LA-UR- 98-4326

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AUG 18 1999
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Submitted to:
INSTITUTE FOR SPACE AND NUCLEAR POWER STUDIES
SPACE TECHNOLOGY & APPLICATIONS
INTRERNATIONAL FORUM (STAIF-99)
JANUARY 31 - FEBRUARY 4, 1999
ALBUQUERQUE, NM

Los Alamos
NATIONAL LABORATORY

Containment of Nitric Acid Solutions of Plutonium-238

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Abstract. The corrosion of various metals that could be used to contain nitric acid solutions of Pu-238 has been studied. Tantalum and tantalum/2.5% tungsten resisted the test solvent better than 304L stainless steel and several INCONEL alloys. The solvent used to imitate nitric acid solutions of Pu-238 contained 70% nitric acid, hydrofluoric acid, and ammonium hexanitratocerate.

INTRODUCTION

Radioisotope heat sources used for outer space applications should be long-lived so that they can endure long interplanetary journeys, but sufficiently radioactive to provide electric power at the destination. Plutonium-238, an alpha-emitting isotope with easily-shielded gamma radiation, is very useful for this purpose. The storage of nitric acid solutions of Pu-238 requires a material that is resistant to a hot mixture of nitric and hydrofluoric acids, water vapor, oxides of nitrogen, and the damaging radioactivity of the ^{238}Pu. We describe the results of a test of metals potentially suitable for containing solutions of the isotope in the acid mixture commonly used to dissolve its oxide.

Our search concentrated on corrosion-resistant metals. Coupons of the candidate metals were individually immersed in a test solvent at room-temperature for 340 hr, while similar coupons of the same metal were individually refluxed in the same solvent for 100 hr. The solvent contained ammonium hexanitratocerate, concentrated nitric acid, and hydrofluoric acid. Ce(IV) is an oxidizing cation like Pu(IV), but it does not produce the intense alpha radiation of the ^{238}Pu. The ratio of fluoride to metal in the test solution was higher than this ratio in acid mixtures commonly used to dissolve $^{238}PuO_2$. The purpose of the higher F/Ce ratio in the test solvent was to enhance its corrosiveness .

EXPERIMENTAL

Limited quantities of ammonium hexanitratocerate were dissolved in aliquots of hot (80-85°C), concentrated (70%) nitric acid. When 219 g of the salt had been dissolved in 2 L of the acid, the solution was cooled, and 6 mL of 49% hydrofluoric acid were slowly added with vigorous stirring. The volume of the cooled solution was slightly greater than 2 L. The solution did not deposit a precipitate on standing for at least two weeks. Analysis of the test solution by Galbraith Laboratories, Knoxville, TN, indicated the concentrations of Ce and F were about 25300 and 1300 ppm, respectively.

INCONEL alloy coupons were obtained from Metal Samples Company of Munford, AL. (INCONEL is a trade name for alloys manufactured by INCO Alloys International of Huntington, WV.) Coupons of these alloys were about 2 in. long, 1 in. wide, and 0.12 in. thick, except the INCO-625 coupons which were 0.05 in. thick. Tantalum and tantalum 2.5% tungsten alloy were obtained from Astrocosmos Metallurgical, Inc., of Camarillo, CA. These coupons were about 2 in. long, 1 in. wide, and 0.02 in. thick. Coupons of stainless steel (304L) were obtained from Reliance Metal Center, Albuquerque, NM. They were 2 in. long, 1 in. wide, and about 0.06 in. thick.

Duplicate coupons of the same metal were weighed and then submerged in separate 300 mL aliquots of the cerium test solution contained in 600 mL, round-bottom TEFLON flasks. In each experiment, one coupon was maintained at room temperature for 340 hr, while its duplicate was refluxed for 100 hr under a water-cooled, TEFLON condenser. At the end of the exposure periods, the metal coupons were removed from the test solution, and the corrosion products carefully removed from the base metals by ultrasonic cleaning. This was followed by abrasion, if required. The coupons were then weighed again and each was examined under a microscope (ASTM: G1-90, ASTM: G31-72). Table 1 summarizes the results of the tests.

RESULTS AND DISCUSSION

Chemical analysis indicated that about 38% of the cerium could be present as the CeF^{3+} complex ion, whereas all of the fluoride could be present in this species. A typical dissolution experiment could contain 100 g of PuO_2 in 1 L of 70% nitric acid containing 0.05$\underline{M}$ hydrofluoric acid. The F to Pu ratio in the typical mixture is about 0.14. Our test solution thus had a higher fluoride-to-metal ratio than in the example case.

The higher F/metal ratio in the test solution probably makes the solution more corrosive than the typical acid mixture used to dissolve PuO_2. The corrosiveness of the test solution is also increased by the presence of the ammonium nitrate: an inert salt raises the boiling point of its solvent. However, the cerium in the test solution cannot imitate the corrosive effects of the intense alpha radiations from ^{238}Pu.

Brown oxides of nitrogen were observed escaping from the refluxing test solutions containing the metal coupons. This phenomenon is also observed when $^{238}PuO_2$ dissolves in a nitric acid/HF mixture. The hot test solution contained nitric acid, oxides of nitrogen, fluoride, and oxidizing cations of tetravalent elements, just like typical batches of dissolving $^{238}PuO_2$. Brown nitrogen oxides were also noticed when the metals in the boiling test solution were Ta or Ta/2.5%W even though these metals were only slightly attacked by the test solvent.

Table 1 summarizes the results of the tests. The table shows that the hot solvent corroded the transition-metal alloys (INCONEL alloys and stainless steel) much more rapidly than the room-temperature solvent. Spent solvent derived from refluxing the INCONEL alloys contained a precipitate and was more darkly colored than the same solvent derived from the unstirred, room-temperature experiment. Tantalum and its 2.5% tungsten alloy resisted attack by hot and cold solvent. The refluxed solvent that contained the Ta or Ta/2.5% W alloy was lighter in color than the same solvent that had been in contact with these metals at room temperature. Coupons of Ta and Ta/2.5%W were partially coated with a light-yellow deposit when they were removed from the boiled test solvent.

Chemical analysis of the spent solvent from the tests indicated that the room-temperature solvent barely corroded the transition-metal alloys, and that the corrosion was uniform. The ratios of the concentrations of Cr, Fe, Mo, and Ni in the solutions (ppm) to the percents of these elements in the alloys were about 5. Greater variations were noted for the heated and filtered test solutions: the same concentration ratios varied erratically from about 10 to about 300. This variation is probably influenced by the appearance of precipitates in the hot solutions. The precipitates were not identified, but analysis indicated that they contained large amounts of cerium.

Surfaces of the metals were examined under a microscope before and after exposure to the test solutions. At room temperature, corrosion of all metals was mostly uniform and even. Severe corrosion was evident for transition metals exposed to the high-temperature solvent. However, Ta and its 2.5%W alloy were hardly corroded by the hot solvent. Localized corrosion, including pitting, was not observed in any of the coupons. INCONEL 686 and 625 exhibited grain-boundary corrosion, particularly at the edges of the coupons. Another study of the corrosion of stainless steel by nitric/hydrofluoric acid mixtures is pertinent [Kranzlein, 1960, Ondrejcin and McLaughlin, 1980). A related study of nitric acid containing chloride is also relevant (Kolman, et.al., 1997).

The solvent exposed to Ta at room temperature contained 160 ppm Ta. Likewise, the test solution containing the Ta/2.5%W coupon contained 133 ppm Ta and 3.7 ppm W. (The observed tungsten concentration was distinctly higher than the background concentrations reported for other alloys that contained no tungsten.) The spent solvent obtained from boiling the Ta coupon contained 15 ppm Ta, while the analogous solution that contained the Ta/2.5%W alloy contained 26 ppm and 0.7 ppm of Ta and W, respectively.

The light-yellow deposit found on the surfaces of the tantalum and its tungsten alloy adhered tightly to the surfaces of the coupons. The deposit required vigorous cleaning to remove it. (The deposit contained cerium, but its composition has not been determined. However, it was not ammonium hexanitratocerate.) The deposit might have acted as a barrier to attack, limiting further corrosion of these metals. The putative barrier could explain the lower rate of corrosion of Ta and Ta/2.5%W in the hot solvent than in the cold solvent.

Weight losses caused by corrosion of the test coupons are reported in Table 1. These weight losses, and the analyses of the spent solvents, show that tantalum and its 2.5% tungsten alloy resist the corrosive cerium solution much better than the other metals. The results suggest the metal of choice for containing nitric acid solutions of ^{238}Pu is tantalum or its 2.5% tungsten alloy. Other properties of these metals, such as price, strength, and workability, also influence the choice.

The conclusion that Ta or its 2.5% tungsten alloy are reasonable choices for the containment of ^{238}Pu solutions is supported by prior experience at another laboratory. In that experience, a tantalum/10% tungsten alloy was used as the inside-liner for a steel vessel in which $^{238}PuO_2$ was routinely dissolved. The liner survived the dissolution of many kilograms of $^{238}PuO_2$. A small white precipitate usually appeared in the plutonium solution during dissolution, however. The precipitate was separated from the plutonium solution by filtration. Its composition does not seem to have been determined, but it probably contained hydrated oxides of tantalum and tungsten.

TABLE 1. Weight Losses (mg) of Metal Coupons After Exposure to Test Solutions at Two Temperatures

Alloy	Room Temp. (340 hr)	115 °C (100 hr)
INCONEL-686	162 [6.4]*	6955 [927]*
INCONEL-625	156 [7.2]	3831 [580]
INCONEL-690	128 [5.4]	2534 [370]
304L-SS	229 [10]	2523 [382]
Ta	43 [1]	2 [0.1]
Ta/2.5% W	39 [0.95]	9 [0.76]

*Approximate corrosion rate, mils per year, is shown in brackets.

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