Carbothermic Synthesis of High Purity Plutonium Nitride from Plutonium Oxide

Tadasumi MUROMURA

Division of Chemistry, Japan Atomic Energy Research Institute*

Received January 27, 1982
Revised April 6, 1982

Synthetic conditions of PuN from carbothermic reduction of PuO₂ has been studied in a mixed 8%H₂+92%N₂ stream at a temperature range of 1,270~1,680°C. In the course of both reactions of the carbothermic synthesis of PuN from PuO₂ and the hydrogenation of C, the vaporization loss of Pu was observed. It increased with temperature in the temperature range of 1,350~1,450°C, and reached to a constant value 1.3% of total Pu in the temperature range of 1,450~1,680°C, at which PuN was synthesized at a reaction rate of high enough. The minimum mixing ratio (C/PuO₂, mole ratio) for the formation of high purity PuN depends on temperature. The value is 2.15 for 1,620°C and 2.35 for 1,680°C. The oxygen and carbon impurities in the PuN obtained were found to be 0.095~0.028 and 0.17~0.012 %, respectively.

KEYWORDS: carbothermic synthesis, plutonium nitrides, plutonium oxides, chemical reaction, mixture, hydrogen, nitrogen, vaporization, plutonium, hydrogenation, carbon, reaction region, temperature dependence

I. INTRODUCTION

The Pu-N system has only one compound, i.e. PuN with a NaCl type structure having the lattice parameter of 0.49025~0.49075 nm(1)(2). Its nonstoichiometric range seems to be small(1)(2).

There are some raw materials for the synthesis of PuN, as seen in the case of UN(3). They are generally classified into three; halide(4), metal(5)(6) or metal hydride(7)~(11) and oxide(12)(13). In an attempt to prepare PuN by the reaction between PuCl₃ and NH₃, a mixture of PuN, PuOCl and PuO₂ was obtained at 800~900°C(4).

By the direct nitrogenation of Pu metal, PuN has been produced. The formation reaction proceeds above 300°C. Conversion of the metal was 78% after 17 h at 1,000°C(5). The value was still about 90% after arc melting in a nitrogen atmosphere(6). The reaction temperature can be lowered by using hydride-nitride method. Plutonium metal is hydrogenated to PuH₃.0~2.7 in a hydrogen atmosphere at room temperature to 200°C(7). The reaction between the hydride and nitrogen or ammonia starts at above 150°C(8)(9). In order to avoid the difficulty in handling hydride, the metal is sometimes allowed to react in an atmosphere of nitrogen containing small amount of hydrogen(10)(11). The PuN thus obtained from the metal contains small amounts of oxygen (less than 0.1%) and carbon (less than 0.1%) as impurities. However, the high cost of the metal production with few impurities is a disadvantage in these methods.

The formation of PuN from PuO₂ is interested from the view point of both economy and handling compared with that from other raw materials because of its high chemical stability. Plutonium mononitride has been reported to be prepared by the carbothermic
reduction of the oxide in a nitrogen atmosphere at 1,400~1,500°C by the following reaction:\(^{(112)}\):

\[ \text{PuO}_2 + 2\text{C} + \frac{1}{2} \text{N}_2 = \text{PuN} + 2\text{CO}. \]

(1)

Recently, the PuN containing 0.095\% C and 0.063\% O with a lattice parameter of 0.49087 nm was reported\(^{(13)}\). It is, nevertheless, considered to be difficult to form PuN purer than that containing 0.2\% C and 0.1\% O\(^{(3)}\).

Prior to the present study, the authors have studied the mechanism and kinetics for the formation of UN from UO\(_2\) by the following reaction:

\[ \text{UO}_2 + 2\text{C} + \frac{1}{2} \text{N}_2 = \text{UN} + 2\text{CO}. \]

(2)

From the results, it has been clarified that the high impurity content in the UN are attributed to both the difficulty of mixing the raw materials in the precise ratio of C/UO\(_2\) = 2.00 and the low reaction rate among the intermediate U(N, C), residual carbon and UO\(_2\)\(^{(14)}\).

To avoid these defects, two methods have been developed. The first is a method avoiding the reaction stage with low reaction rate: A mixture of UO\(_2\) and excess carbon was allowed to react in an ammonia stream or in a mixed hydrogen and nitrogen stream at temperatures of 1,450~1,780°C. The amount of impurities (C+O) in the UN was in the range of 0.05~0.1\%\(^{(15)}\). The second is a method passing through carbide: The oxide was once converted to the carbide in a He stream, which was then allowed to react with an ammonia or a mixed hydrogen and nitrogen stream at temperatures of 1,400~1,750°C. The amount of impurities (C+O) in the UN by this method was in the range of 0.05~0.1\%\(^{(16)}\). From these results, it seems that there is no great differences in the impurity levels between these two methods. These methods seem to be useful for synthesizing high purity PuN from PuO\(_2\).

In the present study, the synthesis of PuN from PuO\(_2\) has been examined by using the first method. A mixture of PuO\(_2\) and excess C was allowed to react in a mixed 8\%H\(_2\)+92\%N\(_2\) stream at high temperatures between 1,270 and 1,680°C. The second one passing through the carbide was not examined here, because the loss of Pu by vaporization in the oxide-carbide process seemed to be a serious problem\(^{(17)}\). The 8\% mixing ratio of hydrogen in nitrogen was chosen from the standpoint of preventing explosion of hydrogen in accident. The reaction conditions were clarified by the thermogravimetric measurement, X-ray and chemical analysis for the formation of high purity PuN from PuO\(_2\).

II. EXPERIMENTAL

1. Materials

Plutonium oxide PuO\(_2\) was obtained as follows: Plutonium was first purified by ion exchange process; The 7 M-HNO\(_3\) solution of Pu(IV) was passed through an anion exchange column (Dowex 1x4) and nearly all the metallic impurities such as Am, Fe, U etc. were removed by washing with 7 M HNO\(_3\) solution\(^{(18)}\). Plutonium(IV) was eluted out of the column with 0.5 M HNO\(_3\) solution. The precipitate of plutonium oxalate was obtained by gradually adding oxalic acid into the Pu solution. It was stirred for a few minutes. After one day standing, the precipitate was filtered and washed thoroughly with water and then dried in a desiccator with Mg(ClO\(_4\))\(_2\)\(^{(19)}\). The plutonium oxalate was heated in an oxygen stream at 950°C for 10 h. The final product was PuO\(_2\), which was identified.
by X-ray analysis.

Carbon used was natural graphite powder of spectroscopically pure grade. Helium and a mixture of 8%H₂+92%N₂ purchased were used after purification.

2. Apparatus

The reaction apparatus consists of a 2 kW induction furnace with a vacuum system in a Pu box, and a gas purification system out of the box, as shown in Fig. 1. It was evacuated to 10⁻³ Pa (10⁻⁸ atm). The induction furnace consists of a Mo heating element in a quartz reaction tube which details were given in the previous paper(14). Temperature of the sample was measured by a two-color eye pyrometer and was recorded.

A mixture of 8%H₂+92%N₂ from cylinder was purified by passing through Pd asbestos at 250°C and then through liquid nitrogen trap. Helium was purified by passing through Cu chips at 450~500°C and then through liquid nitrogen trap.

3. Experimental Procedure

Plutonium oxide and graphite powders were thoroughly mixed in mole ratios C/PuO₂ = 2.00, 2.16, 2.32, 2.63 and 2.95. Each of the mixtures was pressed into pellets of 7 mm in diameter and 0.4 g in weight under 3×10⁶ Pa (3 t/cm²). The pellets were placed in the Mo crucible and were heated in the induction furnace at a constant temperature in 10⁶ Pa (1 atm) reactant gas (8%H₂+92%N₂) stream of 8 cm³/s, which was introduced from the bottom of the reaction tube. The temperature was kept constant within ±20°C. At the pre-determined time of reaction, the temperature was rapidly lowered to room temperature. After the sample was cooled, the atmosphere in the reaction tube was replaced by He. The sample was then subjected to X-ray and chemical analyses after weight change measurement.

The weights of the sample and the crucible were measured in air with an electrobalance with a sensitivity of 0.01 mg. From the results, it was shown that the crucible was stable under the reaction condition of this experiment, as reported in the phase study of Mo-N system(20). Any reactions were not detected between the crucible and the sample during the experiment from the weight change measurement and the observation of appearance of the crucible.

The sintered pellet was crushed into powder in the He-filled dry box. For X-ray analysis, the powdered sample was sealed in the glass capillary evacuated. The X-ray diffraction pattern was obtained within one week after the synthesis to avoid the lattice parameter change by α-radiation damage(21)~(23), using a 114.6 mm diameter Debye-Scherrer camera with Ni-filtered Cu Kα radiation at room temperature.

The amount of carbon was determined by combustion to CO₂: About 20~70 mg powdered sample was ignited in O₂ stream at 950°C. Carbon dioxide thus obtained was adsorbed on CO₂ adsorbent (Molecular Sieve 5A) in a column at room temperature. The CO₂ was then desorbed above 200°C under a controlled condition of a constant heating rate of the adsorbent and a constant flow rate of a carrier gas He, and was determined by the detector which measured the thermal conductivity difference of the filaments. The
The oxygen content was determined as follows. The sample of 100~200 mg was sealed in a tin capsule in the He-filled dry box, which was then stored in the glass tube evacuated. It was fused in the Pt bath in a graphite crucible in a He stream at 2,000°C. Carbon monoxide obtained by the reaction between O in the PuN and C in the Pt bath was passed through the oxidizing agent (Iodine Pentoxide on Silica Gel). The CO₂ thus obtained was determined by the same way as that used for the determination of C.

III. RESULTS AND DISCUSSION

1. Reaction Behavior

The X-ray analysis showed that the solid product was only Pu(N, C) phase. From the reaction condition of excess C and N₂ gas being present, the three-phase equilibrium was possibly attained among N₂ in the atmosphere, C and Pu(N, C) in the sample; Pu(N, C)+C+N₂ → Pu(N, C)+C+N₂, as seen in the case of UN formation from UO₂ (13). In the Pu(N, C), a little amount of oxygen will be dissolved. In some cases, traces of PuO₂ were also detected with Pu(N, C) in the final product in the reaction of C/PuO₂=2.00.

The formation of pure PuN in this method is finally formulated by the following chemical equation:

\[
\text{PuO}_2 + (2+x)C + 2xH_2 + \frac{1}{2}N_2 = \text{PuN} + 2xCO + xCH_4, \quad (x=0\sim0.95). \tag{3}
\]

Accordingly, the final weight change of the sample during PuN formation depends on the mixing ratio C/PuO₂. Figure 2 shows the relation between weight change and reaction temperature after 1 h heating for the samples of mixing ratio 2.00 and 2.95. From the figure, it is seen that the carbothermic synthesis of PuN from PuO₂ proceeds fast above 1,280°C, which is conveniently obtained by extrapolation of the weight change curves to zero value.

Figure 3 shows the relation between the weight change and time for the samples of mixing ratio 2.95 at various temperatures. In the figure, the arrow on the vertical axis is the weight loss calculated from the mixing ratio (17.4%) for PuN formation. The reaction proceeds in monotonous weight loss with time. The formation of PuO₂ or Pu₃O₈ was not observed in the thermogravimetric curves (14). At 1,270°C after 7 h heating, the weight loss of the sample became to be a constant value 13.0%, which was reasonably in agreement with the weight loss of the following reaction:

\[
\text{PuO}_2 + 2.95C + \frac{1}{2}N_2 = \text{PuN} + 0.95C + 2CO, \quad (4)
\]

where the weight loss is 13.7%. It is likely that the hydrogenation of carbon proceeds very slowly at this temperature. From the weight changes at 1,310 and 1,360°C, it is
shown that the hydrogenation proceeds with the carbothermic reduction of PuO\(_2\). The final weight losses of the curves above 1,420°C exceeded the value calculated (17.4%). Some Pu appeared to vaporize above that temperature in the course of PuN formation.

From these results, it is shown that three chemical reactions proceed in the course of PuN formation in this method. They are the carbothermic synthesis of Pu(N, C) from PuO\(_2\), the hydrogenation of C and probably the vaporization of Pu. Their reaction rates largely depend on the temperature.

2. Vaporization of Pu

The weight loss exceeding the calculated value was seen in every mixing ratios of 2.00~2.95 above 1,420°C. From the relation between the weight change and the time, the relation between the loss of sample and the temperature is obtained as seen in Fig. 4; where \(\Delta w_{ob}\) is the weight loss observed after 20 h reaction and \(\Delta w_{cat}\) the weight loss calculated for PuN formation in Eq. (3). The zero value on the vertical axis means that the reaction in Eq. (3) proceeds quantitatively. In the region below the zero value, the reaction would not be complete. The vaporization of Pu appeared to take place in the region above the zero which occurs above 1,350°C. The amount of Pu loss increases with temperature above 1,350°C and reaches to a constant value 1.3% above 1,450°C. The value does not depend on temperature and mixing ratio, as seen in Table 1.

From comparison with vapor pressure of the compounds in this synthetic method\(^{(26)(27)}\), the possible species vaporized seem to be Pu metal obtained by the carbothermic reduction of PuO\(_2\), PuC or Pu\(_2\)C\(_3\) by the carburization of the metal with excess C, and Pu(N, C) under the three-phase equilibrium Pu(N, C)+C+N\(_2\)\(^{(1)}\). The details, however, are not discussed here by the lack of the data on their vaporization behavior.
3. Reaction Temperature

From the results noted in Sec. III-1 and -2, the reaction temperature can be divided into three regions, as follows:

Region 1; 1,280~1,350°C

In this region, the formation of Pu(N, C) proceeds together with the carbothermic reduction of PuO₂. The reaction rate of the hydrogenation of C appeared to be low. The loss of Pu is negligible.

Region 2; 1,350~1,450°C

The vaporization of Pu appears to occur along with both the Pu(N, C) formation and the hydrogenation of C. The amount of Pu loss gradually increases with temperature. It takes more than 20 h for the completion of the synthetic reaction in this region.

Region 3; Above 1,450°C

The rates of the three reactions; i.e., the carbothermic synthesis of Pu(N, C) from PuO₂, the hydrogenation of C, and probably the vaporization of Pu become higher. This range seems to be favorable for the synthesis of PuN by the carbothermic reduction of PuO₂ in a mixed 8%H₂+92%N₂ stream. The amount of Pu loss reaches to a constant value about 1.3% at 1,450~1,680°C.

4. Mixing Ratio C/PuO₂

The effect of mixing ratio on the Pu loss has already been described in Sec. III-2. The effect on the oxygen content in PuN obtained is shown in Fig. 5, in which the oxygen content in the PuN is plotted against the mixing ratio. At 1,620°C, the value is 0.14% at C/PuO₂=2.00. It decreases to about 0.09% at C/PuO₂=2.16~2.95. At 1,680°C, it is 0.23% at C/PuO₂=2.00. It decreases gradually with mixing ratio and attains to a constant value 0.04% at above C/PuO₂=2.63.

From the results in the figure, it seems that the mixing ratios more than 2.15 are favorable at 1,620°C for the formation of high purity PuN containing less than 0.1%O, and more than 2.35 at 1,680°C.

5. Formation of High Purity PuN

From the conditions of both the reaction temperature (Sec. III-3) and the mixing ratio C/PuO₂ (Sec. III-4), a suitable reaction range is obtained for the formation of high purity PuN in a mixed 8%H₂+92%N₂ stream, as seen in Fig. 6. Line (a) in the figure shows the minimum mixing ratio to decrease oxygen content in PuN less than 0.1%, line (b) the lowest temperature 1,450°C to obtain favorable reaction rate for PuN formation, and line (c) the maximum mixing

---

Fig. 5  Effect of mixing ratio C/PuO₂ on oxygen content in PuN

Fig. 6 Reaction range for formation of high purity PuN from PuO₂
ratio examined in this study. In the reaction range enclosed with the three lines, high purity PuN has been synthesized from PuO2.

Some PuNs were synthesized in the reaction range in Fig. 6. The results of chemical and X-ray analyses of the PuNs are shown in Table 2 with varying reaction conditions. The oxygen content in the PuNs is in the range of 0.095~0.28%. The carbon content is in the range of 0.17~0.012%, which will be decreased to lower values with the extended reaction time. The lattice parameter is in the range of 0.49054~0.49062 nm, which agrees with the reported value for the high purity PuN(3). The oxygen and carbon contents in the PuN obtained are in the same order as those of the UN obtained by the same way in this series of work(95)(10).

Table 2 Analysis of PuN obtained by carbothermic synthesis from PuO2

<table>
<thead>
<tr>
<th>No.</th>
<th>Temp. (°C)</th>
<th>Time (h)</th>
<th>C/PuO2 (mole ratio)</th>
<th>Carbon (%)</th>
<th>Oxygen (%)</th>
<th>Lattice parameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>1,520</td>
<td>11.5</td>
<td>2.32</td>
<td>0.17</td>
<td>0.095</td>
<td>0.49060±0.00004</td>
</tr>
<tr>
<td>(2)</td>
<td>1,620</td>
<td>5.5</td>
<td>2.16</td>
<td>0.11</td>
<td>0.089</td>
<td>0.49060±0.00005</td>
</tr>
<tr>
<td>(3)</td>
<td>1,620</td>
<td>5.5</td>
<td>2.63</td>
<td>0.081</td>
<td>0.088</td>
<td>0.49058±0.00004</td>
</tr>
<tr>
<td>(4)</td>
<td>1,620</td>
<td>5.5</td>
<td>2.95</td>
<td>0.12</td>
<td>0.085</td>
<td>0.49062±0.00004</td>
</tr>
<tr>
<td>(5)</td>
<td>1,680</td>
<td>9.0</td>
<td>2.63</td>
<td>0.14</td>
<td>0.028</td>
<td>0.49054±0.00005</td>
</tr>
<tr>
<td>(6)</td>
<td>1,680</td>
<td>9.0</td>
<td>2.95</td>
<td>0.054</td>
<td>0.032</td>
<td>0.49054±0.00005</td>
</tr>
<tr>
<td>(7)</td>
<td>1,680</td>
<td>9.0</td>
<td>2.95</td>
<td>0.054</td>
<td>0.040</td>
<td>0.49055±0.00007</td>
</tr>
<tr>
<td>(8)</td>
<td>1,680</td>
<td>9.0</td>
<td>2.95</td>
<td>0.012</td>
<td>0.061</td>
<td>0.49055±0.00005</td>
</tr>
</tbody>
</table>

IV. CONCLUSIONS

The synthesis of PuN in the reaction of PuO2 and C has been studied in a mixed 8%H2+92%N2 stream at 1,270~1,680°C. The reaction behavior and the conditions for the formation of high purity PuN have been clarified.

1. Three chemical reactions are thought to proceed in the course of PuN formation in this method. They are the carbothermic synthesis of Pu(N, C) from PuO2, the hydrogenation of C and the vaporization of Pu. Their reaction rates are largely affected by the reaction temperature.

2. The reaction temperature can be divided into three regions. Among them, the Region 3 (above 1,450°C) is favorable for PuN formation.

3. There is a minimum mixing ratio (C/PuO2, mole ratio) for the formation of high purity PuN. The value is 2.15 at 1,620°C, and 2.35 at 1,680°C.

4. The amount of oxygen and carbon in the PuN, which is obtained in the suitable reaction range of temperature (1,450~1,680°C) and mixing ratio (2.15~2.95), is in the range of 0.095~0.028% and 0.17~0.012%, respectively. In the course of the reaction, about 1.3% of Pu is lost probably by vaporization.

ACKNOWLEDGMENT

The author expresses his gratitude to Drs. H. Tagawa and T. Fujino for their discussions. He also wishes to thank Dr. A. Hoshino, Mrs. S. Iso, M. Ito and T. Aoyagi for their kind advices on the chemical analysis.
REFERENCES

(9) idem: ibid., 38, 1855 (1976).
(16) idem: ibid., 17[1], 57 (1980).
(24) MUROMURA, T.: To be published.