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DISSOLVING HIGHLY IRRADIATED Pu-AI ALLOY

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DISSOLVING HIGHLY IRRADIATED Pu - Al ALLOY

by

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ABSTRACT

Samples of highly irradiated Pu-Al alloy dissolved at an average rate of $0.5 \text{ mg}/(\text{min})(\text{cm}^2)$ in $6\text{M HNO}_3 - 0.05\text{M Hg}(\text{NO}_3)_2 - 0.02\text{M HF}$ solution. In $2.1\text{M NaOH} - 2.6\text{M NaNO}_3$ the aluminum in the alloy dissolved at an average rate of $14 \text{ mg}/(\text{min})(\text{cm}^2)$, and the actinides dissolved completely when the caustic solution was acidified and boiled.

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DISSOLVING HIGHLY IRRADIATED Pu-Al ALLOY

INTRODUCTION

In a previous report⁽¹⁾ a procedure was described for dissolving Pu-Al alloy that was irradiated to 60% burnup of Pu²³⁹. This procedure involved dissolution of the alloy in HNO₃-Hg(NO₃)₂-HF solution and was used successfully as part of the plant process to recover the plutonium. The present study was aimed at the development of a method for dissolving the same alloy irradiated to over 99% burnup of Pu²³⁹. The method needed to be operable at reasonable production rates in plant equipment.

SUMMARY

Pu-Al alloy irradiated to over 99% burnup of Pu²³⁹ dissolved at impractically slow rates in HNO₃-Hg(NO₃)₂-HF solutions. However, the alloy was successfully dissolved by a two-step procedure:

- (1) Dissolution of the aluminum matrix in a NaOH-NaNO₃ solution.
- (2) Acidification with HNO₃ and digestion of the acid solution.

In this procedure, 99.9% of the actinide elements remained suspended in a metallic sludge after the caustic dissolution step, and were dissolved in the acid digestion step. Laboratory tests of the dissolution gave no evidence of the formation of plutonium polymer.

DISCUSSION

DESCRIPTION OF THE ALLOY

The dissolving studies were made with an aluminum-clad rod of Pu-Al alloy. The one-inch-diameter rod had been fabricated from 7 wt % Pu - Al alloy at Hanford Atomic Products Operation and had been irradiated to over 99% burnup of Pu^{239} at Savannah River. Except for the extent of burnup, the alloy was the same as that described previously in studies of dissolving Pu-Al alloy that was irradiated to about 60% burnup of $\text{Pu}^{239}(1)$.

A metallographic examination⁽¹⁾ of the unirradiated rod showed an extruded structure in the outer 0.1 inch of the core, with particles of PuAl_4 intermetallic compound well dispersed in an aluminum matrix. The center 0.5 inch of the core was predominantly a cast structure, where PuAl_4 particles occur chiefly along grain boundaries and as a eutectic structure around aluminum grains. No metallurgical examination was made on the irradiated alloy.

Since only very small quantities of the fissionable isotopes of plutonium are present in the irradiated alloy, no criticality hazards are involved in the chemical processing of this material.

ACID DISSOLUTION

The aluminum cladding of the irradiated rod dissolved at a normal rate ($37 \text{ mg}/(\text{min})(\text{cm}^2)$) in a solution of 6 to 7M HNO_3 and 0.005M $\text{Hg}(\text{NO}_3)_2$, but the alloy core dissolved at an impractically slow rate. The average dissolving rate of the core was $0.5 \text{ mg}/(\text{min})(\text{cm}^2)$ and was not increased by:

- Adding HF to a concentration of 0.02 to 0.06M
- Increasing the $\text{Hg}(\text{NO}_3)_2$ concentration to 0.09M
- Scratching the surface of the alloy
- Dipping the alloy in a concentrated solution of $\text{Hg}(\text{NO}_3)_2$.

Annealing the alloy at 500°C for 6 hours increased the dissolving rate three-fold in a single test, but the rate was still too low to be practical in a plant process.

The dissolving rate of Pu-Al alloy in $\text{HNO}_3\text{-Hg}(\text{NO}_3)_2$ solution is a function of burnup. The alloy dissolved at 10 to 20 $\text{mg}/(\text{min})(\text{cm}^2)$ under similar test conditions after irradiation to only 60% burnup.⁽¹⁾ However, the aluminum cladding at both burnups dissolved at a normal rate, indicating that neutron irradiation alone has no serious effect on the dissolution of aluminum. The sharp decrease in dissolving rate of the alloy as the Pu^{239} burnup increased from 60 to 99% is apparently related to the number of plutonium fissions rather than to the neutron dose.

CAUSTIC DISSOLUTION

The alloy was dissolved at practical dissolving rates by sequential treatment with caustic and acid. The procedure involves dissolution of the aluminum matrix in boiling NaOH-NaNO_3 solution, followed by acidification with nitric acid and dissolution of the caustic-insoluble residue in the acidified solution. Pu, Am, Cm, and some fission products, which remain as a metallic sludge after the caustic dissolution step, dissolve readily when the acid solution is heated.

Four test specimens were dissolved by this procedure. Based on the following empirical equation

the initial conditions shown in Table I provided an excess of NaOH and NaNO_3 . After complete dissolution of aluminum, the calculated concentrations were 2M NaAlO_2 , 0.7M NaOH , and 1M NaNO_3 . This excess NaOH was sufficient to inhibit crystallization of NaAlO_2 when the solutions were cooled. The presence of a 1M excess of NaNO_3 during the dissolving step reduces the production of H_2 to trace quantities.⁽²⁾

Dissolution began when 50% NaOH was added to a boiling NaNO_3 solution in which the specimen was suspended. The aluminum cladding and the core aluminum dissolved at average rates of 12 to 16 $\text{mg}/(\text{min})(\text{cm}^2)$ without a change in rate when decladding was complete. The reaction slowed sharply whenever the temperature dropped below 100°C. Dissolution required from 2.5 to 4 hours for completion.

TABLE I

Dissolution of Pu-Al Alloy

Size of Test Specimens:

Weight	62.4 $\pm$ 1.0 g
Length	5.0 $\pm$ 0.2 cm
Outer Diameter	2.4 $\pm$ 0.1 cm

	<u>Test 1</u>	<u>Test 2</u>	<u>Test 3</u>	<u>Test 4</u>
<u>Caustic Dissolution</u>				
Initial Solution				
Volume, ml	1500	1000	1300	1500
NaOH, M	2.0	2.6	2.1	1.8
NaNO ₃ , M	3.1	3.2	2.6	2.5
Average Dissolving Rate, mg/(min)(cm ²)	16	15	14	12
Final Solution				
Volume, ml	1300	800	1100	1250
Total Base, M	8.1	12.1	9.4	8.8
Gross α , d/(min)(ml)	1x10 ⁵	1x10 ⁵	1x10 ⁶	2x10 ⁴
Pu α , d/(min)(ml)	-	-	1x10 ⁴	3x10 ²
<u>Acid Digestion</u>				
HNO ₃ Added, mols	(a)	14.1	13.4	14.1
Time at Boiling Point, hr	15	8	7.5	7
Final Solution				
Volume, ml	2000	1900	2100	2300
HNO ₃ , M	0.86	1.94	1.61	1.10
Al, M	0.74	1.32	1.07	0.82
Cm α , d/(min)(ml)	5.4x10 ⁹	5.6x10 ⁹	5.6x10 ⁹	3.9x10 ⁹
Pu α , d/(min)(ml)	3.0x10 ⁷	3.3x10 ⁷	3.1x10 ⁷	3.6x10 ⁷

(a) Solution boiled over during neutralization.

Less than 0.1% of the actinides were dissolved in the caustic solution (Table I). The actinides remained suspended in the solution as a black precipitate, and could be removed by filtration. The precipitate dissolved when the caustic solution was acidified and boiled. The amount of 15.7M HNO₃ added in each test was calculated from the measured volume and total alkalinity of the solution to give an excess of 1-2M acid. In addition to the NaOH-HNO₃ reaction, the following reactions occur:

During the acid addition, considerable Al(OH)₃ precipitated, but with continued acidification, this precipitate dissolved. In the first test, the solution overheated and boiled over. In subsequent tests, the reaction was controlled by cooling the caustic solution below 40°C, mixing the solution with an air jet, and adding the HNO₃ over a period of 30 minutes. The actinides dissolved when the acidified solutions were boiled for two hours; further boiling produced no detectable change in the alpha activity of the solution.

A small quantity of undissolved solids was filtered from one of the four test solutions. Leaching with hot 8M HNO₃ - 0.1M HF showed that only about 0.01% of the actinides were present in this residue. Filtration removed no solids from the other three solutions.

Pu(IV) polymer was not found in the final dissolver solution. The test for polymer consisted of extracting all Pu(IV) from the dissolver solution, adjusting the solution to 0.02M HF, heating the solution 7 to 15 hours, and then testing the solution for the presence of additional extractable plutonium. The absence of additional plutonium indicated that no polymer had been formed.

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