

HYDROTALCITE COATINGS FOR INCREASED AQUEOUS CORROSION RESISTANCE OF ALUMINIUM ALLOYS

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ABSTRACT

Hydrotalcite (HTC) is lithium aluminium-nitrate-hydroxide hydrate and it forms on Al alloys immersed in an appropriate alkaline lithium salt solution. HTC coatings on aluminium alloys AA 1100 and AA 6061 have been prepared from various solutions at different temperatures and its morphology, composition and distribution studied. The corrosion behaviour of HTC coated AA 6061 and AA 1100 in NaCl solutions has been determined and compared with boehmite coated Al alloys. Field tests were carried out in which uncoated, 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 6 and 9 months. All the coatings increased the pitting corrosion resistance of the two alloys and among these, the cerium modified HTC coating was the most efficient.

Key words: Corrosion, aluminum alloys, conversion coating, hydrotalcite, boehmite.

INTRODUCTION

Wet storage facilities for spent aluminium-clad research reactor (RR) fuel often have water quality management programs, to prevent and/or reduce degradation of the fuel cladding. Pitting corrosion is the main form of degradation. 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, corrosion protection of some form is essential for stored spent RR fuel. Conversion coatings have been extensively used

in many industries to control the corrosion of various metals. Rare earth compounds have been also used in corrosion protection systems for aluminium alloys ⁽³⁾. Since cerium hydroxide films form 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 coatings 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. HTC is lithium aluminium-nitrate-hydroxide hydrate and it forms on Al alloys immersed in an appropriate alkaline lithium salt solution ⁽⁹⁾. 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 aluminium 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 6 and 9 months.

METHODS AND MATERIALS

Aluminium 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 x 2 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. 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 field emission 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.

Table 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

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 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. Circular coupons 10 cm in diameter and 3 mm thick of the two alloys were coated with boehmite and HTC using solutions 4 and 5 in Table 2 after appropriate pretreatments, also shown in the same table. The coupons were exposed for 6 and 9 months and then their surfaces were examined with an optical microscope.

RESULTS AND DISCUSSION

The surfaces of the coupons treated in solutions 5 and 6 were analyzed using the grazing angle x-ray diffraction technique. The spectrum of the AA 6061 coupon surface treated in solution 5 at 98 °C and Al powder treated in solution 6 at R.T. are shown in figure 1. The various peaks corresponding to HTC are evident in both the spectra, besides the Al and Mg₂Si peaks on AA 6061. 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. 2. 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.

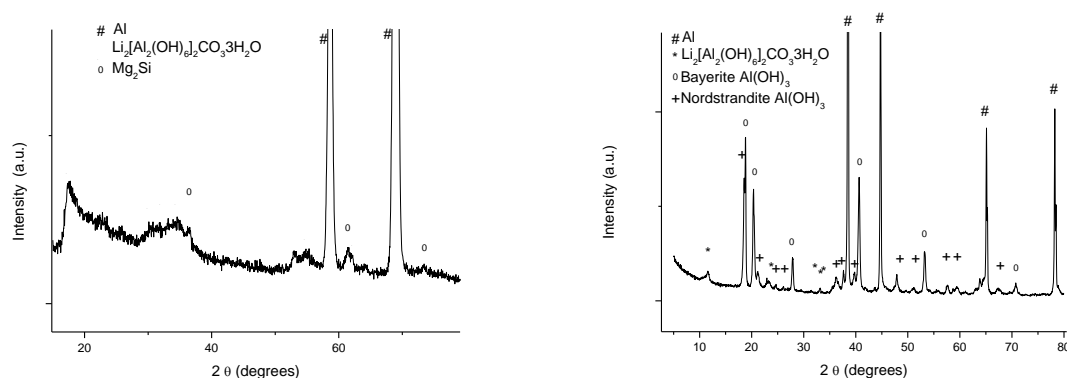


Figure 1. X-ray diffraction spectrum of: (left) AA 6061 treated in solution 5 of table 2 and using Cr K α radiation; (right) AA 1100 powder treated in solution 6 of table 2 and using Cu K α radiation.

The electrochemical behaviour alloy AA 6061, with or without the coatings revealed differences in the anodic as well as the cathodic polarization curves. Table 3 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.

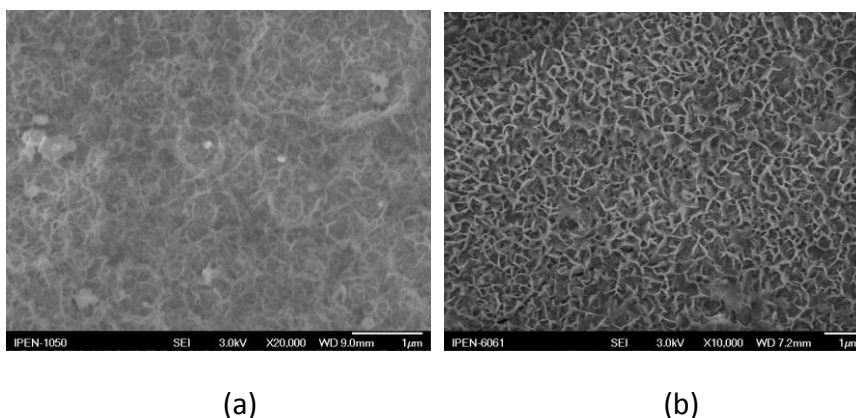


Figure 2. Micrographs of HTC on (a) AA 1050 at RT; (b) AA 6061 at HT.

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, formed from solution 5 of table 2, 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 3. 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

Table 4. Surface features of coupons from the second set of tests after exposure 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 surface features of the coupons are shown in Table 4. 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, where as the untreated coupons revealed many pits of varying size.

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. 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 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.

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. 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.
3. The cerium modified HTC and boehmite coatings increased markedly the pitting resistance of the two alloys.
4. 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.
5. 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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