Coatings for increased protection of aluminium clad spent nuclear fuel during long term wet storage

S.M.C.Fernandes, O.V.Correa, J.A.De Souza, N.B.de Lima, L.V.Ramanathan,
Materials science and Technology Center,
Instituto de Pesquisas Energéticas e Nucleares- IPEN
Av. Prof. Lineu Prestes 2242, Cidade Universitaria
05508-000 São Paulo. Brazil.

R. A. Antunes
Engineering, Modeling and Applied Social Sciences Center (CECS),
Federal University of ABC, 09210-170, Santo André-SP, Brazil.

M.C.L. De Oliveira
Electrocell Ind. Com. Equip. Elet. LTDA, CIETEC, 05508-000 São Paulo-SP, Brazil.

Summary

Aluminium-clad spent fuels from research reactors (RR) are stored in wet facilities. Pitting corrosion of the cladding has been reported during storage and attributed to synergism in the effect of water parameters. Protection of the spent RR fuel with conversion coatings for long term safe storage was considered. Boehmite and hydrotalcite (HTC) coatings were formed on aluminium alloy AA 1100 and AA 6061 specimens and further treated to incorporate Ce and modify the coating. The different coatings were characterized with the aid of SEM/FEG/EDS and x-ray diffraction analysis. The electrochemical behavior of uncoated and coated specimens was determined in 0.01 M NaCl and field tests carried out by immersing boehmite coated, cerium modified boehmite coated, HTC coated and cerium modified HTC coated Al alloy coupons in the spent fuel basin of the IEA-R1 research reactor in São Paulo, Brazil, for extended periods. Most of the coatings increased the pitting corrosion resistance of the two alloys and among the coatings, the cerium modified HTC coating was the most efficient. This paper presents formation of boehmite and HTC on the Al alloys, the electrochemical / field test results and the mechanism of corrosion protection imparted by the different coatings.

1 Introduction

Pitting corrosion of the aluminium cladding of spent research reactor (RR) fuel has been observed in wet storage facilities and attributed to synergism in basin water parameters. [1,2] Conversion coatings have been extensively used in many industries to control the corrosion of various metals and rare earth compounds have been also used to inhibit aqueous corrosion of aluminium alloys [3]. Chemical treatments have been used to form rare earth based conversion coatings on Al alloys. [4-6] Results of preliminary investigations with conversion coated spent Al-clad RR fuels indicated that a cerium hydroxide coating increased the corrosion resistance of Al alloys. Hydrotalcite (HTC) is lithium aluminium-nitrate-hydroxide hydrate and it forms on Al alloys immersed in an appropriate alkaline lithium salt solution. [7-9] Spent fuels after prolonged use in a reactor core have a surface layer of boehmite. Hence the attempts to use boehmite, HTC, cerium modified boehmite and cerium modified HTC coatings to protect spent RR fuel. [10] This paper presents the results of: (a) HTC and boehmite coating preparation; (b) electrochemical measurements with uncoated and coated specimens in NaCl solutions; (c) field tests in which uncoated and coated Al alloy coupons were exposed to the IEA-R1 reactor spent fuel storage basin.

2 Methods and materials

Aluminium alloys AA 1050 and AA 6061 were used in the laboratory and field tests. The aluminium alloy specimens and coupons for the laboratory and the field tests respectively were treated to coat their surfaces with either boehmite or HTC by immersion in solutions and under conditions shown in Table1.

Table 1. 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; 97-100 °C; 5 min.
4	Incorporate Ce in boehmite	0.1% $CeCl_3$; 97 °C; pH 4; 5 min.
5	Form HTC – HT	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 – LT	0.1M Li_2CO_3; LiOH; Al; pH 12; 15 min; R.T.
7	Incorporate Ce in HTC	10 g/L Ce $(NO_3)_{3;}$ 30% $H_2O_{2;}$ R.T.; 5 min.
8	Sealing	$MgC_4H_6O_4$; 82 °C; 15 min.

The electrochemical behaviour of uncoated and coated specimens was determined in 0.01 M NaCl using a standard 3-electrode arrangement. A saturated calomel reference electrode and a platinum counter electrode were used. The potential was scanned from - 0.3 V to +1.0 V at 0.1 mV/s. The field test procedure consisted of preparing Al alloy coupons 10 cm in diameter and 3 mm thick, stacking of the coupons in racks, immersion of the racks in the spent fuel section of the IEA-R1 research reactor in IPEN, Brazil, for 3 and 6 months, removal of the racks followed by disassembly and examination of the coupons with an optical microscope coupled to an image analyzer [1].

3. Results and discussion

3.1 Laboratory tests

The surfaces of the HTC coated specimens were examined in a scanning electron microscope and the coatings identified by x-ray diffraction analysis. The spectra revealed the formation of hydrotalcite. The morphology of HTC formed from solutions 5 is shown in figure 1. The surfaces revealed intersecting blade like HTC crystallites across the surface. The coatings formed inside recesses that developed during pretreatment of the substrate. Typical coating thickness after 10 minutes of immersion was ~2 µm. 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.

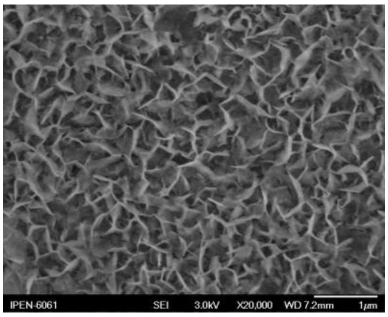

Figure 1. Scanning electron micrographs of HTC coating on AA 6061.

The anodic polarization data shown in Table 2 indicate that specimens with any type of coating, with or without post treatments were more corrosion resistant. Even though the untreated specimen (RC-0) revealed a distinct passive region, the OCP of the coated specimens were close to the breakaway (pitting potential) of RC-0.

Table 2. The corrosion potential E_{corr}, corrosion current I_{corr} and breakdown potentials E_b, as determined from the electrochemical polarization curves. (Breakdown potential was determined only for curves that showed breakdown of passivity)

Specimen	**I_{corr} (µA.cm^{-2})**	**E_{corr} (V)**	**E_b (V)**
RC-0	6.120	-1.23	-0.59
RC-1	0.327	-0.54	-
RC-2	1.749	-0.59	-
RC-3	1.694	-0.58	-
RC-4	0.972	-0.90	-0.59
RC-5	0.085	-0.69	-0.56
RC-6	0.141	-0.62	-
RC-7	0.284	-0.60	-
RC-8	0.134	-0.63	-
RC-9	0.998	-0.61	-

3.2 Coupons exposed to IEA-R1 reactor spent fuel section.

The main features of the coupons exposed for 3 and 5 months to IEA-R1 spent fuel basin, compared with those prior to exposure are summarized in Table 3. The untreated coupons of AA 1050 and AA 6061 revealed staining and many pits respectively. After 3 months of exposure, the HTC – LT coated AA 1050 revealed pits where as the AA 6061 did not. Coupons of both alloys coated with HTC – LT, with or without post treatments revealed pitting. The HTC – HT coated coupons of the two alloys, with or without post treatments revealed no pits on either side after 3 and 5 months of exposure.

Table. 3. Surface features compared to those observed on coupons prior to exposure to the IEA-R1 research reactor spent fuel section

Alloy	**Coating**	**Surface features after exposure for**	
		3 months	**5 months**
AA 1050	None	Stained with oxide	Few pits
	Boehmite	No difference	One pit
	Boehmite + Ce	No difference	Many pits
	HTC – HT	No difference	No difference
	HTC – HT + Ce	No difference	No difference
	HTC – HT + selaed	No difference	No difference
	HTC – HT + Ce + sealed	No difference	No difference
	HTC – LT	No difference	Stained + few pits
	HTC – LT + Ce	Few pits	Stained + few pits
	HTC – LT + sealed	Few pits	Stained + few pits
	HTC – LT + Ce + sealed	No difference	Stained but no pits
AA 6061	None	Many pits	Stained and one pit
	Boehmite	No difference	Many tiny pits
	Boehmite + Ce	No difference	Few pits
	HTC – HT	No difference	No difference
	HTC – HT + Ce	No difference	No difference
	HTC – HT + sealed	No difference	No difference
	HTC – HT + Ce + sealed	No difference	No difference
	HTC – LT	No difference	Dark and some pits
	HTC – LT + Ce	No difference	Dark and some pits
	HTC – LT + sealed	No difference	Very dark and one pit
	HTC – LT + Ce + sealed	No difference	Very dark + two pits

4. General discussion

The laboratory and field tests have indicated marked increase in corrosion resistance of Al alloys coated with HTC – HT. The corrosion resistance was further enhanced by modifying the coating with cerium dioxide. Sealing of the coatings in magnesium acetate also improved pitting corrosion resistance of HTC – HT coated coupons. In the context of eventually protecting Al-clad spent RR fuels during long term wet storage, the coating process for irradiated fuels would be facilitated if treatments were to be carried out at room temperature. Presently, the extent to which HTC – LT imparts protection is lower than that imparted by HTC – HT. Attempts are in progress to increase the HTC – LT layer thickness to increase its protection efficiency. Nonetheless, protecting spent fuel with HTC coatings modified with cerium is the obvious choice. 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 considered to be ‘active corrosion protection’, analogous to chromium coatings. This involves release of Ce^{4+} ions from the coating, transport of Ce^{4+} 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. Hydrotalcite (HTC) coatings on AA 1050 and AA 6061 alloys were prepared from nitrate baths at 98 °C and carbonate baths at room temperature.
2. HTC formed from nitrate bath at 98 °C increased pitting reistance more than HTC formed from carbonate bath 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 HTC – HT when exposed to the IEA-R1 reactor spent fuel section for 5 months did not reveal any pits, indicating its potential for use as a protective coating on spent RR fuel.

6. References

1. Corrosion of Research Reactor Aluminium Clad Spent Fuel in Water", IAEA - TRS 418, (2003).
2. L.V. Ramanathan, R. Haddad, P. Adelfang and I. Ritchie, Corrosion of Spent Aluminium-clad Research Reactor Fuel – Synergism in the Role of Storage Basin Water Parameters, Proceedings of 12th International topical meeting on Research Reactor Fuel Management (RRFM), Hamburg, Germany, (2008).
3. B.R.W. Hinton, D.R. Arnott and N.E. Ryan, Mater. Forum 9, 162, (1986).
4. D.R. Arnott, N.E. Ryan, B.R.W. Hinton, B.A. Sexton and A.E. Hughes, Appl. Surf. Sci., 22/23, 236, (1985).
5. M. Dabalà, L. Armelao, A. Buchberger and I. Calliari. Appl. Surf. Sci., 172, 132, (2001).
6. A.E. Hughes, S.G. Hardin, K.W. Wittel, P.R. Miller, in the Proceedings of the NACE meeting: Corrosion/2000, Research topical Symposium: Surface Conversion of Aluminum and Aluminum alloys for Corrosion Protection, Orlando, USA, (2000).
7. R.G.Buchheit, M.D.Bode and G.E.Stoner, Corrosion, Vol.50, 3, (1994).
8. R.G.Buchheit, S.B.Mamidipally, P.Schmutz and H.Guan, Corrosion, Vol. 58, 1, (2002).
9. W. Zhang and R.G.Buchheit, Corrosion, vol.58, 7, 591, (2002).
10. S.M.C.Fernandes, O.V.Correa, J.A.de Souza and L.V.Ramanathan**,** Coatings for increased corrosion resistance of aluminium-clad spent fuel in wet storage, Transactions of European Research Reactor conference, (RRFM), Prague, Czech Republic, 2012.