

LANTHANIDE BASED CONVERSION COATINGS FOR LONG TERM WET STORAGE OF ALUMINIUM-CLAD SPENT FUEL

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ABSTRACT

Spent fuels from research reactors are stored in basins with water of less than desirable quality at many facilities around the world and instances of cladding failure caused by pitting corrosion have been reported. Conversion coatings have been used in many industries to protect different metals, including aluminium alloys. This paper presents the results of an ongoing investigation in which the corrosion resistance of lanthanide (cerium, lanthanum and praseodymium) based conversion coated RR fuel cladding alloys has been studied. Electrochemical tests in the laboratory revealed higher corrosion resistance of CeO_2 , La_2O_3 and Pr_2O_3 coated AA 1100 and AA 6061 alloys in NaCl solutions. Uncoated and CeO_2 coated coupons of these alloys exposed for 50 days to the spent fuel basin of the IEA-R1 research reactor in IPEN, Brazil, revealed marked reductions in the extent of pitting corrosion.

1. Introduction

A very large number of research reactor spent fuel assemblies are stored in wet facilities around the world and most of these assemblies are clad with aluminium or an aluminium alloy. [1] Pitting corrosion is the main form of degradation that could lead to breach of the cladding and release of fissile material to the environment and contamination of the storage facilities as well as other stored fuels. Corrosion of aluminium cladding of spent RR fuels can be reduced to a large extent by maintaining the storage pool or basin water parameters within specified limits. In spite of maintaining water parameters within specified limits, factors such as bimetallic contact, settled solids and synergism between the effects of many basin water parameters affect the corrosion of aluminium and its alloys. [2, 3]

Conversion coatings have been extensively used in many industries to control the corrosion of various metals. In the early 50's this method of corrosion control was briefly used to protect research reactor fuel prior to use in the reactor and subsequently discarded. Since then, significant progress has been made and new conversion coatings are available to protect Al surfaces. Many facilities around the world store spent fuels in water of less than desirable quality and many instances of cladding failure have been reported. It is imperative that some form of corrosion protection be given to stored spent RR fuel, primarily from the safety standpoint. In the last two decades, rare earth compounds have been considered in the development of corrosion protection systems for aluminium alloys, primarily to substitute chromates, because of the toxicity of the latter. [4] 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. [5-8] Use of conversion coatings to protect spent research reactor fuel assemblies was proposed last year and the results of an exploratory investigation were reported at RRFM 2009. [9]

This paper presents the results of an ongoing investigation at IPEN, Brazil, in which the corrosion resistance of lanthanide (cerium, lanthanum and praseodymium) based conversion coated RR fuel cladding alloys has been studied. In these studies: (a) racks of uncoated and coated Al alloy coupons were exposed to the IEA-R1 research reactor spent fuel basin followed by their examination; (b) the electrochemical behavior of uncoated and coated Al alloy specimens in NaCl solutions was determined.

2. Methods and materials

Aluminium alloys AA 1100 and AA 6061 (Table 1) sheets were used in the laboratory and exposure tests. The laboratory test specimens 2 x 2 x 0.2 cm were prepared using standard procedures, the specimen surfaces acid activated and then coated with oxides of cerium, lanthanum, praseodymium and an oxide concentrate of cerium. [9] Cerium oxide was deposited by immersing the specimen for 5 minutes in a 1 liter solution containing 0.035 M CeCl₃, 0.12 M H₂O₂, 1mM Cu (glycinate), 1 mM Ti(O₂)²⁺ at 43 ° C. [9] The other oxides were deposited by immersing specimens in similar solutions except with the appropriate lanthanide (rare earth – RE) chloride. The electrochemical behavior of uncoated and coated specimens of the two alloys was determined from anodic potentiodynamic polarization measurements carried out with a standard 3-electrode arrangement in 0.1 M NaCl.

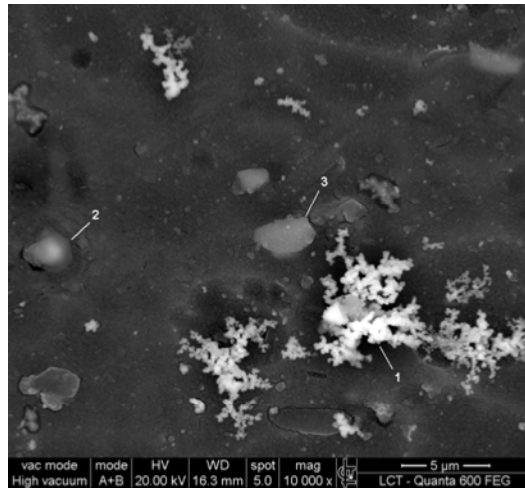
Table 1. Chemical composition of aluminium alloys (wt%)

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

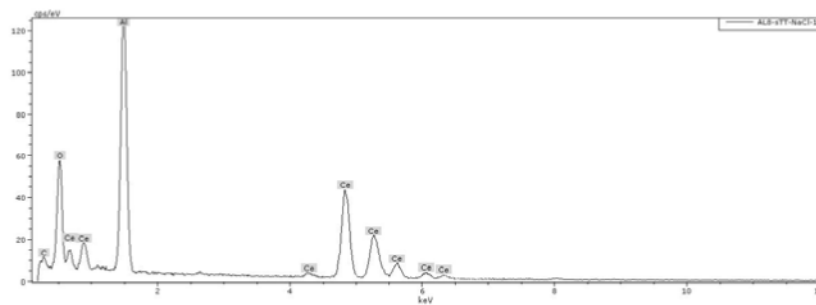
The field exposure test consisted of preparing Al alloy coupons, stacking of these coupons in racks, immersion of the racks in the spent fuel section of the IEA-R1 research reactor in IPEN, Brazil, for predetermined periods, removal of the racks and examination of the coupons. This procedure was used 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 using the procedure described above for the laboratory test specimens. 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 simulating surface conditions of spent fuel plates. This paper presents details of surface features of AA 1050 and AA 6061 coupons exposed for 50 days. Further rack withdrawals are scheduled after coupon exposures to the IEA-R1 reactor spent fuel section for 100, 200, 300 and 500 days. Preparation of and field testing of further coupons of the two alloys coated with these and other lanthanide compounds are also part of this ongoing programme. The surfaces of all the laboratory test specimens and the field test coupons, both prior to and after the tests, were examined in optical microscopes and a scanning electron microscope (SEM) coupled to an energy dispersive spectrometer (EDS),

3. Results and discussion

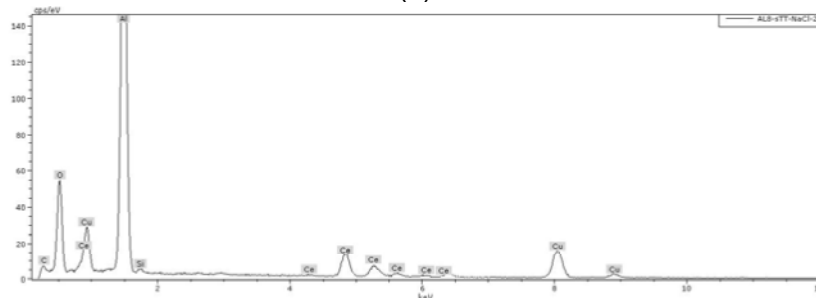
The surfaces of the two alloys immersed in the cerium chloride solution revealed non-uniformly distributed CeO₂ on copper deposits on AA 1100 and preferred formation of CeO₂ at both the intermetallic precipitates (IMP) and on copper deposits on AA 6061, as shown in Fig. 1a and in the EDS spectrums in Figs.1b and 1c.



(a)



(b)



(c)

Figure 1. (a) Scanning electron micrograph of AA 6061 immersed for 5 minutes in the cerium chloride solution; (b) EDS spectrum of region 1; (c) EDS spectrum of region 2.

The anodic polarization curves of the two alloys with or without the coatings were quite similar. The free corrosion potential (E_{corr}) was recorded and the corrosion current densities (I_{corr}) determined by the Tafel extrapolation method [10]. The anodic curves were almost unaffected by the presence of the conversion coatings, whereas the cathodic branches appeared strongly reduced. Table 2 summarizes the corrosion potentials and current densities of the uncoated and RE oxide coated specimens. Lanthanide oxide coatings produce a higher free corrosion potential with respect to the uncoated specimens. The cathodic current densities shown in Table 2 are lower in the presence of cerium and/or cerium concentrate on the specimen surface of both alloys compared to the uncoated specimen, indicating the protective nature of this oxide. The Pr_2O_3 and La_2O_3 coated AA 6061 specimen reveals a similar behavior. However, the invariant current density of the Pr_2O_3 and La_2O_3 coated AA 1050 could be attributed to limited cathodic sites on this alloy and consequent inadequate precipitation of the two rare earth oxides.

Table 2. Corrosion current (I_{corr}) and potential (E_{corr}) of the alloys in 0.1M NaCl

Alloy	Coating	I_{corr} (mA.cm ⁻²)	E_{corr} (mV vs SCE)
AA 1100	None	5.0×10^{-6}	- 850
	CeO ₂	4.1×10^{-7}	- 683
	CeO ₂ from Concentrate	4.1×10^{-7}	- 685
	Pr ₂ O ₃	2.7×10^{-6}	- 690
	La ₂ O ₃	2.8×10^{-6}	- 700
A 6061	None	4.0×10^{-5}	- 770
	CeO ₂	1.4×10^{-6}	-728
	CeO ₂ from Concentrate	4.2×10^{-6}	-705
	Pr ₂ O ₃	8.0×10^{-6}	-723
	La ₂ O ₃	1.5×10^{-6}	- 695

Table 3 summarizes the results of visual and optical microscopic examination of the surfaces of coupons exposed for 50 days to the IEA-R1 research reactor spent fuel section. Pre-oxidized AA 1050 and AA 6061 coupons revealed fewer pits compared to the as-received coupons. The CeO₂ coated as-received and pre-oxidized AA 1050 and AA 6061 coupons continued to be yellow in color indicating the presence of CeO₂ on the coupon surface after 50 days. These coupons revealed very few and extremely small pits indicating the protective nature of this oxide.

Table 3. Number of pits on coupon surfaces after 50 days of exposure to the IEA-R1 spent fuel section. (pit diameters 5-20 μm)

Condition of coupon	AA 1050		AA 6061	
	Top	Bottom	Top	Bottom
As-received	20	15	4	3
Pre-oxidized	8	5	5	3
Pre-oxidized and CeO ₂ coated	5	3	7	2
Pre-oxidized and CeO ₂ concentrate coated	3	2	13	5
As-received and CeO ₂ coated	6	6	-	-
As-received and CeO ₂ concentrate coated	19	18	20	18
As-received or pre-oxidized and Pr ₂ O ₃ coated	Large number of pits			
As-received or pre-oxidized and La ₂ O ₃ coated				

The CeO₂ concentrate coated as-received and pre-oxidized AA 1050 and AA 6061 coupons were grey-white and revealed some pits. Pre-oxidized coupons revealed fewer pits than the as-received coupons in the presence of ceria concentrate. Overall, CeO₂ concentrate was less effective than CeO₂ in terms of corrosion protection. The Pr₂O₃ and La₂O₃ coated AA 1050 and AA 6061 coupons revealed a large number of pits. The AA 6061 coupon had more pits than the AA 1050 coupon. The marked pitting of the Pr₂O₃ and La₂O₃ coated coupons could be attributed to insufficient and non-homogeneous deposition of these two rare earth oxides under experimental conditions similar to that used to deposit CeO₂. Preferred precipitation of Pr₂O₃ and La₂O₃ in the respective solutions occurred while the coupons were

being chemically treated and this was caused by localized pH increase due to Al oxidation. Attempts to prepare solutions to obtain Pr_2O_3 and La_2O_3 deposits on Al alloys are in progress.

4. Conclusions

1. The lanthanide based chemical conversion coatings ennobled the corrosion potential and inhibited both the cathode and anode reactions rates.
2. The experimental condition to deposit Pr_2O_3 and La_2O_3 on Al alloys requires optimization.
3. Long term tests using as-received and pre-oxidized coupons revealed marked improvements in corrosion resistance of the alloys exposed to the IEA-R1 research reactor spent fuel basin.
4. Overall, lanthanide based, and especially cerium dioxide, conversion coatings can be used to improve the pitting corrosion resistance of Al-clad spent RR fuel assemblies.

5. References

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