Gas-phase synthesis of AlN powders from AlCl$_3$–NH$_3$–N$_2$

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Aluminium nitride powders were synthesized by the gas-phase reaction of AlCl$_3$–NH$_3$–N$_2$ system. The yield of AlN powders from AlCl$_3$ and their crystallinity increased as the reaction temperature and the mole ratio of NH$_3$/AlCl$_3$ were increased. AlN powders were also formed outside the reactor and their crystallinity was amorphous. The yield of AlN powders was as high as 80% when the reactor temperature was 1000 °C and the mole ratio of NH$_3$/AlCl$_3$ was 8. Most of the HCl by-product was recovered as NH$_4$Cl outside the reactor. Powder characteristics, such as shape, size distribution and crystallinity, were also studied.

1. Introduction

Aluminium nitride ceramic is considered to be a promising material for electronic packaging because it has many desirable properties, such as high thermal conductivity, high electrical resistivity and a low thermal expansion coefficient [1]. In addition, its mechanical strength and thermal shock resistance are higher than that of alumina ceramics. For ceramic materials, it is important to develop an economically viable powder-manufacturing process which can produce powders with high purity and sinterability.

Aluminium nitride powders have been synthesized through carbothermal reduction of alumina [2, 3], direct nitridation of aluminium [4] and gas-phase synthesis from the reaction of aluminium chloride [5, 6] or other organometallic precursors with ammonia [7]. High-temperature plasmas were also used to make AlN powders [8]. To date, commercial AlN powders have been produced through a carbothermal reduction process and direct nitridation of aluminium [1].

Gas-phase synthesis of ceramics is advantageous to produce high-purity fine powders with uniform particle size, because powders are formed from homogeneous nucleation and it is relatively easy to control the nucleation process. Gas-phase reaction is fast compared to solid–solid reactions in the carbothermal reduction process and potentially high throughput can be achieved through continuous operation.

On the other hand, it is relatively difficult to recover fine powders from the gas stream and the powder handling in the system also imposes a formidable problem. It is also not easy to obtain a high yield of the product intrinsically from the thermodynamic equilibrium limitations or the reactor design problem associated with chemical reaction kinetics. It is also important to suppress the formation of by-products as low as possible or to find out how to handle them if unavoidable.

In this work, AlN powders were synthesized through the vapour-phase reaction of AlCl$_3$ and NH$_3$. Important operating variables which affect the yield of AlN powders from AlCl$_3$ were identified and the characteristics of AlN powders were evaluated.

2. Experimental procedure

Fig. 1 shows the experimental setting used in this experiment.

As an aluminium source, aluminium chloride of 98% purity was used. Aluminium chloride has a sublimation temperature of 177.8 °C. It was packed in a glass tube and heated at 180 °C in an oil bath. Nitrogen gas was flowed through the packed column to remove moisture and oxygen and passed through the AlCl$_3$ sublimation bed. Aluminium chloride vapour was mixed with nitrogen of 99.99% purity in the sublimation bed and introduced at the centre of the furnace.

From the sublimation bed to the reactor, a heating tape was used to prevent the condensation of AlCl$_3$. The electric furnace was 85 cm long and had a uniform heating zone of about 60 cm in the middle. Ammonia of 99.999% purity was measured with a mass-flow controller and introduced at the forefront of the uniform heating zone. The reactor was made of a 92 cm quartz tube with 3.5 cm inside diameter and was heated inside the electric furnace. At the outlet of the reactor, a 500 ml round flask was connected to recover the powders coming out of the reactor and to damp out any pressure variations inside the reactor. To facilitate the recovery of the powders and prevent cracking of the reactor, a quartz boat 40 cm long, was placed in the bottom of the reactor. The exhaust gas leaving the flask was passed through a water column and vented outside. The operating conditions are summarized in Table I
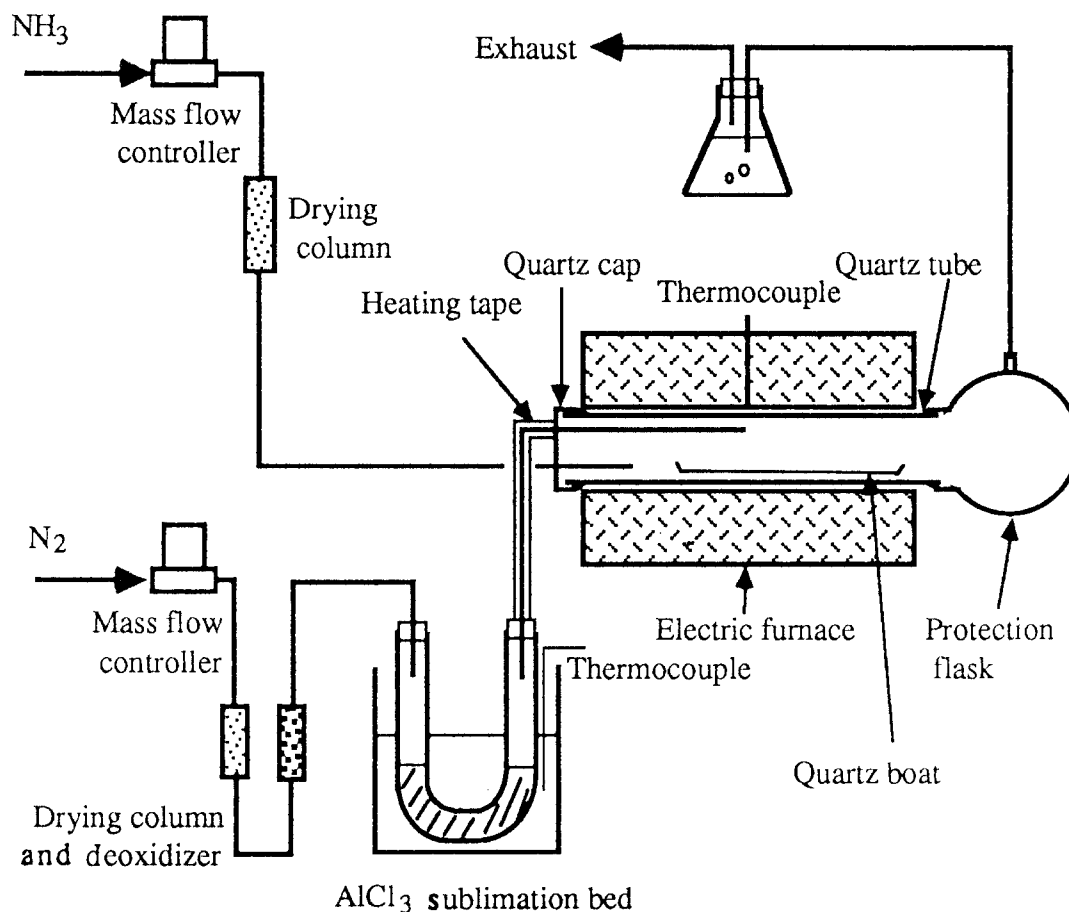
Figure 1 Experimental apparatus used for the synthesis of AlN powders.

TABLE I Experimental conditions

Reaction temperature	700–1000 °C
Flow rate of N_2	150 cm^3 min^{-1}
Flow rate of NH_3	55–370 cm^3 min^{-1}
Input amount of $AlCl_3$	0.22 g min^{-1}

The flow rate of ammonia corresponds to a mole ratio of NH_3 and $AlCl_3$ from 1.5–10. For each run, the experiment was carried out for about 1 h. After each run, the amount of product recovered inside the reactor and inside the flask was measured and the chemical composition of the powders was analysed. The production rate was 0.15–5.5 g h^{-1} AlN powders depending on the operating conditions. Powder characteristics, such as crystallinity, shape and size distribution, were also measured.

3. Results and discussion
3.1. Yield
One of the most important goals in the development of the chemical synthesis process is to obtain a maximum yield of the product. In this experiment, most of the product was recovered inside the reactor and from the flask connected to the outlet of the reactor. Powders recovered inside the reactor were from the homogeneous nucleation at a given reactor temperature. Powders recovered from the flask were probably a mixture of those powders carried out of the reactor and those products formed at low temperatures inside

the flask from the reactant gases coming out of the reactor.

Fig. 2 shows the equilibrium constant of the reactions considered to be important in the $AlCl_3$–NH_3–N_2 system as a function of the reaction temperature.
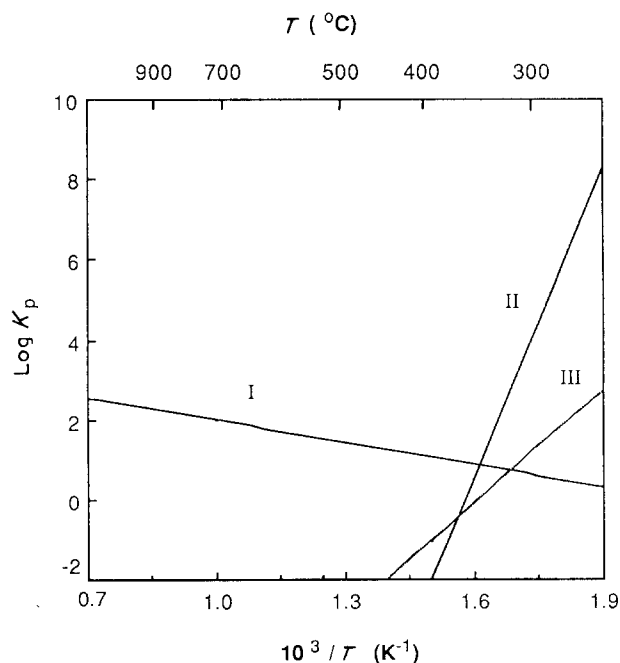

Figure 2 Thermodynamic equilibrium constant versus temperature. I, $AlCl_3(g) + NH_3(g) = AlN(s) + 3HCl(g)$; II, $AlCl_3(g) + 4NH_3(g) = AlN(s) + 3NH_4Cl(s)$; III, $NH_3(g) + HCl(g) = NH_4Cl(s)$.

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It is generally known that the equilibrium constant should be large, preferably larger than 2, to have powders formed from homogeneous nucleation [6]. From this criterion, we know that AlN powders can possibly be formed from the following reaction

$$AlCl_3(g) + NH_3(g) = AlN(s) + 3HCl(g) \tag{1}$$
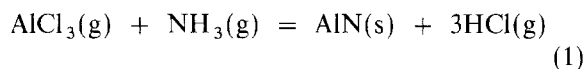
above about 700 °C. AlN can also be formed at low temperatures around 350 °C via the following reaction

$$AlCl_3(g) + 4NH_3(g) = AlN(s) + 3NH_4Cl(s) \tag{2}$$
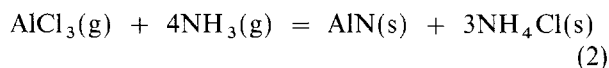
with the formation of a by-product, ammonium chloride. Ammonium chloride can also be formed below about 250 °C via the reaction

$$NH_3(g) + HCl(g) = NH_4Cl(s) \tag{3}$$
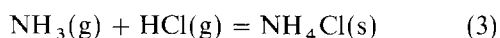
This suggests that only AlN and HCl can be formed inside the reactor if the reaction temperature is high enough to suppress Reactions 2 and 3. At the same time, AlN and NH_4Cl can also be formed out of the reactor through Reactions 2 and 3 from unreacted $AlCl_3$, NH_3 and HCl. This is when the temperature inside the flask is low enough. Of course, these thermodynamic data give us only the necessary conditions for the reaction to proceed, and this can only be achieved when the reaction rate is fast enough or the residence time of the reactant gases is long enough to reach a thermodynamic equilibrium.

Nickel et al. [9] calculated the maximum possible yield of AlN from a thermodynamic analysis of the Al–H–Cl–N system, which is shown in Fig. 3. This calculation was done with the mole ratio of $NH_3/AlCl_3$ fixed at 1.5. They showed that the yield was low because ammonia decomposes into hydrogen and nitrogen according to

$$2NH_3 = N_2 + 3H_2 \tag{4}$$
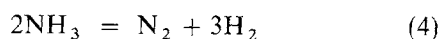
at temperatures above 130 °C. Nitrogen is not as reactive as ammonia and does not react readily with aluminium chloride. They also showed that almost complete conversion of $AlCl_3$ was possible by suppressing the dissociation of ammonia. This was possible by introducing ammonia and aluminium chloride at the same position and keeping the temperature of that position at 400 °C to form $AlCl_3 \cdot x\,NH_3$ $(x = 1\text{–}6)$ adducts. These adduct compounds decompose at temperatures above 700 °C to form AlN and HCl. One of the problems of this approach is that a large fraction of AlN formed from this adduct is in the form of a coating inside the quartz wall [9]. The powders formed through this adduct were amorphous. These thermodynamic calculations give a good guide to how to design a reaction system and how to operate a synthesis process.

In this experiment, aluminium chloride was introduced at the centre of the reactor and ammonia was introduced at the low-temperature region near the inlet, as reported by Kimura et al. [6].

Fig. 4 shows the yield of AlN as a function of the reactor temperature for mole ratios of ammonia to aluminium chloride of 1.5 and 6, in the inlet reactant gases. The yield was calculated from the number of moles of AlN recovered in the form of powder inside the reactor or the flask, divided by the number of moles of $AlCl_3$ introduced. The total yield is the summation of both. When the mole ratio was 1.5, the yield was very low, i.e., less than 20% for all the reaction temperatures between 700 and 1000 °C. This is probably due to the fact that ammonia is dissociated into H_2 and N_2 and not enough active nitrogen
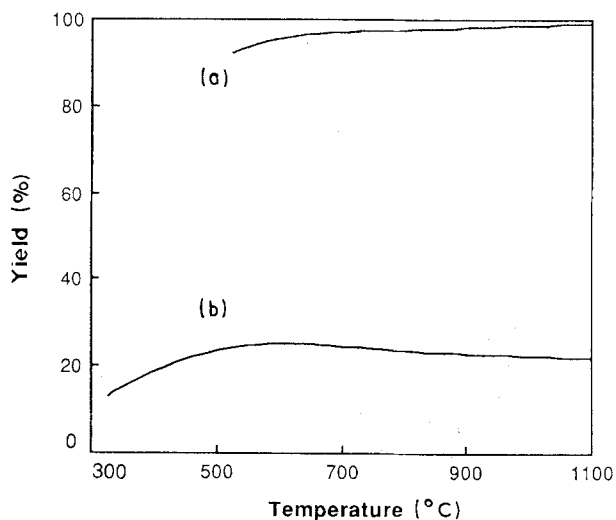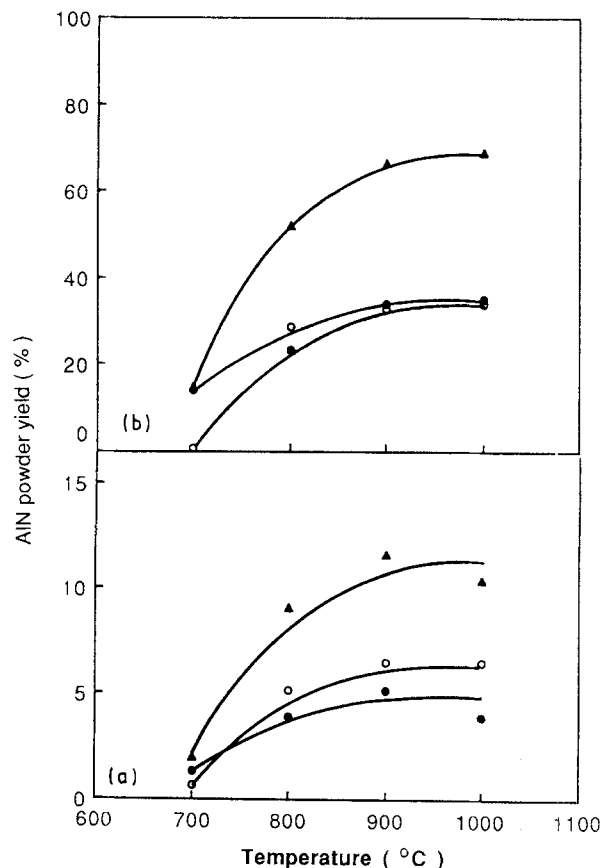

Figure 3 Maximum possible yield of AlN from thermodynamic calculations plotted against temperature at $NH_3/AlCl_3$ mole ratio of 1.5 [9], (a) without and (b) with dissociation of ammonia.

Figure 4 Experimental yield of AlN powders from $AlCl_3$ versus reactor temperature at $NH_3/AlCl_3$ mole ratio (R) of 1.5 and 6: (○) recovered in the reactor, (●) recovered in the flask, (▲) total.
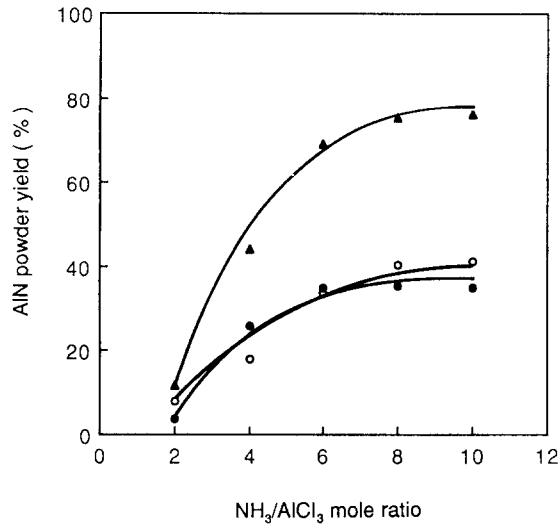
Figure 5 Experimental yield of AlN powders from $AlCl_3$ versus $NH_3/AlCl_3$ mole ratio at a reactor temperature of 1000 °C: (○) recovered in the reactor, (●) recovered in the flask, (▲) total.

source is available. In fact, the thermodynamic calculations reported by Nickel *et al.* [9] shown in Fig. 3 predicted that maximum yield cannot be higher than 20% in this case. At 700 °C, the yield was extremely low presumably because the reaction rate was very slow.

When the mole ratio of NH_3 to $AlCl_3$ was 6, the yield became much higher than when it was 1.5. The yield increased as the reaction temperature increased. When the mole ratio was 6, it seemed that there was enough ammonia to participate in the formation of
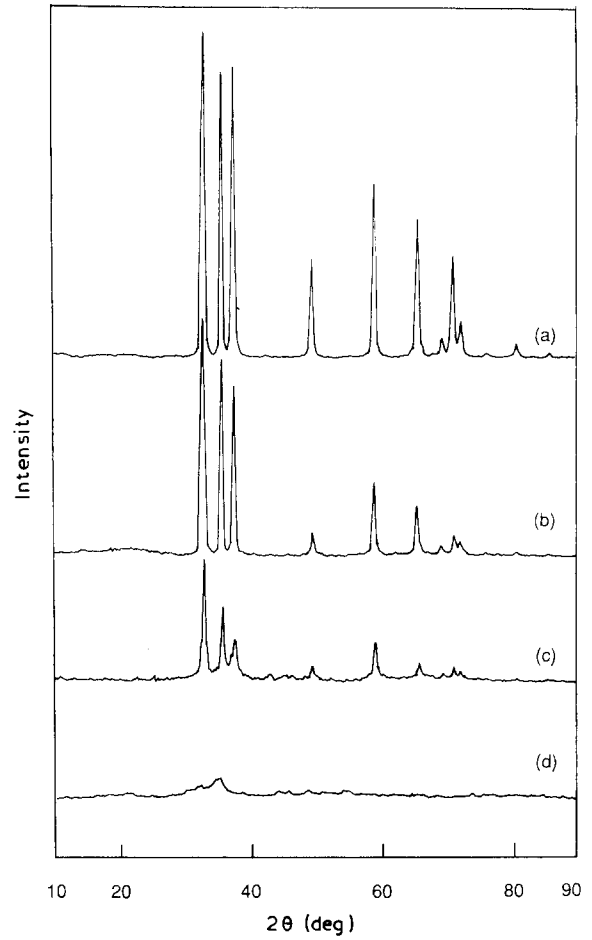

Figure 6 X-ray diffraction pattern of powders recovered in the reactor at a reactor temperature of (a) 1000, (b) 900, (c) 800 °C, and (d) heat-treated powders recovered from the flask.
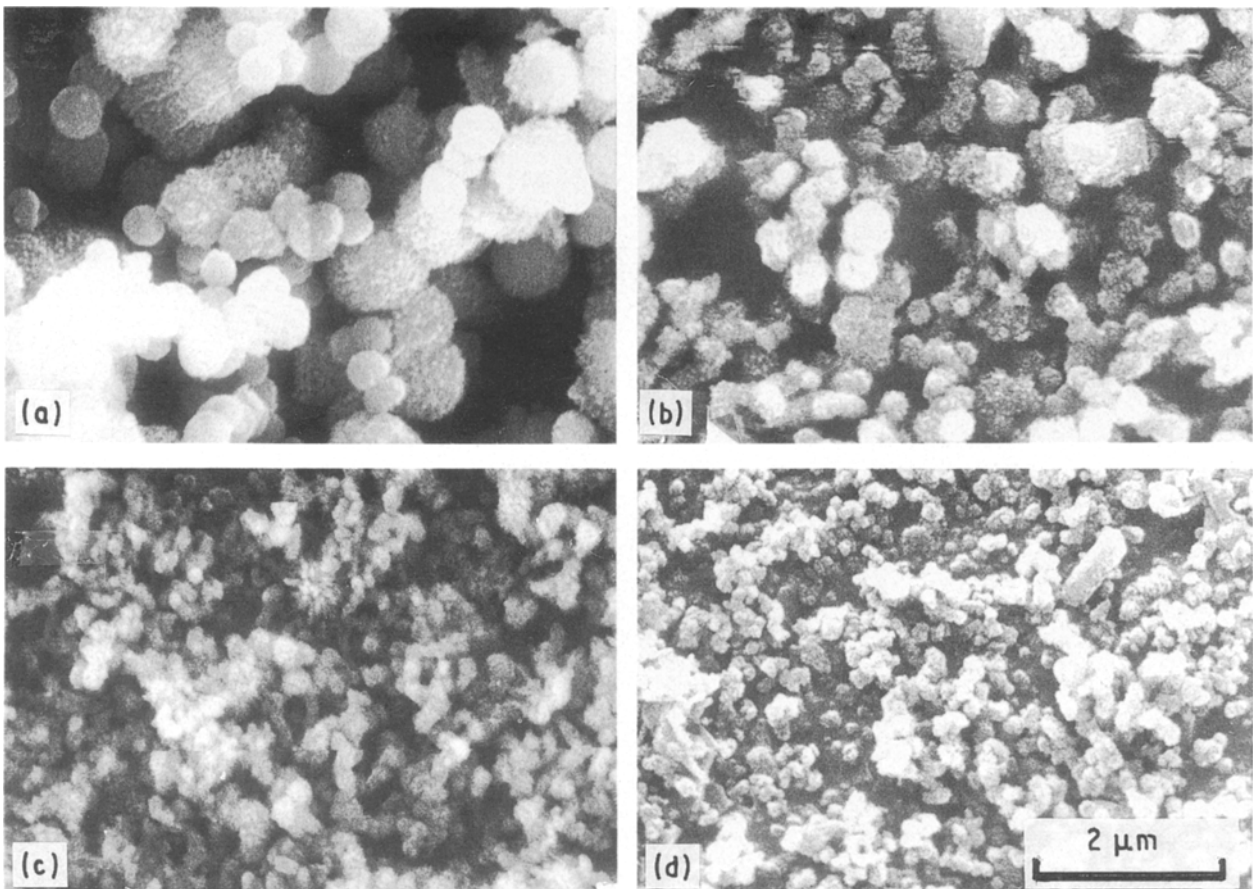

Figure 7 Scanning electron micrographs of powders synthesized at a reactor temperature of (a) 700, (b) 800, (c) 900 and (d) 1000 °C.

AlN even though the dissociation reaction of ammonia took place. As the temperature went up, the nucleation rate of AlN in the gas phase became higher, so that the system approached equilibrium more closely. The yield can approach 70% when the mole ratio is 6 and the reactor temperature is 1000 °C. This is lower than the theoretical maximum shown in Fig. 3 when there is no dissociation of ammonia. Maybe the reaction rate or the residence time of the reactant gases is not high enough to reach thermodynamic equilibrium, or the amount of ammonia available to participate in the reaction is not high enough, because of the dissociation, even though the mole ratio of $NH_3/AlCl_3$ is 6. The real conversion of $AlCl_3$ could be higher because some of the AlN is deposited as a film on the reactor wall and on the boat. It is almost impossible to recover all the powders formed without any loss. When the reaction temperature was 1000 °C, the amount of $AlCl_3$ captured in the water trap was negligible.

When the mole ratio was 6 and the reactor temperature was 700 °C, most of the AlN powders were recovered from the flask, i.e., at this reactor temperature, homogeneous nucleation of AlN through Reaction 1 inside the reactor was not appreciable. On the other hand, AlN could be formed through Reaction 2 in the flask where the temperature is much lower than inside the reactor. This is exactly what the thermodynamic calculations shown in Fig. 2 predict. At low temperatures, AlN can be formed through Reaction 2 because the equilibrium constant of this reaction is much bigger than Reaction 1. At temperatures higher than 700 °C, the amounts of AlN powders formed inside the reactor and the flask are about the same. This means that some part of the reactant gases formed AlN inside the reactor through Reaction 1 and also an appreciable amount of unreacted gases leaving the reactor formed AlN at the low temperatures through Reaction 2 in the flask. If we increase the length of the reactor, the portion of AlN powders formed inside the reactor could be higher.

The characteristics of the powders recovered from inside the reactor and from the flask will be discussed in the next section.

Fig. 5 shows the yield of AlN powders as a function of the mole ratio of ammonia and aluminium chloride at the reactor temperature of 1000 °C. As the mole ratio increases, the yield of AlN goes up and becomes almost constant above 8. At this point, the yield can reach as high as 80%. When the mole ratio is higher than 6, the amount of AlN formed inside the reactor becomes larger than the amount formed in the flask. That means as we increase the amount of ammonia, more $AlCl_3$ can be converted into AlN inside the reactor.

Most of the ammonium chloride formed was recovered from the flask and more than 80% of the HCl formed was captured through the reaction with ammonia. This suggests that most of the HCl formed as a by-product can be recovered in a solid form through the reaction with ammonia. The recycling of ammonium chloride may be required in the development of this process.

3.2 Powder characteristics

The crystallinity of AlN powders have already been discussed by Kimura et al. [6] and it was shown that the crystallinity increased with increasing reactor temperature. In this experiment, XRD analysis of powders recovered inside the reactor showed exactly the same trend as shown in Fig. 6.

Those powders synthesized at high reactor temperatures around 1000 °C contain a negligible amount of NH_4Cl and unreacted $AlCl_3$. Those AlN powders formed through Reaction 2 at low temperatures and recovered from the flask showed little crystallinity as shown in Fig. 6d. These powders recovered from the
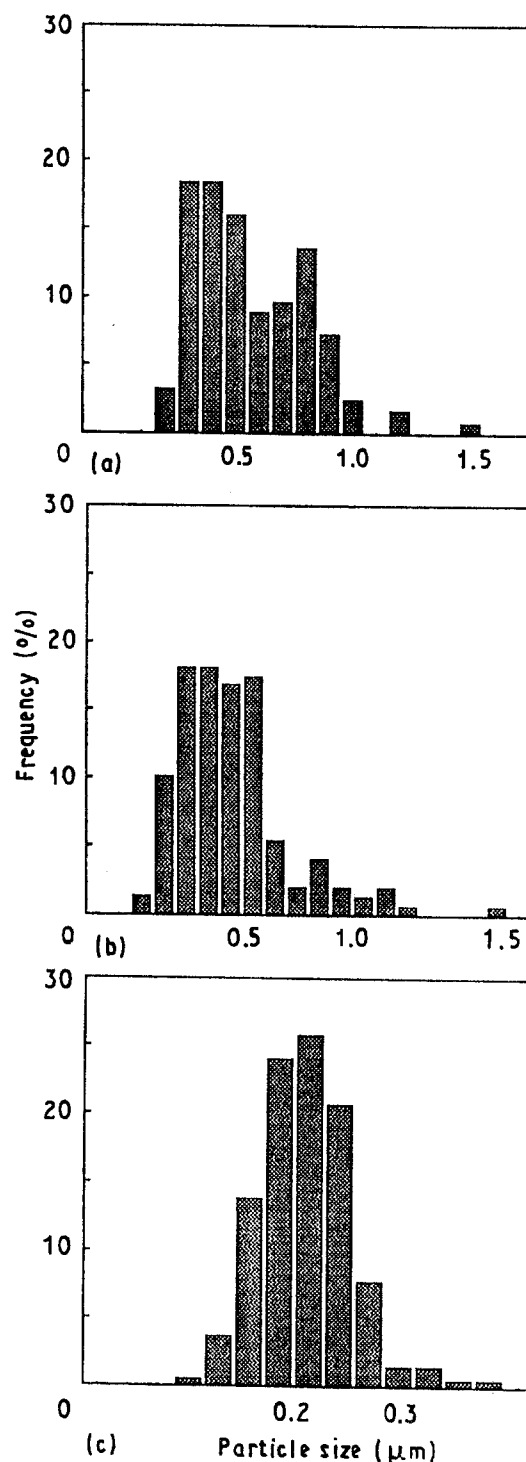

Figure 8 Particle-size distribution diagram of AlN powders synthesized and recovered in the reactor at reactor temperature of (a) 800, (b) 900 and (c) 1000 °C.

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flask were mixtures of AlN, NH_4Cl and unreacted $AlCl_3$. These were treated for 4 h at 600 °C in a nitrogen atmosphere to drive out NH_4Cl and unreacted $AlCl_3$.

Scanning electron micrographs of those powders synthesized at various reaction temperatures and recovered inside the reactor are shown in Fig. 7. As the reactor temperature rose, the size of the powders decreased. Image analysis results for the particle size distribution are shown in Fig. 8. In our reactor, the temperature profile in the uniform temperature zone was almost flat and we could not find any differences in the powder characteristics depending on the location inside the reactor where the powders were recovered.

Fig. 9 shows the transmission electron micrographs of powders synthesized at 900 °C. Three different types of powder were observed as shown in the figure. Bar-like powders (× 50 000) shown in Fig. 9c were crystalline, as shown in the selective-area diffraction pattern of Fig. 9f. Those powders, with radially grown small columns shown in Fig. 9b, had a selected-area diffraction pattern as shown in Fig. 9e. These small columnar crystals may have a high crystallinity as the bar-like powders in Fig. 9c, but dots are formed in a ring pattern as shown in Fig. 9e perhaps because they are small. Round particles are shown in Fig. 9a and their crystallinity is less than the columnar structure. The amounts of the bar-like powders were extremely small and most of the powders were either round or had a
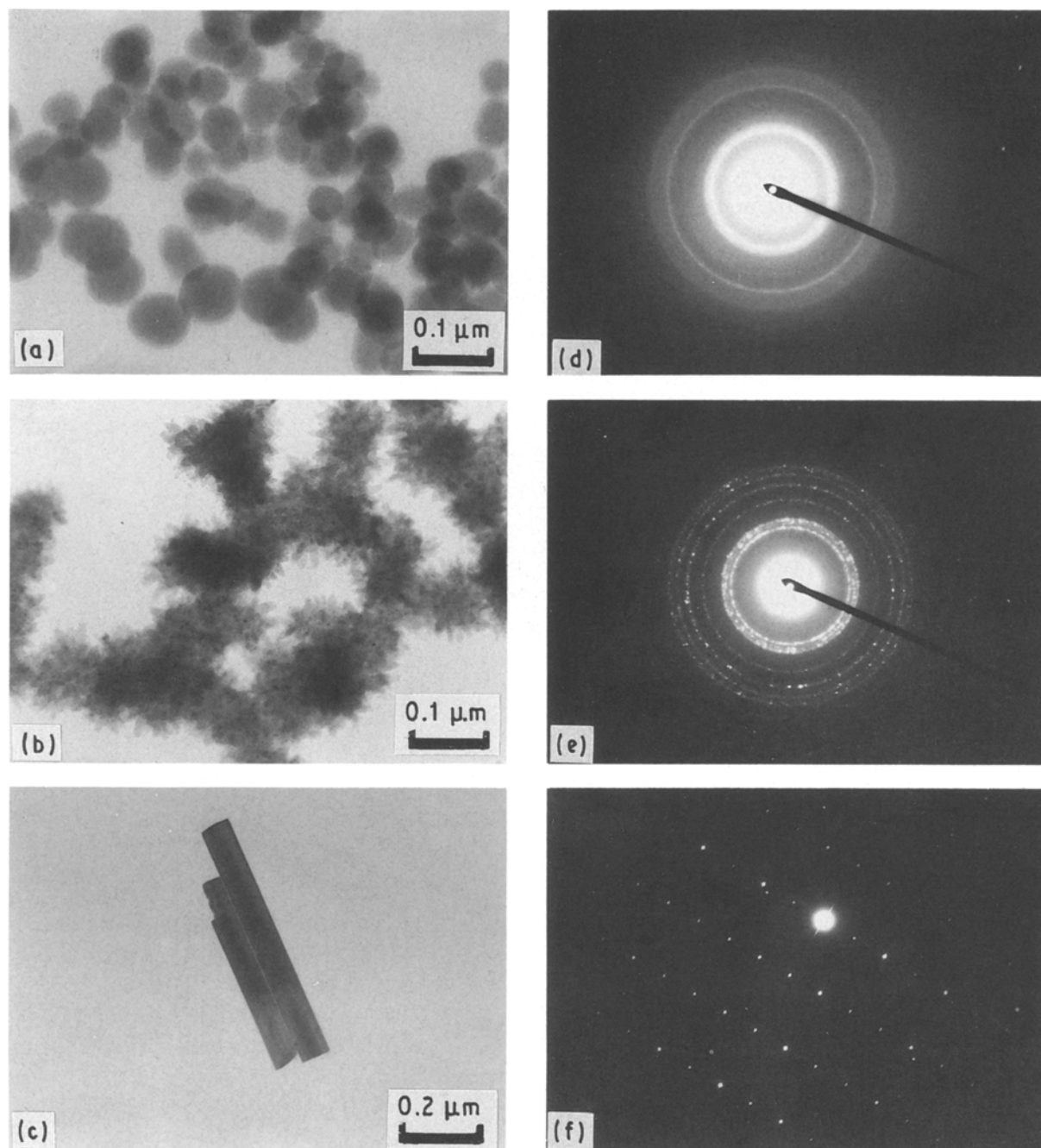

Figure 9 (a–f) Transmission electron micrographs of AlN powders of various shapes synthesized in the reactor at 900 °C. (d–f) selected-area diffraction patterns of (a–c) respectively.
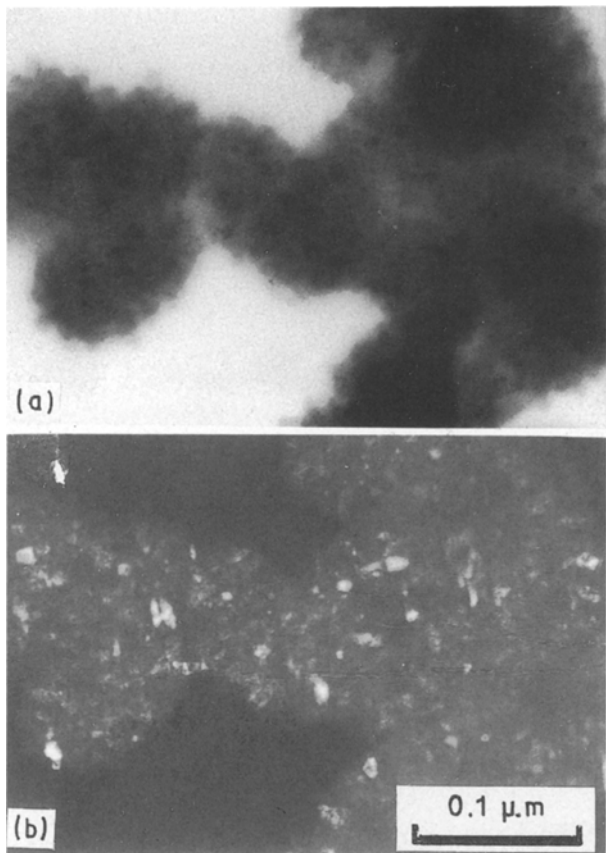
Figure 10 Transmission electron micrographs of powders with columnar structure on the surface: (a) bright-field image, and (b) dark-field image.

Figure 11 FT–IR spectra of powders recovered in the reactor at a reaction temperature of (a) 800, (b) 900 and (c) 1000 °C, (d) as-recovered powder from the flask (reactor temperature 900 °C, $NH_3/AlCl_3$ mole ratio = 4), (e) heat-treated powders of (d).

columnar structure on the surface. In fact, the powders with columnar structure on the surface were most abundant.

Fig. 10 shows a bright and dark image of powders with columnar structure (× 200 000) on the surface. It seems that many small crystallites in a columnar structure were embedded in a relatively large particle. Fig. 11 shows the Fourier transform-infrared spectrum of the powders recovered inside the reactor at reactor temperatures of 800, 900 and 1000 °C, respectively. Fig. 11d is the spectrum of as-recovered powders from the flask when the reactor temperature was 900 °C and the mole ratio of NH_3 and $AlCl_3$ was 4. As-recovered powders showed N–H and Al–Cl bonds because NH_4Cl and unreacted $AlCl_3$ were also deposited. Fig. 11e is the spectrum when these powders were heat treated at 600°C for 4 h in a nitrogen atmosphere.

The O–H peak around 3400 cm^{-1} may be due to the fact that $Al(OH)_3$ was formed at the powder surface from the reaction between AlN and adsorbed moisture. AlN bonds were observed at around 700 cm^{-1}. Surface reactivity could be higher for those powders synthesized at high temperatures because their size is smaller with larger surface area. However, the FT–IR spectrum shows that those powders synthesized at low temperatures are more hygroscopic. This is quite evident with those powders recovered from the flask, as shown in Fig. 11e. This tendency
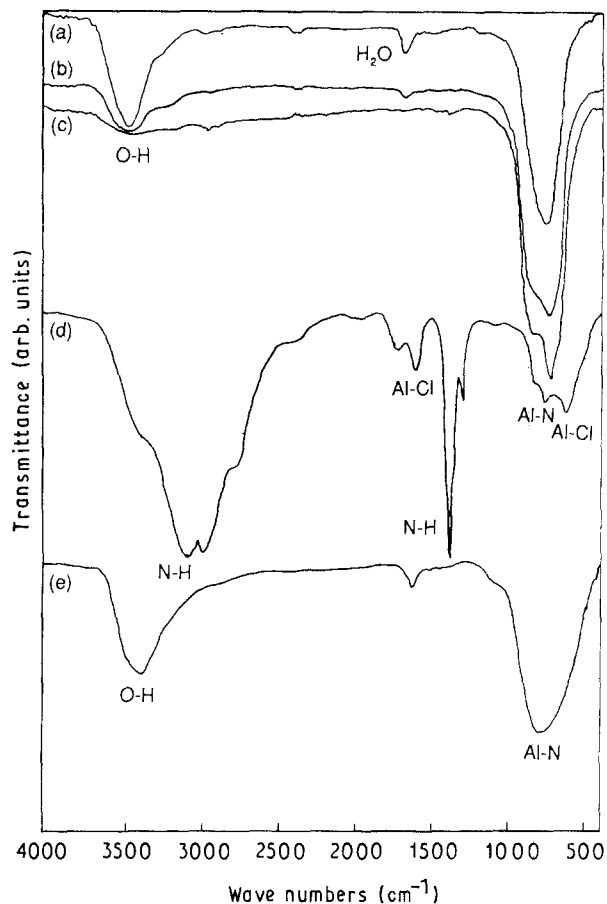
may be related to the crystallinity of the powders. Powders with low crystallinity may have stronger tendency to absorb moisture.

As the reactor temperature goes up, the Al–N peak becomes stronger and for those powders synthesized at 1000 °C showed a shoulder in the Al–N peak. This phenomenon was observed for SiC powders with the structure of an unreacted silicon core covered with a carbonized SiC shell [10, 11]. It is not clear in our case whether this shoulder indicates a similar structure of unreacted aluminium covered with an AlN shell.

4. Conclusions

Through the gas-phase synthesis of aluminium nitride powders from $AlCl_3$–NH_3–N_2, the following conclusions were obtained about the process and the powder characteristics.

1. Aluminium nitride powders were formed both at high temperatures inside the reactor and at low temperatures in the flask outside the reactor. The yield of AlN powders from $AlCl_3$ and the crystallinity of the powders were increased as the reaction temperature and the $NH_3/AlCl_3$ mole ratio were increased. The yield was about 80% when the reactor temperature was 1000 °C and the $NH_3/AlCl_3$ ratio was 8.

2. AlN powders recovered at high temperatures inside the reactor were crystalline and contained negligible amounts of NH_4Cl and unreacted $AlCl_3$. AlN

powders recovered from the flask were amorphous with NH_4Cl and unreacted $AlCl_3$. Most of HCl by-product was recovered as NH_4Cl in the flask.

3. Most of the powders were round with or without small columns around the surface and in the size range 0.1–1 μm. Bar-like particles of high crystallinity were also obtained in a relatively small amount.

Acknowledgement

References

1. L. M. SHEPPARD, *Amer. Ceram. Soc. Bull.* **69** (1990) 1801.
2. M. MITOMO and Y. YOSHIOKA, *Adv. Ceram. Mater.* **2** (1987) 253.
3. L. D. SILVERMAN, *Adv. Ceram. Mater.* **3** (1988) 418.
4. I. KIMURA, K. ICHIYA, M. ISHII, N. HOTTA and T. KITAMURA, *J. Mater. Sci. Lett.* **8** (1989) 303.
5. I. KIMURA, N. HOTTA, H. NUKUI, N. SAITO and S. YASUKAWA, *ibid.* **7** (1988) 66.
6. *Idem, J. Mater. Sci.* **24** (1989) 4076.
7. K. TSUCHIDA, Y. TAKESHITA, A. YAMANE and A. KATO, *Yogyo-Kyokai-Shi* **95** (1987) 54.
8. K. BABA, N. SHOHATA and M. YONEZAWA, *Appl. Phys. Lett.* **54** (1989) 2309.
9. K. G. NICKEL, R. RIEDEL and C. PETZOW, *J. Amer. Ceram. Soc.* **72** (1989) 1804.
10. L. CHEN, T. GOTO and T. HIRAI, *J. Mater. Sci.* **24** (1989) 3824.
11. C. H. PAI, K. KOUMOTO, S. TAKEDA and H. YANAGIDA, *ibid.* **24** (1989) 3679.