 M NaCl for 5, 10, 15 and 30 days.

Coating	**Observations**
Boehmite	No pits after 5 and 10 days in NaCl of either concentration. Few pits in 0.1 M NaCl.
Boehmite + Ce	Few small pits in 0.01 M NaCl, that increased in number with duration. In 0.1 M NaCl, large pits after 5 days that increased in number and size with time.
HTC – HT	No pits after 5 and 10 days. Few pits after 15 days in 0.1 M NaCl.
HTC – HT + Ce	Some pits after 15 and 30 days in both NaCl solutions. Increased with concentration and duration.
HTC – LT	Many pits, in both solutions and increased in number and size with duration.
HTC – LT + Ce	Fewer pits compared to HTC – LT.
HTC – HT + sealed	Very few tiny pits after 30 days in 0.01 M NaCl even after 30 days. Many pits in 0.1 M NaCl that increased with duration.
HTC – LT + sealed	Many small pits in 0.01 M NaCl, increased in number with NaCl concentration and duration.

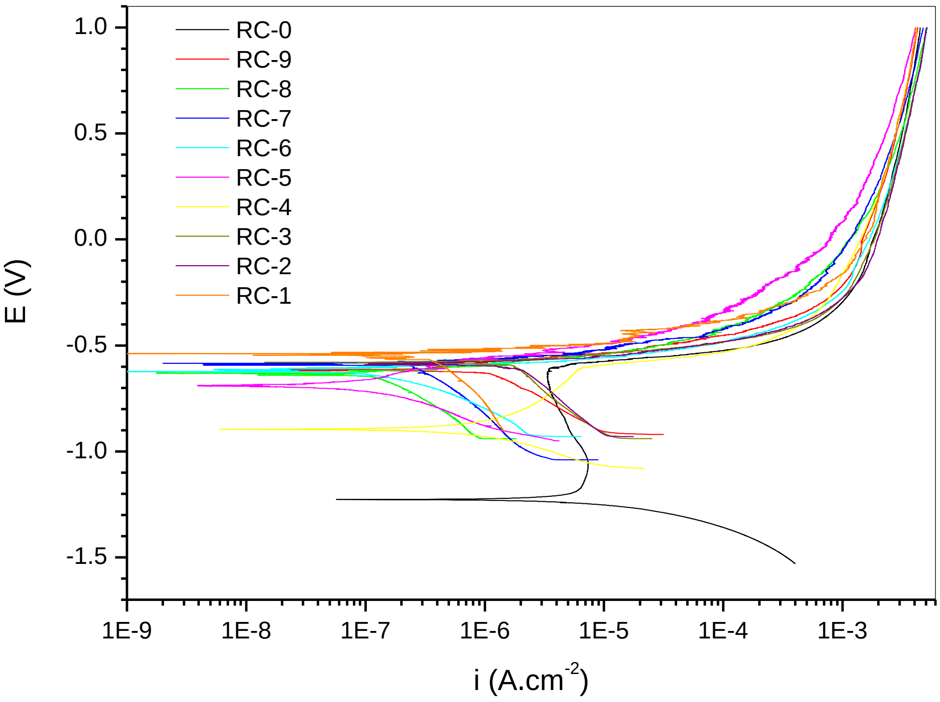


Fig. 3. Potentiodynamic polarization curves of uncoated and coated AA 6061 specimens in 0.01 M NaCl at room temperature and at scan rate of 0.1 mV/s.

The anodic polarization data shown in Fig. 3 and in Tab. 4. clearly indicate 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) to more anodic values. Even though the untreated specimen (RC-0) revealed a distinct passive region, the OCP of the coated specimens were close to the breakaway (pitting potential) of RC-0.

Tab.4. The corrosion potential E_{corr}, corrosion current I_{corr} and breakdown potentials E_b, as determined from the electrochemical polarization measurements. (Breakdown potential was determined only for curves in figure 2 that showed breakdown of passivity)

Specimen	**I_{corr} (μA.cm^{-2})**	**E_{corr} (V)**	**E_b (V)**
RC-0	6.120	-1.23	-0.59
RC-1	0.327	-0.54	-
RC-2	1.749	-0.59	-
RC-3	1.694	-0.58	-
RC-4	0.972	-0.90	-0.59
RC-5	0.085	-0.69	-0.56
RC-6	0.141	-0.62	-
RC-7	0.284	-0.60	-
RC-8	0.134	-0.63	-
RC-9	0.998	-0.61	-

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 compared to those observed on coupons prior to exposure to the IEA-R1 research reactor spent fuel section

Alloy	Coating	Surface features after exposure for	
		3 months	5 months
AA 1050	None	Stained with oxide	Few pits
	Boehmite	No difference	One pit
	Boehmite + Ce	No difference	Many pits
	HTC – HT	No difference	No difference
	HTC – HT + Ce	No difference	No difference
	HTC – HT + selaed	No difference	No difference
	HTC – HT + Ce + sealed	No difference	No difference
	HTC – LT	No difference	Stained + few pits
	HTC – LT + Ce	Few pits	Stained + few pits
	HTC – LT + sealed	Few pits	Stained + few pits
	HTC – LT + Ce + sealed	No difference	Stained but no pits
AA 6061	None	Many pits	Stained and one pit
	Boehmite	No difference	Many tiny pits
	Boehmite + Ce	No difference	Few pits
	HTC – HT	No difference	No difference
	HTC – HT + Ce	No difference	No difference
	HTC – HT + sealed	No difference	No difference
	HTC – HT + Ce + sealed	No difference	No difference
	HTC – LT	No difference	Dark and some pits
	HTC – LT + Ce	No difference	Dark and some pits
	HTC – LT + sealed	No difference	Very dark and one pit
	HTC – LT + Ce + sealed	No difference	Very dark + two pits

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 Tab. 5. The untreated coupons of AA 1050 and AA 6061 revealed staining and many pits respectively. After 3 months of exposure, the HTC – LT coated AA 1050 revealed pits where as the AA 6061 did not. Coupons of both alloys coated with HTC – LT, with or without post treatments revealed pitting. The HTC – HT coated coupons of the two alloys, with or without post treatments revealed no pits on either side after 3 and 5 months of exposure.

4. General discussion

The laboratory and field tests have indicated the marked increase in corrosion resistance of Al alloys coated with HTC – HT. The corrosion resistance was further enhanced by modifying the coating with cerium dioxide. Sealing of the coatings in magnesium acetate also improved pitting corrosion resistance of HTC – HT coated specimens and coupons. 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. Presently, the extent to which HTC – LT imparts protection is lower than that imparted by HTC – HT. Attempts are in progress to increase the HTC – LT layer thickness to increase its protection efficiency. Nonetheless, protecting spent fuel 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 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.

5.Conclusions

1. Hydrotalcite (HTC) coatings on AA 1050 and AA 6061 alloys were prepared from nitrate baths at 98 °C and carbonate baths at room temperature.
2. HTC formed from nitrate bath at 98 °C increased pitting reistance more than HTC formed from carbonate bath at room temperature.
3. The cerium modified HTC and boehmite coatings increased markedly the pitting resistance of the two alloys.
4. Sealing of cerium modified boehmite and HTC coatings further increased pitting corrosion reistance of the two alloys.
5. Coupons of the two types of alloys coated with HTC – HT when exposed to the IEA-R1 reactor spent fuel section for 5 months did not reveal any pits, indicating its potential for use as a protective coating on spent RR fuel.

6.References

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