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Test Protocol for Aluminum Based Spent Nuclear Fuel

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Abstract

Aluminum based spent nuclear fuel (Al-SNF) will be treated and then stored in a geological repository. A series of corrosion tests, including coupon, galvanic, and electrochemical, were performed to measure the effects of degradation on U-Al alloys, which simulated various Al-SNF forms. The test solutions were variants of a J-13 well water chemistry. As part of the degradation characteristics, the dissolution of uranium, which is the primary radionuclide, was measured. The degradation and dissolution were changed by the type of water chemistry and the temperature. The alloy composition and fabrication were not significant variables.

Introduction

The Department of Energy (DOE) is pursuing several options for the disposition of aluminum-based spent nuclear fuel (Al-SNF) in the national repository. The degradation of Al-SNF in the repository will differ from that of the commercial nuclear fuels and the high level waste glasses. The Al-SNF is less stable and more reactive than the other waste forms, in part due to the aluminum cladding and the aluminum-rich matrix of the fuel. Aluminum may also be susceptible to galvanic corrosion when coupled with a canister material, such as stainless steel. The fuel meat of the Al-SNF, which has a two-phase structure, is more highly enriched than commercial fuels. Therefore, an understanding of the corrosion of the Al-SNF and its release of radionuclides is necessary.

A test program was undertaken at the Savannah River Site to develop a database that will provide preliminary input for the performance assessment of Al-SNF. The database will consist of information on both the environmental degradation and redistribution of radionuclides. This paper focuses on the results of testing to evaluate the corrosion and degradation mechanisms of Al-SNF in waters anticipated during the long-term repository storage. Static coupon, galvanic corrosion, and electrochemical tests were performed on U-Al alloys in modified waste chemistries of J-13 well water. J-13 well water is a characterized water stream near the Yucca Mountains, a possible repository site. Test temperatures were 25 and 95 °C.

The results from all three tests showed that the test environment, which included J-13 water chemistry and temperature, had the greatest effect on the corrosion of U-Al alloys. Alloy composition and fabrication technique had a minimal effect on corrosion behavior. A galvanic couple with stainless steel had greater degradation and uranium dissolution than a couple with aluminum. The degradation of the U-Al alloys was observed to follow a two-stage process. During the initial stage, preferential corrosion of the aluminum matrix adjacent to U-Al particles occurred independent of the environmental variables. During the second stage, an oxide film formed on the surface of the coupon; the thickness depended on the environmental conditions. The alloys were also susceptible to pitting in certain environments.

Experimental Procedure

The experimental procedures of the three techniques, static, galvanic, and electrochemical, differed slightly, but maintained constancy of test variables to determine the effects on the degradation of U-Al alloys and the uranium dissolution. The variables were the J-13 water chemistry, the U-Al alloy composition, temperature, type of galvanic coupling, and fabrication.

Static Test

For the static tests, the procedures and apparatus were developed from ASTM G31-71 [1]. The test apparatus consisted of a 2.5 L glass vessel, heating mantle, and temperature controller. The static tests were conducted so that the U-Al samples were coupled to either a stainless steel or aluminum plate for investigating galvanic and crevice corrosion. Figure 1 shows a schematic of the test apparatus. Temperatures of 25 and 90 °C were used.

The samples were bolted to the plates with nylon hardware, which passed through a central hole drilled through the sample. The samples were 0.5-inch cubes with surfaces ground to a 1000 grit finish. Pre- and post- test characterization, including optical metallography and SEM, were performed for each sample to detect changes in structure. Samples were also weighed to monitor weight changes resulting from corrosion or oxidation.

Figure 1 - Schematic of Static Test Apparatus

The tests were performed for one month. Samples were removed from the vessel at intervals of 7, 14, and 28 days which provided data for the time dependence of the degradation process. Samples of the test solution were taken to determine concentrations of aluminum and uranium. Chemical analyses included ICPES for aluminum and Chemcheck$^{(tm)}$ for uranium. After the test, the solution was filtered to remove any particulate, which was subsequently analyzed using SEM and EDS.

Galvanic Corrosion Test

The galvanic corrosion tests were configured to quantify the galvanic interaction between the U-Al alloys and stainless steel, which is a candidate canister material. The galvanic test cell was similar to that for the static tests. The samples were 0.5-inch cubes which were mounted in a cold cure epoxy. For an electrical contact, a wire was attached with a silver epoxy prior to mounting. The surface was polished to a 600 grit surface finish and cleaned prior to immersion. The sample was placed one inch over a stainless steel plate with the face of the sample directed towards the plate. The electrode areas were 126.6 cm2 for the plate and 1.6 cm2 for the sample.

The solution was brought to temperature with the stainless steel plate in the test cell. The sample was immersed and the test initiated. The tests were conducted for four days. The current was measured either with a computer controlled EG&G Princeton Applied Research Model 273 potentiostat or a Keithley current amplifier and portable analog data logger. After testing, the samples were examined with a SEM/EDS system. Solution samples were taken for chemical analysis to determine the uranium and aluminum concentrations.

Electrochemical Tests

The electrochemical tests included linear and cyclic potentiodynamic polarization. The test procedures were based on ASTM standards [2,3]. The samples were similar to those used for the galvanic corrosion test except that a 800 grit surface finish was used. Corrosion parameters and characteristics that were determined from the data included the corrosion potential, a general corrosion rate (linear polarization resistance), and pitting susceptibility. After the test, a sample was visually evaluated for corrosion morphology. Solution samples were taken after testing for chemical analysis of the uranium and aluminum concentrations.

The tests were performed with an EG&G Princeton Applied Research Model 273 potentiostat under computer control. For the linear and cyclic tests, the samples were polarized from the natural or open-circuit potential at a rate of 0.2 mV/sec. The linear polarization was performed on the sample prior to the cyclic scan. The samples were placed into standard glass electrochemical cells after the solution had come to temperature. Test temperatures included 25 and 95 °C. The counter electrodes were graphite rods and the reference electrode was a high temperature Ag/AgCl electrode. Air was bubbled slowly through the solution during the test.

U-Al Alloys

A range of U-Al alloys was tested to cover a range indicative of Al-SNF. The compositions were 10, 13.2 (eutectic), and 25 wt % U with the balance aluminum (10 UAl, 13 UAl, and 25 UAl).

The U-Al alloys were produced from a supply of bulk aluminum ingots (1100 Al) and depleted uranium. The materials were melted in an induction furnace between 800 and 1400 °C, depending on the alloy composition. The alloys were cast into molds and cooled in air. Metallographic analyses indicated that the microstructures were fairly uniform throughout the cross-section of the ingots. Several ingots of the 13.2 and 25 UAl alloys were extruded and rolled to produce a wrought structure. The wrought and cast structures were representative of either unprocessed or melt and diluted Al-SNF, respectively. Samples were cut from the ingots with either an electric discharge machine or a mill.

The surfaces of the coupons were examined with a scanning electron microscope (SEM) prior to initiating the tests. Figure 2 (a) shows a micrograph of the 10 UAl cast material. The dark area was the primary aluminum phase, while the light, skeletal areas are the eutectic phase. The eutectic consists of the lamellae of aluminum and the UAl_4 phase. The cast microstructure consists mostly of aluminum dendrites with eutectic filling the interdendritic regions. Figure 2 (b) shows a micrograph of the 13.2 UAl cast material, which was the eutectic composition. A greater fraction of the surface is covered with eutectic than was observed for the 10 UAl cast. Additionally, several blocky structures of the UAl_3 phase are present in the midst of the aluminum matrix. Figure 2 (c) shows a micrograph of the 25 UAl cast material. The UAl_3 phase was much more apparent at this composition. Small regions of the eutectic phase were also seen. The diamond shape particles with the dark center (i.e., aluminum phase) are also the UAl_4 phase. Figure 2 (d) shows a micrograph of 13.2 UAl wrought material. Due to the rolling of the material the particles were crushed and are aligned in the rolling direction.

Figure 2 - Microstructures of U-Al Test Samples: a) 10 UAl cast, b) 13.2 UAl cast, c) 25 UAl cast, d) 13.2 UAl wrought

Test Solutions

The solutions for all the tests were based on the composition of a water stream characterized from a well near a proposed repository site. Variations of the J-13 water were used to simulate various scenarios due to interactions with soils and other waste forms. The J-13 water with a pH of ~8 had a nominal composition similar to that of Beavers et al. [4]. Three other variants of J-13 were used for the remaining tests: low pH (~3), high pH (~11), and high chloride (60 ppm versus 7 ppm Cl^-). The low and high pH J-13 waters were made by additions of either nitric acid or sodium hydroxide, respectively. Additional sodium chloride was added to make the high Cl J-13. The conductivities of these J-13 waters ranged as follows: nominal J-13, 250-350 µS; low pH, 450-600 µS; high pH, 1200-7500 µS; high Cl, 400-450 µS. The solutions were made from distilled water and reagent grade chemicals.

Experimental Results

The experimental results from the three test methods gave similar results. Each method produced different insights into the corrosion of U-Al alloys. In general, the degradation changed with the water chemistry, temperature, and galvanic coupling, but not the alloy composition or fabrication technique.

Static Test Results

The overall degradation that occurred during the static tests was small with the majority of the corrosion occurring on the sides of the coupon rather than the bottom crevice area. The corrosion of the U-Al alloys depended primarily upon the test environment and not the U-Al microstructure or the fabrication method. Coupling the coupons to stainless steel increased the severity of attack for a given test solution, as did increasing the temperature of the environment. Concentrations of dissolved uranium and aluminum were consistent with the observed degradation of the coupon. Relatively small changes in the weights of the coupons were measured; however, general trends were consistent with the observed degradation.

Morphology of Corroded U-Al Alloys. Coupons immersed in nominal J-13 showed only slight evidence of degradation with few white corrosion products that were indicative of pitting of the aluminum matrix. Figure 3 shows the corroded surface of a 13.2 UAl cast coupon that was exposed to nominal J-13. Original grinding marks were seen on the surface indicating that minimal general corrosion occurred. However, the aluminum matrix adjacent to the U-Al eutectic was preferentially corroded leaving the particles in relief. The micrograph also shows evidence that eutectic particles became dislodged from the surface. U-Al particles were collected by filtering the solution after the test. The degradation features of preferential corrosion of aluminum near U-Al particles and particle dislodging were observed in all solutions.

Figure 3 - Post-test Microstructure of 13.2 UAl Cast from Nominal J-13 at 90ºC

In low pH J-13, a whitish film was observed on the surface of the coupon with no associated white deposits. A thick oxide film covered the surface indicating a more general form of attack. The oxide contained many cracks and fissures with many U-Al particles embedded in the film. Figure 4 shows a cross-sectional view after exposure to the low pH J-13. Note the preferential dissolution of the aluminum matrix and the dislodging of the U-Al particles which are embedded in the oxide film.

Figure 4 - Cross-sectional View of Post-test Microstructure of 13.2 UAl Cast from Low pH J-13 at 90ºC

Exposure of the coupons to high Cl J-13 resulted in a blackening of the surface with numerous white corrosion products indicative of pitting. As with the nominal J-13, minimal general attack of the aluminum surface was observed. Pitting of the aluminum matrix was more severe than with the nominal J-13. Several large volcanic-like aluminum oxide formations were observed on the surface.

The high pH J-13 also resulted in the coupon becoming dark, but without white corrosion deposits. Figure 5 shows the degraded microstructure of the 13.2 UAl cast coupon that was exposed to the high pH J-13. Large, skeletal-like regions of the eutectic remained due to the high corrosion rate of aluminum. The corrosion of the aluminum was the most severe of all the test solutions.

Figure 5 - Post-test Microstructure of 13.2 UAl Cast from High pH J-13 at 90ºC

The test alloys had similar degradation or corrosion mechanisms. The aluminum matrix corroded preferentially leaving a surface rich in U-Al particles. The corrosion morphology of the 10 and 13.2 UAl samples were similar since both had only the eutectic UAl_4 phase. The 25 UAl alloy on the other hand consisted of both UAl_3 and UAl_4. Figure 6 shows a cross-sectional view of a 25 UAl cast coupon, which contained both phases, from the test in nominal J-13 at 90°C. The blocky UAl_3 particles at the surface were cracked and dislodged. The formation of a voluminous aluminum oxide beneath the particles created pressure on the brittle UAl_3 particle.

Thus, both UAl_3 and UAl_4 can be dislodged from the aluminum matrix without significant degradation of the particle.

Figure 6 - Cross-sectional View of Post-test Microstructure of 25 UAl Cast from Nominal J-13 at 90ºC

The fabrication process of the material affected the corrosion morphology of the, but did not change the corrosion mechanism. Figure 7 shows a cross-sectional view of a 13.2 UAl wrought coupon that had been immersed in low pH J-13 at 90 ºC. As was observed for the 13.2 UAl cast coupons, the U-Al particles became embedded in the oxide, however, the wrought particles are smaller in size and more easily engulfed in the oxide.

Figure 7 - Cross-sectional View of Post-test Microstructure of 13.2 UAl Wrought from Low pH J-13 at 90ºC

The type of galvanic couple and the temperature of the environment affected the severity of attack. For example, in the high Cl J-13 the number of pits was much greater for coupons attached to the stainless steel disk than to the aluminum disk. Increasing temperature also increased the severity of attack, both pitting and general corrosion. The number of deposits on the surface were less at the lower temperature than at the higher, although the deposits were more voluminous than at the higher temperature. This result probably reflects the lower solubility of the aluminum oxide at the lower temperature.

The crevice area of the coupons demonstrated little evidence of attack. The primary site of degradation was near the edge of the coupon. Figure 8 shows a typical crevice surface with a relatively thick oxide that contained striations. These markings were similar to the grinding marks from the stainless steel and aluminum disks as shown in the figure. Areas where this oxide had cracked and spalled were observed intermittently. Preferential dissolution of the aluminum was also seen at these local areas.

FIGURE 8 - Post-test Surface of Crevice Area of 13.2 UAl Wrought from Nominal J-13 at 90ºC

The uranium and aluminum concentrations in solution after testing were consistent with the degree of degradation or corrosion. The effects of alloy composition, water chemistry, coupling, fabrication and temperature were similar to those reported above. Table 1 shows the aluminum and uranium concentrations for 13.2 and 25 cast alloys coupled to stainless steel in the different waters. Table 2 shows the same concentrations except for the aluminum couple. As can be seen from the tables the alloy composition did not change the resultant concentrations. Although not shown, the fabrication process also did not alter the concentrations.

Table 1
Dissolved Uranium and Aluminum Concentrations at 90ºC Stainless Steel Couple

	Uranium (ppm)		**Aluminum (ppm)**	
Solution	**13.2 UAl cast**	**25 UAl cast**	**13.2 UAl cast**	**25 UAl cast**
J-13	0.6-0.7	0.5-0.6	2-3	2.5-4
Low pH	2.5	1-2	4-9	1-3
High Cl^-	0.25-0.3	0.25-0.4	3.5-6.2	2.2-9.6

High pH	3.5-4.5	3-4	36-40	11-15

Table 2
Dissolved Uranium and Aluminum Concentrations at 90ºC Aluminum

	Uranium (ppm)		**Aluminum (ppm)**	
Solution	**13.2 UAl cast**	**25 UAl cast**	**13.2 UAl cast**	**25 UAl cast**
J-13	0.05	0.1	5-6.5	2.5-4
Low pH	1-1.5	0.25-0.75	3.5-6	0.5-4
High Cl^-	0.05	0.08-0.1	8-15	2.5-4.2
High pH	0.1	2	63-80	12-13

The most significant effect on concentration was the water chemistry and the coupling, although the effect differed for uranium and aluminum. The uranium concentrations increased in the following order: high cl~nominal<low pH<high pH. The relative ratio differed depending on the couple, but were 2-10 times greater for the stainless steel couple than the aluminum.

The aluminum concentrations for the U-Al alloys were similar in the nominal, low pH and high Cl J-13 for the stainless steel couple. In the high pH J-13, the concentration was 5-10 times greater due to the higher solubility of aluminum in alkaline solutions. For the low pH solution a maximum aluminum concentration occurred after one week. This was attributed to the precipitation of an aluminum oxide film which was observed on the test samples. With the aluminum couple, the concentration was greater than the stainless steel couple in the nominal, high Cl, and high pH J-13. This result reflects the dissolution of the aluminum plate. The concentration was greater for the stainless steel couple than the aluminum for the low pH due to the formation of the aluminum oxide.

Galvanic Test Results

The galvanic interaction between the U-Al alloys and stainless steel varied with environmental or solution conditions, but appeared to be independent of the alloy composition. The results from the galvanic corrosion tests consisted of the measured galvanic current, the uranium and aluminum concentrations after testing, and the corrosion morphology of the samples.

The initial and steady state galvanic currents are shown in Table 3 for the U-Al alloys as a function of solution chemistry and temperature. For each solution chemistry and temperature combination, the galvanic currents were similar for the U-Al alloys, although a few anomalies occurred, such as the 10UAl alloy in nominal J-13 at 97 °C. The current trends either increased or decreased in changing from the initial to the steady state values. The current levels changed significantly with the solution chemistry, differing by two orders of magnitude. The order of aggressiveness, as indicated by increasing current values, was: High pH>>High Cl>Low pH, nominal J-13. The currents also decreased with temperature, approximately by an order of magnitude.

Table 3
Initial and Steady State Galvanic Current for U-Al Alloys

U-Al Alloy	Solution	Galvanic Current (µA) at 97°C		Galvanic Current (µA) at 25°C	
		Initial	Steady State	Initial	Steady State
10	Nominal	60	60	60	90
13.2		225	340	50	70
25		370	230	55	75
10	Low pH	340	140	65	45
13.2		220	160	55	50
25		450	140	55	45
10	High pH	5700	5000	4000	1150
13.2		5300	4000	3500	No Data
25		5900	3600	2800	675
10	High Cl	950	1000	220	200
13.2		1360	900	220	200
25		980	600	No Data	250

Similar trends were also observed for the aluminum and uranium concentrations shown in Table 4. The concentrations were independent of the alloy, but varied with solution chemistry and temperature. The uranium concentration did not show as strong a trend as the galvanic current, which was probably associated with the minimal degradation of the U-Al particles.

Table 4
Uranium and Aluminum Concentrations From Galvanic Corrosion Test

U-Al Alloy	Solution	Concentrations at 97°C		Concentrations at 25°C	
		Uranium	Aluminum	Uranium	Aluminum
10	Nominal	0.03	<0.017	0.03	<0.017
13.2		0.1	<0.017	0.02	<0.017
25		0.1	<0.017	0.02	<0.017
10	Low pH	0.12	3.5	0.09	0.73
13.2		0.12	3.7	0.11	0.92
25		0.13	3.0	0.18	0.58
10	High pH	0.07	105.5	0.005	32.7
13.2		0.05	107.7	0.004	25.1
25		0.68	58.9	0.011	35.7
10	High Cl	0.13	4.3	0.03	0.04
13.2		0.19	6.2	0.03	<0.03
25		0.19	0.6	0.03	0.07

The corrosion morphology was reflective of the galvanic currents and concentrations. The high pH J-13 caused significant and uniform corrosion of the alloys. The aluminum matrix was heavily attacked, leaving the surface rich in U-Al particles. Few corrosion products were formed. In the high Cl J-13, however, the alloys were heavily pitted with the formation of voluminous corrosion products at the high temperature. At the lower temperature, the number of pits and corresponding corrosion products were decreased. Within the pits and at the surface, the aluminum matrix was again preferentially attacked.

For both the low pH and nominal J-13, the surfaces had irregular oxide/corrosion product distribution. In low pH J-13, a white surface film was observed at 97 °C but not at room temperature. A powdery corrosion product formed on the samples exposed to the nominal J-13, although only at 97 °C. The attack was not as great in the nominal J-13 where initial grinding marks were observed after testing. Slight pitting occurred in the nominal J-13, but not in the low pH J-13.

Electrochemical Test Results

The results from the electrochemical test reflect those of the other tests. The corrosion behavior and polarization characteristics for the three cast alloys, 10, 13.2, and 25 UAl, were similar. The variable effects were evaluated for the corrosion potential, the linear polarization resistance, and the characteristics of the polarization scan (the potential-current plot). A corrosion rate (CR) was calculated from the linear polarization resistance (R_P) using the density ([rho]) and equivalent weight (EW) of aluminum.

The polarization curves displayed two distinct patterns indicative of changes in the corrosion characteristics that were dependent on the water chemistry and temperature. The primary degradation mechanism was low general corrosion accompanied by some degree of pitting. The pitting was dependent on the chloride concentration. The corresponding cyclic polarization curve is shown in Figure 9 for a 13.2 UAl sample in nominal J-13 at 90°C. In the high pH J-13, the alloys underwent general corrosion as shown by the polarization curve in Figure 10 for 10 UAl in high pH J-13 at 25°C.

The UAl alloys in low pH J-13 at 90 °C also showed an oxide-induced passivity which was susceptible to pitting. This passivity attributed to the more noble potential of the alloys. A pitting potential occurred at approximately -0.2 V. The UAl alloys grew a thick oxide/corrosion product layer during exposure as shown in Figure 4 from the static test. In the other waters, these layers were either not observed or not as thick. For the other conditions in which pitting was observed, the alloys probably did not manifest a pitting potential since their corrosion potentials were near or above the pitting potential.

Figure 9 - The Polarization Curve for 13.2 UAl in Nominal J-13 at 90 C

Figure 10 - The Polarization Curve for 10 UAl in High pH J-13 at 25 °C

The other electrochemical parameters, corrosion potential and corrosion rate, are shown in Table 5 as a function of the test variables. For any given water chemistry and temperature, the corrosion potentials of the alloys were similar. The most active values were those in the high pH J-13, ranging from -1.2 to -1.5 V. The corrosion potentials of the alloys in the nominal and high Cl J-13 waters were similar, typically -0.3 to -0.53 V. The corrosion potentials in the low pH J-13 were the most noble, -0.25 to -0.46 V. The potentials of the alloys became more active, that is more electronegative, with an increase in temperature in the nominal and high Cl waters. In the low and high pH J-13, the potentials became more noble. This potential shift for the low pH was not always steady but at times fluctuated between passive and active values indicating an unstable oxide or partial coverage by the oxide.

Table 5
Corrosion Potentials and Rates for Cast U-Al Alloys in J-13 Waters

Corrosion Potential (V)

Alloy	Temp (°C)	J-13	Low pH	High pH	High Cl
10	25	-0.385	-0.505	-1.525	-0.460

	90	-0.450	-0.260/ -0.320	-1.22	-0.530
13.2	25	-0.295	-0.275/ -0.480	-1.470	-0.460
	90	-0.375	-0.330	-1.190	-0.825
25	25	-0.460	-0.400	-1.510	-0.480
	90	-0.450	-0.340	-1.225	-0.530

Corrosion Rate (mpy)

Alloy	**Temp (°C)**	**J-13**	**Low pH**	**High pH**	**High Cl**
10	25	1	3	56	1.5
	90	6	2.25	50	2.4
13.2	25	0.6	0.1/2.1	60	0.8
	90	3.4	3.7	59	1.0
25	25	0.5	2	58	1.3
	90	6	3.5	50	4.9

The corrosion rates of the alloys were similar for the J-13 waters at a given temperature as indicated in Table 12. The rates in the high pH J-13 were the largest at approximately 60 mpy, which corresponded to the most active corrosion potentials. The rates in the other waters were all similar ranging from 1-6 mpy. Changing temperature affected the corrosion rates in nominal, low pH, and high Cl J-13. However, the corrosion rate in the high pH J-13 surprisingly was unaffected. The increased corrosion rates occurred with a shift to more active corrosion potentials as discussed above.

From macroscopic observations, the corrosion morphologies of the alloys after the polarization tests were similar and dependent on the J-13 water chemistry. In the nominal J-13, the surface had a smooth, mottled appearance of light and dark regions. The surfaces appeared to be pitted at 25 °C, whereas at 90 °C the overall surface was rougher indicating the higher corrosion rate. White corrosion deposits were observed near pits or voids. The morphology resulting from exposure to the low pH J-13 at 90 °C appeared flat with a dark tarnished appearance and random white deposits. At 25 °C, the surface was not darkened and fewer corrosion products were observed. Corrosion product formation and surface roughness was greater in the high pH J-13 which indicated the higher corrosion rate than in the other waters. Voluminous, volcanic-like deposits covered a dark surface. The corrosion products that formed in high Cl J-13 formed a more uniform surface layer with fewer discrete deposits. Surface roughening appeared minimal, although pits were numerous as expected.

Discussion

The three test methods had similar results for the effects of water chemistry, alloy composition, and the other test variables on the degradation of the U-Al alloys. The primary degradation characteristic was that the aluminum matrix corroded preferentially to the U-Al particles. A micro-galvanic cell was established between the aluminum and the U-Al particles with the attack of the aluminum being most severe in the region adjacent to the particle or in between eutectic lamellae. Figures 3-5 show this degradation for the various water chemistries. As a result of this preferential corrosion, many of the particles became dislodged from the surface. The presence of the particle in the solution depended on whether or not an oxide film formed to entrap the particle.

Degradation of the U-Al particle was not apparent from the post-test metallography. The dissolved uranium concentration, however, was greater than that expected from the uranium present in the aluminum matrix alone, which has a maximum uranium solubility of 0.52 wt %. Therefore, uniform corrosion of the particles was likely. Other investigators have seen some physical evidence of the U-Al particles in low pH solutions [5]. This attack may have occurred while the particle was part of the aluminum matrix or after it had become dislodged.

The solution composition had the most significant effect on the dissolution, degradation, and formation of corrosion products. The severity of attack generally increased in the following order: nominal~ high Cl < low pH < high pH J-13.

The nominal and high Cl J-13 were at a pH and corrosion potential where a protective oxide formed on aluminum [6], so the general attack was minimal but pitting occurred. The pitting attack in the high Cl J-13 was greater than in nominal J-13 as indicated by the higher dissolved aluminum concentration, shown in Tables 1,2, and 4 for the static and galvanic corrosion tests. As shown in Table 5, the galvanic currents were also greater for the high Cl J-13. The dissolved uranium concentrations were similar since the dissolution of uranium was not affected by the presence of chloride.

The low pH J-13 was at pH levels where the degradation of the aluminum matrix and the U-Al particles occurred. The thick oxide film produced in the low pH J-13 (Figure 4) was the result of precipitation on the surface. The mechanism involved an initial rapid corrosion and dissolution of both aluminum and uranium. Al dissolution also resulted in the removal of the U-Al particulate from the matrix. Once the dissolved Al concentration reached saturation near the surface; an oxide precipitated on the surface. The surface was then protected, entrapping U-Al particles in the oxide and slowing further degradation and dissolution.

An oxide film did not form on the surface of test samples immersed in the high pH J-13. In this case, the U-Al particles were continuously exposed to the solution. The measured U and Al concentrations and dissolution from the static test shown in Tables 1 and 2 indicated that the dissolution was greater than the other water chemistries. The dissolved uranium concentrations reached a constant level after one week so saturation was reached quickly. The aluminum concentration continued to increase with time over the duration of the test. From a thermodynamics perspective [6], a greater U concentration would be expected in the low pH J-13 due to the higher solubility of uranium as was observed in the galvanic corrosion test. The difference between the results was attributed to sample variations. In the high pH J-13 the corrosion was also accelerated most by the increase in temperature.

The coupling of the U-Al alloys to stainless steel had a significant effect on the severity of attack in the static and galvanic tests. The stainless steel and aluminum plates both were large cathodic areas relative to the U-Al alloys. In the static tests, the stainless steel plate accelerated the corrosion of the Al matrix as compared to the corrosion that occurred when coupled to the aluminum plate as shown by the larger concentrations after testing. Coupling between the packaging and the fuel, therefore, would accelerate the degradation and the release of the uranium and other radionuclides. A couple between the fuel meat and any remaining aluminum cladding would have less of an impact on the fuel degradation.

The heterogeneity of the surface microstructure attributed to the data variability. This heterogeneity was due to the area fraction of U-Al particles and the formation of a non-uniform aluminum oxide film. The area fraction of the U-Al particles exposed to the environment differed during the test. A large area fraction of the cathodic U-Al particles enhanced aluminum corrosion and the dislodging of U-Al particles. The presence of an oxide film retarded the degradation of the aluminum except in localized areas where film breakdown occurred. The presence of the particles in the aluminum matrix may create a strain in the oxide film and result in mechanically weak sites in the oxide film. The distribution of these sites again would be variable.

Conclusions

The effect of the degradation mechanism on the dissolution and corrosion of U-Al alloys was investigated with static coupon, galvanic corrosion, and electrochemical tests. The first stage of the degradation mechanism was consistent in all environments. The aluminum matrix adjacent to the U-Al particles preferentially corroded leaving the particles in relief. Many times the particles became dislodged and were relocated into the solution. At unsaturated conditions, the U dissolution rates are highest in the low pH J-13 and lowest in the high Cl J-13.

The second stage of the degradation mechanism depended on the environment in which the material was immersed. In the nominal and high Cl J-13, a thin protective oxide film deposited on the surface of the coupon. The coupon was susceptible to pitting of the aluminum matrix at localized sites. The amount of pitting was greatest in the high Cl J-13, however, the dissolution rate of U was insensitive to chloride concentration in the range tested. In low pH J-13 general corrosion of the aluminum occurred. Once the solution became saturated with aluminum, a thick, aluminum oxide precipitated on the surface. When the solution was saturated the dissolution of uranium was reduced. In high pH J-13 solutions, general dissolution of the aluminum also occurred. However, in this case the aluminum remains dissolved and continues to corrode without the formation of a surface oxide. The dissolved U concentration was limited by the solubility of uranium at the high pH. In the static test, the dissolved U concentration was greatest for the high pH J-13.

In addition to solution chemistry, the effects of other experimental variables such as temperature and galvanic coupling on the degradation of U-Al alloys was investigated. In solutions where a thin oxide or no oxide formed (i.e., nominal, high Cl, and high pH J-13), the degradation increased with temperature. However, in cases where a thick oxide (5-10 µm) was formed (i.e., low pH J-13) the degradation was less sensitive to temperature changes. The stainless steel galvanic couple resulted in a significant increase in the degradation and dissolution in all solutions.

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Figure 1. Schematic of Static Test Apparatus

(a)

(b)

(c)

(d)

Figure 2. Microstructures of U-Al Test Samples: a) 10 UAl cast, b) 13.2 UAl cast, c) 25 UAl cast, d) 13.2 UAl wrought

Figure 3. Post-test Microstructure of 13.2 UAl Cast from Nominal J-13 at 90ºC

Figure 4. Cross-sectional View of Post-test Microstructure of 13.2 UAl Cast from Low pH J-13 at 90ºC

Figure 5. Post-test Microstructure of 13.2 UAl Cast from High pH J-13 at 90ºC

Figure 6. Cross-sectional View of Post-test Microstructure of 25 UAl Cast from Nominal J-13 at 90ºC

Figure 7. Cross-sectional View of Post-test Microstructure of 13.2 UAl Wrought from Low pH J-13 at 90ºC

Figure 8. Post-test Surface of Crevice Area of 13.2 UAl Wrought from Nominal J-13 at 90ºC

Figure 9. The Polarization Curve for 13.2 UAl in Nominal J-13 at 90 °C

Figure 10. The Polarization Curve for 10 UAl in High pH J-13 at 25 °C