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Lanthanide based conversion coatings to protect aluminum alloys

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Abstract

Degradation of aluminum alloy clad spent nuclear fuel is caused by pitting corrosion and this can be reduced to a large extent by maintaining the spent fuel storage basin water parameters within specified limits. Nevertheless it has been shown that in spite of well controlled water parameters, synergism between the effects of many of the basin water parameters contribute to and cause aluminum alloys to corrode. Conversion coatings have been extensively used in a variety of industries to protect and/or to control the corrosion of many metals, including aluminum alloys. The use of conversion coatings to protect spent Al-clad spent fuel surfaces has never been considered. 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 CeO₂, La₂O₃ and Pr₂O₃ coated AA 1100 and AA 6061 alloys in NaCl solutions. Uncoated and CeO₂ 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.

Key words: Aluminum alloy, conversion coating, rare earth.

Introdução

According to the IAEA's Research Reactor Spent Fuel Data Base, there are over 62,000 spent fuel assemblies (SFA) stored in facilities around the world. (1) Most of the research reactor (RR) fuels are clad with relatively pure aluminum or an aluminum alloy. The main form of degradation of aluminum alloy clad RR fuel is that caused by corrosion. Pitting is the main form of corrosion and could lead to breach of the cladding, release of fissile material to the environment and contamination of the storage facilities as well as other fuels in the storage basin. The corrosion of spent RR fuel cladding can be reduced to a large extent by maintaining the storage pool or basin water parameters within specified limits. Nevertheless it has been shown that in spite of stringent water parameters, factors such as bimetallic contact, settled solids and synergism between the effects of many of the basin water parameters could result in corrosion of Al and its alloys. (2, 3)

The use of inhibitors or the application of conversion coatings to protect metals is well known. These methods of controlling corrosion were considered very briefly in the early

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50's to protect fuels during use in the reactor and subsequently discarded. In the last 60 years, significant progress has been made and a wide range of new inhibitors and conversion coatings are available to protect Al surfaces. The use of inhibitors or conversion coatings to protect spent fuel surfaces has never been considered. Many facilities around the world store spent fuels in water of less than desirable quality and many instances of cladding failure have been reported. A corrosion protected spent RR fuel could be stored for extended periods in waters of less than optimum quality. This would reduce the cost of water quality maintenance. During the last two decades, rare earth compounds have been considered to develop corrosion protection systems for aluminum alloys to replace chromates, due to its toxic nature. (4-6) Based on the formation of cerium hydroxide films on Al alloys immersed in solutions containing cerium compounds as inhibitors, other treatments have been proposed to develop rare earth based conversion coating on Al alloys. (7-12)

This paper presents (a) the results of an ongoing investigation to prepare and characterize cerium based conversion coatings on Al alloys AA 1100 and AA 606, used as RR fuel cladding material; (b) the corrosion resistance of lanthanide based conversion coated (which includes cerium dioxide, cerium dioxide concentrate, lanthanum dioxide and praseodymium dioxide) Al alloy specimens in NaCl solutions; (c) the effect of conversion coatings on the corrosion behavior of Al alloy coupons exposed for 50 days to the spent fuel basin of IEA-R1 research reactor.

Methods and materials

Aluminium alloys AA 1100 and AA 6061 (Table 1) sheets were used in the laboratory and the reactor exposure tests. The laboratory test specimens ($2 \times 2 \times 0.2$) cm³ were prepared using standard procedures used for the preparation of fuel plates. In the preliminary tests, these sheet specimens were chemically treated by immersion in one or a combination of solutions shown in Table 2. Solution-1 was used to pickle and remove the surface oxide. Solutions 2 and 3 were used to form the coating. (12) After treatment, the specimens were rinsed and their surfaces examined. The surfaces of specimens: (a) untreated; (b) after treatment in the Ce ions containing solutions; (c) after exposure to NaCl solutions were examined in a scanning electron microscope (SEM) coupled to an energy dispersive spectrometer (EDS). The electrochemical behavior of untreated and treated specimens of the two alloys was determined from anodic potentiodynamic polarization measurements carried out with an electrochemical system using a standard 3-electrode arrangement in 0.1 mol.L⁻¹ NaCl. Having observed CeO₂ deposits on Al surfaces dipped in solution 3, similar solutions containing cerium dioxide concentrate, La₂O₃ and Pr₂O₃ were prepared with the respective lanthanide oxides and specimens immersed in these solutions to form the respective lanthanide oxides on the specimen surfaces. The electrochemical behavior of Al specimens treated in these solutions was also determined in 0.1 mol.L⁻¹ NaCl.

The field exposure test consisted of preparing 3 mm thick and 10 cm diameter circular coupons, stacking of these coupons in racks, as shown in Figure 1, 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) The coupons of the two alloys were coated with RE oxides 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 of the coupons were oxidized at 300 °C in air for 4 h to form a surface aluminum oxide layer simulating surface conditions of spent fuel plates. This paper presents the surface features of AA 1100 and AA 6061 coupons exposed for 50 days. Further rack withdrawals are scheduled after 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 program. 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).

Results and discussion

The surfaces of AA 1100 and AA 6061 specimens immersed in Solution-2 revealed non-uniformly distributed CeO_2 on the former and preferred formation of CeO_2 at intermetallic precipitates (IMP) on the latter, as shown in Figure 2a and in the EDS spectrum in Figure 2b. The AA 1100 and AA 6061 specimens immersed in Solution-3 revealed CeO_2 on the deposited Cu islands. CeO_2 was also observed on IMP in AA 6061. Other regions of the surface also revealed CeO_2 , but to a lesser extent as shown in Figure 3. The EDS at region 2 in Figure 3a is shown in Figure 3b, revealing Cu and Ce peaks. The Cu and IMP free regions revealed significantly less CeO_2 , due probably to the aluminum oxide on the surface. Specimens that were treated first in Solution-1, to remove surface oxide followed by treatments in Solutions 2 or 3 revealed CeO_2 even at regions without Cu or IMP.

The micrographs of CeO_2 coated AA 1100 and AA 6061 specimens did not reveal any marked changes upon exposure to NaCl solutions of varying concentrations and for duration of up to 2 hours. 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. (13) The anodic curves were almost unaffected by the presence of the conversion coatings, whereas the cathodic branches appeared strongly reduced. The results of the preliminary electrochemical measurements are summarized in Table 3. The cerium dioxide coated specimens had higher corrosion potentials and lower corrosion currents. Specimens coated with CeO_2 from Solution-3 were even more corrosion resistant compared to those coated in solution-2. Increase in immersion time in either solution had no significant effect on the potential or the corrosion current.

Table 4 summarizes the corrosion potentials and current densities of specimens that were uncoated and coated with the different RE oxides. The different lanthanide oxide coated specimens had higher free corrosion potentials compared to the uncoated specimens. The cathode current densities of the specimens, shown in Table 4, are lower in the presence of cerium and/or cerium concentrate on the specimen surface of both alloys, compared to the uncoated specimen. This indicated the protective nature of this oxide. The Pr_2O_3 and La_2O_3 coated AA 6061 specimen revealed a similar behavior. However, the invariant current density of the Pr_2O_3 and La_2O_3 coated AA 1100 could be attributed to limited cathode sites on this alloy and consequent inadequate precipitation of the two rare earth oxides. Attempts are in progress to address this issue.

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 1100 and AA 6061 coupons revealed fewer pits compared to the as-received coupons. The CeO₂ coated as-received and pre-oxidized AA 1100 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 CeO₂

The CeO₂ concentrate coated as-received and pre-oxidized AA 1100 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, the CeO₂ concentrate was less effective than CeO₂ in terms of corrosion protection. The Pr₂O₃ and La₂O₃ coated AA 1100 and AA 6061 coupons revealed a large number of pits. The AA 6061 coupon had more pits than the AA 1100 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. Insufficient deposition of these RE oxides on the coupon surfaces could be attributed to precipitation of Pr₂O₃ and La₂O₃ in the respective solutions caused by pH increase resulting from Al oxidation. Attempts to prepare solutions that would enable deposition of Pr₂O₃ and La₂O₃ on Al alloys are in progress.

General discussion

To explain the formation of Ce(III) / Ce(IV) hydrated oxides on aluminum alloy surfaces in the presence of oxygen, two theories have been proposed. (14,15) The first claims local pH increase due to the oxygen reduction reaction which enables Ce(III) hydroxide precipitation followed by oxidation to hydrated CeO₂. (16,17) The second theory postulates that first Ce(III) to Ce(IV) oxidation takes place in the solution followed by precipitation of CeO₂ at areas on the surface where local reduction in pH takes place due to the oxygen reduction reaction. (13) In the solutions that were used to deposit cerium oxides, the role of H₂O₂ was twin-fold. First, its presence causes rapid increase in pH due to its reduction which favors hydrated CeO₂ precipitation. Second, it enhances Ce(III) to Ce(IV) oxidation in solution resulting in predominant Ce (IV) hydroxide film formation. (18)

The cathode regions on aluminum alloy surfaces are the preferred sites for CeO₂ formation. In Cu containing 2xxx and 7xxx Al alloys, CuAl₂ intermetallic precipitates are the preferred sites for CeO₂ formation. On non-copper containing alloys such as AA 6061, the cathode sites are Mg₂Si intermetallic sites, and these are not as efficient as CuAl₂. Consequently immersion of this alloy or other non-Cu containing Al alloys in Cu containing solutions with other additives such as Ti compounds result in Cu as well as Ti compound deposition, increasing markedly the cathode sites for oxygen reduction and subsequent RE oxide formation. (12)

Overall, on Al alloys with rare earth oxide conversion coats, increase in the corrosion potential and inhibition of both the cathode and anode reaction rates occur.

Conclusions

1. Immersion of AA 1100 and AA 6061 alloy specimens in CeCl_3 containing solutions resulted in formation of CeO_2 on the surface.
2. The CeO_2 on the alloy surface increased the corrosion resistance of the alloys in NaCl solutions.
3. Immersion of the alloys in Cu containing CeCl_3 solutions resulted in formation of increased amounts of CeO_2 , mainly at the Cu islands.
4. The lanthanide (Ce, Pr and La) based chemical conversion coatings ennobled the corrosion potential and inhibited both the cathode and anode reactions rates.
5. The experimental condition to deposit Pr_2O_3 and La_2O_3 on Al alloys requires optimization.
6. 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.
7. 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.

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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. Composition of solution and treatment conditions

Treatment conditions	Solution		
	1	2	3
Composition	0.5 mol.L ⁻¹ H ₂ SO ₄ 1.28 mol.L ⁻¹ HNO ₃ 0.05 mol.L ⁻¹ Ce(SO ₄) ₂ 0.04 mol.L ⁻¹ HF 0.1 mol.L ⁻¹ (NH ₄) ₂ SO ₄ 1 litre	10 g.L ⁻¹ CeCl ₃ .6H ₂ O 3 ml.L ⁻¹ 100vol% H ₂ O ₂ 1 litre pH 1.6	0.035 mol.L ⁻¹ CeCl ₃ 0.12 mol.L ⁻¹ H ₂ O ₂ 1mmol.L ⁻¹ Cu (glycinate) 1 m mol.L ⁻¹ Ti(O ₂) ²⁺ 1 litre pH 2.0
Temperature (° C)	35	43	45
Duration (minutes)	10	4	5



Figure 1. A typical rack with a stack of circular coupons.

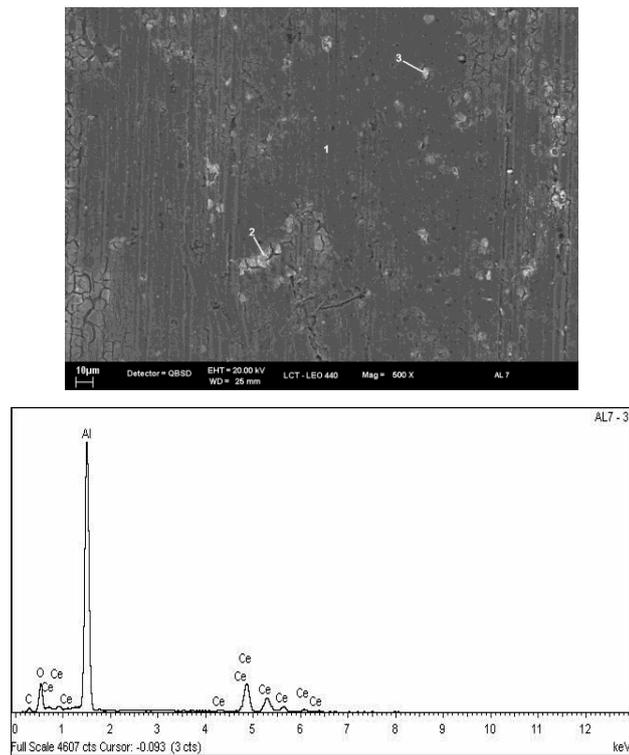


Figure 2. (a) Scanning electron micrograph of AA 6061 surface treated in Solution-2.
(b) EDS spectrum of surface at region 3 in Figure 2a.

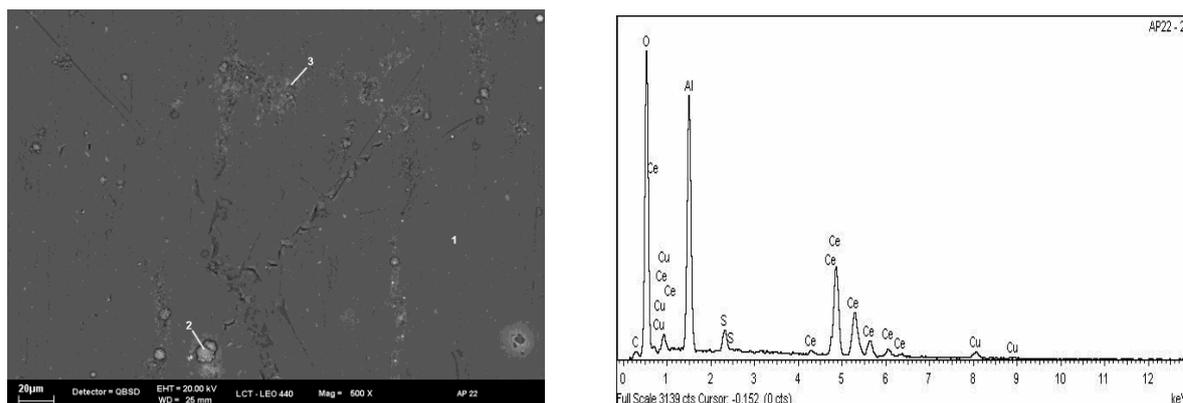


Figure 3. (a) Scanning electron micrograph of AA 6061 surface treated in Solution-3.
(b) EDS spectrum of surface at region 2 in Figure 3a.

Table 3. Corrosion current density (i_{corr}) and potential (E_{corr}) of the alloys in 0.1M NaCl

Alloy	Treatment	i_{corr} ($\text{mA}\cdot\text{cm}^{-2}$)	E_{corr} (mV vs SCE)
AA 1100	None	5×10^{-6}	- 850
	Solution - 2	2×10^{-6}	- 730
	Solution - 3	5×10^{-7}	- 660
AA 6061	None	4×10^{-5}	- 770
	Solution - 2	4×10^{-6}	- 790
	Solution - 3	1×10^{-6}	- 630

Table 4. Corrosion current density (i_{corr}) and potential (E_{corr}) of the alloys in 0.1M NaCl

Alloy	Coating	i_{corr} ($\text{mA}\cdot\text{cm}^{-2}$)	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 5. Number of pits on coupon surfaces after 50 days of exposure to the IEA-R1 spent fuel section. (pit diameters 5 μm - 20 μm)

Condition of coupon	AA 1100		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				