CERIUM MODIFIED CONVERSION COATINGS TO PROTECT ALUMINUM CLADDING OF SPENT NUCLEAR FUEL DURING EXTENDED WET STORAGE[1]

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Abstract

Pitting of Al-clad spent nuclear fuel in wet storage facilities could lead to cladding breach and contamination. Maintenance of water parameters within specified limits does not prevent pitting due to synergism between many water parameters that affect corrosion of aluminum alloys. Five types of coatings for Al alloys have been studied: (i) lanthanide oxides (Ce, La and Pr); (ii) boehmite; (iii) cerium modified boehmite; (iv) hydrotalcite (HTC); (v) cerium modified HTC. This paper will present: (a) preparation of and characteristics of the these coatings on alloys AA 1100 and AA 6061; (b) corrosion resistance of coated alloys in NaCl solutions; (c) results of field tests in which un-coated and coated Al alloy coupons were exposed to a spent fuel storage basin for a year. The cerium modified HTC coatings imparted the highest corrosion resistance. The mechanism of corrosion protection of Al alloys by these coatings and the role of cerium is discussed.

Key words: Cerium; Conversion coating; Aluminum alloys; Corrosion.

RECOBRIMENTOS DE CONVERSÃO MODIFICADOS COM CÉRIO PARA PROTEGER REVESTIMENTO DE ALUMÍNIO DE COMBUSTIVEL NUCLEAR DURANTE ESTOCAGEM ÚMIDA E PROLONGADA

Resumo

Corrosão por pite do revestimento de Al de combustiveis nucleares queimados durante estocagem pode contaminar as facilidades de estocagem. A manutenção da qualidade da água não evita corrosão devido sinergismo entre parâmetros da água que afetam a corrosão de alumínio. Foram estudados cinco tipos de recobrimentos de conversão para Al; (i) óxidos lantanidios (de Ce, La, Pr); (ii) boemita; (iii) beomita modificada com cério; (iv) hidrotalcita (HTC); e (v) HTC modificada com cério. Este trabalho apresenta: (a) preparação e caracterização destes recobrimentos sobre ligas AA 1100 e AA 6061; (b) resistência à corrosão em NaCl destas ligas recobertas; e (c) resultados de ensaios de campo, nos quais cupons de Al, sem e com recobrimentos, foram expostos na seção de estocagem de combustíveis queimados do reator IEA-R1 por um ano. HTC modificada com cério foi o melhor entre o recobrimento. O mecânismo de proteção de Al por estes recobrimentos é discutido.

Palavras-chave: Cério; Recobrimento de conversão; Ligas de alumínio; Corrosão.

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1 INTRODUCTION

Storage facilities like basins, pools or ponds for spent aluminum-clad research reactor (RR) fuels usually have water quality control programs to prevent pitting corrosion of the cladding. This form of corrosion often leads to release of fissile material and contamination of the storage facilities. Maintenance of storage facility water parameters within specified limits, although efficient, has been shown to reduce but not prevent pitting corrosion of the fuel cladding, due to synergism between different water parameters that affect corrosion of aluminum and its alloys.(1,2) Hence, some form of corrosion protection of spent RR fuel was considered imperitive. Use of conversion coatings is a well-established corrosion control technique and is used extensively. Rare earth compounds have been used in corrosion protection schemes for aluminum alloys.(3) Having observed cerium hydroxide films on Al alloys that were 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 revealed that cerium hydroxide coating increased the corrosion resistance of Al alloys.(7,8) The investigations were subsequently extended to include boehmite, and hydrotalcite (HTC) coatings. Inclusion of 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.(9) Immersion of Al alloys in this solution results in formation of a polycrystalline barrier film composed mainly of HTC like compounds. These studies were further extended to include cerium modified boehmite and cerium modified HTC coatings on Al alloy surfaces. Recently, studies were also carried out to obtain HTC coatings at room temperature to facilitate the process to coat spent fuels.

This paper presents: (a) HTC coating preparation from different aqueous solutions; (b) the corrosion resistance of aluminum alloys AA 1100 and AA 6061 specimens coated with different types of boehmite and HTC in NaCl solutions; (c) results of 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 months and 9 months.

2 METHODS AND MATERIALS

Aluminum alloys AA 1100 and AA 6061 (Table 1) were used in all the tests. In the laboratory tests, the Al alloy specimens 2 x 2 x 0.2 cm were degreased and deoxidised in solutions 1 and 2 respectively of Table 2 and then boehmite or HTC coated in solutions 5, 6 and 7. The boehmite and HTC coatings on some specimens were modified by treatment in solutions 4 and 8 respectively. The composition of the coatings was determined by x-ray diffraction analysis and the morphology examined in a scanning electron microscope coupled to an energy dispersive spectrometer. The corrosion resistance of the coated Al alloy specimens in 0.1 M NaCl was determined from anodic potentiodynamic polarization measurements carried out with a standard 3-electrode arrangement.

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_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°C-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_2CO_3; LiOH; Al; pH 12; 15 min; R.T.
7	Form HTC	6.9 g/L $LiNO_3$; 28.3 g/L KNO_3; 2.4 g/L LiOH; 2.5 g/L $K_2S_2O_8$; 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_2O_2; R.T.; 5 min

The field tests consisted of preparing circular 10 cm Ø and 3 mm thick 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.(2) Two sets of field tests were carried out. In the first set, coupons 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 of Table 3 that was altered according to the type of rare earth ion.(10) 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 months 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 shown in Table 2 after appropriate pretreatments. The coupon stacking sequence in racks 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 months and 9 months and then their surfaces were examined.

Table 3. Composition of solutions and treatment conditions

Treatment conditions	Solution	
	1	2
Composition	0.5 M H_2SO_4 1.28 M HNO_3 0.05 M $Ce(SO_4)_2$ 0.04 M HF 0.1 M $(NH_4)_2SO_4$ 1 litre	0.035 M $RECl_3$ 0.12 M H_2O_2 1mM Cu (glycinate) 1 mM $Ti(O_2)^{2+}$ 1 litre pH 2.0
Temperature (°C)	35	45
Duration (minutes)	10	5

3 RESULTS AND DISCUSSION

3.1 Laboratory Tests

The main features of the coatings formed from the different solutions of Table 2 are summarized in Table 4. 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 also 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 Figure 1. Below the outer layer a dense layer of amorphous or nanocrystaline lithium aluminate formed.(9) The coating thickness varied with the type of alloy, bath (composition, age) and immersion time. Typical coating thickness after 10 minutes of immersion was ~2 µm.

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_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	$NO_3 + S_2O_8$	No HTC
6061	7	95	$NO_3 + S_2O_8$	No HTC, Mg_2Si 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

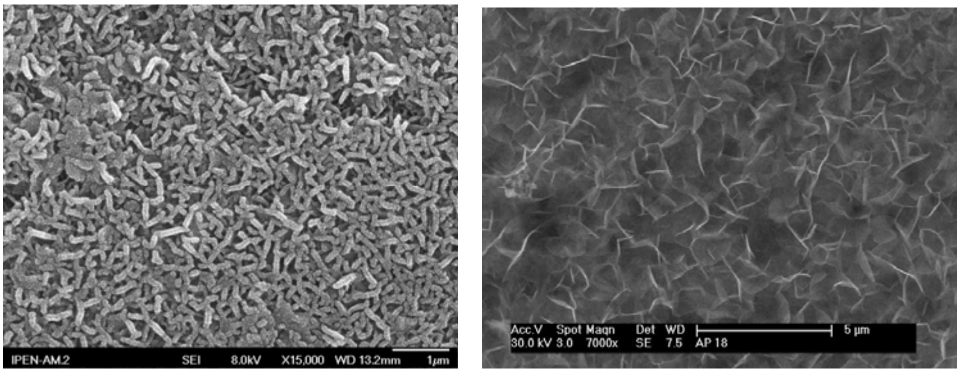

Figure 1. Micrographs of: (a) HTC on AA 6061 from NO_3 solution at 95°C; (b) HTC on AA 1100 from CO_3 solution at RT + Ce impregnation.

The electrochemical behaviour alloy AA 6061, with or without the coatings revealed differences in the anodic and cathodic polarization curves. Table 5 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 when boehmite coated, the E_{pit} increased to -650 mV. Cerium modification of the boehmite increased E_{pit} even more to -600 mV, indicating increased pitting corrosion resistance upon introduction of Ce. With a HTC layer on the alloy surface the pitting resistance increased even more and E_{pit} increased from -750 mV to -580 mV. The 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} (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 Field Tests

The coupons from the different racks were dismounted, 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.

Table 6. Surface features of uncoated and lanthanide coated AA 1100 and AA 6061 coupons exposed for 2 months 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	*Yellow bright, no pits*	*Mostly bright, no pits*
	+ La_2O_3	Bright, many pits	Dark, many pits
	Oxidized	Dull, no pits	Dark, few pits
	Oxidized + CeO_2	*Yellow bright, no pits*	*Dark, few pits*
	Oxidized +CeO_2 conc	Bright, few pits	Dark, many pits
	Oxidized + La_2O_3	Bright, many pits	Brown, many pits
	Oxidized + Pr_2O_3	Bright, many pits	Dark, many pits
AA 6061	None	Dull, no pits	Dark brown, many pits
	+ CeO_2	*Yellow, no pits*	*Very dark, very few pits*
	+ CeO_2 conc	Light brown, few pits	Dark surface, many pits
	+ La_2O_3	Dull, many pits	Dark surface, many pits
	Oxidized	Almost bright, no pits	Dark, some pits
	Oxidized + CeO_2	*Semi bright, no pits*	*Dark, few pits*
	Oxidized + La_2O_3	Semi-bright, many pits	Dark, many pits
	Oxidized + Pr_2O_3	Semi-bright, many pits	Dark, many more pits

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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 CeO_2 coated coupons were the most resistant to pitting corrosion. The coupons coated with La_2O_3 and Pr_2O_3 were heavily pitted after just 2 months of exposure. Even though preliminary laboratory tests indicated improved corrosion resistance of La_2O_3 and Pr_2O_3 coated specimens, to the same extent as CeO_2 coated specimens, long term field tests have shown otherwise.(4) This is attributable to formation of soluble Pr and La hydroxides on the coupon surface, and inability therefore to provide ‘active corrosion protection’, like cerium to the coupons. 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, where 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 months 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.

4 GENERAL DISCUSSION

The laboratory and field tests have indicated a marked increase in corrosion resistance of Al alloys coated with boehmite and HTC. The corrosion resistance increased even more with modification of the two types of coatings with cerium dioxide. Protection of Al-clad spent RR fuels during long term wet storage with a coating of cerium modified HTC would be facilitated if treatments could be carried out at room temperature. In this context the use of a carbonate bath for HTC coating and its modification with cerium from a nitrate bath would be the right option. 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.

5 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 a nitrate bath at 95°C and a carbonate bath 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 a carbonate bath 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 spent Al-clad fuels for long term wet storage.

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