JOURNAL OF MATERIALS SCIENCE 24 (1989) 4076–4079

Particulate characteristics and deposition features of fine AlN powder synthesized by vapour-phase reaction

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Fine AlN powder was synthesized by the vapour-phase reaction of $AlCl_3$ and NH_3 at 600 to 1100° C, and the particulate characteristics and the deposition features were investigated. The powder deposited near the $AlCl_3$-feeding nozzle included radially-grown particles with columnar crystals. The powder deposited apart from the $AlCl_3$-feeding nozzle consisted of only fine, spherical particles. Vapour-phase reaction at 1100° C produced fine powder, which was characterized by uniform and fine particle size; its distribution width was from 0.1 to 0.3 μm, and median diameter was 0.18 μm. Deposition area of the powder was affected by the reaction temperature and the temperature profile in the reactor.

1. Introduction

AlN ceramics have excellent thermal conductivity and high electrical resistivity and are eminently suitable for LSI substrates [1]. The mechanical strength and thermal shock resistance of AlN ceramics are so much greater than those of Al_2O_3 ceramics [2] that applications as structural materials are also of importance. For all applications, it is necessary to establish a method to yield fine AlN powder with high sinterability and purity.

Kato *et al.* have reported [3] the synthesis of TiN powder by vapour-phase reaction in the $TiCl_4$–NH_3–N_2–H_2 system. They presumed that a great degree of supersaturation or great thermodynamic driving-force is necessary to produce TiN powder, concretely log $K_p > 2$. Equilibrium constants [4], K_p, of conceivable reactions in the system of $AlCl_3$–NH_3 were plotted against reaction temperature in Fig. 1. AlN powder was produced above 600° C in the present work. From Fig. 1, it can be confirmed that this temperature corresponds to log $K_p = 2$. Accordingly, log $K_p > 2$ is also a requirement for powder synthesis in the present system.

Homogeneous nucleation is more predominant with greater K_p, so that a fine powder with uniform particle size is obtained. A lower value of K_p makes the heterogeneous nucleation predominant, so that formation of bulky crystals, whiskers and films becomes easy. We have been trying to find conditions under which the homogeneous nucleation is predominant, that is, a fine powder with excellent characteristics is obtained.

We have reported [5, 6] that fine AlN powder can be synthesized by the vapour-phase reaction of aluminium chloride ($AlCl_3$) and ammonia (NH_3). Compared with other methods such as direct nitridation and reduction nitridation, this method has several advantages — AlN powder is synthesized in a shorter time; it is more energy saving, requiring no special heat source; and so on. Thus, it is appropriate to produce AlN powder as a raw material for AlN ceramics at a low cost.

In the present work, we synthesized fine AlN powder by the vapour-phase reaction of $AlCl_3$ and NH_3 and investigated its particulate characteristics and deposition features. Shape, size, size distribution and crystallinity were evaluated as the particulate characteristics.

2. Experimental procedures

The raw materials used in the experiment are commercially available $AlCl_3$ powder (purity 98.0%) and NH_3 gas (purity 99.9%). Commercially available nitrogen gas (purity 99.999%) was used as the carrier gas and the protective gas.

Fig. 2 shows schematic illustrations of the reactor assembly. The reaction was performed in a flow reactor (r) measuring 35 mm inner diameter and 600 or 1000 mm long, made of mullite. The $AlCl_3$-feeding tube (a) is a concentrically double tube, which was heated with a ribbon heater to prevent gaseous $AlCl_3$ from depositing prior to the reaction. $AlCl_3$ was heated at 180° C to be sublimed and carried by a nitrogen stream through the inner tube of the feeding tube into the centre of the furnace (f, fI). Nitrogen gas was passed also through the outer tube of the feeding tube to protect the nozzle from being shut by a bulky AlN, which was easily formed. NH_3 was dried with soda lime and potassium hydroxide (KOH) and fed into the reactor through another tube (b). The reaction temperature was measured using a chromel–alumel thermocouple positioned immediately above the $AlCl_3$-feeding nozzle.

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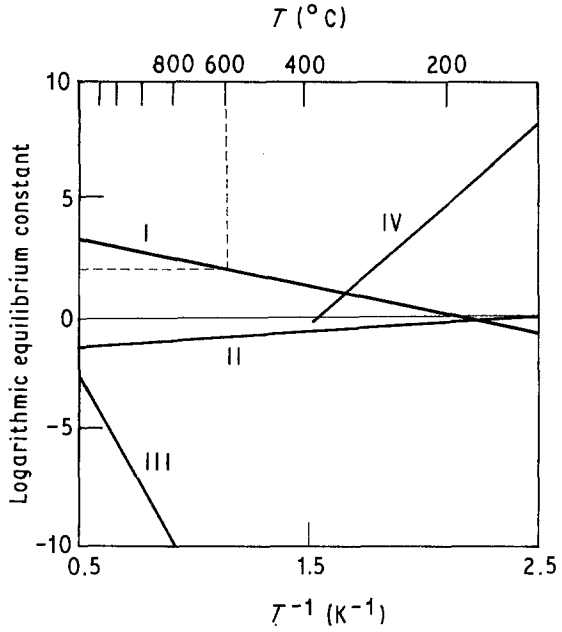

Figure 1 Change of equilibrium constants with reaction temperature. (I, $AlCl_3(g) + NH_3(g) = AlN(s) + 3HCl(g)$, II, $AlCl_3(g) + \frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) = AlN(s) + 2HCl(g)$, III, $AlN(s) = Al(l) + \frac{1}{2}N_2(g)$, IV, $NH_3(g) + HCl(g) = NH_4Cl(s)$).

Another thermocouple was used to measure the temperature profile in the reactor. The reaction conditions are listed in Table I.

The phase and the crystallinity were measured by powder X-ray diffraction. The particle shape and size distribution were measured using a scanning electron microscope and a centrifugal settling type particle-size analyser. The mean particle size was evaluated as median diameter, corresponding to particle size at the cumulative frequency of 50%.

3. Results and discussion

3.1. General characteristics

The product powder was deposited on the reactor wall above 400° C. The only AlN was detected in X-ray diffraction patterns of the powders synthesized at any reaction temperatures. It is reported [7, 8] that the impure AlN powders were coloured pale yellow, bluish black, or greyish black, and the pure one white. The colour of the AlN powder obtained in the present study was white, indicative of high purity.

At the reaction temperature of 700° C, particulate characteristics of the powder deposited near the $AlCl_3$-feeding nozzle were quite different from those of the powder deposited apart from the $AlCl_3$-feeding

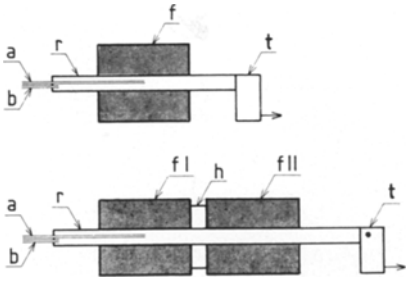

Figure 2 Schematic illustrations of the reactor assembly. (a) $AlCl_3$-feeding tube, (b) NH_3-feeding tube, (f, fI, fII) electric furnace, (h) heat insulator, (r) reactor, (t) trap.

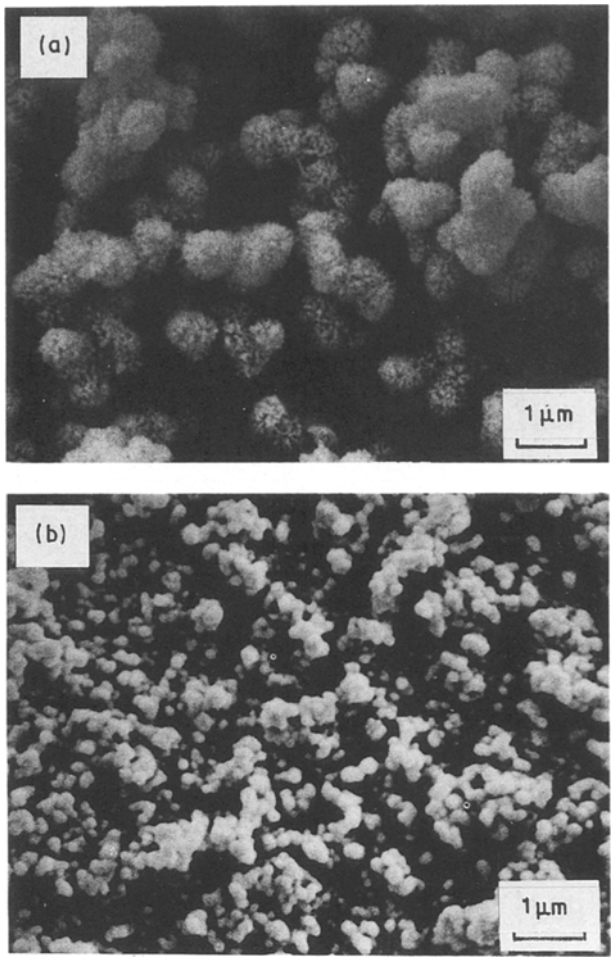

Figure 3 Scanning electron micrographs of the AlN powders synthesized at 700° C. (a) Deposited near the $AlCl_3$-feeding nozzle. (b) Deposited apart from the $AlCl_3$-feeding nozzle.

nozzle. Scanning electron micrographs of them are shown in Fig. 3. Radially grown particles with columnar crystals are observed in the powder deposited near the $AlCl_3$-feeding nozzle (a) as well as spherical particles. As stated later, such columnar crystals were grown by the heterogeneous nucleation on a surface of a spherical particle. Agglomeration also can be observed on the many particles. On the other hand, the powder deposited apart from the nozzle (b) consists of fine, sperical particles alone. The particle size is uniform, and agglomeration is observed a little.

Particle-size distribution diagrams of them are shown in Fig. 4. The powder deposited near the nozzle had a broader distribution between 0.5 to 40 μm, and the median diameter was 1.91 μm. The second peak, which corresponds to agglomeration, exists over a range of 8 to 40 μm. Its frequency is considerable, demonstrating significant agglomeration. On the other hand, the powder deposited apart from the nozzle (b) had a narrow distribution range from 0.15

TABLE I Conditions in vapour-phase reaction

Reaction temperature	600 to 1100° C
$AlCl_3$ feed rate	0.58 g cm^{-3}
NH_3 flow rate	400 cm^3 min^{-1}
N_2 flow rate	400 cm^3 min^{-1} as carrier gas
	200 cm^3 min^{-1} as protective gas
Temperature of furnace II	500 to 900° C

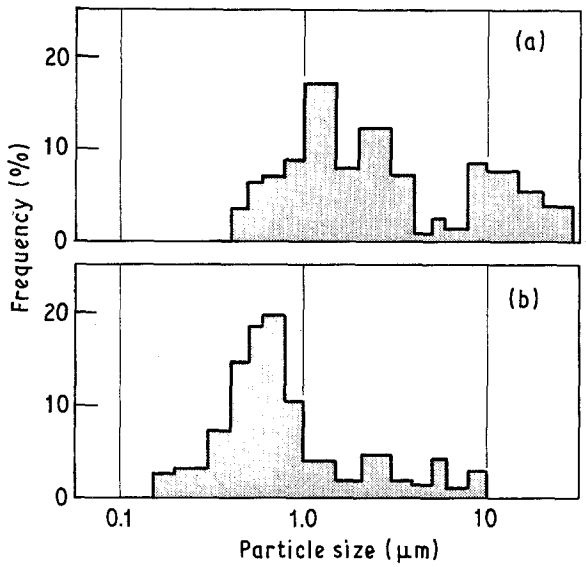

Figure 4 Particle-size distribution diagrams of the AlN powder synthesized at 700° C. (a) Deposited near the $AlCl_3$-feeding nozzle. (b) Deposited apart from the $AlCl_3$-feeding nozzle.

to 10 μm. Most of it was concentrated at 0.4 to 1.0 μm, and the median diameter was 0.62 μm. The second peak was not distinguishable, demonstrating less agglomeration.

3.2. Effect of the reaction temperature

Fig. 5 shows the relation between deposition area and reaction temperature. While the powder formed at 600° C was deposited from just behind the nozzle, the deposition area was shifted downstream with elevating reaction temperature. Formation of the radially grown particles was reduced with the shift of the deposition areas. At 1100° C, the radially grown particles were not observed, but fine, spherical particles alone were deposited.

We may deduce these phenomena as follows: As soon as fine particles are formed by homogeneous nucleation, the partial pressure of $AlCl_3$ decreases instantly. Thus, unreacted $AlCl_3$ cannot contribute to further formation of particles but to the heterogeneous nucleation on the surfaces of particles already formed, resulting in the formation of columnar crystals. Therefore, the radially grown particles are formed only near

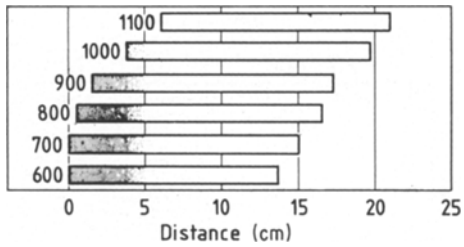

Figure 5 Relation between deposition area and reaction temperature. The numbers by the bars designate reaction temperatures. The abscissa is the distance from the $AlCl_3$-feeding nozzle. The shaded areas correspond to deposition of the radially grown particles.

the $AlCl_3$-feeding nozzle. Since homogeneous nucleation becomes more predominant at higher reaction temperature, almost all the $AlCl_3$ is consumed in the formation of fine particles so that the amount of $AlCl_3$ remaining is not enough to cause even the heterogeneous nucleation, so that formation of the radially grown particles decreases. In addition, the size of the particles decrease and, simultaneously, the gas speed in the reactor increases with increasing reation temperature, so that the particles are transported further.

Fig. 6 shows the X-ray diffraction patterns of the AlN powders synthesized at different reaction temperatures for comparison in the crystallinity. Any diffraction lines become high and sharp with elevating temperature, indicating promotion of the crystallinity. A comparison of the powders deposited near the $AlCl_3$-feeding nozzle and those apart from it shows high crystallinity in the former. This is because each columnar crystal may be a single crystal. The low crystallinity of the latter powders is one of the advantages for fabricating the ceramics.

3.3. Effect of the temperature profile in the reactor

In the experiment using two furnaces, the temperature of furnace I was fixed at 1100° C, and that of furnace II was varied between 500, 700 and 900° C, resulting in temperature profiles as shown in Fig. 7. The areas in which the AlN powders were deposited are designated by shading. The powders were only deposited in the zones with negative temperature gradients not in the zones with zero or positive gradients. Moreover, the

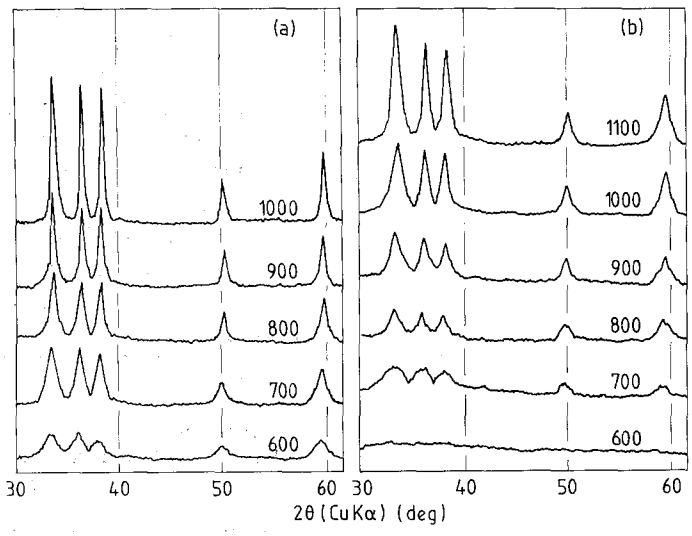

Figure 6 X-ray diffraction patterns of the AlN powders. The numbers on the diffraction lines designate reaction temperatures. (a) Deposited near the $AlCl_3$-feeding nozzle. (b) Deposited apart from the $AlCl_3$-feeding nozzle.

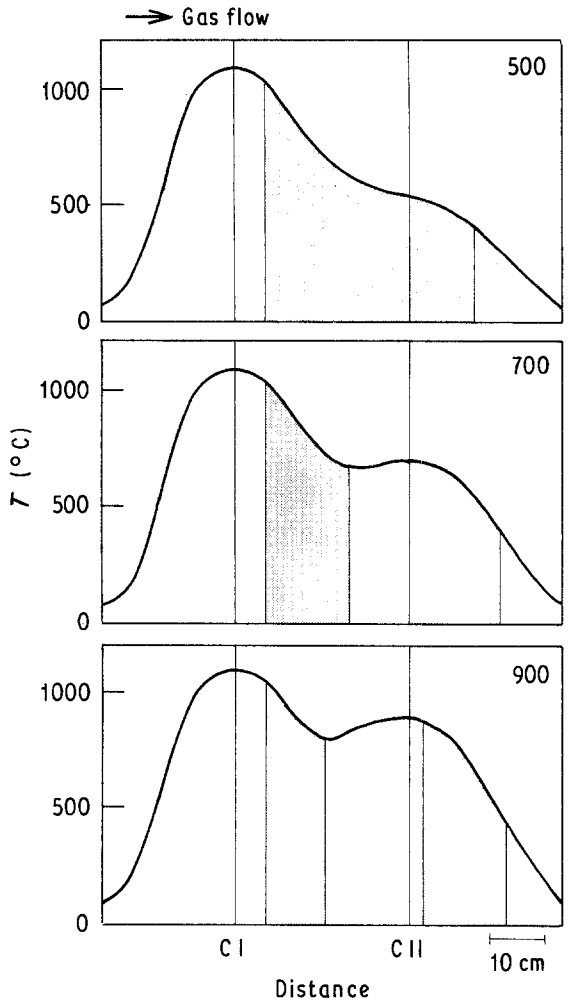

Figure 7 Temperature profiles in the reactor (curves) and deposition ranges of the AlN powders (shaded areas). The abscissa is distance from an end of the reactor. "CI" and "CII" correspond to the centres of furnaces I and II, respectively. Reaction temperature, i. e., temperature of the furnace I was fixed at 1100° C. The numbers in the frames designate the temperatures of furnace II.

greater the gradient, the greater the deposit. These facts demonstrate that a negative temperature gradient is closely related to the driving force of the deposition. The force, which allowed the powder to reach the reactor wall, is probably of the thermophoresis.

The particulate characteristics of all the powders obtained in this experiment are the same and are not dependent on the distance from $AlCl_3$-feeding nozzle or on the temperature of furnace II. If unreacted $AlCl_3$ were reacted with NH_3 during transportation, some differences in their characteristics would be observed. Thus, it is recognized that the reaction zone lies only near the $AlCl_3$-feeding nozzle and, therefore, whatever temperature profile would be permitted behind the reaction zone. The AlN powder was yielded most efficiently when the temperature gradient was negative everywhere, in practice.

The particle-size distribution of this powder is shown in Fig. 8. The powder was distributed over a very narrow range from 0.08 to 0.6 μm, and most of it was concentrated at 0.1 to 0.3 μm. The median diameter was very fine, 0.18 μm. The second peak was very small, indicative of little agglomeration. These characteristics suggest that the AlN powder obtained by this method is a promising raw material for the ceramics.

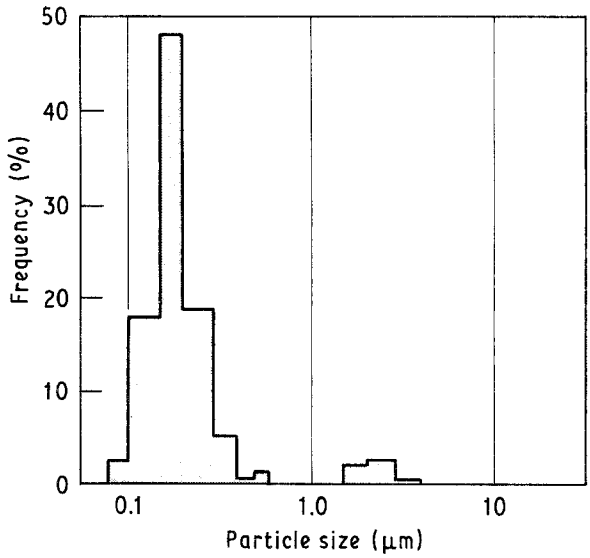

Figure 8 Particle-size distribution diagram of AlN powder synthesized at 1100° C.

4. Conclusions

The particulate characteristics and the deposition features of the AlN powder synthesized by the vapour-phase reaction of $AlCl_3$ and NH_3 were summarized as follows:

(1). Below 1000° C, the powder deposited near the $AlCl_3$-feeding nozzle included radially grown particles with columnar crystals, which have been formed by heterogeneous nucleation. The powder deposited apart from $AlCl_3$-feeding nozzle consisted of fine, spherical particles alone. Vapour-phase reaction at 1100° C produced the fine particles alone. The colour was white, indicative of high purity.

(2). The deposition area of the powder was shifted downstream with elevating reaction temperature. The experiment, in which several temperature profiles were set in the reactor, indicated that the powders formed were deposited in zones with a negative temperature gradient.

Acknowledgements

We thank Mr S. Takahashi and Mr Y. Yokota (Industrial Research Institute of Niigata Prefecture) for making their particle size analyser available.

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Received 19 July
and accepted 21 November 1988.