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CORROSION AND PROTECTION OF SPENT AL-CLAD RESEARCH REACTOR FUEL DURING EXTENDED WET STORAGE

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ABSTRACT

A variety of spent research reactor fuel elements with different fuel meats, geometries and ^{235}U enrichments are presently stored under water in basins throughout the world. More than 90% of these fuels are clad in aluminum (Al) or its alloy and are susceptible to corrosion. This paper presents an overview of the influence of Al alloy composition, galvanic effects (Al alloy/stainless steel), crevice effects, water parameters and synergism between these parameters as well as settled solids on the corrosion of typical Al alloys used as fuel element cladding. Pitting is the main form of corrosion and is affected by water conductivity, chloride ion content, formation of galvanic couples with rack supports and settled solid particles. The extent to which these parameters influence Al corrosion varies. This paper also presents potential conversion coatings to protect the spent fuel cladding.

1. INTRODUCTION

Over 62,000 research reactor spent fuel assemblies are stored in a variety of facilities around the world. A significant part of these fuels are clad in aluminium or its alloys and stored in different types of light water pools for periods of up to 50 years. Concerns related to degradation of the stored spent fuels lead to determining the corrosion behavior of a variety of aluminum alloys normally used to clad different types of research reactor fuels. This was done by exposing circular coupons to spent fuel basin water for different duration followed by examination and evaluation of the coupon surface features. This paper summarizes the results obtained over a period of 6 years from a number of tests in which many racks with coupons were exposed to the spent fuel basin of the IAE-R1 research reactor in São Paulo, Brazil. The effect of aluminum alloy composition, bimetallic contact with stainless steel, crevices, water parameters and synergism between these parameters as well as settled solids on the corrosion behavior of the coupons are presented. The results of an exploratory investigation to develop conversion coatings to protect Al clad spent research reactor fuel is also presented.

2. MATERIALS AND METHODS

Circular coupons of aluminum alloys AA 1100 (or AA 1050) and AA 6061 (chemical composition shown in Table 1) were assembled in stainless steel racks with alumina separators as shown in Figure 1. The separators were used to avoid metallic contact between coupons and between the coupons and the rack. A typical stack of coupons in the rack consisted of not only a coupon of each alloy but also coupled coupons such as AA 1100 - AA 1100, AA 1100 - AA 6061, AA 6061 - AA 6061, AA 1100 - SS 304 and AA 6061 - SS 304. The Al alloy-Al alloy and Al alloy-stainless steel couples were included to simulate crevices and bimetallic (galvanic) contacts. The racks were immersed both vertically (with its coupons horizontal) and horizontally (with its coupons vertical) [1]

Table 1. Chemical composition of the aluminium alloys.

Alloy	Cu	Mg	Mn	Si	Fe	Ti	Zn	Cr	Al
AA1100	0.16	<0.1	0.05	0.16	0.48	0.005	0.03	0.005	Balance
AA1050	<0.05	<0.03	<0.03	<0.25	<0.35	<0.03	<0.05	<0.03	>99.5
AA6061	0.25	0.94	0.12	0.65	0.24	0.04	0.03	0.04	Balance

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

The coupons and the racks were photographed prior to and after stacking and the assembled racks were immersed in the IAE-R1 reactor spent fuel storage basin for periods of up to 3 years. During this period the spent fuel basin water parameters such as pH, conductivity, chloride content, temperature and other ions were monitored periodically. Graphs of variations in temperature, conductivity and pH as a function of time were plotted to help correlate coupon corrosion with water parameters. After pre-determined periods the racks were withdrawn from the basins, photographed and disassembled. The pH in the crevices of the crevice and bimetallic couples were measured. The coupons were examined in an optical microscope coupled to an image analysis system.

3. RESULTS AND DISCUSSION

The racks were withdrawn from the basin after 0.5, 1, 2 and 3 years. Figure 2 shows a typical plot of variations in temperature, conductivity and pH during the year 2004. The pH of the water in the crevice between the various couples was found to be about 4.5-5.0, one half to one point below that of the bulk water pH.

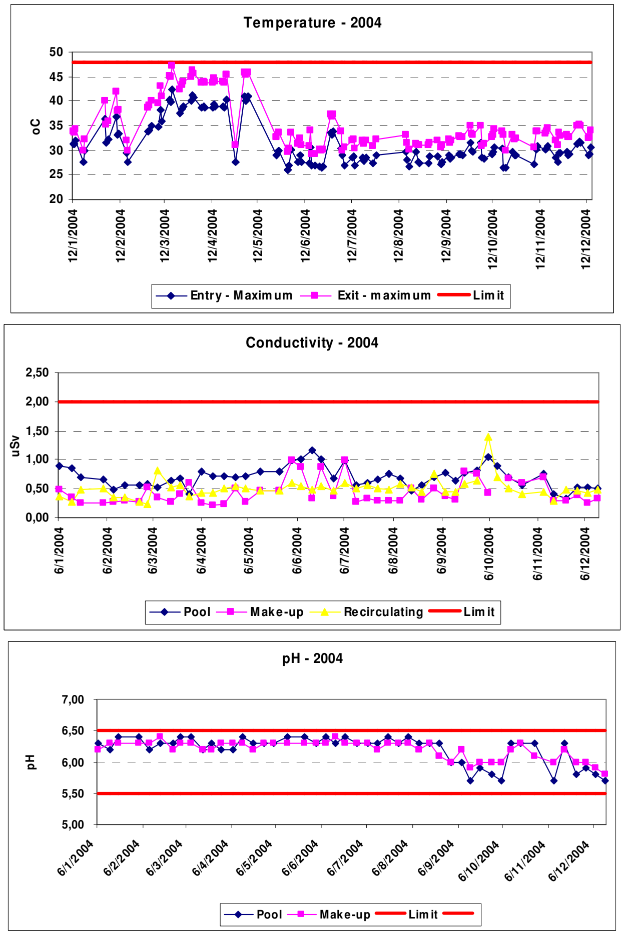

Figure 2. Temperature, conductivity and pH profiles during 2004 in the spent fuel basin of the IEA-R1 research reactor in São Paulo, Brazil.

3.1. Coupon surface features

The two sides of the coupons were examined and the main features with respect to corrosion were recorded photographically. The features and/or the extent of corrosion of the coupons were correlated to basin water parameters. This section presents the main findings with typical examples.

3.1.1. Pitting corrosion

The surfaces of the different aluminium alloy coupons revealed pits, and these increased in number and size with increase in conductivity and chloride content of the basin water. However, many features such as pit distribution, pit shape, stained regions around pits, oxide nodules, general coupon staining, oxide formation, color and texture of oxides were specific to the alloy, whether the coupon was or not in contact with another coupon of the same material or a different alloy, the position of the coupon in the rack and the orientation of the coupon. [2] Most pits revealed a bright region around the pit, characteristic of a cathode region around a localized anode region. The shape of this bright region also varied from circular to elliptical. (Figure 3) Pit distributions on the different coupon surfaces were examined. Histograms of number of pits (counts) as a function of pit diameter were plotted. Comparison of pit histograms of the different coupons revealed that alloy AA 1050 or AA 1100 pitted more than AA 6061. [3]

Comparison of pit features on horizontal and vertical coupons revealed that the bright regions around pits on vertically oriented coupons were shaped like a comet with a tail, unlike those around pits on a horizontal coupon, giving thereby a clear indication of the orientation of the coupon. (Figure 4)

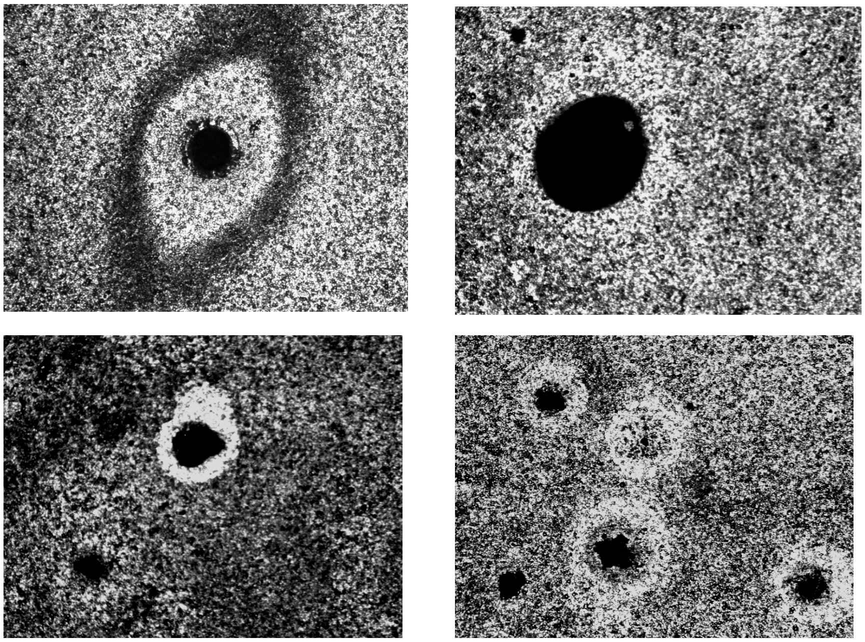

Figure 3. Micrographs showing pits and bright regions on horizontal AA 1050 surfaces.

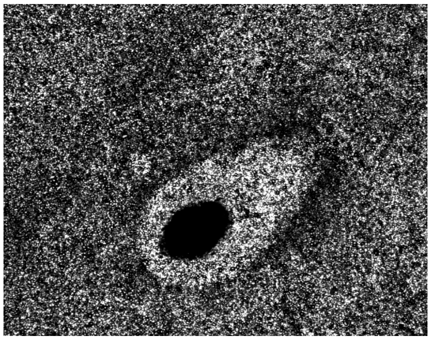

Figure 4. Optical micrograph of vertically oriented AA 1050 surface revealing comet shaped bright region around a pit.

3.1.2. Crevice and galvanic corrosion

The facing surfaces of the crevice couple coupons, AA 1050-AA 1050, AA 1050-AA 6061 and AA 6061-AA 6061 were stained and/or covered with a thick layer of oxide. The stains on the surfaces of the two alloys were distinct and characteristic of the alloy. The number and size of pits were higher in cases where the coupons were in contact with stainless steel. (Figure 5) [2, 3]

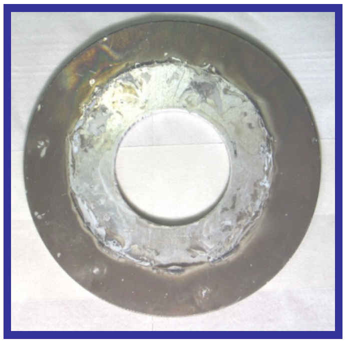

Figure 5. Corrosion of AA 6061 coupon in contact with a SS coupon.

3.1.3. Pitting as a function of coupon orientation

Comparison of pit histograms obtained for the horizontally oriented top surface of AA 1050 coupon exposed for one year, with that obtained for one of the surfaces of the same alloy oriented vertically (Figure 6) revealed that twice as many pits (size range 40-50 μm) form on the horizontal coupon as compared to that on the vertical coupon. [3]

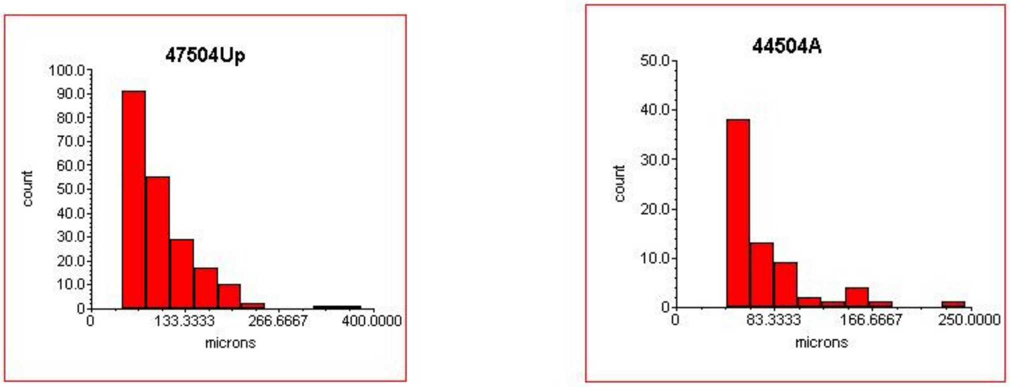

Figure 6. Histograms of pit count versus pit size on the upward facing surface (47504Up) and vertical surface (44504A) of AA 1050 coupon.

This indicated that among the many parameters that control pit formation, such as alloy composition, metallurgical state and water parameters, settled solids contribute to pit initiation and formation. The top surfaces of horizontal coupons corroded more than the bottom surfaces of the same coupon. The nature of the settled solid particles affected the nature of pitting attack on the Al surface. These observations lent further proof of the dominant role of settled solids on the corrosion of Al coupons and by extension on the corrosion of Al-clad spent research reactor fuel. Consequently, this aspect was studied in detail by installing a sediment collector for 4 months and the solids were analyzed. Quantitative x-ray fluorescence analysis revealed that the settled solids were primarily oxides of Al, Si, Fe and Ca.

3.2. Conversion Coatings For Spent Al-Clad Fuels

The use of inhibitors or conversion coatings to protect spent fuel surfaces has never been considered. Exploratory investigations were carried out to prepare cerium based conversion coatings on Al alloys used as RR fuel cladding material, namely AA 1100 and AA 6061. The electrochemical behavior of uncoated and cerium dioxide coated specimens of the two alloys in 0.1 M NaCl was determined. The results, summarized in Table 2, revealed that the cerium dioxide coated specimens had higher corrosion potentials and lower corrosion current densities. 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. [4]

Table 2. Corrosion current density (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
AA 6061	None	4×10^{-5}	- 770
	Solution - 2	4×10^{-6}	- 790
	Solution - 3	1×10^{-6}	- 630

Solution -2: $CeCl_3$, H_2O_2 and solution-3: $CeCl_3$, H_2O_2, Cu (glycinate) [4]

4. GENERAL DISCUSSION

Pitting was the main form of corrosion. The number, size and distribution of the pits on the coupons varied. The factors that contributed to corrosion of aluminum alloys were: (a) high water conductivity (100-200µS/cm); (b) aggressive ion concentration (Cl^-); (c) galvanic coupling between dissimilar metals (stainless steel/aluminum); (d) settled solids that were cathodic with respect to aluminum; (e) sludge; (f) scratches and imperfections in the surface oxide; (g) poor water circulation. Direct correlations between these parameters and pitting corrosion of Al alloy coupons were observed. [5-7] Synergism has been observed in the effect of these parameters on Al corrosion. That is, the combined effect of two or more of the parameters on Al corrosion was greater than the sum of the effects of individual parameters.

Laboratory test data and Al coupon evaluation data have indicated that even though no pits formed in chloride ion free neutral pH waters with conductivity of 10-20 $\mu S\ cm^{-1}$ and in distilled water with chloride ions in the ppm range, pitting was observed in waters with even lower conductivity (~2 $\mu S\ cm^{-1}$) and with some chloride ions. [8] This indicated synergism in the effects of conductivity and chloride ion content on pitting corrosion of Al. Proof of synergism in the effects of galvanic coupling and conductivity/chloride ions was evident when the contact surfaces of coupons in the crevice couple and in the galvanic couple (in the same rack) was compared. The surface of the Al alloy in the crevice couple was stained with Al oxide but had no pits. However, the surface of the same Al alloy in contact with the stainless steel (SS) coupon revealed many pits. (Figure 2). In a similar manner synergism was observed between settled solids and galvanic contacts.

5. CONCLUSIONS

1. Pitting was the main form of corrosion. The number, size and distribution of pits on the Al alloy coupons varied with alloy composition, basin water parameters, galvanic contact and settled solids.
2. The Al alloy coupons were also prone to crevice and galvanic corrosion.
3. Synergism was observed in the effect of the different parameters that affected Al corrosion.
4. Cerium dioxide conversion coatings improved the pitting corrosion resistance of Al alloys. Further evaluations are necessary before these can be considered for protecting spent Al-clad research reactor fuel during extended wet storage.

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