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REDUCTION OF PLUTONIUM DIOXIDE TO PLUTONIUM METAL

by

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ABSTRACT

Attempts were unsuccessful to reduce PuO_2 with calcium or barium to form a coalesced mass of plutonium metal. Molten fluoride fluxes to dissolve CaO or BaO were not effective in promoting the reaction, nor was mechanical agitation. The major difficulty was the rapid separation of the reactant phases.

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INTRODUCTION

Plutonium metal is generally prepared by the reduction of a plutonium halide with calcium metal,(1,2,5) for example, by the reaction:

$$PuF_4 + 2Ca = Pu + 2CaF_2 \quad \Delta H = -156 \text{ kcal/mole Pu.}$$

Such reactions are usually carried out in a pressure vessel that is heated inductively to initiate the reduction. The heat of reaction is sufficient to maintain the temperature of the slag above the melting point long enough for the molten plutonium to coalesce into a single button in the bottom of the reaction crucible. The melting point of the slag produced by the above reaction is approximately the melting point of pure CaF_2 (1418°C). In one production system,(2) a mixture of about 75% PuF_4 and 25% PuO_2 is reduced with calcium; the CaO formed is presumably dissolved in the molten CaF_2, yielding a slag that melts below 1400°C. The reduction yields in systems such as these range from 95 to greater than 99% of the plutonium, recoverable as a single metal button.

In the work described in this report, tests were made of direct reduction of PuO_2 to plutonium metal, with calcium or barium as the reductant and with a flux of fused salt to dissolve the alkaline earth oxide. The method would be attractive because it would obviate the costly preparation of intermediate plutonium fluoride. For ^{238}Pu metal, it would also significantly reduce the troublesome neutron radiation that arises from the (α,n) reaction with fluorine.(3) A production facility for ^{238}Pu metal based on a direct reduction of PuO_2 could be constructed more economically because the shielding requirements would be reduced substantially.

Reduction of PuO_2 by calcium at 1000-1050°C in 90 to 100% yield, has been reported,(4-7) but the product is a metal powder. Presumably, coalescence of the metal is prevented by the CaO formed in the reaction. The reaction cannot be practically carried out above the melting point of CaO (2570°C); however a low-melting flux may be used to dissolve the CaO as it is formed. This reduction with flux has been accomplished with some success on a scale of ~1 gram of plutonium with a mixed flux of chloride and fluoride salts, with yields of coalesced metal of approximately 90%.(4,8,11) In the present studies, attempts were made to extend the work to larger scale, and to use a flux consisting of fluoride salts only in order that reduction residues could be reprocessed in stainless steel equipment.

SUMMARY

The direct reduction of PuO_2 with calcium or barium to produce a coalesced metal product in good yield was tried unsuccessfully. Attempts were made 1) without flux, 2) with flux consisting of fluoride salts only, and 3) with a mixed flux of chloride and fluoride salts. Although finely divided plutonium was produced in each case, the metal coalesced only with the mixed flux, and then in very small yield (1-2%).

Plutonium as Al-Pu alloy was produced in ~70% yield with aluminum as reductant and a fluoride-salt flux.

DISCUSSION

The reaction of PuO_2 with calcium or other alkaline earth metals is thermodynamically favorable.

$$PuO_2 + 2Ca = Pu + 2CaO$$

$$\Delta H_{298°K} = -53 \text{ kcal/mole Pu}$$

$$\Delta F_{1500°K} = -38 \text{ kcal/mole Pu}$$

It would be expected that the reaction would be essentially complete at temperatures in the region of 1000°C. However, because 1000°C is above the melting temperatures of Pu(640°C) and Ca(850°C) but below the melting temperatures of PuO_2 (~2300°C) and CaO(2570°C), the reaction mixture will consist of both solid and liquid phases. Even with the addition of a molten salt flux, the major experimental difficulty was expected to be interruption of the reaction by rapid separation of the phases, which are of widely different densities. However, CaO is soluble in molten fluoride salts to the extent of about 10 mole % in 70% LiF-30% CaF_2;(9) the addition of a fluoride flux to dissolve the CaO was expected to promote the reaction and improve the coalescence of molten plutonium droplets.

The relatively low heat of reaction of PuO_2 and alkaline earth metals limits self-heating, which is useful in promoting reductions of plutonium halides. External induction heating was provided to maintain the reaction mixture at the desired temperature.

Experimental

Experiments were performed in the apparatus shown schematically in Figure 1, with minor changes for some tests. The "Vycor"* or quartz tube was 18" long and approximately 3-1/4" ID. The ends of this tube were closed by aluminum plates with elastomer O-ring gaskets to obtain a gastight seal between tube and plate. The plates were provided with various fittings. Helium flowed from a bottom fitting to an outlet in the top. The magnesia crucibles were 2" OD and 5-3/8" high. The graphite susceptor crucibles were 2-1/16" ID and 5-1/4" deep with a groove at one point in order that the sheathed chromel-alumel thermocouple could be inserted for monitoring the reaction temperature. In some tests, a tantalum crucible 2" ID, 5" high, and with 1/8"-thick walls was used in place of the magnesia crucible. A tantalum paddle attached to a 1/4"-diameter stainless steel rod was used for stirring. The rod passed through a "Teflon"** fitting at the aluminum plate which acted as a seal and a bearing. A variable speed motor turned the paddle at 400-500 rpm.

To prevent penetration of the crucible by the flux (observed in several early runs), the magnesia crucibles were coated with calcium fluoride before use. To coat the magnesia, CaF_2 was slurried with water and poured into a crucible; the excess water was decanted; the crucible and coating were dried for 2 hours at 800°C and stored in a dessicator over silica gel. To assure good heat transfer to the bottom of the magnesia crucible, graphite powder was packed in the bottom of the graphite crucible.

Heating was accomplished by use of a 100-kilocycle, 15-kva "Tocco"*** radiofrequency generator and heat station with a water-cooled copper coil 3-3/4" ID and 5-3/8" high with 18 turns of flattened copper tubing.

Reagent grade LiF, CaF_2, AlF_3, BaF_2, and $CaCl_2$ were dried several hours under vacuum at 300°C and used in the various flux compositions. The barium rod, granular calcium, and aluminum turnings were reagent grade. Plutonium dioxide was prepared by precipitation of Pu(III) oxalate and calcination in air at 450°C.(10)

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* Trademark of Corning Glass Company.

** Trademark of E. I. du Pont de Nemours & Co.

*** Ohio Crankshaft Corporation.

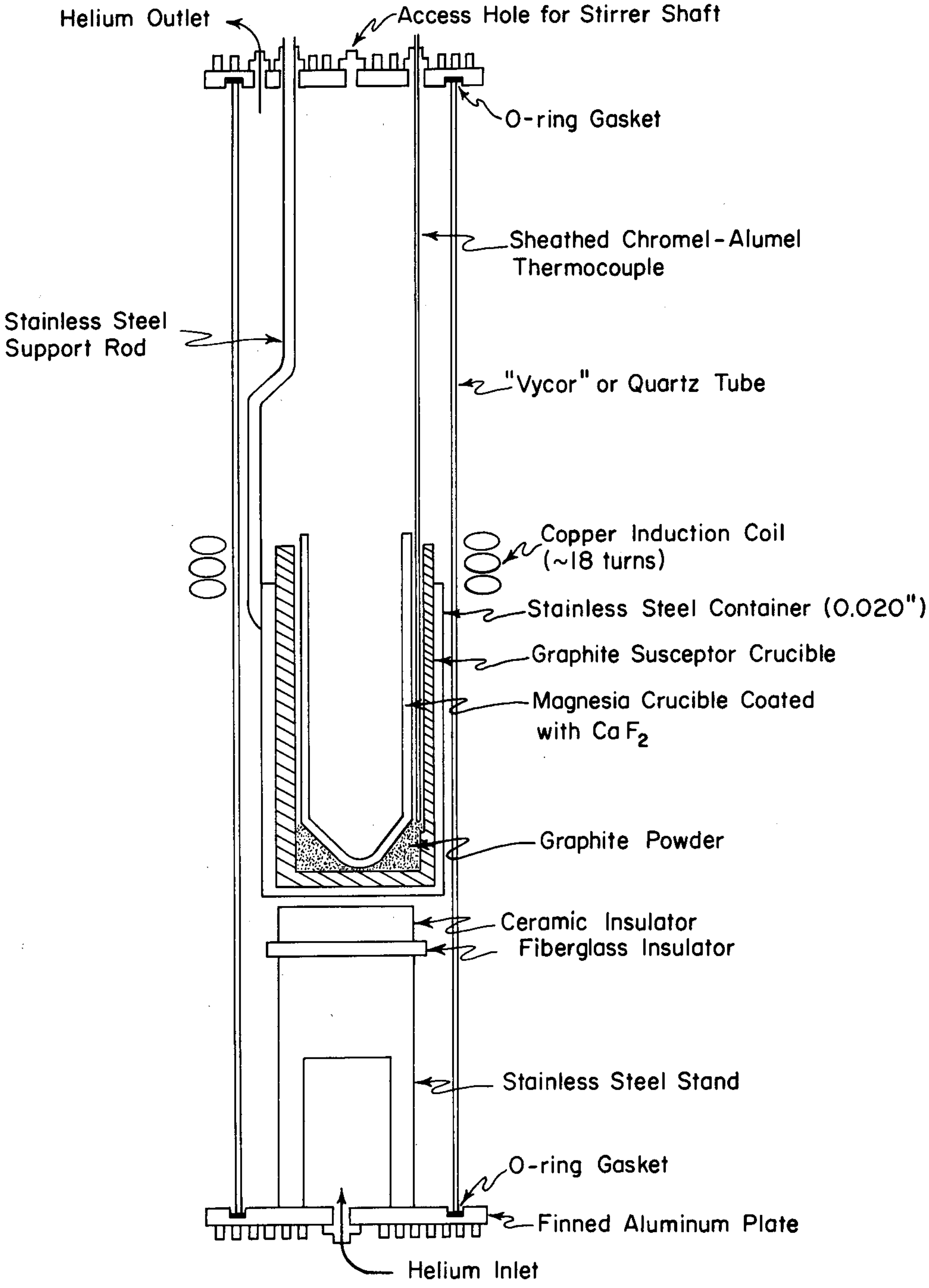

FIG. 1 REDUCTION TEST APPARATUS

Heating and cooling times were varied in different tests. Rapid heating produced thermal stresses that cracked the magnesia crucibles. To prevent cracking, the crucibles were held at 300°C for five minutes, then at 600°C for five minutes, and then were heated to reaction temperature as rapidly as possible.

The method of packing the reaction mixture in the crucible varied. For each run, about 10 grams of PuO_2, 0-180 grams of flux, and 100-150% excess calcium or barium metal were charged to the crucible. The calcium or barium was placed either on the bottom of the crucible charge or on a thin layer of flux near the bottom of the crucible. The PuO_2 powder was placed directly on top of the reductant, or above the reductant in narrow layers alternating with layers of flux.

Results

The conditions and results for 18 reduction tests are summarized in the table. In general, no coalesced plutonium metal was obtained without flux or with fluoride flux. In these runs a black dispersion of finely divided plutonium metal was usually observed in the bottom of the crucible after the test, but accurate determination of the extent of reaction was not practical. Variations in flux composition (in the region of the eutectic), in the ratio of flux to PuO_2, in the temperature and time of reaction, and in the method of packing the reactants into the reaction crucible had no significant effect. In Run 12, plutonium metal was added to the reaction mixture in an attempt to promote coalescence; the metal in the button was essentially that added to the reaction mixture.

In Run 14, no flux was used and no coalesced Pu was produced. The reaction mixture was analyzed to determine the extent of reaction. The CaO and the excess Ca were leached from the products with 1M acetic acid, leaving the Pu metal powder and unreacted PuO_2. The Pu metal was then dissolved in dilute HCl. The exposure of the oxide to the dilute HCl was limited to several minutes at room temperature; so only a small fraction of the oxide was dissolved. This test indicated that about 80% of the PuO_2 had been reduced to Pu metal powder.

In Run 8, the PuO_2 was first reduced with calcium without flux; then flux was added and the mixture was heated. No coalesced Pu was obtained.

Observable yields of coalesced plutonium metal were obtained only in Run 15, in which a $CaCl_2$-CaF_2 flux was used, and in Run 18, in which aluminum metal was used as the reductant. Run 15 confirmed qualitatively the Canadian work(11) on this system, and indicates the advantage of a chloride-containing flux, due presumable to a lower melting point and a greater solubility of CaO. Run 18 confirmed the previous results of Runnalls.(4) In this system the product is Al-Pu alloy.

The reaction mixture was stirred in Run 13 in an effort to improve contact between molten calcium metal and PuO_2. The temperature was somewhat lower than planned, but was above the melting point of calcium. No significant yield of coalesced Pu was observed.

In summary, reductions were not successful due mainly to the rapid separation of the metal and flux phases before an appreciable amount of oxide was reduced. In addition, the fluxes were not effective in dissolving the CaO or BaO formed during reduction. Mechanical agitation was not effective, possible because of inadequate mixing action. With the $CaCl_2$-CaF_2 flux and calcium metal reductant, the limited success was due to enhanced solubility of CaO, possibly some solubility of Ca and PuO_2, and the lower melting point of the flux.(4)

Results of Reduction Tests

Run No.	Flux Composition, mole %	Weight Ratio, flux/PuO_2	Reductant	Crucible Material	Reaction Temp, °C	Time at Reaction Temp, minutes	Pu Yield, % in button
1	65% LiF-35% CaF_2	10/1	Ca	MgO	1000	15	0
2	↓	5/1	Ca	Ta	1000	20	0
3	70% LiF-30% CaF_2	18/1	Ca	MgO	1000	20	0
4	↓	3/1	Ca	MgO(a)	1050	30	0
5	↓	15/1	Ca	MgO(a)	1050	45	0
6	80% LiF-20% CaF_2	14/1	Ca	MgO(a)	1000	25	0
7	↓	13/1	Ca	MgO(a)	1050	30	0
8	↓	7/1	Ca	MgO(a)	1050	30	0
9	↓	13/1	Ca	MgO(a)	1050	30	0
10	↓	13/1	Ca	MgO(a)	1050	50	0
11	↓	13/1	Ca	MgO(a)	1050	55	0
12	↓	13/1	Ca	MgO(a)	1050	55	0(c)
13	↓	13/1	Ca	Ta(b)	~875	35	0
14	None	-	Ca	MgO(a)	1050	30	0
15	80% $CaCl_2$-20% CaF_2	13/1	Ca	MgO	1000	20	1-2
16	80% LiF-20% CaF_2	14/1	Ba	MgO(a)	1025	60	0
17	55% LiF-45% BaF_2	16/1	Ba	MgO(a)	1000	30	0
18	75% LiF-25% AlF_3	9/1	Al	MgO(a)	1050	60	70

(a) CaF_2 coated crucible.

(b) Reaction mixture stirred.

(c) Pu metal added, which coalesced as button.

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