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

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The reaction products of gaseous VCl_4 with ammonia were $VCl_4 \cdot 4NH_3$ at 200 °C, $VCl_4 \cdot 4NH_3$, VN_x, and NH_4Cl at 250—550 °C, and VN_x and NH_4Cl at 600—1000 °C. At 1100 °C, small amounts of VCl_2 and HCl were formed in addition to VN_x and NH_4Cl. The N/V atomic ratio, x, of the VN_x formed was 1.20 at 600 °C, 1.15 at 700 °C, 1.14 at 800 °C, and 1.13 at 900 and 1000 °C. The lattice constants of the VN_x formed were shown. The reaction process of gaseous VCl_4 with ammonia can be represented as follows: The reaction of gaseous VCl_4 with ammonia first occurs to form $VCl_4 \cdot 4NH_3$. Above about 215 °C, the reaction of $VCl_4 \cdot 4NH_3$ with ammonia also occurs to form VN_x. At 1100 °C, in addition to these reactions, the reaction of gaseous VCl_4 with hydrogen formed by the thermal dissociation of ammonia occurs to form VCl_2. On heating the VN_x, formed by the vapor-phase reaction, at temperatures higher than 500 °C in an argon atmosphere, the value of x decreased with the increase in the heating temperature to 1.03 at 900—1000 °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, which are acquiring importance as new industrial materials. Concerning the formation of vanadium nitride powders by the vapor-phase reaction of vanadium tetrachloride (VCl_4) with ammonia, Hojo *et al.*[1] have studied the preparation of fine vanadium nitride powders by a vapor-phase reaction of the VCl_4–NH_3–H_2–N_2 system at 700—1200 °C with emphasis on the effects of reaction conditions on particle size and chemical composition. However, no information is at present available on the reaction process of VCl_4 with ammonia in the vapor phase.

In this paper, the reaction products of gaseous VCl_4 with ammonia at 200—1100 °C were examined in detail. In order to elucidate the reaction process of gaseous VCl_4 with ammonia, the behavior of $VCl_4 \cdot 4NH_3$, which was newly-found during the reaction process, on heating in an ammonia stream and the thermal dissociation of ammonia under the experimental conditions in this work were examined. The N/V atomic ratios, lattice constants, and thermal stability in an argon atmosphere of the vanadium nitrides formed at various temperatures were examined. The vanadium nitrides formed were also examined by electron microscopy.

Experimental

Materials. The VCl_4 used was prepared by the reaction of vanadium (V>99.8%, Atomergic Chemetals Corp., U.S.A.) with chlorine at 500 °C.[2] The chemical analysis gave V, 26.4; Cl, 73.5% (calcd for VCl_4:V, 26.43; Cl, 73.57%). The Ammonia was dried by passing it over sodium hydroxide granules.

Experimental Procedures. A transparent quartz reaction tube (1000 mm length) was used for examining the reaction products of gaseous VCl_4 with ammonia at various temperatures. Gaseous VCl_4 was formed by heating liquid VCl_4 (22 g) at 125 °C and 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 VCl_4 inlet tube consisted of two concentric tubes. Gaseous VCl_4 carried by argon was introduced through the inner tube and the outer tube was used for introducing argon (50 cm^3/min) as a sheath gas to prevent formation of vanadium 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 VCl_4 was 6.0 cm^3/min. A quartz 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 ammonium chloride (NH_4Cl) which deposited outside the reaction zone together with the vanadium nitride formed was separated by heating the mixture in an argon stream at 400 °C (the sublimation point of NH_4Cl: 339 °C)[3] for 10—15 h.

Analytical. The vanadium, chlorine and ammonia contents of the product formed were determined by chelatometric titration,[4] gravimetric method as AgCl, and the Kjeldahl method, respectively, after dissolving the sample in dilute nitric acid.

X-Ray analysis of the solid product was performed with an X-ray powder diffractometer equipped with a proportional counter 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 with atmospheric moisture during the irradiation. The lattice constant of the vanadium nitride was calculated based on the X-ray diffraction data obtained by using silicon powders as an internal standard under a scanning speed of 1/2—1/4°/min.

The sensitivity of the quartz helix used for thermogravimetry (TG) was approximately 72 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/V atomic ratio of the vanadium nitride formed was evaluated as follows: The sample vanadium nitride was oxidized to V_2O_5 by heating in an oxygen atmosphere up to 550 °C, using a Shimazu high-sensitive thermal balance Model TGA31. The amount of vanadium in the sample was calculated from the amount of V_2O_5 formed. The amount of nitrogen was determined as the difference between the amount of initial sample and that of the vanadium. The value of the N/V atomic ratio was evaluated with an accuracy within ± 0.01.

Throughout this work, the VCl_4 and the reaction products were handled in an argon atmosphere to prevent any contamination with atmospheric moisture.

Results and Discussion

Reaction Products of Gaseous Vanadium Tetrachloride with Ammonia. The products formed by heating gaseous VCl_4 in an ammonia stream at various temperatures were examined by X-ray analysis[5-7] and chemical analysis. Reaction temperatures above 200 °C were employed, because gaseous VCl_4 was generated at 125 °C. The results are shown in Table 1. Unreacted VCl_4 was not observed throughout the temperature range in this work. The products were obtained inside and outside the reaction zone below 550 °C. The portion of the product obtained outside the reaction zone increased with the increase in the reaction temperature and above 600 °C all the products were obtained outside the reaction zone.

The product formed at 200 °C showed a hitherto unknown X-ray diffraction pattern which was different from those of known vanadium compounds. The chemical analysis of the product gave V, 19.3; Cl, 54.5; NH_3, 26.2%. The ratio of V:Cl:NH_3 was calculated to be 1:4.06:4.06. This result was considered to indicate that the product formed at 200 °C had a composition of $VCl_4 \cdot 4NH_3$ (calcd for $VCl_4 \cdot 4NH_3$: V, 19.53; Cl, 54.36; NH_3, 26.11%). But the observed values for chlorine and ammonia were slightly higher than the calculated values. The evaporation of VCl_4 on heating liquid VCl_4 is accompanied by the decomposition of liquid VCl_4, $VCl_4(l) \rightarrow VCl_3(s) + 1/2Cl_2(g)$.[8] The resulting chlorine was considered to react with ammonia to form NH_4Cl. Accordingly, the amount of chlorine formed by heating liquid VCl_4 at 125 °C for 2 h was examined. The result showed that 0.07 g of chlorine was formed during the heating. From this result, the product formed at 200 °C was considered to be $VCl_4 \cdot 4NH_3$ containing a small amount of NH_4Cl. The chemical analysis of the sample obtained after the removal of the NH_4Cl from the product at 190 °C in an ammonia atmosphere gave V, 19.5; Cl, 54.3; NH_3, 26.0%. From the results, the product formed at 200 °C was confirmed to have the composition of $VCl_4 \cdot 4NH_3$.

The products formed at 250 and 300 °C were identified by X-ray analysis as a mixture of $VCl_4 \cdot 4NH_3$ and a small amount of NH_4Cl. However, it was found that when the products were treated with 1 M hydrochloric acid, $VCl_4 \cdot 4NH_3$ and NH_4Cl were dissolved leaving a small residue of black powder which was identified as vanadium nitride (VN_x) by X-ray and chemical analyses. These results indicated that a small amount of VN_x was formed in addition to $VCl_4 \cdot 4NH_3$ and NH_4Cl at 250 and 300 °C. The products formed at 500 and 550 °C were identified as a mixture of VN_x and NH_4Cl by X-ray analysis. But, the formation of a small amount of $VCl_4 \cdot 4NH_3$ in addition to these products was found by chemical analysis. Contrary to the experimental results obtained for the reaction products at temperatures below 1000 °C, a small amount of VCl_2 was formed in addition to VN_x and NH_4Cl at 1100 °C. It was also found that hydrogen chloride (HCl) was formed.

Table 1. Reaction products of gaseous VCl_4 with ammonia at various temperatures

Temp/°C	Products
200	$VCl_4 \cdot 4NH_3$
250	$VCl_4 \cdot 4NH_3 \gg VN_x$; NH_4Cl
300	$VCl_4 \cdot 4NH_3 \gg VN_x$; NH_4Cl
350	$VCl_4 \cdot 4NH_3 > VN_x$; NH_4Cl
400	$VCl_4 \cdot 4NH_3 > VN_x$; NH_4Cl
450	$VN_x > VCl_4 \cdot 4NH_3$; NH_4Cl
500	$VN_x \gg VCl_4 \cdot 4NH_3$; NH_4Cl
550	$VN_x \gg VCl_4 \cdot 4NH_3$; NH_4Cl
600—1000	VN_x; NH_4Cl
1100	$VN_x > VCl_2$; NH_4Cl, HCl

Reaction Process of Gaseous Vanadium Tetrachloride with Ammonia. To elucidate the reaction process of gaseous VCl_4 with ammonia, the behavior of $VCl_4 \cdot 4NH_3$, formed during the reaction process, on heating in an ammonia stream and the thermal dissociation of ammonia[9] under the experimental conditions in this work were examined.

Behavior of $VCl_4 \cdot 4NH_3$ on Heating in an Ammonia Stream: TG of $VCl_4 \cdot 4NH_3$ (0.2 g) in an ammonia stream (50 cm^3/min) was carried out. When ammonia was introduced at room temperature, the sample gained weight gradually and reached a constant value after 6 h, showing about 10% increase in weight. After the weight increase, the sample gave the same X-ray diffraction pattern with the initial sample. When the heating of the sample was started, the sample lost weight gradually and reached the initial weight at 190 °C. The TG curve of $VCl_4 \cdot 4NH_3$ in an ammonia stream above 200 °C is shown in Fig. 1.

$VCl_4 \cdot 4NH_3$ lost weight above 215 °C. The weight loss was accompanied by the vaporization of NH_4Cl and a small amount of $VCl_4 \cdot 4NH_3$. The sample after heating up to 450 °C was found to be VN_x by X-ray analysis.

In order to obtain more detailed information on the behavior of $VCl_4 \cdot 4NH_3$ on heating in an ammonia stream, $VCl_4 \cdot 4NH_3$ (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

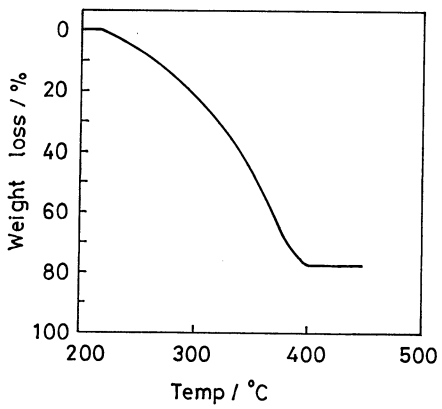


Fig. 1. TG curve of $VCl_4 \cdot 4NH_3$ in an ammonia stream.

Table 2. Experimental results for $VCl_4 \cdot 4NH_3$ on heating in an ammonia stream

Heating temp/°C	Products		Unreacted $VCl_4 \cdot 4NH_3$/%
	In the boat	Outside the boat	
250	$VN_x(<1)$	$VCl_4 \cdot 4NH_3(1)$, NH_4Cl	98
300	$VN_x(7)$	$VCl_4 \cdot 4NH_3(7)$, NH_4Cl	86
350	$VN_x(86)$	$VCl_4 \cdot 4NH_3(10)$, $VN_x(<1)$, NH_4Cl	3
400	$VN_x(92)$	$VCl_4 \cdot 4NH_3(5)$, $VN_x(2)$, NH_4Cl	<1
450	$VN_x(95)$	$VCl_4 \cdot 4NH_3(3)$, $VN_x(2)$, NH_4Cl	—

Note: the value in parentheses is mole percentage of $VCl_4 \cdot 4NH_3$ converted to the product.

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 inside and outside the boat were examined by X-ray and chemical analyses. The results are shown in Table 2.

The results showed that $VCl_4 \cdot 4NH_3$ reacted with ammonia to form VN_x above about 215 °C and a part of the $VCl_4 \cdot 4NH_3$ vaporized. The formation of a small amount of VN_x outside the boat was considered to indicate that the reaction of gaseous $VCl_4 \cdot 4NH_3$ with ammonia also occurred above about 350 °C.

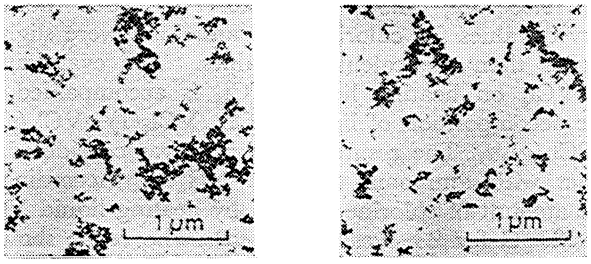
Thermal Dissociation of Ammonia: Ammonia alone was introduced at a flow-rate of 100 cm³/min into the reaction zone held at a specified temperature and the total volume of nitrogen and hydrogen, formed by the dissociation of ammonia, was measured. From the results, the percentage of the dissociated ammonia was found to be <1% at 800 °C, 1% at 900 °C, 2% at 1000 °C, and 6% at 1100 °C.

Based on the experimental results mentioned above, the reaction process of gaseous VCl_4 with ammonia was discussed. As shown in Table 1, $VCl_4 \cdot 4NH_3$ alone was formed at 200 °C. This fact indicates that the reaction of gaseous VCl_4 with ammonia first occurs to form $VCl_4 \cdot 4NH_3$. The VN_x formed by the vapor-phase reaction above 250 °C (Table 1) are considered to be due to the reaction of $VCl_4 \cdot 4NH_3$ with ammonia, because the $VCl_4 \cdot 4NH_3$ reacts with ammonia above about 215 °C to form VN_x. The formation of VCl_2 at 1100 °C (Table 1) is considered to be due to the reaction of gaseous VCl_4 with hydrogen[2] formed by the thermal dissociation of ammonia.

Properties of the Vanadium Nitride Formed. The N/V atomic ratios of VN_x formed by the vapor-phase reaction at 600—1000 °C are shown in Table 3. Prior to this examination, the VN_x obtained after the removal of by-product NH_4Cl at 400 °C in an argon stream was dissolved in dilute nitric acid and the presence of residual NH_4Cl was checked by chemical analysis.[10] From the results, the VN_x formed at 1000 °C was found to contain no residual NH_4Cl. The VN_x formed at 600—900 °C was found to contain a small amount of residual NH_4Cl; The NH_4Cl content was 0.3% for the VN_x formed at 900 °C, 2.4% at 800 °C, 2.6% at 700 °C, and 3.6% at 600 °C. But, further separation of the NH_4Cl was not possible as the N/V atomic ratio of VN_x decreased on heating

Table 3. N/V atomic ratio and lattice constant of the VN_x formed by the reaction of gaseous VCl_4 with ammonia

Formation temp/°C	x in VN_x	a_0/Å
600	1.20	Not determined
700	1.15	4.115
800	1.14	4.126
900	1.13	4.133
1000	1.13	4.133



(a) 900 °C (b) 1000 °C

Fig. 2. Electron micrographs of $VN_{x(x=1.13)}$ formed at 900 and 1000 °C.

at temperatures higher than 500 °C in an argon atmosphere, as described later. So, for the evaluation of the N/V atomic ratios of the VN_x formed below 900 °C, 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.

It has been known that VN_x phase has a NaCl structure.[7] The lattice constant of VN_x formed at each temperature is also shown in Table 3. As X-ray diffraction lines of the $VN_{1.20}$ formed at 600 °C were relatively weak and diffuse, the exact value of the lattice constant was not calculated.

The VN_x formed by the vapor-phase reaction at 600—1000 °C was examined by electron microscopy. The typical micrographs of the VN_x are shown in Fig. 2. The VN_x formed is relatively uniform, ultrafine powders with particle diameters of the order of 1/100 μm.

Finally, to obtain knowledge of the thermal stability of the VN_x formed by the vapor-phase reaction, the N/V atomic ratio of the sample obtained by heating $VN_{1.20}$ formed at 600 °C, which had the largest N/V atomic ratio in the VN_x formed in this work, at various temperatures in an argon atmosphere was examined. The results are shown in Fig. 3. In addition,

it was found that the residual NH_4Cl in the VN_x was completely removed by the heating above 900 °C.

The results indicated that when the VN_x formed by the vapor-phase reaction was heated in an argon atmosphere at temperatures higher than 500 °C, the N/V atomic ratio decreased and became close to that of the stoichiometric nitride; The value of x was 1.03 at the heating temperatures of 900 and 1000 °C. Hojo *et al.*[1] reported that when the VN_x with $x>1$ was heated *in vacuo* up to 1150 °C, the x value reduced to 1.02.

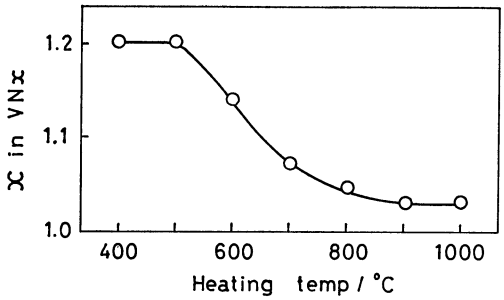


Fig. 3. N/V atomic ratio of VN_x obtained after heating $VN_{1.20}$ at various temperatures in an argon atmosphere for 1 h.

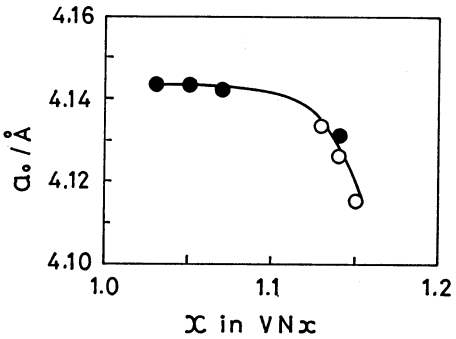


Fig. 4. Lattice constants (a_0) of VN_x with various x values.
●: From VN_x obtained after the heating of $VN_{1.20}$,
○: from VN_x formed by the reaction of gaseous VCl_4 with ammonia (Table 3).

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

The N/V atomic ratio of VN_x obtained after heating $VN_{1.20}$ in an argon atmosphere at each temperature was found to be lower than that of the VN_x formed by the vapor-phase reaction at the same temperature (Table 3). The difference in the N/V atomic ratio became larger with the increase in the temperature. These facts are considered to be due to the presence of nitrogen during the reaction, because the dissociation pressure of ammonia is relatively high even at low temperatures and markedly increases with the increase in the temperature.[9] This consideration was supported by the fact that no change in the N/V atomic ratio of the $VN_{1.13}$ formed at 1000 °C by the vapor-phase reaction was observed after heating at 1000 °C in an ammonia stream for 1 h.

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