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W. B. Tolley
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THE PREPARATION OF PLUTONIUM(IV) AMMONIUM FLUORIDE
AND ITS DECOMPOSITION TO PLUTONIUM TETRAFLUORIDE
FOR SUBSEQUENT REDUCTION TO METAL

By

W. B. 43147

W. B. Tolley

Metallurgy Unit
Applied Research Sub-Section

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THE PREPARATION OF PLUTONIUM(IV) AMMONIUM FLUORIDE
AND ITS DECOMPOSITION TO PLUTONIUM TETRAFLUORIDE
FOR SUBSEQUENT REDUCTION TO METAL

I. INTRODUCTION

In the current Hanford process plutonium metal is produced by the reduction of plutonium tetrafluoride with metallic calcium in a stationary, hermetically sealed bomb. Plutonium tetrafluoride is prepared by hydrofluorination of plutonium dioxide at 600 C. A small amount of oxygen is continuously introduced during fluorination to prevent the reduction of plutonium tetrafluoride to the trifluoride by traces of hydrogen always present in the hydrogen fluoride. Since water is also present as a product during fluorination, the hydrogen fluoride, oxygen, and water vapor form an extremely corrosive atmosphere at elevated temperatures. External corrosion due to hydrogen fluoride leakage at the furnace gaskets and in the piping lines is especially troublesome.

II. OBJECTIVE

The purpose of this investigation was to study the preparation of plutonium(IV) ammonium fluoride by the reaction of plutonium dioxide with ammonium bifluoride and the subsequent thermal decomposition of this double salt at elevated temperatures to form plutonium tetrafluoride. Reduction to metal of plutonium tetrafluoride prepared in this manner was to be studied concurrently, utilizing methods presently employed in Hanford operation.

III. SUMMARY AND CONCLUSIONS

An exothermic reaction has been shown to take place between plutonium dioxide and excess ammonium bifluoride forming a plutonium(IV) ammonium fluoride double salt. The reaction is initiated by warming a

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mixture of the powdered reactants to 50 C at which temperature the reaction becomes self sustaining, going essentially to completion. Plutonium(IV) ammonium fluoride double salt and excess ammonium bifluoride can then be decomposed at 300 C and the volatile constituents collected in a cold trap.

The plutonium tetrafluoride remaining in the reaction vessel can be dehydrated in deoxygenated argon at 500 C. Since the volatile fluorides can be flushed from the furnace at 300 C, before the temperatures are raised for dehydration, the corrosion of furnace parts is expected to be lower than that experienced when using gaseous hydrogen fluoride at 600 C. Plutonium tetrafluorides prepared in this manner can be reduced to the metal by reaction with metallic calcium in a hermetically sealed bomb. Yields greater than 97 percent are obtained on a twenty gram scale when an iodine-calcium booster is employed.

IV. DISCUSSION

Due to the hazards associated with the handling of plutonium, a few preliminary investigations were employed using cerium. Previous work⁽¹⁾ has indicated its usefulness as a plutonium stand-in for compound preparation and reduction studies.

A. Preparation and Reduction of Cerous Fluoride

Ammonium bifluoride is known to react with the rare earth oxides yielding a mixture of metal ammonium fluorides which can be decomposed thermally to give a relatively pure mixture of the rare earth fluorides. This metal trifluoride mixture can be reduced to "mischmetall" by the bomb method with yields of 78 to 80 percent on a 150 gram scale.⁽²⁾ Since

(1) Smith, R. C., and W. E. Roake, Plutonium Trifluoride; Preparation by Reaction with Freon-12 and Bomb Reduction to Metal, HW-30040, September 15, 1953, (SECRET), p. 7.

(2) Decroly, C., D. Tytgat, and J. Van Impe, "Preparation of Mischmetall by Thermal Reduction," Journal of the Electrochemical Society, September, 1953, p. 388.

temperatures for preparation and decomposition of the rare earth intermediates are low, the process seemed worthy of investigation of its application to the preparation of plutonium metal.

Two experiments were performed using the cerium stand-in. Thirty-three percent excess ammonium bifluoride was ground and mixed with powdered cerium dioxide. This mixture was heated in an argon atmosphere for several hours at low temperature to form a cerium ammonium fluoride double salt. The white intermediate was decomposed at elevated temperature to cerous fluoride and volatile ammonium fluoride which was collected in a cold trap. Although the mechanism for the reduction of Ce(IV) to Ce(III) in this preparation of cerous fluoride has not been investigated, it is believed to occur during preparation of the intermediate salt, yielding cerous ammonium fluoride. Several reactions involving the oxidation of ammonium ion are thermodynamically possible. The potentials for reduction of plutonium(IV) to plutonium(III) are less favorable. Although some reduction was observed during the high temperature dehydration of plutonium tetrafluoride, it did not appear to be serious.

Reductions to cerium metal were carried out in a stationary, hermetically sealed, 50 gram size, reduction bomb. A thermocouple well located on the side of the bomb provided a means for thermal tracing of the firing cycle. A calcium-iodine booster was employed to provide additional heat and to lower the melting point of the calcium fluoride slag formed during reduction. Although analyses indicated the cerous fluoride to be over 93 percent converted to the trifluoride the reductions resulted in only fair yields of metal. This was attributed to the use of a reduction bomb in which the thermocouple well was apparently fabricated from a different stainless steel than the bomb proper. Since the thermocouple well was heated inductively to red heat while the bomb itself was still relatively cold, the time of charge firing could not be determined by thermal

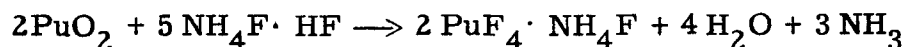
tracing and heating was probably discontinued at or before the charges fired, resulting in a lower yield than would normally be expected. The data obtained for the preparation and reduction of cerous fluoride are presented in Table I.

B. Preparation and Reduction of Plutonium Tetrafluoride

Plutonium dioxide ignited at temperatures above 400 C has been found to be much less reactive to halogenation than that produced by the ignition of plutonium oxalate to the dioxide at low temperatures. For this reason, only the low temperature oxides were used in the preparations.

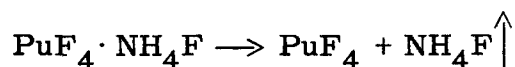
The same general procedures which were used with cerium were duplicated in the preparation of plutonium tetrafluoride. No difficulty was experienced in preparing the plutonium(IV) ammonium fluoride intermediate. The plutonium dioxide and 40 percent excess ammonium bifluoride mixture was found to react at any temperature between 50 and 250 C. The reaction indicated in equation I is exothermic, going essentially to completion even at 50 C.

Equation I.



Decomposition of the bright pink plutonium ammonium fluoride is accomplished without intermediate handling by merely increasing the furnace temperature. This decomposition begins at approximately 250 C and proceeds rapidly at 300 C. To prevent the oxidation of the plutonium tetrafluoride to the dioxide the decomposition was carried out in a deoxygenated argon atmosphere. The ammonium fluoride is volatilized during decomposition as indicated in equation II and is then efficiently collected in a cold trap with the excess ammonium bifluoride.

Equation II.



Plutonium tetrafluoride which remains in the reaction vessel is easily powdered. Bulk densities of four samples ranged from 1.95 to 2.10 grams/cm³. This compares favorably with the bulk densities of plutonium tetrafluorides presently prepared by hydrofluorination in 234-5 operation.

Although a highly converted tetrafluoride (F/Pu mole ratio of 3.7 to 3.9) was obtained at 300 to 400 C attempts at reduction to metal always resulted in bomb pressures of over 350 psig and broken, poorly coalesced, pyrophoric reguli. The high pressures are attributed to incomplete dehydration of the tetrafluoride at these temperatures. Whenever decomposition was completed between 450 to 500 C the bomb pressures during reduction were not excessive. However, the resulting regulus was always poorly coalesced and usually extremely pyrophoric. In three preparations 10 through 12, in which plutonium tetrafluoride was dehydrated at 500 C for one and a half hours or longer, reduction to the metal produced buttons of high yield and purity.

In practice, on a nominal twenty gram scale, the optimum method for the preparation of plutonium tetrafluoride by reaction of plutonium dioxide with ammonium bifluoride has been found to be as follows. Freshly precipitated plutonium(IV) oxalate is placed in a reaction vessel and dried in a stream of air at 125 to 150 C for one hour. The temperature is raised to 300 C and held for two hours to decompose the plutonium(IV) oxalate to plutonium dioxide. Forty percent excess ammonium bifluoride is mixed with the plutonium dioxide and the mixture heated in a stream of argon for one hour at 150 C. The double salt, plutonium(IV) ammonium fluoride, which forms rapidly at 150 C, is decomposed at 300 C for one and one-half hours in an atmosphere of argon. Ammonium fluoride from the decomposition of the double salt and the volatilized excess bifluoride are collected in a cold trap. The plutonium tetrafluoride is then dehydrated for two

hours at 500 C. Since the temperature need never exceed 300 C while fluoride is present, the corrosion of furnace equipment may be reduced considerably from that experienced using hydrogen fluoride at 600 C. The data on the preparation and reduction of plutonium tetrafluoride are presented in Table II.

V. RECOMMENDATION

It is recommended that batches of approximately 300 grams of plutonium dioxide be fluorinated by this procedure. Plant time cycle data necessary for preparation of the intermediate, its decomposition and dehydration will be provided by such experiments. Since several reductions on a twenty gram scale were characterized by high gas pressures during reduction, the gas pressure during the large scale reductions should be measured to ascertain whether or not this will be a limitation in such a process.

W. B. Tolley
W. B. Tolley

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TABLE I
CEROUS FLUORIDE PREPARATION AND REDUCTION

33 percent excess ammonium bifluoride used in each preparation.
33 percent excess calcium reductant used in each reduction.
Bomb charges were fired by induction heating.

<u>Run</u>	<u>Intermediate Preparation</u>		<u>Intermediate Decomposition</u>		<u>Product F/Ce</u>	<u>Booster Ca-I₂/Ce</u>	<u>Yield</u>
	<u>Time, hr</u>	<u>Temp, C</u>	<u>Time, hr</u>	<u>Temp, C</u>	<u>Mole Ratio</u>	<u>Mole Ratio</u>	<u>Percent</u>
1	3	200	1	400	2.73	0.76	61.1 ^(a)
2	3	200	1	400	2.80	1.00	85.5 ^(b)

(a) Poorly coalesced button with much small shot.

(b) Rough button in one piece.

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TABLE II
PLUTONIUM TETRAFLUORIDE PREPARATION AND REDUCTION

40 percent excess ammonium bifluoride used in each preparation. 33 percent calcium reductant used in each reduction. Bomb charges were fired by induction heating. Heating was continued three minutes after charges fired.

Run	<u>Intermediate Preparation</u>		<u>Intermediate Decomposition</u>		<u>Product F/Pu</u>	<u>Booster Ca-I₂/Pu</u>	<u>Yield</u>	<u>Pressure</u>
	<u>Time, hr</u>	<u>Temp, C</u>	<u>Time, hr</u>	<u>Temp, C</u>	<u>Mole Ratio</u>	<u>Mole Ratio</u>	<u>Percent</u>	<u>psig</u>
1	1	250	3/4	400-500	3.67	0.5	79.7	
2	1	250	1	400-500	3.79	0.5	95.5	
3	1 1/2	250-350	1	350	3.91	1.0	10.0	>400 ^(a)
4	1 1/2	150	1	400	3.20	1.0	78.4	>350 ^(a)
5	1 1/2	150	1	415	3.42	1.0	92.0	350
6	1	150	1	400-450	3.63	1.0	(b)	200
7	3	200-250	1	425-470	3.77	1.0	93.8	200
8	1/5	50	2/3	450-480	3.85	1.0	84.1	250
9	12	25	1	500	3.59	1.0	86.3	75
10	1/5	50	1 1/2	500-525	3.49	1.0	97.8	200
11	2	250	2	500	3.49	1.0	98.2	200
*12	2	150-200	2	300	3.5(est.)	1.0	97.0	150

* Decomposition was completed at 300 C, the furnace flushed free of fluoride and the plutonium tetrafluoride dehydrated at 510 C.

(a) Heating was discontinued when pressure reached 350 psig with the charge apparently firing after heating was discontinued.

(b) Button burned to oxide.

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ABSTRACT

An exothermic reaction has been shown to take place between low temperature plutonium dioxide and ammonium bifluoride at 50 to 250 C. The reaction goes essentially to completion with the formation of the pink plutonium(IV) ammonium fluoride. This compound can be decomposed at 300 C and the resulting plutonium tetrafluoride dehydrated at 500 C. Analyses have shown that plutonium tetrafluoride prepared in this manner is approximately 90 percent converted from the dioxide. On a twenty gram scale average reduction yields of over 97 percent can be obtained by reaction with metallic calcium in a hermetically sealed, stationary bomb when a calcium-iodine booster is employed.

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