Preparation of ThN by Thermal Decomposition of Th_3N_4*

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Thorium mononitride, ThN, has been prepared in the following two ways. Olson and Mulford [1] obtained ThN through the direct nitriding of Th metal under 2 atm N_2 at 2000 °C. Benz *et al.* [2] and Ozaki *et al.* [3] prepared ThN by the thermal decomposition of Th_3N_4 in a vacuum (about 1×10^{-4} Pa) at about 1500 °C. Although pure ThN can be obtained by the direct nitriding of metallic thorium, it is very difficult to avoid oxidation of the sample using the method of thermal decomposition.

The present study also deals with the preparation of ThN by the thermal decomposition of Th_3N_4. Thermal decompositions have been performed under various conditions and the products have been examined as a function of temperature and time.

In the Th–N–O system there exist ThN, Th_3N_4, ThO_2 and Th_2N_2O as solid phases, and gaseous O_2 and N_2. The thermodynamic stability of these solid compounds has been evaluated as a function of $P(O_2)$ and $P(N_2)$ and compared with the experimental results.

Experimental

Apparatus and Procedure

Thermal decomposition of Th_3N_4 was performed in an alumina reaction tube in which a molybdenum tube was inserted in order to avoid the reaction of samples with oxygen released from the reaction tube. The reaction tube could be evacuated up to 1×10^{-4} Pa with a diffusion pump and could be heated up to 1400 °C by means of a furnace with an SiC heater.

Th_3N_4 was prepared by the reaction of Th_4H_{15} with flowing N_2 at 800 °C, as reported previously [4]. The Th_3N_4 powder was placed in the center of the alumina reaction tube and it was heated up to the desired temperature in a vacuum or in flowing gas (H_2 or He) at a flow rate of 100 ml/min. After the temperature was maintained for the desired period of time, the sample was cooled to room temperature. The product was taken out of the reaction tube and transferred to an Ar-filled glove box for analysis.

Analysis

The decomposition product was embedded in an aluminum sample holder with epoxy resin in order to minimize oxidation of the sample, and its X-ray diffraction powder patterns were obtained with a diffractometer (Geigerflex rad-γA, Rigaku Denki Co., Ltd.) using Ni-filtered Cu Kα radiation at room temperature.

Thorium and nitrogen contents of the decomposition products were determined by combustion of the products to ThO_2 at 900 °C in an oxygen-filled furnace connected to a gas chromatograph (Sumigraph NC-80; Sumitomo Chemical Industry Co., Ltd.)

Results

Thermal Decomposition in a Vacuum

The phases identified by X-ray diffraction measurements and the N/Th atom ratios determined by chemical analyses for the products obtained by thermal decomposition in a vacuum are summarized in Table I, where the conditions for the thermal decomposition are also given. The product obtained on heating at 1400 °C for 2 h contained ThN as a

TABLE I. Analyses of the Thermal Decomposition Products of Th_3N_4 in a Vacuum

Run no.	Temperature (°C)	Time (h)	N/Th atom ratio	Phases			
				Th_3N_4	ThN	Th_2N_2O	ThO_2
1	1400	2	0.95	–	+ + +	–	+ +
2	1300	2	0.96	–	+ + +	+	+
3	1300	1	0.97	–	+ + +	+	+
4	1300	1/3	0.97	–	+ + +	+	+
5	1250	1	0.98	–	+ + +	+	–
6	1100	14	1.12	+ + +	+ + +	–	–

+ + + major phase; + + minor phase; + trace; – not detected.

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major phase and ThO_2 as a minor phase. According to the Th–ThO_2 phase diagram reported by Benz [5], ThO_2 is stoichiometric at the temperatures examined in the present study. Thus, from the value of 0.95 for the N/Th atom ratio, it follows that the product contains 95 mol% of ThN.

Decreasing the temperature from 1400 to 1300 °C (Run 2), the minor phases changed from ThO_2 to a mixture of ThO_2 and Th_2N_2O, but the amounts of these impurities decreased, judging from the X-ray diffraction patterns. With decreasing time at the fixed temperature (Runs 2 and 3), the N/Th ratio became higher although little significant difference in the X-ray diffraction patterns could be observed.

The thermal decomposition on heating at 1250 °C for 1 h yielded the product containing ThN as a major phase and only Th_2N_2O as a trace. The N/Th ratio of the product was 0.98. Thus, it is seen that a decrease in time and temperature of the heat treatment reduces undesirable oxidation of the sample.

It should be noted that the product in Run 6 did not contain the oxide phases (ThO_2 and Th_2N_2O) even though a time as long as 14 h was allotted to the thermal decomposition. From these results it is expected that pure ThN phase may be prepared by choosing suitable conditions between those of Run 5 and Run 6.

Thermal Decomposition in Flowing Gas

The experimental results for the thermal decomposition of Th_3N_4 in flowing gas are summarized in Table II. No appreciable difference in the results was observed whether H_2 gas or He gas was employed.

In order to know the effect of reaction time on the type of products, three experiments were performed at 1400 °C (Runs 7–9). It is seen from the results given in the Table that the amounts of oxide phases ThO_2 and Th_2N_2O decrease with decreasing time. Thus, a decrease in the time reduces the oxidation of the sample.

In order to clarify the effect of temperature on the kind of reaction products, four experiments were made (Runs 8, 10–12). The reaction time was kept constant at 2 h. On decreasing the temperature of the heat treatment, the Th_2N_2O content decreased and the Th_3N_4 content increased. In other words, a decrease in temperature suppresses the undesirable oxidation of the sample, although the complete thermal decomposition cannot be established.

Discussion

According to studies on the preparation of ThN by thermal decomposition of Th_3N_4 performed by Benz *et al.* [2] and Ozaki *et al.* [3], ThO_2 always exists as the impurity phase together with ThN. They did not mention the occurrence of Th_2N_2O as the impurity phase. However, the present study shows that the impurity oxide changes from ThO_2 to Th_2N_2O with decreasing reaction temperature and time. Therefore, it may be important to consider the phase stability of the Th–N–O system, including Th_2N_2O as well as ThO_2, ThN and Th_3N_4 as the solid phases.

For this purpose, the thermodynamic stabilities for ThN, Th_3N_4, Th_2N_2O and ThO_2 have been evaluated. The reactions to be considered are:

$$Th_3N_4 + 3O_2 = 3ThO_2 + 2N_2 \qquad (1)$$

$$ThN + O_2 = ThO_2 + \tfrac{1}{2}N_2 \qquad (2)$$

$$2Th_3N_4 + \tfrac{3}{2}O_2 = 3Th_2N_2O + N_2 \qquad (3)$$

$$Th_2N_2O + \tfrac{3}{2}O_2 = 2ThO_2 + N_2 \qquad (4)$$

$$2ThN + \tfrac{1}{2}O_2 = Th_2N_2O \qquad (5)$$

$$Th_3N_4 = 3ThN + \tfrac{1}{2}N_2 \qquad (6)$$

The following data for the free energies of formation in cal/mol have been used [6]:

TABLE II. Analyses of the Thermal Decomposition Products of Th_3N_4 in Flowing Gas

Run no.	Temperature (°C)	Time (h)	N/Th atom ratio	Phases			
				Th_3N_4	ThN	Th_2N_2O	ThO_2
7	1400	5	1.01	–	+ + +	+ +	+
8	1400	2	1.04	–	+ + +	+ +	–
9	1400	0.5	1.12	+ + +	+ + +	+	–
8	1400	2	1.04	–	+ + +	+ +	–
10	1350	2	1.19	+ + +	+ + +	+	–
11	1300	2	1.25	+ + +	–	–	–
12	1250	2	1.24	+ + +	–	–	–

+ + + major phase; + + minor phase; + trace; – not detected.

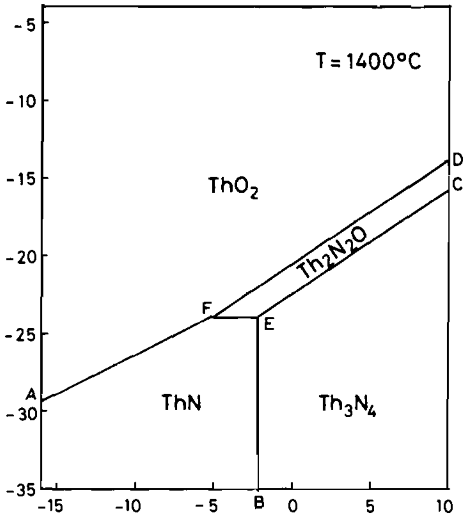

Fig. 1. The Th–N–O phase stability diagram at 1400 °C.

$$\Delta G_f = -89\,810 + 20.53T \quad \text{for } Th + \tfrac{1}{2}N_2 = ThN \quad (7)$$

$$\Delta G_f = -308\,880 + 80.05T \quad \text{for } 3Th + 2N_2 = Th_3N_4 \quad (8)$$

$$\Delta G_f = -291\,930 + 43.50T \quad \text{for } Th + O_2 = ThO_2 \quad (9)$$

$$\Delta G_f = -305\,840 + 61.69T \quad \text{for } 2Th + N_2 + \tfrac{1}{2}O_2 = Th_2N_2O \quad (10)$$

Figure 1 is the Th–N–O phase stability diagram at 1400 °C constructed by the above method. In this Figure ThN is stable in the segment AFEB, Th_3N_4 in the segment BEC, Th_2N_2O in the segment CEFD, and ThO_2 in the segment AFD. As seen from this Figure, thorium nitrides are stable with respect to thorium oxides only at very low oxygen pressure. And at such a low oxygen pressure, if the nitrogen pressure is lower than about 1×10^{-2} atm (1×10^3 Pa), ThN is stable with respect to Th_3N_4. Thus, in order to prepare ThN with no other phases, thermal decomposition of Th_3N_4 at 1400 °C must be performed at a nitrogen pressure lower than about 1×10^{-2} atm. However, the oxygen pressure required is so low that it cannot be attained easily under ordinary experimental conditions. Even in a vacuum which can normally be achieved in a laboratory, for example, 1×10^{-9} atm (1×10^{-4} Pa), ThO_2 is very stable with respect to ThN.

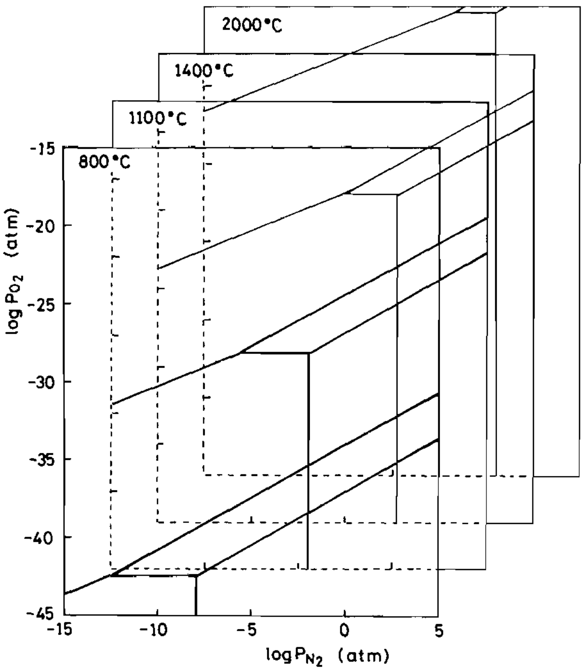

Fig. 2. The Th–N–O phase stability diagrams at 800, 1100, 1400 and 2000 °C.

Figure 2 shows the phase stability diagrams at 800, 1100, 1400 and 2000 °C. The stable region of ThN, which corresponds to the segment BEFA in Fig. 1, moves downwards with decreasing temperature. Thus, the oxygen and nitrogen pressures required for preparation of pure ThN become lower with decreasing temperature. It can therefore be concluded that it is very difficult to prepare ThN by thermal decomposition of Th_3N_4 at a low temperature, say 1400 °C, from the thermodynamic point of view.

Nevertheless, the products containing ThN together with ThO_2 and/or Th_2N_2O could be prepared experimentally. The ratio of ThN to the oxides varied according to the experimental conditions, in particular temperature and time. This means that both the thermal decomposition of Th_3N_4 and the oxidation of thorium nitrides take place simultaneously. It is, therefore, a kinetic matter whether ThN containing no oxide phases can be prepared or not. Judging from the experimental results which showed products containing more than 95 mol% ThN could be obtained, it may be possible to prepare the ThN phase without the oxide phase by choosing suitable conditions of temperature and time, in such a way that only the decomposition of Th_3N_4 occurs without the oxidation of nitrides.

The comparison between the results in a vacuum and those in flowing gas suggests that the thermal decomposition in a vacuum is more favorable than that in flowing gas. An explanation of the results may be that the nitrogen gas resulting from the reaction $Th_3N_4 = 3ThN + \frac{1}{2}N_2$ may be removed more rapidly in a vacuum than in flowing gas.

Conclusions

(1) Material containing more than 95% ThN could be obtained by thermal decomposition of Th_3N_4.

(2) The Th–N–O phase stability diagrams were constructed from thermodynamic calculations.

(3) Although ThN is extremely unstable from a thermodynamic point of view, the present experimental results suggest that the kinetics play an important role in preparing ThN containing no thorium oxide phases.

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