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Formation Process of Niobium Nitride by the Reaction of Niobium Pentachloride with Ammonia in the Vapor Phase and Properties of the Niobium Nitride Formed

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The reaction products of gaseous $NbCl_5$ with ammonia were $NbCl_5 \cdot 5NH_3$ at 200 °C, $NbCl_5 \cdot 5NH_3$, Nb_4N_5, and NH_4Cl at 250—500 °C, Nb_4N_5 and NH_4Cl at 550—950 °C, δ-NbN and NH_4Cl at 1000 °C, δ-NbN, Nb_2N, NH_4Cl, and HCl at 1100 °C, and δ-NbN, Nb_2N, Nb_4N_3, δ′-NbN, ε-NbN, NH_4Cl, and HCl at 1200—1300 °C. In the vapor-phase reaction of gaseous $NbCl_5$ with ammonia, the reaction of gaseous $NbCl_5$ with ammonia to form $NbCl_5 \cdot 5NH_3$ occurs first. Above *ca.* 235 °C, the $NbCl_5 \cdot 5NH_3$ reacts with ammonia to form Nb_4N_5. Above *ca.* 1000 °C, the Nb_4N_5 decomposes to δ-NbN. Above about 1100 °C, in addition to these reactions, the nitriding of niobium, formed by the reduction of gaseous $NbCl_5$ with the hydrogen resulting from the thermal dissociation of ammonia, also occurs to form Nb_2N at 1100 °C and Nb_2N, Nb_4N_3, δ′-NbN, and ε-NbN at 1200—1300 °C. When the Nb_4N_5, formed by the vapor-phase reaction, is heated in an argon atmosphere, it changes to δ-NbN at *ca.* 1000 °C, to δ-NbN and ε-NbN at 1100—1200 °C, and then to Nb_4N_3 and δ-NbN at 1300 °C. The niobium nitrides formed above 1200 °C are uniform, ultrafine powders with particle diameters of the order of 1/100 μm.

The vapor-phase reaction of transition-metal chlorides with ammonia has recently become important for the preparation of fine powders or thin films of transition-metal nitrides, which are aquiring importance as new industrial materials. However, no information has been available on the reaction process of transition-metal chloride with ammonia in the vapor phase. The present authors have previously reported the formation processes of some nitrides of transition metals of Groups IV and V by the reaction of the chloride with ammonia.[1,2]

Concerning the vapor-phase reaction of niobium pentachloride ($NbCl_5$) with ammonia, little information has been available apart from the work of Gavrilko and Kornilov.[3] They reported the preparation of fine niobium nitride powders by a vapor-phase reaction of the $NbCl_5$–NH_3–N_2 system at 5300—9200 K, with emphasis on the effect of the reaction temperature on the specific surface area and the particle size.

In this paper, the reaction products of gaseous $NbCl_5$ with ammonia at 200—1300 °C were examined in detail. The possible reactions which were considered to occur during the reaction process on the basis of the above experiments were examined. Further, the thermal stability of the niobium nitride formed was examined. The niobium nitride formed was also examined by electron microscopy.

Experimental

Materials. The $NbCl_5$ used was prepared by the reaction of niobium powder (Nb 99.8%, Hermann C. Starck Berlin) with chlorine at 300 °C.[4] Found: Nb, 34.3; Cl, 65.6%. Calcd for $NbCl_5$: Nb, 34.39; Cl, 65.61%. Ammonia was dried by passing it over sodium hydroxide granules and barium oxide powders.

Experimental Procedures. A transparent quartz or alumina reaction tube (1000 mm length) was used for examining the reaction products of gaseous $NbCl_5$ with ammonia. Gaseous $NbCl_5$ was formed by heating solid $NbCl_5$ (12 g) at 190 °C and was carried by a stream of argon (50 cm^3/min) into the reaction zone (28 mm i.d., 250 mm length), held at a specified temperature. The $NbCl_5$ inlet tube consisted of two concentric tubes. Gaseous $NbCl_5$ carried by argon was introduced through the inner tube, and the outer tube was utilized for introducing argon (50 cm^3/min) as a sheath gas to prevent the formation of product deposits in the chloride inlet tube. Ammonia was simultaneously introduced at a flow-rate of 100 cm^3/min into the reaction zone through a separate tube. The mean flow-rate of gaseous $NbCl_5$ was 6.0 cm^3/min. A quartz or alumina tube was inserted into the reaction tube to make the removal of the reaction product easier. The reaction was allowed to proceed for 2 h.

The by-product, ammonium chloride (NH_4Cl), which was deposited outside the reaction zone, together with the niobium nitride formed, was separated by heating the mixture in an argon stream at 400 °C for 10—15 h.

Analytical. The chemical analysis of the reaction product was performed as follows. The niobium content of the $NbCl_5$–NH_3 adduct was gravimetrically determined as Nb_2O_5 after hydrolyzing the sample in 3 M†-nitric acid. The chlorine and ammonia contents were determined by the gravimetric method as AgCl and by the Kjeldahl method, respectively, from the filtrate. In the case of a mixture of the adduct and niobium nitride, the niobium and chlorine contents were gravimetrically determined after the fusion of the sample with sodium carbonate. The NH_3 content was determined by the Kjeldahl method from the filtrate after hydrolyzing the sample in 3 M-nitric acid.

The X-ray analysis of the solid product was performed with an X-ray powder diffractometer equipped with a proportional counter and using Ni filtered Cu radiation. The sample chamber of the diffractometer was maintained under a dry nitrogen atmosphere, if necessary, to prevent any contamination of the sample by atmospheric moisture during the irradiation.

The sensitivity of the quartz helix used for thermogravimetry (TG) was approximately 113 mm/g. The sample (0.2 g) was heated at a rate of 2.5 °C/min, and the flow-rate of ammonia was maintained at 50 cm^3/min.

Throughout this work, the $NbCl_5$ and the reaction products were handled in an argon atmosphere to prevent any contamination by atmospheric moisture.

Results and Discussion

Reaction Products of Gaseous Niobium Pentachloride with Ammonia. The products formed by heating

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† 1 M = 1 mol dm^{-3}.

gaseous $NbCl_5$ in an ammonia stream at various temperatures were examined by both X-ray analysis[5—11] and chemical analysis. Reaction temperatures above 200 °C were employed, because gaseous $NbCl_5$ was generated at 190 °C.

The product formed at 200 °C showed no clear X-ray diffraction pattern. Found: Nb, 26.1; Cl, 49.8; NH_3, 24.0%. The ratio of Nb:Cl:NH_3 was calculated to be 1:5.00:5.02. This was considered to indicate that the product formed at 200 °C had a composition of $NbCl_5 \cdot 5NH_3$ (calcd for $NbCl_5 \cdot 5NH_3$: Nb, 26.15; Cl, 49.89; NH_3, 23.96%). The reaction products at various temperatures above 200 °C are shown in Table 1. Unreacted $NbCl_5$ was not observed throughout the temperature range of this work.

At 550—1000 °C, all the products were obtained outside the reaction zone. Above 1100 °C, in addition to the δ-NbN formed outside the reaction zone, Nb_2N was formed inside the reaction zone at 1100 °C, while Nb_2N, Nb_4N_3, δ′-NbN, ε-NbN, were formed both inside and outside the reaction zone at 1200—1300 °C. The products formed below 1000 °C and the products formed outside the reaction zone above 1100 °C were in the form of powder, while the products formed inside the reaction zone at 1100—1300 °C were in the form of film. The mole percentage of $NbCl_5$ converted to the nitrides formed inside the reaction zone was 16% at 1100 °C, 21% at 1200 °C, and 44% at 1300 °C. Also, it was observed that HCl was formed in addition to NH_4Cl above 1100 °C.

The presence of the following niobium nitrides has been reported: Nb_2N (hexagonal, a_0=3.055 Å, c_0=4.994 Å;[6] N/Nb 0.40—0.50[12]), Nb_4N_3 (tetragonal, a_0=4.382 Å, c_0=4.316 Å;[7] N/Nb 0.75—0.79[12]), δ-NbN (cubic, a_0=4.376—4.392 Å; N/Nb 0.86—1.06[10]), δ′-NbN (hexagonal, $a_0=2.96_7$ Å, $c_0=5.53_8$ Å;[5] metastable phase[13]), ε-NbN (hexagonal, a_0=2.960 Å, c_0=11.270 Å;[8] N/Nb 1.000—1.018[12]), Nb_4N_5 (tetragonal, $a_0=6.87_3$ Å, $c_0=4.29_8$ Å),[5] and Nb_5N_6 (hexagonal, $a_0=5.19_3$ Å, $c_0=10.38_0$ Å).[5] It was found that all the above nitrides except Nb_5N_6 were formed by the reaction of gaseous $NbCl_5$ with ammonia.

Table 1. Reaction products of gaseous $NbCl_5$ with ammonia at various temperatures

Temp/°C	Products
200	$NbCl_5 \cdot 5NH_3$
250—300	$NbCl_5 \cdot 5NH_3 \gg Nb_4N_5$; NH_4Cl
400—450	$NbCl_5 \cdot 5NH_3$, Nb_4N_5; NH_4Cl
500	$Nb_4N_5 \gg NbCl_5 \cdot 5NH_3$; NH_4Cl
550—950	Nb_4N_5; NH_4Cl
1000	δ-NbN; NH_4Cl
1100	δ-NbN>Nb_2N; NH_4Cl, HCl
1200	δ-NbN>Nb_2N>Nb_4N_3, δ′-NbN, ε-NbN; NH_4Cl, HCl
1300	Nb_4N_3>Nb_2N, ε-NbN>δ-NbN, δ′-NbN; NH_4Cl, HCl

Reaction Process of Gaseous Niobium Pentachloride with Ammonia. To elucidate the reaction process of gaseous $NbCl_5$ with ammonia, the behavior of the $NbCl_5 \cdot 5NH_3$ and the Nb_4N_5, which had been formed during the reaction process, on heating in an ammonia stream were examined.

Behavior of $NbCl_5 \cdot 5NH_3$ on Heating in an Ammonia Stream: The TG curve of $NbCl_5 \cdot 5NH_3$ in an ammonia stream showed that the sample weight decreased continuously above about 235 °C and reached a constant value at about 460 °C. The sample after the heating to 500 °C was found by X-ray analysis to be Nb_4N_5.

In order to obtain more detailed information on the behavior of $NbCl_5 \cdot 5NH_3$ on heating in an ammonia stream, $NbCl_5 \cdot 5NH_3$ (1.0 g) in a quartz boat (70 mm length, 15 mm width, 7 mm depth) was placed in a straight reaction tube (28 mm i.d., 1000 mm length). Ammonia was introduced into the reaction tube at a flow-rate of 100 cm³/min. The sample part was then placed in the centre of an electric furnace (300 mm heating length) maintained at a specified temperature for 1 h. The products obtained both inside and outside the boat were examined by X-ray analysis and chemical analysis. The results are shown in Table 2.

The results showed that $NbCl_5 \cdot 5NH_3$ reacted with ammonia to form Nb_4N_5 and NH_4Cl above about 235 °C and that a small part of the $NbCl_5 \cdot 5NH_3$ vaporized above about 350 °C. The formation of a small amount of Nb_4N_5 above 400 °C outside the boat was considered to indicate that the reaction of gaseous $NbCl_5 \cdot 5NH_3$ with ammonia to form Nb_4N_5 also occurred above about 400 °C.

Behavior of Nb_4N_5 on Heating in an Ammonia Stream: The samples obtained by heating Nb_4N_5 (0.1 g) in an ammonia stream (100 cm³/min) at various temperatures of 900—1300 °C for 2 h were examined by X-ray analysis.[5,8,9] The Nb_4N_5 used was prepared by the reaction of gaseous $NbCl_5$ with ammonia at 900 °C, based on the experimental results shown in Table 1. The results are shown in Table 3. The results indicated that, on heating Nb_4N_5 in an ammonia stream above 1000 °C, Nb_4N_5 changed according to the following path: $Nb_4N_5 \rightarrow$ δ-NbN $\rightarrow$ ε-NbN $\rightarrow$ δ′-NbN.

Based on the above experimental results, the reac-

Table 2. Experimental results for $NbCl_5 \cdot 5NH_3$ on heating in an ammonia stream

Heating temp/°C	Products		Unreacted
	In the boat	Outside the boat	$NbCl_5 \cdot 5NH_3$/%
250	Nb_4N_5(11)	NH_4Cl	89
300	Nb_4N_5(46)	NH_4Cl	54
350	Nb_4N_5(75)	$NbCl_5 \cdot 5NH_3$(1), NH_4Cl	24
400	Nb_4N_5(88)	$NbCl_5 \cdot 5NH_3$(3), Nb_4N_5(<1), NH_4Cl	8
450	Nb_4N_5(91)	$NbCl_5 \cdot 5NH_3$(4), Nb_4N_5(2), NH_4Cl	3
500	Nb_4N_5(95)	$NbCl_5 \cdot 5NH_3$(4), Nb_4N_5(<1), NH_4Cl	—

The values in parentheses are the mole percentages of $NbCl_5 \cdot 5NH_3$ converted to the product.

Table 3. Products obtained by heating Nb_4N_5 at various temperatures in an ammonia stream

Temp/°c	Products
900	Nb_4N_5
1000	δ-NbN > ε-NbN
1100	ε-NbN > δ-NbN > δ'-NbN
1200	ε-NbN > δ-NbN > δ'-NbN
1300	ε-NbN > δ-NbN > δ'-NbN

Table 4. Products obtained by heating niobium at various temperatures in a nitrogen stream

Temp/°c	Products
900	Nb > Nb_2N
1000	Nb > Nb_2N > δ'-NbN, ε-NbN > Nb_4N_3
1100	Nb_2N, ε-NbN > Nb, Nb_4N_3 > δ'-NbN
1200	Nb_4N_3 > Nb_2N, ε-NbN > δ'-NbN
1300	Nb_4N_3, ε-NbN

tion process of gaseous $NbCl_5$ with ammonia can be discussed. As shown in Table 1, $NbCl_5 \cdot 5NH_3$ alone was formed at 200 °C. This fact indicates that the reaction of $NbCl_5$ with ammonia to form $NbCl_5 \cdot 5NH_3$ occurs first. The Nb_4N_5 formed at 250—950 °C is considered to be due to the reaction of $NbCl_5 \cdot 5NH_3$ with ammonia, because the $NbCl_5 \cdot 5NH_3$ reacts with ammonia above about 235 °C to form Nb_4N_5, as described above. The δ-NbN formed above 1000 °C is considered to be due to the decomposition of the Nb_4N_5, because Nb_4N_5 decomposes above about 1000 °C to form δ-NbN, as described above.

As mentioned before, Nb_2N was formed in addition to δ-NbN at 1100 °C. At 1200—1300 °C, Nb_4N_3, δ'-NbN, and ε-NbN were formed in addition to δ-NbN and Nb_2N. Above 1100 °C, HCl was formed in addition to NH_4Cl. The percentage of HCl formed to the total amount of chlorine introduced as $NbCl_5$ was 18% at 1100 °C, 51% at 1200 °C, and 92% at 1300 °C. This amount of HCl formed is considerably higher than that of HCl formed by the thermal decomposition of NH_4Cl at each temperature under the experimental conditions in this work.[1] Also, it has been reported that the thermal dissociation of ammonia under the experimental conditions in this work proceeds markedly above about 1100 °C to form hydrogen and nitrogen[1] and that the reduction of gaseous $NbCl_5$ with hydrogen proceeds markedly above about 900 °C to form niobium.[14] Considering these facts, it was considered that the reduction of gaseous $NbCl_5$ with the hydrogen resulting from the thermal dissociation of ammonia also occurred to form niobium and HCl and that the niobium formed reacted with nitrogen or ammonia to form niobium nitrides.

Then, the products obtained by heating niobium (1.0 g) in a nitrogen stream and in an ammonia stream (100 cm^3/min) at various temperatures of 900—1300 °C for 2 h were examined by X-ray analysis.[5-8,15] The experimental results in a nitrogen stream are shown in Table 4. The results in an ammonia stream were similar to those in a nitrogen stream.

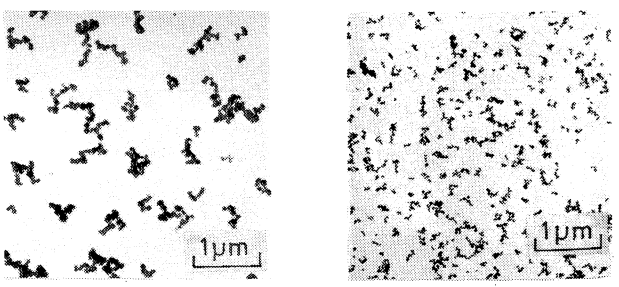
Based on the above experimental results, the formation processes of the Nb_2N, Nb_4N_3, δ'-NbN, and ε-NbN, which were formed above 1100 °C by the reaction of gaseous $NbCl_5$ with ammonia, can be discussed. As seen from the results shown in Tables 3 and 4, Nb_2N and Nb_4N_3 were not formed by the heating of Nb_4N_5 in an ammonia stream, but they were formed by the nitriding of niobium. This fact was considered to indicate that the formation of Nb_2N and Nb_4N_3 was due to the nitriding of the niobium resulting from the hydrogen reduction of $NbCl_5$. δ'-NbN and ε-NbN were considered to be formed by the heating of Nb_4N_5 in an ammonia stream or by the nitriding of niobium (Tables 3 and 4). However, as shown in Table 1, δ'-NbN and ε-NbN were always obtained, together with Nb_2N and Nb_4N_3, which were formed only by the nitriding of niobium. This fact was considered to indicate that δ'-NbN and ε-NbN were formed also by the nitriding of niobium.

From the above mentioned results, the formation process of niobium nitride by the vapor-phase reaction of $NbCl_5$ with ammonia can be represented as follows. The reaction of gaseous $NbCl_5$ with ammonia occurs first to form $NbCl_5 \cdot 5NH_3$. Above about 235 °C, the $NbCl_5 \cdot 5NH_3$ reacts with ammonia to form Nb_4N_5. Above about 1000 °C, the Nb_4N_5 decomposes to δ-NbN. Above about 1100 °C, in addition to these reactions, the nitriding of niobium, formed by the reduction of gaseous $NbCl_5$ with the hydrogen resulting from the thermal dissociation of ammonia, also occurs to form Nb_2N at 1100 °C and Nb_2N, Nb_4N_3, δ'-NbN, and ε-NbN at 1200—1300 °C.

Properties of the Niobium Nitride Formed. To obtain knowledge on the thermal stability of the niobium nitride formed by the reaction of gaseous $NbCl_5$ with ammonia, the Nb_4N_5 (0.1 g), formed at 900 °C, was heated in a argon atmosphere at various temperatures for 2 h. X-ray analysis of the samples obtained after the heating showed them to be unchanged Nb_4N_5 at 900 °C, δ-NbN at 1000 °C, δ-NbN $\gg \varepsilon$-NbN at 1100—1200 °C, and $Nb_4N_3 > \delta$-NbN at 1300 °C.

A comparison of the above results with the results on heating Nb_4N_5 in an ammonia stream (Table 3) showed that δ'-NbN was not formed by the heating of Nb_4N_5 in an argon atmosphere, and that in an argon atmosphere Nb_4N_5 decomposed to Nb_4N_3, while in an ammonia stream Nb_4N_5 did not give the nitride with a N/Nb atomic ratio of less than 1, Nb_4N_3.

Finally, the niobium nitrides obtained outside the reaction zone by the reaction of gaseous $NbCl_5$ with ammonia at various temperatures were examined by electron microscopy. Some typical micrographs of the niobium nitride are shown in Fig. 1.



(a) 1100 ℃ (b) 1200 ℃

Fig. 1. Electron micrographs of the niobium nitrides formed at various temperatures.

As seen from Fig. 1, the niobium nitrides formed above 1200 °C under the experimental conditions in this work were uniform, ultrafine powders with particle diameters of the order of 1/100 μm.

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