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Reaction Process of Titanium Tetrachloride with Ammonia in the Vapor Phase and Properties of the Titanium Nitride Formed

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The reaction products of gaseous $TiCl_4$ with ammonia were $TiCl_4 \cdot 5NH_3$ at 200 °C, $TiCl_4 \cdot 5NH_3$, TiClN, and NH_4Cl at 250—400 °C, $TiCl_4 \cdot 5NH_3$, TiClN, TiN_x, and NH_4Cl at 450—650 °C, TiN_x and NH_4Cl at 700—1000 °C, and TiN_x, NH_4Cl, and HCl at 1100—1400 °C. The N/Ti atomic ratio, x, of the TiN_x formed was 1.21 at 700 °C, 1.16 at 800 °C, 1.13 at 900 °C, and 1.10 above 1000 °C. The lattice constants of the TiN_x formed are shown. The reaction process can be represented as follows: The reaction of gaseous $TiCl_4$ with ammonia occurs first to form $TiCl_4 \cdot 5NH_3$. Above *ca.* 220 °C, the $TiCl_4 \cdot 5NH_3$ decomposes to TiClN. Above *ca.* 430 °C, the TiClN reacts with ammonia to form TiN_x. Above *ca.* 1100 °C, in addition to these reactions, the reaction of $TiCl_2$, formed by the reduction of $TiCl_4$ with hydrogen resulting from the thermal dissociation of ammonia, with ammonia occurs to form TiN_x. On heating the TiN_x, formed by the vapor-phase reaction, at temperatures higher than 500 °C in an argon atmosphere, the value of x decreased and became close to that of the stoichiometric nitride, being 1.02 at 900—1100 °C.

The vapor-phase reaction of transition metal chlorides with ammonia has recently become important for the preparation of fine powders of transition metal nitrides; these are acquiring importance as new industrial materials. Concerning the formation of titanium nitride from titanium tetrachloride ($TiCl_4$) by a vapor-phase reaction, Kato *et al.*[1] have studied the preparation of fine titanium nitride powders by a vapor-phase reaction of the $TiCl_4$–NH_3–H_2–N_2 system at 700—1500 °C with emphasis on the effects of reaction conditions on the particle size and chemical composition. However, no information is at present available on the reaction process of $TiCl_4$ with ammonia in the vapor phase.

In this paper, the reaction products of gaseous $TiCl_4$ with ammonia at 200—1400 °C were examined in detail. The possible reactions which were considered to occur on the basis of the above experiments were examined. The N/Ti atomic ratios, lattice constants, and thermal stability of the titanium nitrides formed at various temperatures were examined. The titanium nitrides formed were also examined by electron microscopy.

Experimental

Materials. The $TiCl_4$ was prepared by the reaction of titanium sponge (Ti 99.7%) with chlorine at 500 °C and purified by fractional distillation. The chemical analysis gave Ti, 25.2; Cl, 74.7% (calcd for $TiCl_4$: Ti, 25.24; Cl, 74.76%). The ammonia was dried by passing it over sodium hydroxide granules.

Experimental Procedures. A transparent quartz or alumina reaction tube (1000 mm length) was used for examining the reaction products of gaseous $TiCl_4$ with ammonia. Gaseous $TiCl_4$ was formed by heating liquid $TiCl_4$ (17 g) at 105 °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 specified temperature. The $TiCl_4$ inlet tube consisted of two concentric tubes. Gaseous $TiCl_4$ carried by arogn 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 formation of titanium nitride deposits at 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 $TiCl_4$ was 6.0 cm^3/min. A quartz or alumina tube was inserted inside the reaction tube to make the removal of the reaction product easier. The reaction was allowed to proceed for 2 h.

The by-product NH_4Cl which deposited outside the reaction zone together with the titanium nitride formed was separated by heating the mixture in an argon stream at 400 °C (the sublimation point of NH_4Cl: 339 °C)[2] for 10—15 h.

Analytical. The chemical analysis of the reaction products was performed as follows: The titanium content was gravimetrically determined as TiO_2 using cupferron as a precipitating agent, after dissolving the sample in 3 M-nitric acid. The chlorine content was gravimetrically determined as AgCl from the filtrate. The ammonia content was determined by the Kjeldahl method from the nitric acid solution.

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

The sensitivity of the quartz helix used for thermogravimetry (TG) was approximately 94 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.

The N/Ti atomic ratio of the titanium nitride formed was evaluated as follows: The sample titanium nitride was oxidized to TiO_2 by heating in an oxygen atmosphere to 700 °C, using a Shimazu high-sensitive thermal balance Model TGA31. The titanium content of the sample was calculated from the amount of TiO_2 formed. The amount of nitrogen was determined as the difference between the amount of the initial sample and that of the titanium. The value of the N/Ti atomic ratio was evaluated with an accuracy within ± 0.01.

The lattice constant of the titanium nitride was calculated based on the X-ray diffraction data obtained by using silicon powders as an internal standard and under the scanning speed of 1/2—1/4°/min.

Throughout this work, the $TiCl_4$ and the reaction products were handled in an argon atmosphere to prevent contamination by atmospheric moisture.

Results and Discussion

Reaction Products of Gaseous Titanium Tetrachloride with Ammonia. The products formed by heating gaseous

Table 1. Reaction products of gaseous $TiCl_4$ with ammonia at various temperatures

Temp/°C	Products	
	In the reaction zone	Outside the reaction zone
200	$TiCl_4 \cdot 5NH_3$	$TiCl_4 \cdot 5NH_3$
250	$TiCl_4 \cdot 5NH_3 \gg TiClN$	$TiCl_4 \cdot 5NH_3$; NH_4Cl
300	$TiCl_4 \cdot 5NH_3 \gg TiClN$	$TiCl_4 \cdot 5NH_3$; NH_4Cl
350	$TiCl_4 \cdot 5NH_3 > TiClN$	$TiCl_4 \cdot 5NH_3$; NH_4Cl
400	TiClN	$TiCl_4 \cdot 5NH_3$; NH_4Cl
450	$TiClN > TiN_x$	$TiCl_4 \cdot 5NH_3$; NH_4Cl
500	TiClN, TiN_x	$TiCl_4 \cdot 5NH_3$; NH_4Cl
550	$TiN_x > TiClN$	$TiCl_4 \cdot 5NH_3$, TiN_x; NH_4Cl
600	$TiN_x > TiClN$	$TiN_x \gg TiCl_4 \cdot 5NH_3$; NH_4Cl
650	$TiN_x > TiClN$	$TiN_x \gg TiCl_4 \cdot 5NH_3$; NH_4Cl
700—900	TiN_x	TiN_x; NH_4Cl
1000	—	TiN_x; NH_4Cl
1100—1400	—	TiN_x; NH_4Cl, HCl

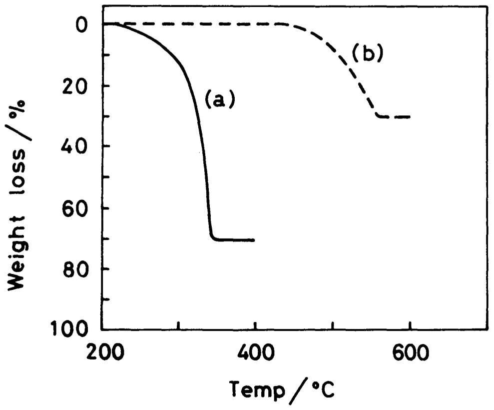


Fig. 1. TG curves of $TiCl_4 \cdot 5NH_3$ and TiClN in an ammonia stream.
(a): $TiCl_4 \cdot 5NH_3$, (b): TiClN.

$TiCl_4$ in an ammonia stream at various temperatures above 200 °C were examined both by X-ray analysis[3–5] and chemical analysis. The product formed at 200 °C showed a hitherto unknown X-ray diffraction pattern which was clearly different from those of known titanium compounds. The chemical analysis of the product gave Ti, 17.4; Cl, 51.6; NH_3, 30.8%. The ratio of Ti : Cl : NH_3 was calculated to be 1 : 4.00 : 4.98. This was considered to indicate that the product formed at 200 °C had a composition of $TiCl_4 \cdot 5NH_3$ (calcd for $TiCl_4 \cdot 5NH_3$: Ti, 17.42; Cl, 51.60; NH_3, 30.98%). The reaction products at various temperatures are shown in Table 1. Unreacted $TiCl_4$ was not observed throughout the temperature range of this work.

Reaction Process of Gaseous Titanium Tetrachloride with Ammonia. To elucidate the reaction process of gaseous $TiCl_4$ with ammonia, the behavior of the $TiCl_4 \cdot 5NH_3$ and the TiClN, which had been formed during the reaction process, on heating in an ammonia stream were examined. The thermal dissociation of ammonia[6] and the thermal decomposition of NH_4Cl[7] under the experimental conditions in this work were also examined.

Behavior of $TiCl_4 \cdot 5NH_3$ and TiClN on Heating in an Ammonia Stream: The TG curve of $TiCl_4 \cdot 5NH_3$ in an ammonia stream is shown in Fig. 1(a). $TiCl_4 \cdot 5NH_3$ lost weight above 220 °C. The weight loss was accompanied by the vaporization of NH_4Cl and a small amount of $TiCl_4 \cdot 5NH_3$. The sample after heating to 400 °C was found to be TiClN by X-ray analysis.

In order to obtain more detailed information on the behavior of $TiCl_4 \cdot 5NH_3$ on heating in an ammonia stream, $TiCl_4 \cdot 5NH_3$ (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 cm^3/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 inside and outside the boat were examined by X-ray analysis and chemical analysis. The results are shown in Table 2.

From the results, it was found that $TiCl_4 \cdot 5NH_3$ decomposed to TiClN above about 220 °C and a part of $TiCl_4 \cdot 5NH_3$ vaporized above about 300 °C in an ammonia stream.

The TG curve of TiClN in an ammonia stream is shown in Fig. 1(b). The TiClN used was prepared by the reaction of gaseous $TiCl_4$ with ammonia at 400 °C. The chemical analysis gave Ti, 49.1; Cl, 36.4% (calcd for TiClN: Ti, 49.19; Cl, 36.42%). TiClN lost weight above 430 °C. The weight loss was accompanied by the vaporization of NH_4Cl alone. The sample after heating to 600 °C was found to be TiN_x. From these results, it was found that TiClN reacted with ammonia above about 430 °C to form TiN_x.

Table 2. Experimental results for $TiCl_4 \cdot 5NH_3$ on heating in an ammonia stream

Heating temp/°C	Products		Unreacted $TiCl_4 \cdot 5NH_3$ (%)
	In the boat	Outside the boat	
250	TiClN(4)	NH_4Cl	96
300	TiClN(41)	$TiCl_4 \cdot 5NH_3$(15), NH_4Cl	44
350	TiClN(71)	$TiCl_4 \cdot 5NH_3$(29), NH_4Cl	—

Note: the value in( ) is mole percentage of $TiCl_4 \cdot 5NH_3$ converted to the product.

Thermal Dissociation of Ammonia and Thermal Decomposition of NH_4Cl: Ammonia alone was introduced at a flow-rate of 100 cm^3/min into the reaction zone held at a specified temperature and the total volume of nitrogen and hydrogen, formed by the dissociation of ammonia, was measured. From the results, the percentage of the dissociated ammonia was found to be <1% at 800 °C, 1% at 900 °C, 2% at 1000 °C, 6% at 1100 °C, 23% at 1200 °C, 88% at 1300 °C, and 98% at 1400 °C.

Gaseous NH_4Cl was formed by heating solid NH_4Cl and was carried by a stream of argon at a flow-rate of 100 cm^3/min into the reaction zone held at a specified temperature for 2 h. The amount of NH_4Cl introduced, 6.5 g, was the same as that formed during the reaction of gaseous $TiCl_4$ with ammonia for 2 h at 700—1000 °C (Table 1). The percentages of the decomposed NH_4Cl at various temperatures were evaluated from the amount of HCl formed by the decomposition. From the results, the percentage of the decomposed NH_4Cl was found to be <1% at 1100 °C, 8% at 1200 °C, 29% at 1300 °C, and 65% at 1400 °C.

Based on the above experimental results, the reaction process of gaseous $TiCl_4$ with ammonia was discussed. As shown in Table 1, $TiCl_4 \cdot 5NH_3$ alone was formed at 200 °C. This fact indicates that the reaction of gaseous $TiCl_4$ with ammonia to form $TiCl_4 \cdot 5NH_3$ occurs first. The TiClN formed at 250—650 °C (Table 1) is considered to be due to the decomposition of $TiCl_4 \cdot 5NH_3$, because the $TiCl_4 \cdot 5NH_3$ decomposes above about 220 °C to TiClN, as described above. The TiN_x formed above 450 °C is considered to be due to the reaction of TiClN with ammonia, because the TiClN reacts with ammonia above about 430 °C to form TiN_x.

Above 1100 °C, HCl was formed in addition to TiN_x and NH_4Cl (Table 1). The percentage of HCl formed to the total amount of chlorine introduced as $TiCl_4$ was 36% at 1100 °C, 75% at 1200 °C, 92% at 1300 °C, and 93% at 1400 °C. This amount of HCl is considerably larger than the amount of HCl formed by the thermal decomposition of NH_4Cl at each temperature, as described above. Also, it has been reported that gaseous $TiCl_4$ reacts with hydrogen above about 800 °C to form gaseous titanium dichloride ($TiCl_2$) and HCl.[8] From these facts, it was considered that the reduction of gaseous $TiCl_4$ with hydrogen, formed by the thermal dissociation of ammonia, to $TiCl_2$ also occurred above 1100 °C and that the $TiCl_2$ reacted with ammonia to form TiN_x. Therefore, the reaction of gaseous $TiCl_2$ with ammonia was examined.

TABLE 3. N/Ti ATOMIC RATIO AND LATTICE CONSTANT OF THE TiN_x FORMED

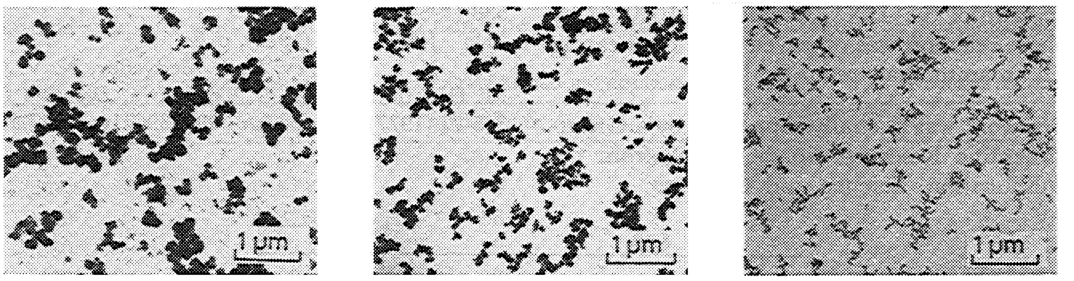
Formation temp/°C	x in TiN_x	a_0/Å
700	1.21	4.224
800	1.16	4.228
900	1.13	4.230
1000—1400	1.10	4.233

The $TiCl_2$ used was prepared by the disproportionation of commercial titanium trichloride ($TiCl_3$) *in vacuo* at 475 °C.[9] The chemical analysis gave Ti, 40.2; Cl, 59.7% (calcd for $TiCl_2$: Ti, 40.31; Cl, 59.69%). Gaseous $TiCl_2$ was formed by heating $TiCl_2$ at 800 °C and was carried by a stream of argon (50 cm^3/min) into the reaction zone held at a specified temperature. Ammonia was simultaneously introduced at a flow-rate of 100 cm^3/min through a separate tube into the reaction zone.

The products formed were TiN_x and NH_4Cl at 1000 °C and TiN_x, NH_4Cl, and a small amount of HCl at 1100 °C. The HCl formed at 1100 °C was considered to be formed by the reduction of $TiCl_4$, formed by the disproportionation of $TiCl_2$,[8,10] with hydrogen resulting from the thermal dissociation of ammonia. The results indicate that gaseous $TiCl_2$, formed by the reduction of gaseous $TiCl_4$ with hydrogen, reacts with ammonia to form TiN_x.

From these results, the reaction process of $TiCl_4$ with ammonia in the vapor phase can be represented as follows: The reaction of gaseous $TiCl_4$ with ammonia occurs first to form $TiCl_4 \cdot 5NH_3$. Above about 220 °C, the $TiCl_4 \cdot 5NH_3$ decomposes to TiClN. Above about 430 °C, the TiClN reacts with ammonia to form TiN_x. Above about 1100 °C, in addition to these reactions, the reaction of $TiCl_2$, formed by the reduction of $TiCl_4$ with hydrogen resulting from the thermal dissociation of ammonia, with ammonia occurs to form TiN_x.

Properties of the TiN_x Formed. The N/Ti atomic ratios of TiN_x formed at 700—1400 °C are shown in Table 3. Prior to this examination, the presence of residual NH_4Cl in the TiN_x, obtained after the removal of NH_4Cl at 400 °C in an argon stream, was checked by chemical analysis,[11] after the fusion of the TiN_x sample with sodium carbonate. From the results, the NH_4Cl content in the TiN_x was 6.9% for the TiN_x formed at 700 °C, 5.9% at 800 °C, 3.6% at 900 °C, 1.5% at



(a) 1200 °C (b) 1300 °C (c) 1400 °C

Fig. 2. Electoron micrographs of the $TiN_{x(x=1.10)}$ formd at various temperatures.

1000 °C, 1.0% at 1100 °C, 0.5% at 1200 °C, 0.2% at 1300 °C, and trace at 1400 °C. Further separation of the NH_4Cl at higher temperatures could not be carried out, by considering the thermal stability of the TiN_x formed, as described later. For the evaluation of the N/Ti atomic ratio of the TiN_x formed, the initial weight of the sample was corrected by subtracting the amount of NH_4Cl contained, because the NH_4Cl was vaporized during the oxidation.

Kato *et al.*[1] reported that the N/Ti atomic ratio of the TiN_x formed by a vapor-phase reaction of the $TiCl_4$–NH_3–H_2–N_2 system at 700—1500 °C was 1.1—1.4. Vorob'ev *et al.*[12] reported that the stoichiometric TiN was identified as a main component of the reaction products of gaseous $TiCl_4$ with ammonia at 800—1100 °C. But, the details of this study are not available.

It has been known that the TiN_x phase has a NaCl structure.[1,3] The lattice constant of TiN_x formed at each temperature is also shown in Table 3.

The TiN_x formed by the reaction of gaseous $TiCl_4$ with ammonia above 1000 °C were examined by electron microscopy. The typical micrographs of the TiN_x are shown in Fig. 2.

As seen from Fig. 2, the TiN_x formed at 1400 °C is uniform, ultrafine powders with the particle diameters of the order of 1/100 μm. The range of the particle sizes of the TiN_x formed at lower temperatures was found to be wide.

Finally, to obtain knowledge of the thermal stability of the TiN_x formed, the N/Ti atomic ratios of the samples obtained by heating $TiN_{1.21}$ at various temperatures in an argon atmosphere for 1 h were examined. The results are shown in Fig. 3. In addition, it was found that the residual NH_4Cl in the TiN_x was compeletely removed by the heating at 1100 °C.

The results indicated that when the TiN_x formed was heated in an argon atmosphere at temperatures higher than 500 °C, the N/Ti atomic ratio decreased and became close to that of the stoichiometric nitride; The value of x was 1.02 at the heating temperatures of 900—1100 °C.

The lattice constants of the TiN_x with various x values, obtained in this work, are shown in Fig. 4.

The N/Ti atomic ratio of TiN_x obtained after heating $TiN_{1.21}$ in an argon atmosphere at each temperature was found to be lower than that of the TiN_x formed by the vapor-phase reaction at the same temperature (Table 3). The facts are considered to be due to the presence of nitrogen during the reaction. This consideration was supported by the fact that no change in the N/Ti atomic ratio of the $TiN_{1.10}$ formed at 1000 °C by the vapor-phase reaction was observed after the heating at 1000 °C in an ammonia stream for 1 h.

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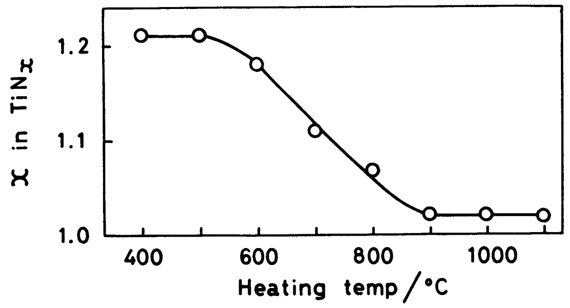

Fig. 3. N/Ti atomic ratios of TiN_x obtained after heating $TiN_{1.21}$ at various temperatures in an argon atmosphere.

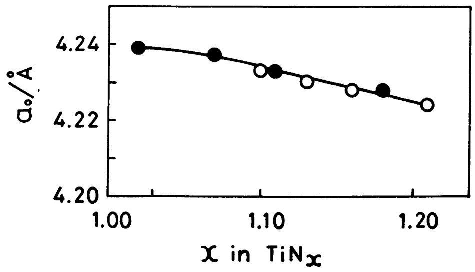

Fig. 4. Lattice constants of the TiN_x with various x values. ○: From TiN_x formed by the reaction of gaseous. $TiCl_4$ with ammonia, ●: from TiN_x obtained after the heating of $TiN_{1.21}$.

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