



CORROSION BEHAVIOUR OF CLADDING MATERIALS OF RESEARCH REACTOR SPENT FUEL DURING WET STORAGE

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The present investigations deal with the study of the effect of water chemistry of spent fuel storage bay on corrosion properties of cladding materials of research reactor. Coupons of four different alloys of stainless steel (SS 316) and aluminium alloys (Al 6063, Al 6061 and Al 1100) in form of discs were assembled on a rack forming galvanic couples and crevice sandwiches. The rack was immersed in the spent fuel storage bay for a period of one year exposure. The monthly inspection of specimens was conducted out based on visual observation and photography. The analyses of water were done on weekly basis. After exposure of one year the rack was withdrawn and disassembled in the laboratory. The surface of each individual coupon was observed visually and by means of optical microscope. Visual observation revealed relatively more deposits of scale on aluminium samples in the galvanic couples compared to stainless steel (SS) samples. In the crevice sandwiches (Al+Al) both upper and lower samples were found almost identical with respect to scale deposits. The microscopic observations showed no pitting on any sample except at selective areas only in contact with ceramic spacers.

Keywords: Pitting & crevice corrosion, Aluminium alloys, Stainless steel, Optical microscope, Research reactor

1. Introduction

Aluminium clad spent fuel from research and test reactors worldwide are currently being stored in water filled basins while awaiting final disposition. The spent fuel has been in water at the reactor sites for upto several years in some cases. As a result of corrosion issues that developed from the long term storage of the aluminium clad fuel the International Atomic Energy Agency (IAEA) implemented a Coordinated Research Programme (CRP) to assess the corrosion behaviour of fuel cladding materials in research reactor spent fuel storage bay water. Aluminium and its alloys have lower thermal neutron capture cross section, good tensile strength and thermal conductivity. These alloys are frequently used as fuel cladding and construction materials in water-cool reactors. Aluminium owes its excellent corrosion resistance in most environments due to the protective barrier oxide film formed and strongly bonded to its surface. This oxide film is relatively inert and tends to resist further oxidation. In the wet storage of aluminium clad spent fuel, a number of corrosion mechanisms plays a role. When the films is damaged under conditions, where normal self-healing does not occur, localized corrosion in the form of pitting or intergranular attack can occur

[1,2]. There is no significant general corrosion or gradual thinning of aluminium as may occur with steel [3] and highly susceptible to failure by galvanic attack [4]. However, in chloride bearing solutions these are susceptible to galvanic corrosion [5]. The primary mechanism of corrosion of aluminium alloys is pitting. It has been observed [6-8] that pits usually start at small points on the surface and enlarge with time. A number of studies have been conducted in synthetic waters containing several metal and salt ions alone and in combination [9-11]. Amin et al. [12] studied the pitting corrosion of Al in perchlorate solutions and found that the rate of pit nucleation increases with increase in ClO_4^- concentration. It has been reported [13] the successful storage of Al1100 clad fuel in its pool for over 25 years, where continuously deionized water at typically $1 \mu\text{S}/\text{cm}$ or better has been used. Kain et al. [14] concluded in their study that pure aluminium clad research spent fuels are susceptible to crevice and pitting corrosion under condition of galvanic and crevice.

The main objective of the present study is to assess the pitting and crevice corrosion behaviour of aluminium and stainless steel in research reactor spent fuel storage bay water with respect

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Table 1. Chemical composition of alloys*.

Alloy	C (%)	Cu (%)	Mg (%)	Mn (%)	Si (%)	Fe (%)	Ti (%)	Zn (%)	Mo (%)	Cr (%)	Ni (%)	Al (%)
SS 316	0.08	-	--	2.0	1.0	Balance	-	-	2-3	16-18	10-14	-
6061	-	0.25	0.94	0.12	0.65	0.24	0.04	0.03	-	0.04	-	Bal.
6063	-	0.16	0.73	<0.05	0.37	0.24	0.04	0.03	-	0.055	-	Bal.
1100	-	0.16	<0.1	0.05	0.16	0.48	0.005	0.03	-	0.055	-	Bal.

*Analysis provided by IAEA

to its water management facilities. The rack was immersed in bay water near to stored spent fuel racks. The results have been reported, which are based on the conditions maintained at fuel storage bay. The results of visual examination and microscopic observation have been described alongwith weight gain data and water analysis.

2. Experimental

2.1. Immersion and monthly inspection of rack

The chemical analysis of stainless steel (SS) and Al-alloys provided by IAEA are given in Table 1. As required all the specimens (total 10) alongwith rack and insulating (separating) washers were degreased ultrasonically using alcohol, rinsed with water, dried, weighed, measured the dimensions of each sample and finally assembled on the rack according to the plan shown in Fig. 1. A nylon cord was used to suspend the rack in the basin pool and immersed in pool and allowed to remain there for one year. The exposure dose rate in the region of fuel rack was initially $7.68 \mu\text{Sv}$, which decreased down to $1.96 \mu\text{Sv}$ at the termination of test time. During the exposure water samples were regularly collected from the pool on weekly basis and analysed for their temperature, pH, conductivity, anion and chloride contents. The visual inspection of the rack was conducted after every month of exposure to the basin water. Each inspection was carried out after withdrawing the rack from the pool for a very short time. The camera photographs were made and visual observations were recorded regularly.

2.2. Withdrawal of rack

After the period of one year the rack was withdrawn permanently from the basin water. The rack was dismantled and cleaned the test specimens. The specimens were decontaminated with 5% phosphoric acid solution, rinsing with deionized water and dried at room temperature. After decontamination each sample was immersed

in a 50% phosphoric acid solution, in order to clean/dissolved oxide in the pits, and specimens were removed from the solution as soon as bubbles start to increase [15]. The weight was measured and corrosion rates were calculated of each test specimen by weight loss technique [16]. Surface condition for general and pitting corrosion of each specimen was observed under an optical microscope-Litez-400.

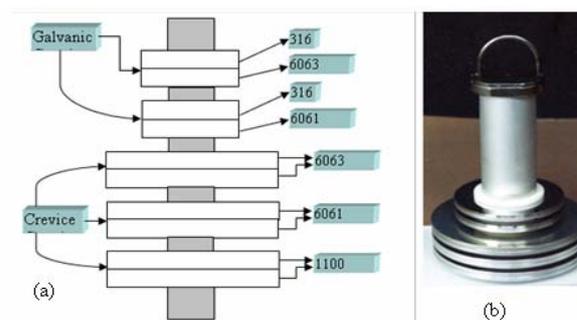


Figure 1. Depicts (a) schematic arrangement of specimens (b) test specimens assembled on rack.

3. Results and Discussion

3.1. Visual observations

Exposed specimens were visually inspected every month and the overall observations are presented in Table 2. Water samples were collected weekly and their pH and conductivity were measured. The data obtained during the whole exposures time are plotted in Fig. 2. The monitoring results have indicated that the pH remains in the range 5 to 6 and conductivity falls between 1 and 0. The chlorides ions were also measured by Ion Chromatographic technique and result showed that the water quality meets the standard requirements. The radiation level near the specimen rack was continually checked during inspection and was found below the detection limit. At the time of withdrawal the following observations were recorded in the laboratory during their dismantling.

Table 2. Monthly inspection of specimens for corrosion.

Exposure Days	Observations / Conditions
31	Pitting was not observed in the samples but discolouration was noticed
61	No corrosion, however, samples were slightly bright in colour
92	No pitting corrosion in the samples
123	No Pitting Corrosion. Samples were found dull in colour
151	Samples were dull but no corrosion found
182	No corrosion but samples were dull in colour
212	The same observation as noticed in the previous inspection
243	Samples were dull. No indication of pitting corrosion
273	No any type of corrosion was observed but discoloration was noticed
304	Corrosion was not observed
335	Samples were dull in colour and corrosion was not observed
365	No pitting corrosion was observed on exposed surfaces.

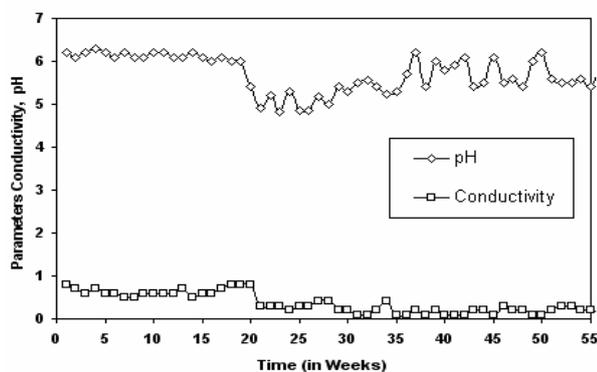


Figure 2. Data obtained during one year for pH and conductivity of water samples.

- Galvanic and crevice specimens could be removed by sliding and pulling.
- No loose deposits were found on the surface of specimens.
- No change in the appearance of stainless steel specimen was found while Al-specimens had turned dull white.
- No pitting was observed on exposed surfaces by visual inspection.
- No staining, loose oxide or embedded particles were found on the surfaces.

The corrosion rates of specimens after 365 days exposure in the basin water are presented in Fig. 3. These results indicate that the aluminium samples were relatively more affected as compared to stainless steel samples. Visual observation of galvanic samples showed that there were more deposits of scale on aluminium samples as compared to stainless steel (SS) samples. In the crevice couples both aluminium samples (Al + Al) were found almost identical with respect to scale deposits on their surfaces.

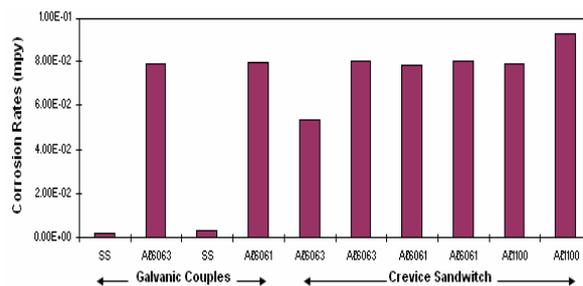


Figure 3. Corrosion rates of galvanic couples and crevice sandwich.

3.2. Optical microscopic observations

3.2.1. Galvanic couples

Exposed specimens of galvanic couples were observed under optical microscope. In stainless steel sample (SS316/112) no pitting and deposition were observed. Only boundary marks of insulating washer and some scratches which had occurred during assembling on the specimens. In sample Al6063/114 (surface exposed to water) areas under washer remained bright but showed pitting of 4µm under washer surface. These pitting were mostly round, elliptical, shallow and a few undercutting as shown in Fig. 4a. No pitting was observed on the coupled surface. In other galvanic couples the stainless steel sample (SS316/119), in the surface exposed to water, a band of etched out area as a boundary line (without any pitting) was produced under and along the outer edge of insulating washer. On the coupled surface some steaks of scale 2µm thick formed due to seepage of water. However, on the surface of the sample Al6061/143 (exposed to water surface) 6 to 20µm deep pitting was observed only under ceramic washer, mostly having round openings and grain boundaries were also etched out as shown in Fig. 4b. No pitting on coupled surface was observed.

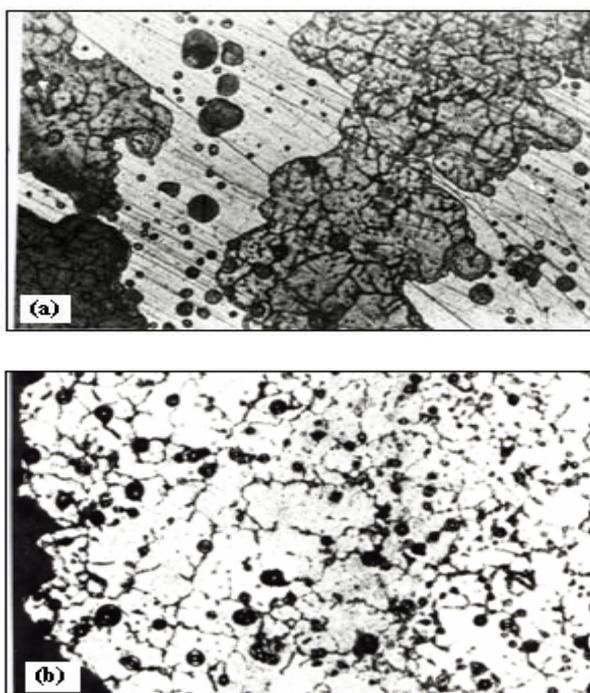


Figure 4. Micrographs of galvanic couple (a) Aluminium 6063/114 exposed surface and (b) Aluminium 6063/143 exposed surface.

3.2.2. Crevice sandwiches

In the first crevice sandwich (Al6063/167-Al6063/187) of aluminium the top surface under ceramic washer of sample Al6063/167 having round & irregular shape of pittings 8 to 18 μ m in size and mostly found at grain boundaries as shown in Fig. 5a. Some shallow pits of 2 μ m depth were observed on coupled surface while most of the area remained un-attacked, (Fig. 5b). In the case of sample Al6063/187 no pitting was observed on exposed surface. On the coupled surface scale formed at some areas due to water seepage between two coupled surfaces while other areas remained bright and un-attacked.

In the second crevice sandwich (Al6061/241 and Al6061/237), the area under insulation washer of sample Al6061/241 has showed some pealed off scales where region without scale showed very shallow pits are shown in Fig. 5c. The thickness of scale was measured which is about 10 μ m thick on the exposed surface. No pitting observed on the coupled surface and areas in contact with each other remained bright. In sample Al6061/237 the pits with maximum 20 μ m depth were observed in the area remained under insulation washer

(Fig. 5d). Uniform scale observed along the water channels on the surface exposed to water.

In the third crevice sandwich (Al1100/228 and Al1100/221) a few undercut type of pits 10 to 16 μ m deep were found in the sample Al1100/228 (Fig. 5e). The dense scale at surface exposed to water was observed and no appreciable pitting found. In the sample, Al1100/221, thick and uniform scale observed on the exposed surface (Fig. 5f). Contact areas (Coupled surface) remained bright and no pitting was observed either on exposed or coupled surfaces.

The overall observations of surface conditions of each specimen after exposure are presented in Table 3.

As discussed before the results of water analyses have indicated that the water quality meet up the standard requirements. However, it seems that the water chemistry in the crevice (for Al-Al samples) could be more aggressive than that of the pool, and it would determine the susceptibility to pitting. In addition to water chemistry parameters other factors may also play a vital role to promote pitting of aluminum alloys [17-19] such as high conductivity of pool water, aggressive ions, sludge having concentrated Fe⁺⁺⁺ and Cl⁻ impurities, scratches/imperfections in protective oxide film.

4. Conclusions

1. In galvanic couple of SS 316 + 6063Al and SS316 + 6061Al general, pitting corrosion or any other forms have been observed on coupled surfaces.
2. The crevice sandwich of Al-alloys 6063, 6061 and 1100 respectively has not shown any symptoms of general, pitting or crevice corrosion on the coupled surfaces of similar alloys.
3. The surfaces of Al-alloys 6063, 6061 and 1100 suffered pitting of the sizes 4-18, 6-20 and 10-16 μ m depth respectively.
4. The surfaces of the stainless steel (SS316) specimens exposed to water have not shown any corrosion and scale deposition. Only thin scale has developed on the opened surfaces of all Al-alloys exposed to water.

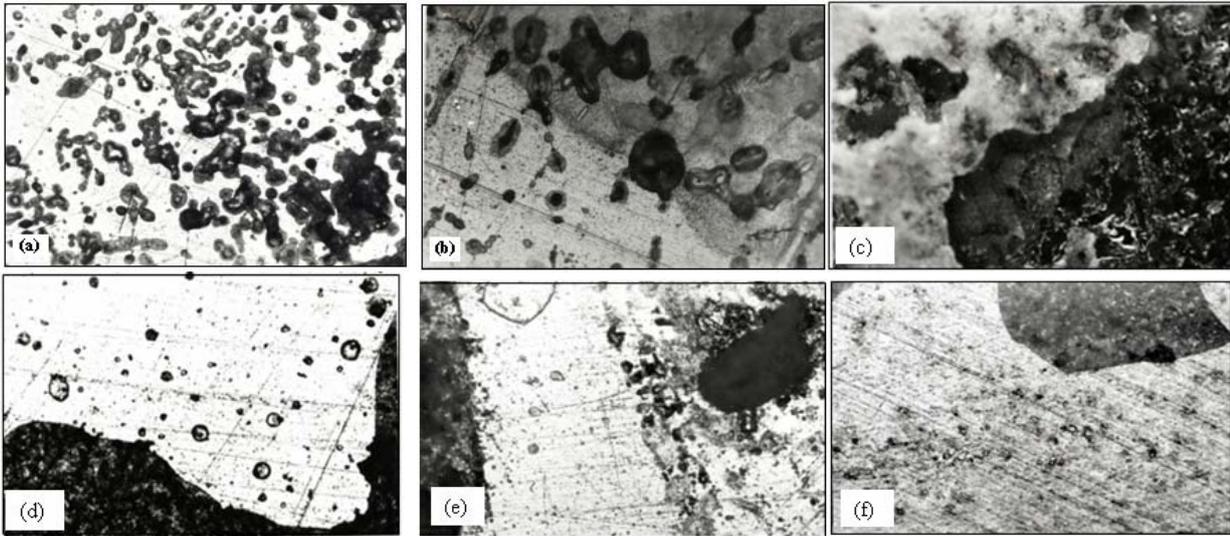


Figure 5. Micrographs of crevice sandwich of exposed surfaces of Al specimens (a) 6063/167 (b) 6063/167 coupled surface (c) 6061/241 (d) 6061/237 (e) 1100/228 (f) 1100/221.

Table 3. Microscopic observations of exposed specimens.

	Sp.#	Microscopic Observations
Galvanic couple	316/112	No pitting and deposition only boundary marks of insulating washer and some scratches which had occurred during assembling on the specimens
	6063/114	Pitting of 4 μm under washer surface. These pitting were mostly round, elliptical, shallow and a few undercut (Fig. 4a).
Galvanic couple	316/119	On the surface exposed to water, a band of etched out area as a boundary line (without any pitting) and on the coupled surface some steaks of scale 2 μm thick formed due to seepage of water
	6061/143	On the surface exposed to water, 6 to 20 μm deep pitting under ceramic washer (Fig. 4b). No pitting on coupled surface was observed.
Crevice sandwich	6063/167	Pitting (round & irregular) of 8 to 18 μm (Fig. 5a) under ceramic washer. Pits of 2 μm depth on coupled surface (Fig. 5b).
	6063/187	No pitting on exposed surface. On the coupled surface scale formed at some areas due to water seepage, while other areas remained bright and un-attacked
Crevice sandwich	6061/241	The area under insulation washer showed some peeled off scales where region without scale showed very shallow pits (Fig. 5c). No pitting on the coupled surface
	6061/237	Pits with maximum 20 μm depth in the area remained under insulation washer (Fig. 5d). Uniform scale observed along the water channels on the surface exposed to water
Crevice sandwich	1100/228	A few undercut type of pits 10 to 16 μm deep on coupled surface (Fig. 5e). No appreciable pitting on surface exposed to water
	1100/221	Thick and uniform scale on the exposed surface (Fig. 5f). Coupled surface remained bright and no pitting

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References

- [1] H.G. Godard, The Corrosion of Light Metall, Wiley, New York (1967) 3.
- [2] H.G. Godard, Mater. Performance **20** (1981) 9.

- [3] H.G. Godard, Can. J. Chem. Eng. **38** (1960) 167.
- [4] Metals Handbook, ASM International, 9th edn. Vol. 13, Metals Park, OH (1987) 18.
- [5] J. P. Howell, Corrosion/95, Natl Assoc. of Corrosion Engineers, Houston, TX (1995) paper 429.
- [6] M.G. Fontana, Corrosion Engineering, 3rd Edn, McGraw Hill, New York (1986).
- [7] C.A. Hampel, Editor, Encyclopedia of Electrochemistry, Reinhold, New York (1964) 925.
- [8] P. M. Aziz, H. P. Godard, J. Ind. Eng. Chem. **44** (1952) 1791.
- [9] F. C. Porter and S. E. Hadden, J. Appl. Chem. **3** (1953) 385.
- [10] D. E. Davies, J. Appl. Chem. **9** (1959) 651.
- [11] L. C. Rowe and M. S. Walker, Corrosion **17** (1961) 105.
- [12] M. A. Amin, S. S. Abd El Rehim and E.E.F. El Sherbini, Electrochimica Acta, **51** (2006) 4754.
- [13] J P. Howell, Corrosion of aluminum-clad spent fuel in reactor basin water storage, Corrosion/96, Natl. Assoc. of Corrosion Engineers, Houston, TX (1996).
- [14] V. Kain, K. Agarwal, P.K. De and P. Seetharamaih, J. Mat. Eng. Perform., **9** (2000) 317.
- [15] Test Protocol, IAEA-CRP (1995).
- [16] M.G. Fontana, N.D. Greene, Corrosion Engineering, 2nd edition , McGraw-hill, (1978) p. 9.
- [17] H. Bohni and H.H. Uhlig: J. Electrochem. Soc. **116** (1969) 906.
- [18] J.P. Howell and P.E. Zapp. Corrosion 94 Houston, TX, 1 (994) paper No. 118
- [19] J.P. Howell, Corrosion 96, Houston, TX, (1996) paper No. 128.