Synthesis of spherical AlN particles by gas-reduction-nitridation method

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Abstract

Spherical AlN particles were synthesized by reduction-nitridation of spherical Al_2O_3 particles using NH_3 and propane (C_3H_8) as reactant gases. Phase analysis of the reaction products was performed by XRD and the extent of nitridation was evaluated by weight loss measurement. Experimental results indicated that C_3H_8 addition was effective in accelerating the rate of nitride formation. SEM analysis revealed that the product powder maintained the particle morphology of the initial Al_2O_3 powder. Up to 94% of the starting material was converted to AlN at 1500°C within 0.5 h via a single-step synthesis process. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Aluminium nitride (AlN) has attracted much interest in recent years, particularly in the electronics industry as a substrate material, because of its high intrinsic thermal conductivity (~ 320 W m^{-1} K^{-1}), high electrical insulation and thermal expansion coefficient close to that of silicon. In addition, AlN has been added in a powder or fibre form as filler for polymer compounds to optimize the thermal properties of electronic-packaging.[1–3]

At present, commercial AlN powders are produced via the direct nitridation of aluminium metal, the carbothermal reduction-nitridation of alumina, or via the CVD process using triethyl aluminium.[4] In addition to these processes, various attempts have been made on the laboratory-scale production of AlN powder.[5] Among them, the reduction-nitridation of alumina using ammonia gas (referred to as gas-reduction-nitridation method hereafter) is noteworthy. In comparison with existing synthesis techniques, there are significant advantages in producing a fine powder by this method. First, no mixing step or post-synthesis processing is necessary, and hence high-purity powder can be produced in a single-step

process. Second, the original particle morphology of the starting alumina may be retained, owing to the gas–solid reaction between ammonia and alumina. Thus, the particle shape and size of the product AlN can be tailored by selecting particular alumina raw materials. Third, starting materials of high purity and fine particle size are commercially available. Despite the commercial importance, this process has received limited attention and there appear to have been only a few published studies. Hoch and Nair[6] used amorphous alumina and aluminium hydroxide as starting materials and heated them in a dry ammonia flowing furnace. They reported that up to 80% of the amorphous alumina was converted to AlN at 1200°C for 24 h, and the rest of the starting material was crystallized to α-Al_2O_3. More recently, Rocherulle et al.[7] claimed that they could produce pure AlN powder by heating alumina (~ 1 μm) in a NH_3 flow of 15 l/h at 1300°C for 48 h, but no further description of the reaction has been given. Colque and Grange[8] studied the formation of AlN through the reaction of alumina-carbon mixtures in a flow of diluted ammonia, instead of N_2 gas generally used in the almost all carbothermal syntheses. The authors showed that a high conversion to AlN was observed even when the carbon and alumina were physically separated, and proposed the gas-solid reaction mechanism between hydrogen cyanide

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(HCN) and alumina. From the viewpoint of thermodynamics, the gas phase carbon transport mechanism such as that through hydrocarbons appears to be important. However, investigations of the reduction-nitridation reaction of alumina in a hydrocarbon-containing atmosphere can hardly be found among literature.

The main purpose of the present work is to establish a method to obtain a pure and fine AlN powder endowed with a characteristic particle morphology via a simple and cost-effective synthesis technique. In the present paper, we propose a new process for synthesizing AlN powder which comprises micro particles of spherical shape by gas-reduction-nitridation method using NH_3 and C_3H_8 as reactant gases. The phase compositions of the reaction products were analysed by X-ray diffractometry (XRD) and microstructural analyses were performed to examine the powder morphology. The effects of reaction temperature, time and the gas composition on nitridation extent were also investigated systematically.

2. Thermodynamic considerations

A comparison of the change in free energy for various overall reactions in the systems Al_2O_3–NH_3 and Al_2O_3–NH_3–C_3H_8 is shown in Fig. 1. All ΔG_f° data were obtained from the JANAF tables[9] except those of C_3H_8.[10] The direct reduction and nitridation of Al_2O_3 to AlN by NH_3 can occur according to the reaction:
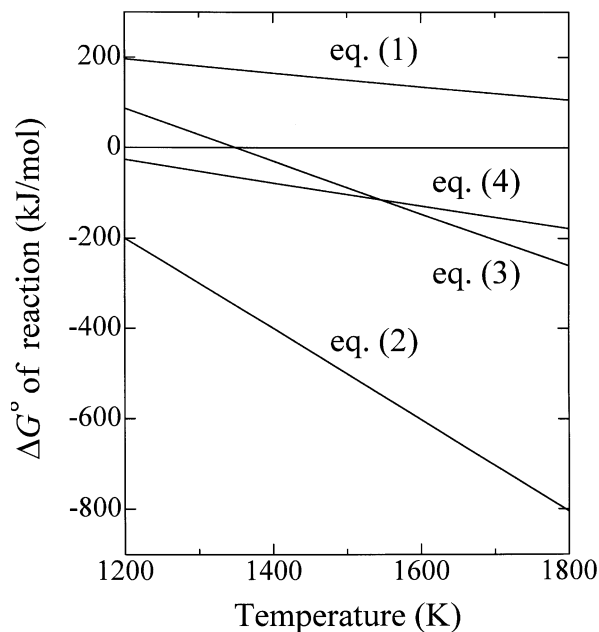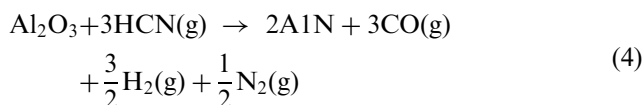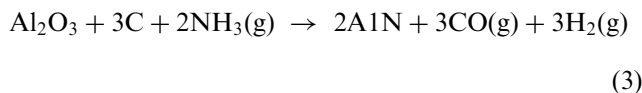
$$Al_2O_3 + 2NH_3(g) \rightarrow 2AlN + 3H_2O(g) \tag{1}$$

Fig. 1. Change in Gibbs free energy as a function of temperature for various overall reactions in the systems Al_2O_3–NH_3 and Al_2O_3–NH_3–C_3H_8.

To promote the formation of AlN in Eq. (1), it is important to maintain the partial pressure of H_2O well below the equilibrium value, which is calculated to be 1.4×10^2 Pa (1.4×10^{-3} atm) at 1200 K for δ-Al_2O_3. In contrast, the thermodynamic calculations show that the formation of AlN in the system Al_2O_3–NH_3–C_3H_8 following the overall reaction

$$Al_2O_3 + 2NH_3(g) + C_3H_8(g) \rightarrow 2AlN + 3CO(g) + 7H_2(g) \tag{2}$$
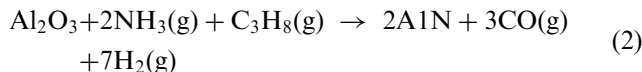
is favoured by having a negative value of free energy change at temperatures above ~1000 K. In the temperature range of interest, there are several competitive processes that may occur: the cracking of C_3H_8 as well as the reaction between C_3H_8 and NH_3 yielding HCN.[11] Hence, other possible reactions such as

$$Al_2O_3 + 3C + 2NH_3(g) \rightarrow 2AlN + 3CO(g) + 3H_2(g) \tag{3}$$

$$Al_2O_3 + 3HCN(g) \rightarrow 2AlN + 3CO(g) + \frac{3}{2}H_2(g) + \frac{1}{2}N_2(g) \tag{4}$$

should be considered in the system Al_2O_3–NH_3–C_3H_8. In all cases, highly active forms of nitrogen and hydrogen induced by the dissociation of ammonia may play an important role in the reduction-nitridation reaction.

3. Experimental procedure

A commercially available spherical alumina powder with a minimum purity of 99.8% and a median particle size of 0.91 μm was used as a starting material. Particles in the size range of 2–5 μm constituted about 15% of this powder material. The powder was synthesized via the vapourized metal combustion method and composed of δ- and θ-Al_2O_3. Its particle morphology is shown in Fig. 2. The transition temperature to α-Al_2O_3 was measured to be 1270°C by the differential thermal analysis in the present experiment. The powder was first screened through a 150 μm sieve to disperse any large agglomerates. The weighed sample was then placed in a high-purity alumina boat and set in an alumina tube furnace (inner diameter of 42 mm) with air-tight end gaskets. The reactor was flushed with argon to eliminate oxygen in the system during the heating-up period. As the temperature reached 900°C, a gas mixture of NH_3 (99.999% purity) and C_3H_8 (99.99%) with a predetermined proportion (0–1 vol.% C_3H_8) was introduced from the extremity of the reactor, at a flow rate of 4 l/min (stp). The furnace was heated to the experimental reaction temperature (1200–1500°C) at a rate of 8°C/min. The temperature was
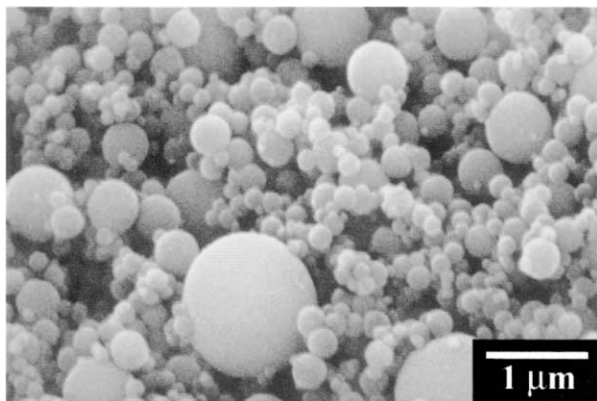
Fig. 2. SEM photograph of the initial Al_2O_3 powder showing the particles to have spherical shape.

Fig. 3. Relationship between C_3H_8 concentration of the reactant flow and the extent of nitridation.

subsequently maintained for a reaction time of 0–2 h, then the sample was cooled at approximately 6°C/min in an ammonia atmosphere. A reaction time of zero is defined as the time at which the furnace reached the set point. After cooling, the sample powders were reweighed and the degree of conversion was calculated for each run from the mass loss. The experimental error was normally less than 1%.

Phase analysis of the product powder was performed by X-ray diffractometer (RINT 2500, Rigaku) operated at 50 kV and 300 mA using CuK_α radiation. A scanning electron microscope (SEM, JSM-5200, JEOL) was used to analyse the particle morphology. Samples for SEM analyses were coated with thin films of sputtered gold to reduce the tendency for electrical charge buildup.

4. Results and discussion

The dependence of nitridation extent, calculated from the weight loss, on C_3H_8 concentration of the reactant flow is shown in Fig. 3. The reaction was performed at 1400°C for 0.5 h with the C_3H_8/NH_3 molar ratio varying from 0 to 0.01. A marked increase in conversion was observed with the addition of 0.25 vol.% of C_3H_8 and the addition in excess of 0.5 vol.% resulted in only a slight increase in AlN yield. Measurements by XRD confirmed that the final reaction products consisted exclusively of AlN and unreacted alumina. No diffraction peaks assigned to aluminium oxynitride or aluminium oxycarbide were detected. XRD analysis also revealed that the unreacted alumina consisted mainly of α-Al_2O_3 in the sample treated in pure NH_3 gas, while δ- and θ-Al_2O_3 phases were still dominant in cases where NH_3–C_3H_8 gas mixtures were used. This result seems to indicate that the polymorphic transformation of alumina is suppressed in the Al_2O_3–NH_3–C_3H_8 system. Although literature on this subject is scarce, some studies on carbothermal syntheses[12–14] have also found the
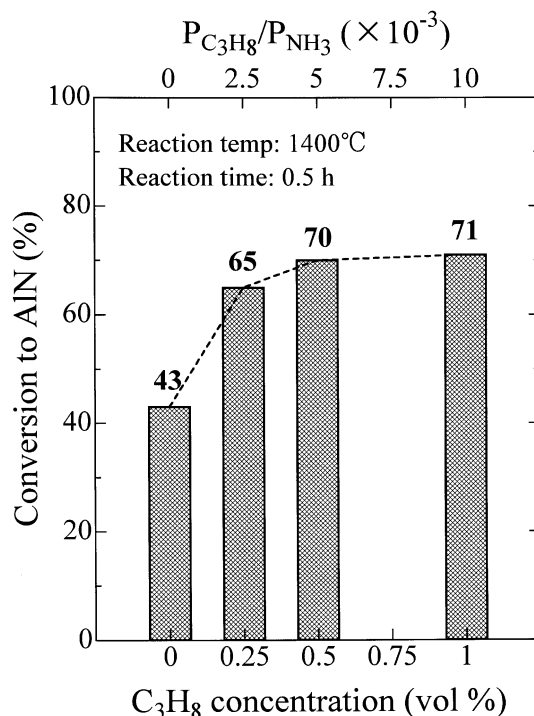
presence of transition aluminas such as γ- and θ-Al_2O_3 which persisted to temperatures as high as 1300°C.

The extent of nitridation as a function of reaction time are shown in Fig. 4 for the samples synthesized at 1400°C in NH_3 and NH_3–0.5 vol.% C_3H_8 gas streams. The reaction rate increased significantly with the addition of
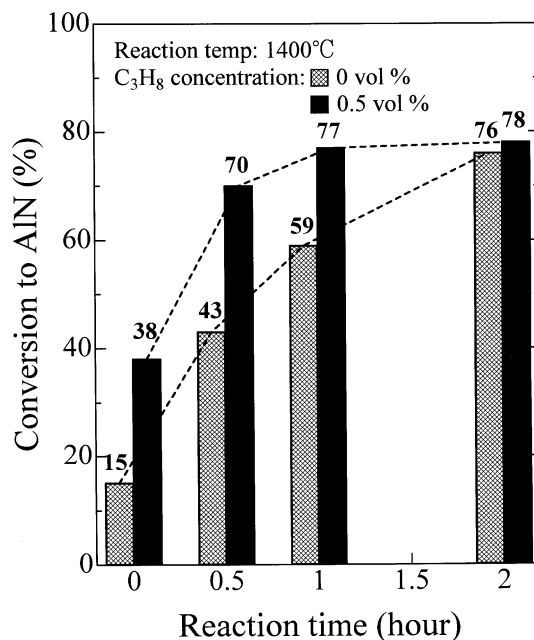

Fig. 4. Effect of the addition of C_3H_8 on the nitridation extent as a function of reaction time.

0.5 vol.% of C_3H_8, and the percent AlN conversion reached about 77% within 1 h in the system containing C_3H_8. However, the nitridation extent was found to be almost saturated at this value, presumably due to the relatively broad particle size distribution of the starting powder.

XRD patterns of the samples synthesized at 1400°C for times up to 2 h under NH_3 and NH_3–0.5 vol.% C_3H_8 gas streams are shown in Figs. 5 and 6, respectively. For nitridation in the pure NH_3 stream, most of the starting alumina was transformed to the stable α phase (corundum) upon reaching the reaction temperature, and subsequent formation of AlN through α-Al_2O_3 was observed. Thus, α-Al_2O_3 remained in the final products as noted before. On the other hand, in the system containing C_3H_8, a considerable amount of AlN was formed at the reaction time of zero, and nitridation proceeded rapidly without the phase transformation from δ- and θ-Al_2O_3 to α-Al_2O_3. According to thermodynamic calculations using $\Delta G°$ data in Fig. 1, the degree of reaction in equilibrium ($\Delta G = 0$) at atmospheric pressure and $T = 1200$ K reaches almost unity for Eq. (2) and 0.875 for Eq. (4). These results suggest that AlN can be formed below the transition temperature to α-Al_2O_3 in the system Al_2O_3–NH_3–C_3H_8. Therefore, the observed suppression of the θ-α transition of Al_2O_3 can be regarded as the result of the nitride formation during heating prior to reaching the transition temperature. Furthermore, since formation of

AlN is accompanied by a change in coordination number of aluminium atoms, nitridation of Al_2O_3 may be favoured by the suppression of the polymorphic transformation. Aluminium is tetracoordinated in the Würtzite
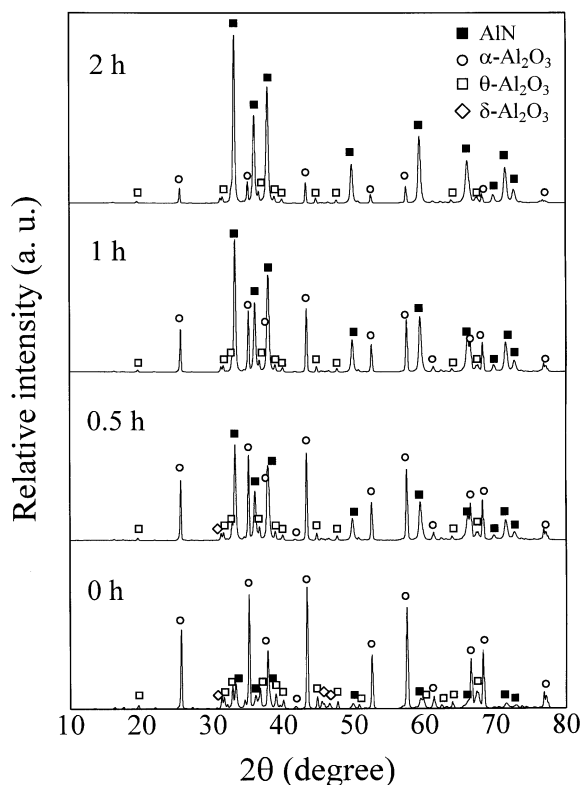

Fig. 6. XRD patterns of the samples synthesized at 1400°C for times up to 2 h in NH_3–C_3H_8 stream.
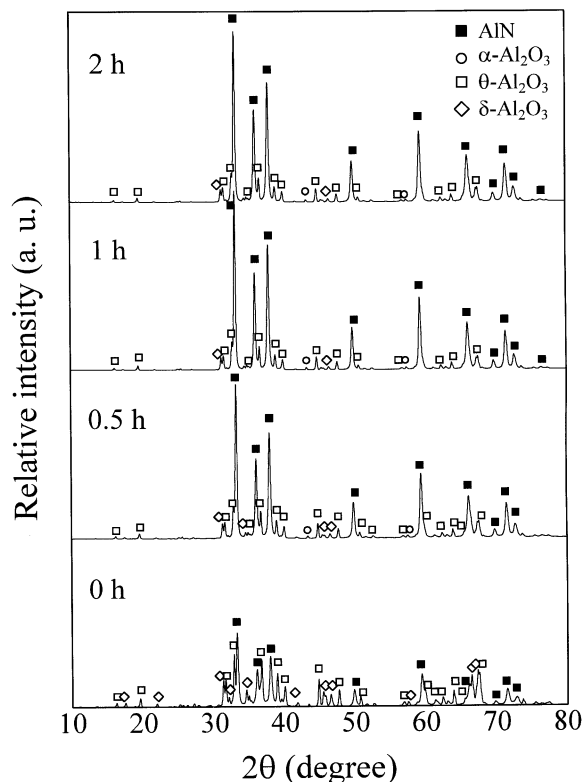

Fig. 5. XRD patterns of the samples synthesized at 1400°C for times up to 2 h in NH_3 stream.
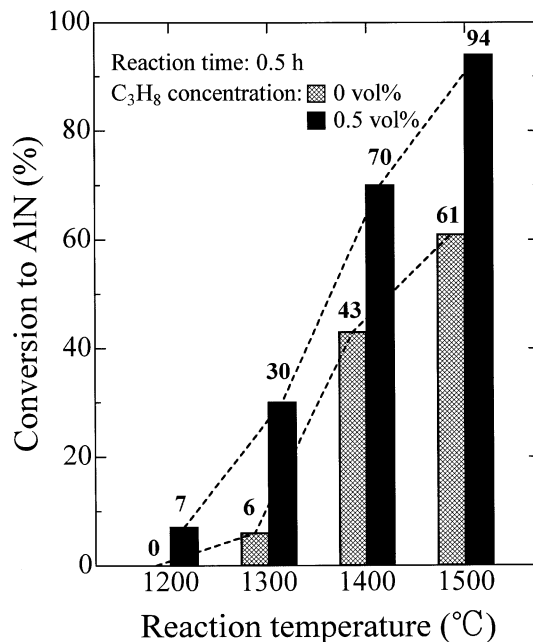

Fig. 7. Extent of nitridation as a function of reaction temperature for 0.5 h runs.
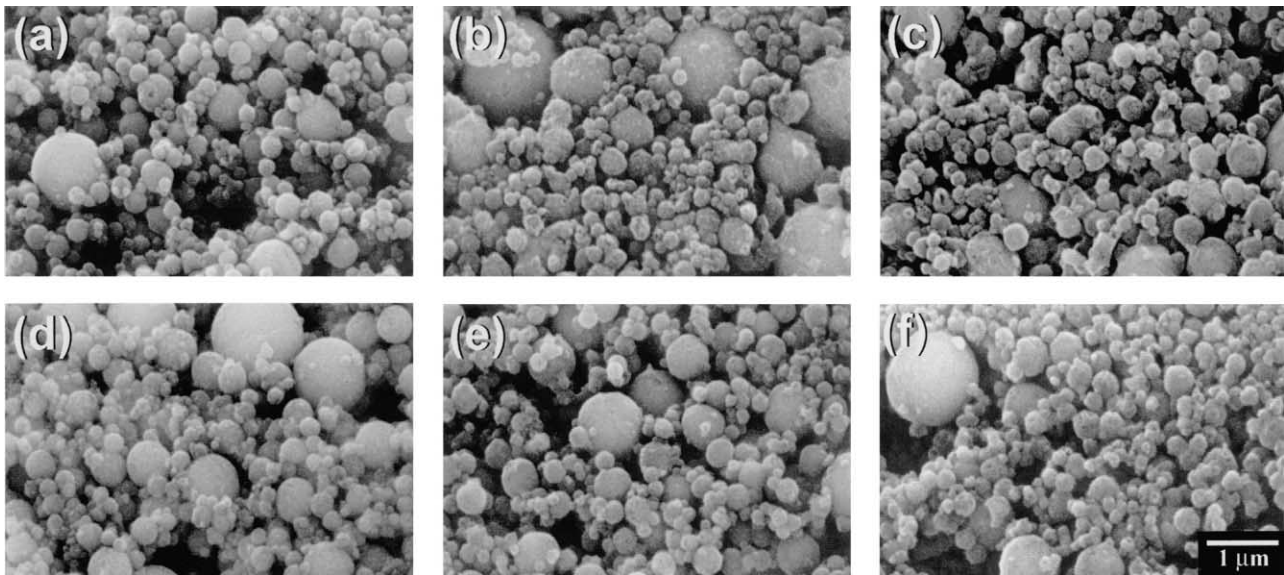
Fig. 8. SEM photographs of the product powders synthesized at 1400°C for various heat treatment times: (a) 0 h, (b) 0.5 h, (c) 1 h in NH_3, and (d) 0 h, (e) 0.5 h, (f) 1 h in NH_3–0.5 vol.% C_3H_8 gas stream.

structure of AlN, tetra- and hexacoordinated in the transition aluminas, but solely hexacoordinated in the corundum structure of α-Al_2O_3. Consequently, it is expected that the enhancement of the rate of reaction observed in the C_3H_8 containing system originated not only from the thermodynamic advantages of the C_3H_8 addition but also from the favoured formation of AlN from transition aluminas.

Fig. 7 shows the effect of reaction temperature on nitridation in both reaction systems for soaking time of 0.5 h. The extent of nitridation increased drastically with rising temperature, and the percentage conversion to AlN reached about 94% at 1500°C in the system containing C_3H_8. These reaction conditions are obviously more efficient than those required in the conventional carbothermal reduction method, and comparable to those of the carbothermal synthesis[4] where additives such as CaF_2 and rare-earth oxides were used as reaction promoters. For the Al_2O_3–NH_3 system, no conversion could be detected by the weight loss in the sample heated at 1200°C, while in the system containing C_3H_8, 7% of the starting alumina was converted to AlN at this temperature. These observations support the view that formation of a surface nitride layer prior to reaching the polymorphic transition temperature prevents the transformation of transition aluminas into α-Al_2O_3.

Fig. 8 shows SEM photographs of the product powders synthesized at 1400°C for various heat treatment times in NH_3 and NH_3–0.5 vol.% C_3H_8 gas streams. It is clear that the particle morphologies of the nitrided powders are exactly the same as that of the alumina raw material and have retained its spherical shape. Several irregular-shaped particles were observed in the samples

heated in NH_3 stream for 0.5 and 1 h [Fig. 8(b) and (c)]. This is likely to be a result of sintering of agglomerated alumina particles during conversion, due to the lower nitriding capability of NH_3 relative to NH_3–C_3H_8 gas. Although agglomeration of as-prepared powders was very weak, prolonged heat treatment should cause coalescence of AlN particles and hard agglomerates. Hence, addition of C_3H_8, which leads to shorter reaction times and increased yields of AlN, is thought to be beneficial also from the viewpoint of integrity of the morphological retention.

5. Conclusion

Preparations of AlN powder by the gas-reduction-nitridation reaction of alumina using NH_3–C_3H_8 gas were investigated and compared with the reaction utilizing pure NH_3 gas. A high conversion to AlN (94%) was achieved with the addition of 0.5 vol.% of C_3H_8 at 1500°C within 0.5 h. The marked enhancement of the nitridation rate observed for the system containing C_3H_8 could be attributed to the effects of the thermodynamic advantages of the C_3H_8 addition, and the suppression of the polymorphic transformation of alumina. Observation by SEM clearly demonstrated that the particle morphology of the product powder was exactly the same as that of the alumina raw material and retained the original spherical shape. This morphological retention was more evident in the system containing C_3H_8. It is concluded that the gas-reduction-nitridation method developed in the present work is a promising way of producing pure and fine AlN powder, morphology of which can be controlled by specifying morphology of the raw material.

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