

A COATING TO PROTECT SPENT ALUMINIUM-CLAD RESEARCH REACTOR FUEL ASSEMBLIES DURING EXTENDED WET STORAGE

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ABSTRACT

Pitting corrosion of aluminium (Al) alloy clad research reactor (RR) fuel in wet storage facilities can be reduced to a large extent by maintaining water parameters within specified limits. However, factors like bimetallic contact, settled solids and synergistic effects of many storage basin water parameters provoke cladding corrosion. Increase in corrosion resistance of spent Al-clad RR fuels can be achieved through the use of conversion coatings. This paper presents: (a) details about the formation of cerium dioxide as a conversion coating on Al alloys used as RR fuel cladding; (b) the corrosion resistance of cerium dioxide coated Al alloy specimens exposed to NaCl solutions. Marked improvements in corrosion resistance of cerium dioxide coated Al specimens were observed. This paper also presents details of a Latin American Project to develop conversion coatings for long term safe wet storage of spent Al-clad RR spent fuel assemblies.

1. Introduction

According to the IAEA's Research Reactor Spent Fuel Data Base, there are about 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 aluminium or an aluminium alloy. The main form of degradation of aluminium alloy clad RR fuel is that caused by corrosion. Pitting is the main form of corrosion and 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 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. Work carried out within the context of two IAEA coordinated research projects on the "Corrosion of Al-clad spent RR fuel in water", and within the corrosion activities of the IAEA supported Regional Project for Latin America on "Management of RR spent nuclear fuel" revealed that in spite of such stringent water parameters, factors such as bimetallic contact, settled solids and synergism between the effects of many of the basin water parameters result in corrosion of Al and its alloys. [2, 3]

Among the many forms of controlling corrosion of metals in general, the use of inhibitors or the application of conversion coatings are widely known and these are extensively used in a variety of industries. These methods of controlling corrosion were considered very briefly in the early 50's to protect fuel cladding prior to use in the reactor and subsequently discarded. During 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. It is imperative that some form of corrosion

protection be given to stored spent RR fuel, primarily from the safety standpoint. A corrosion protected spent RR fuel could be stored for extended periods in waters of less than optimum quality. This in turn would reduce cost of water quality maintenance. During the last two decades, rare earth compounds have been investigated to develop corrosion protection systems for aluminium alloys as an alternative to chromates, which need to be replaced because of their 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 the results of an exploratory investigation carried out to prepare cerium based conversion coatings on Al alloys used as RR fuel cladding material, namely AA 1100 and AA 6061. The effects of chemical pretreatments and processing parameters on cerium dioxide coating characteristics were determined. The corrosion resistance of cerium dioxide coated Al alloy specimens in NaCl solutions of varying concentrations was also determined. This paper also presents details of a Latin American Regional Project to develop coatings for long term safe wet storage of RR spent fuel assemblies.

2. Methods and materials

Specimens 2 x 2 x 0.2 cm were cut from AA 1100 and AA 6061 (Table 1) sheets prepared using standard procedures used for making RR fuel plates. These specimens were oxidized at 300° C in air for 4 h to form a surface oxide layer, simulating thus the surface conditions of a spent fuel plate. Table 2 shows the chemical composition of the solutions used in this study and also the treatment conditions to form cerium dioxide conversion coatings on the specimen surfaces.

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

Table 2. Composition of solution and treatment conditions

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

The treatment consisted of simple immersion of the specimens in the solutions. Solution-1 was used to pickle and remove the surface oxide. Solutions 2 and 3 were used to form the coating. After treatment, the specimens were rinsed and their surfaces examined. Untreated and treated specimens were exposed to 0.001 M and 0.1 M NaCl solutions for 1 and 4 hours to determine their corrosion resistance. The surfaces of specimens: (a) untreated; (b) after treatment in the Ce 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 M NaCl.

3. 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 AA 6061, as shown in Fig. 1a and in the EDS spectrum in Fig.1b. The AA 1100 and 6061 specimens immersed in Solution-3

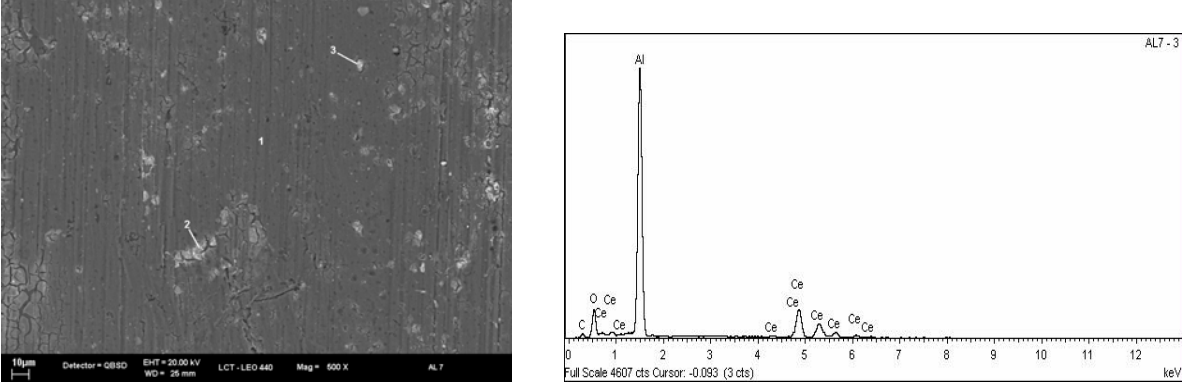


Figure 1. (a) Scanning electron micrograph of AA 6061 surface treated in Solution-2. (b) EDS spectrum of surface at region 3 in Fig. 1a.

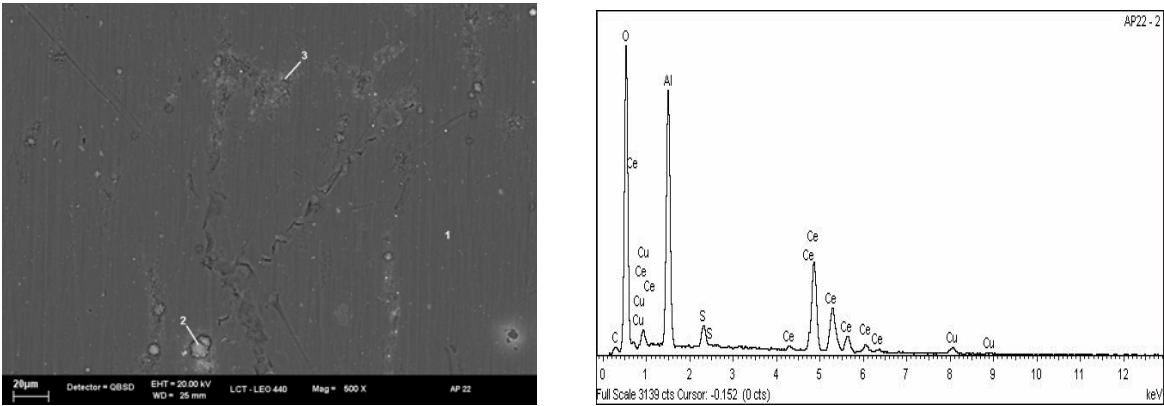


Figure 2. (a) Scanning electron micrograph of AA 6061 surface treated in Solution-3. (b) EDS spectrum of surface at region 2 in Fig. 2a.

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 Fig. 2. The EDS at region 2 in Fig.2a is shown in Fig.2b, revealing Cu and

Ce peaks. The Cu and IMP free regions revealed significantly less CeO₂, due probably to the Al 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 CeO₂ even at regions without Cu or IMP.

The micrographs of CeO₂ coated AA 1100 and AA 6061 specimens did not reveal any marked changes upon exposure to NaCl of either concentration and for the two different durations. The results of the electrochemical measurements are summarized in table 3. The cerium dioxide coated specimens had higher corrosion potentials and lower corrosion currents. Specimens coated with CeO₂ 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.

Overall, these data indicate that cerium dioxide conversion coatings on AA 1100 and AA 6061 clad spent RR fuel assemblies would significantly improve the pitting corrosion resistance of the assemblies in spent fuel basins with significantly lower quality water than that in use presently.

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

Alloy	Treatment	I_{corr} (mA.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
A 6061	None	4×10^{-5}	- 770
	Solution - 2	4×10^{-6}	- 790
	Solution - 3	1×10^{-6}	- 630

4. The ARCAL project

A Latin American project titled "Development of novel cost effective conversion coatings for long term safe wet storage of spent aluminium-clad research reactor fuels" has been approved for execution during 2009-2012 and awaiting funding. The participating countries are Argentina, Brazil, Chile and Peru. The different stages of the project include: (a) development of transition metal (TM) and/or lanthanide conversion coatings on Al alloys; (b) evaluation of corrosion resistance of conversion coated mock fuel plates in Latin American spent fuel basins; (c) design and construction of a rig and remote handling equipment to conversion coat spent fuel assemblies; (e) Definition of procedures to prepare conversion coatings on spent fuel assemblies.

5. Conclusions

1. Immersion of AA 1100 and AA 6061 specimens in CeCl_3 containing solutions resulted in the 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 corrosion potentials of CeO_2 coated specimens in 0.1M NaCl solution were higher and the corrosion currents lower, indicating higher corrosion resistance, compared to uncoated specimens.

6 References

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