Preparation of Plutonium Metal, (II)

Preparation of Plutonium Metal by Calcium Reduction of Sodium Plutonium (IV) Fluoride

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A method of producing Pu metal by the reduction of sodium plutonium (IV) fluoride is reported. After the valency of Pu in acidic solution was adjusted to tetravalent state by addition of nitrite (e.g. NaNO₂), sodium plutonium (IV) fluoride was precipitated by adding hydrofluoric acid in the presence of sodium ion in the solution.

The double salt obtained by the wet method was dried under reduced pressure at 110°C, and then reduced with Ca metal in Ar atmosphere. Over 80% Pu yield was obtained by reducing 1g batch of the double salt.

I. INTRODUCTION

As reported in Part (I), Pu metal is usually prepared by reducing anhydrous fluoride, which is obtained by dry method using hot HF gas. The drawback of the dry method, however, is that the dry fluorination apparatus must be air tight, and expensive corrosion-resistant materials must be used for the hot HF gas, and the apparatus is not easy to handle.

As an alternative method, we have attempted to prepare anhydrous PuF₃ by thermal decomposition of ammonium plutonium (IV) fluoride, obtained as precipitate from acidic solution, as described in the preceding paper Part (I).

In the present study, sodium plutonium (IV) fluoride was used as the starting material instead of ammonium double salt, because the sodium double salt can be reduced directly with Ca or other reducing metals without requiring thermal decomposition.

II. EXPERIMENTAL

1. Purification of Pu

The method used for purification of Pu in acidic solution was as described in the preceding paper.⁰

2. Precipitation

The purified Pu(III) solution was adjusted to tetravalent state by addition of sodium nitrite, and then 10% hydrofluoric acid was added to this solution until the precipitation ceased. After 24 hr of standing, the precipitate was filtered and washed thoroughly with methanol. It was then dried in a desicador with Mg(ClO₄)₂.

3. Calcium Reduction of Sodium Plutonium (IV) Fluoride

The sodium plutonium (IV) fluoride was reduced with Ca in Ar atmosphere by induction heating. The sample was placed in a tantalum crucible provided with an inner surface thickly lined with calcium fluoride, as shown in Fig. 1. The lining at the bottom was made over 10 mm thick in order to prevent Pu penetrating to the crucible bottom. Calcium metal, in grains of 1 to 2 mm diameter, was mixed with the double salt, and mixture was placed in the crucible.

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III. RESULTS AND DISCUSSION

1. Preparation of Sodium Plutonium(IV) Fluoride

The valency of the Pu in acidic solution was adjusted to tetravalent state by addition of sodium nitrite (NaNO₂). Then 10% hydrofluoric acid was added to the Pu(IV) solution. A light brown colored salt was obtained. The X-ray pattern of the double salt agreed with that of PuF₄·7/₆NaF₂.

2. Preparation of Pu Metal

About 1g of sodium plutonium (IV) fluoride was mixed in a tantalum crucible with a large excess of Ca metal. The crucible was heated in Ar atmosphere to 1,100°C, when the reduction reaction occurred violently with a yellow flame. After 10 min of heating the product was cooled in Ar atmosphere. Crushing the sintered slag in a crucible, glittering Pu metal was obtained from the slag. A typical yield was 0.58 g of Pu metal from 1.05 g of sodium plutonium (IV) fluoride. A plutonium yield exceeding 80% was obtained by reducing a batch of about 1 g of the double salt. The purity of Pu metal was not determined.

The usual process for producing Pu metal, proposed by Johnson, is shown in Fig. 2. The dry fluorination process used in this method was replaced by a wet process (Fig. 3) by Orth. In the first procedure, the reaction heat is not sufficient for the reduction of kilogram quantities of PuF₃, so that the use of an iodine booster is necessary.

The process using double salt obtained by wet method is shown in Fig. 4. The method (A) corresponds to the wet method proposed by Orth, but has the advantage of producing anhydrous plutonium fluoride. The method (B) embodies the very useful simplification of dispensing with the thermal decomposition process of the method (A). Moreover, sodium ion in the sodium nitrite which is used for adjusting the valency of Pu can be re-used for preparing the source material of the sodium plutonium (IV) fluoride. The excess of sodium ion from the nitrite is coprecipitated as sodium fluoride with the double salts by reaction with fluorine ion.
Fig. 4 Double fluoride method

(A) Ammonium Plutonium (IV) fluoride method

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\begin{align*}
\text{N}\text{H}_4\text{NO}_2 + \text{HF} & \rightarrow \text{Ammonium plutonium (IV) fluoride} \\
\text{Filtration} & \rightarrow \text{Waste (liquid)} \\
\text{Thermal decomposition} & \rightarrow \text{Anhydrous plutonium trifluoride} \\
\text{Ca} & \rightarrow \text{Reduction} \rightarrow \text{Waste (solid)} \\
& \rightarrow \text{Plutonium metal}
\end{align*}
\]

(B) Sodium Plutonium (IV) fluoride method

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\begin{align*}
\text{NaNO}_2 + \text{HF} & \rightarrow \text{Sodium plutonium (IV) fluoride} \\
\text{Filtration} & \rightarrow \text{Waste (liquid)} \\
\text{Ca} & \rightarrow \text{Reduction} \rightarrow \text{Waste (solid)} \\
& \rightarrow \text{Plutonium metal}
\end{align*}
\]

Fig. 4 Double fluoride method

To lower the melting point of the slag, to simplify thereby the separation of the metal from the slag and to enhance the yield. In the present method of reducing the double salt, sodium fluoride is already contained as its component and also in the coprecipitate. This should contribute to lowering the melting point of the slag. The double salt method is "wet" through a large part of the process, and organic resins such as acryl and polyethylene can be extensively used as structural material.

This should place the method (B) using the double salt in a most advantageous position for preparing Pu metal.

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