

PROTECTIVE COATINGS FOR WET STORAGE OF ALUMINIUM-CLAD SPENT FUEL

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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 and lanthanide-based conversion coated Al alloy coupons were exposed to the IEA-R1 reactor spent fuel basin for durations of up to a year; (b) preparation of cerium modified hydrotalcite coatings and cerium sealed boehmite coatings on AA 6061 alloy; (c) corrosion resistance of coated specimens in NaCl solutions. The field studies indicated that the oxidized and cerium dioxide coated coupons were the most corrosion resistant. The cerium modified hydrotalcite and cerium sealed boehmite coated specimens showed marked increase in pitting corrosion resistance.

1. Introduction

It is well known that over 62,000 Al-clad research reactor spent fuel assemblies are stored in wet facilities around the world. [1] Most of the storage facilities have water quality management programmes, to prevent and/or reduce degradation of the fuel cladding. Pitting corrosion is the main form of degradation which could breach the cladding and release fissile material, contaminating thereby storage facilities as well as other stored fuels. 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. [2-4] Therefore it is important to consider some form of corrosion protection for stored spent RR fuel. Use of conversion coatings is a well established corrosion control technique in many industries.

Formation of cerium hydroxide films on Al alloys immersed in solutions containing cerium compounds as inhibitors has led to the development of rare earth based conversion coatings on Al alloys, mainly to substitute hexavalent chromium, a known human carcinogen. [5-9] Use of conversion coatings, to protect spent research reactor fuel assemblies, was proposed in 2007 and laboratory as well as field investigations carried out at IPEN in Brazil. Preliminary results revealed that the pitting corrosion resistance of aluminium alloys AA 1100 and AA 6061, used as cladding of RR fuel plates or elements, increased when coated with lanthanide-based compounds. [4, 10] These investigations were subsequently extended to include cerium modified boehmite and hydrotalcite coatings on Al alloy surfaces. Inclusion of cerium impregnated with boehmite was motivated by the fact that a thick layer of boehmite forms on spent fuel surfaces. Hydrotalcite (HTC) is lithium aluminium-nitrate-hydroxide hydrate (a form of talc) and it forms on Al alloys, when the alloy is immersed in an appropriate alkaline Li salt solutions. [11-13]. Immersion of Al alloys in such solutions result

in formation of a polycrystalline barrier film composed mainly of HTC like compounds. The main advantage of this coating process is its simplicity.

This paper presents the results of: (a) on-going field tests in which uncoated and lanthanide-based conversion coated Al alloy coupons were exposed to the IEA-R1 reactor spent fuel basin for durations of up to a year; (b) the formation of and the corrosion resistance of cerium modified hydrotalcite coatings and cerium sealed boehmite coatings on AA 6061.

2. Methods and materials

Aluminium alloys AA 1100 and AA 6061 (Table 1) were used in the first set of laboratory and exposure tests. However, only AA 6061 was used to study boehmite and hydrotalcite (HTC) coatings. Details of specimen and coupon preparation, surface treatment, application of lanthanide coatings and laboratory corrosion testing in the first set of experiments can be found elsewhere. [4]

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

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 2 and 12 months, 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". [2] Circular coupons 10 cm in diameter and 3 mm thick of the two alloys were coated with oxides of cerium, lanthanum, praseodymium and an oxide concentrate of cerium. [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 surface features of AA 1050 and AA 6061 coupons exposed for 2 and 12 months were examined, both visually and with an optical microscope.

Table 2. Aqueous solutions, their composition and experimental conditions used to prepare and to coat AA 6061 specimens.

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 minutes.
2	Deoxidize	10% HNO ₃ ; 3% NaBrO ₃ ; 55 °C; 3 minutes.
3	Form boehmite	Deionized water; 97-100° C; 5 minutes.
4	Incorporate Ce in boehmite	0.1% CeCl ₃ ; 97 °C; pH 4; 5 minutes.
5	Incorporate Ce, Li and Al in boehmite	0.1% CeCl ₃ ; 1% LiNO ₃ ; 1% AlNO ₃ ; 97 °C; pH-4; 5 minutes.
6	Form hydrotalcite	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 minutes.
7	Incorporate Ce in hydrotalcite	10 g/L Ce (NO ₃) ₃ ; 30% H ₂ O ₂ ; room temperature.

To prepare boehmite and HTC coatings, AA 6061 specimens (2 x 2 x 0.2 cm) were first degreased in solution 1 and deoxidized in solution 2, under conditions shown in Table 2. The specimens were then boehmite or HTC coated by immersion in solutions 3 or 6 respectively.

HTC formed on a specimen surface is shown in figure 1. Some of the boehmite coated specimens were further treated in solution 4 or 5 to incorporate Ce or Ce+Li+Al respectively. Similarly, some HTC coated specimens were treated in solution 7 to modify it with Ce. 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 electrode (SCE) as the reference electrode.

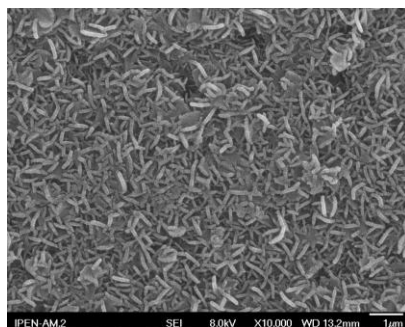


Fig 1. Hydrotalcite layer on the surface of AA 6062 specimen.

3. Results and discussion

3.1. 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 3 summarizes the main features observed on the top surfaces of the different coupons. 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 3. Surface features of coated and lanthanide coated AA 1050 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
	+ CeO₂	Yellow bright, no pits	Mostly bright, no pits
	+ La ₂ O ₃	Bright, many pits	Dark, many pits
	Oxidized	Dull, no pits	Dark, few pits
	Oxidized + CeO₂	Yellow bright, no pits	Dark, few pits
	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
	+ CeO₂	Yellow, no pits	Very dark, very few pits
	+ 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	Semi bright, no pits	Dark, few pits
	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

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 tests have shown otherwise. [4] 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.

3.2. Corrosion behavior of boehmite and HTC coated specimens.

The electrochemical behaviour alloy AA 6061, with or without the coatings revealed differences in the anodic as well as the cathodic polarization curves. The free corrosion potential (E_{corr}) and the pitting potential (E_{pit}) were recorded and the corrosion current densities (i_{corr}) determined by the Tafel extrapolation method. [10]

Table 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
Boehmite + Ce + Li + Al	7.1×10^{-7}	- 741	- 565
Hydrotalcite	3.5×10^{-7}	- 718	- 580
Hydrotalcite + Ce	4.0×10^{-7}	- 764	- 420

Table 4 summarizes the corrosion current, the corrosion potential and the pitting potential 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. With boehmite on the surface, the E_{pit} increased to -650 mV. Modification of the boehmite with cerium hydroxide increased E_{pit} even more to -600 mV. This indicates an increase in the pitting corrosion resistance upon introduction of Ce into the pores of the boehmite coating. Impregnation of the boehmite with Ce, Li and Al resulted in a further increase in the pitting corrosion resistance by increasing the E_{pit} to -565 mV. 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 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.

The mechanism by which HTC imparts pitting corrosion protection is referred to as 'passive corrosion protection', in other words, the HTC acts as a physical barrier between the solution and the surface. On the other hand the mechanism by which the cerium modified HTC imparts protection is considered to be 'active corrosion protection', analogous to that in chromium coatings. This involves release of Ce ions from the coating, transport through the solution and 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 Ce^{3+} , which forms an insoluble hydroxide and precipitates. The precipitated Cerium hydroxide at the defect then stifles further corrosion.

4. Conclusions

1. The CeO_2 coated coupons were the most resistant to pitting corrosion after 12 months of exposure to the spent fuel section of the IEA-R1 reactor.
2. The electrochemical measurements 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.
3. The pitting corrosion resistance of HTC coated AA 6061 specimens was higher than those coated with boehmite. Cerium modification of the HTC coating increased pitting corrosion resistance further.
4. A coating process involving simple immersion in several solutions to form cerium containing conversion coats on Al alloys, and thereby increasing the pitting corrosion resistance of the alloy, has the potential for scale-up to increase the corrosion resistance of Al-clad spent RR fuel assemblies during long term wet storage.

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