FULL PAPER

Synthesis of AlN particles via direct nitridation in a drop tube furnace

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We propose a facile and continuous direct nitridation method for synthesizing fine aluminum nitride (AlN) particles using a drop tube furnace. Aerosolized Al powder as the raw material was continuously supplied through the top of the furnace together with N₂ as a carrier gas. Once in the furnace, the Al powder reacted with the N₂ to form AlN. A particular advantage of this process is that it allows the continuous synthesis of fine AlN particles. In this study, either a mullite (Al₂O₃-SiO₂) or an alumina tube was used to fabricate the furnace, and the products were collected in a crucible placed at the bottom. Upon heating the mullite tube from 1200 to 1400°C, AlN was formed once the temperature exceeded 1250°C, and its product content increased with temperature. When the flow rate of the N₂ carrier gas was decreased from 4 to 2 L min⁻¹, the amount of AlN formed increased due to the increased residence time in the reactor. The morphology of the particles obtained was radially aligned nanofibers with droplets on the tips of the fibers. Transmission electron microscopy revealed that the Si in the mullite tube reacted with Al to form eutectic Al-Si droplets on the Al surface, in which these droplets acted as a catalyst of vapor-liquid-solid AlN fiber growth. When the alumina tube was used (1800°C), nitridation of Al was enhanced and radially aligned AlN nanofibers with no droplets on the tips were collected, mainly in a filter at the exhaust port. These AlN nanofibers are thought to form via vapor-solid growth and are easily carried along with the N₂ gas flow, resulting in their deposition on the filter. The products collected in the crucible contained coarse Al particles, which are formed via Al particle agglomeration and coarsening through melting.

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1. Introduction

Aluminum nitride (AlN) is an essential ceramic material with high thermal conductivity, excellent electrical insulative properties, and a low thermal expansion coefficient.^{1),2)} Because of these favorable characteristics, AlN powders or fibers may be used as highly thermally conductive fillers in resins to improve their heat dissipation.^{3),4)} AlN sintered bodies are also important substrate materials for integrated circuits.^{1),5),6)} Currently, Al₂O₃ is conventionally used for thermally conductive fillers owing to its low price and high chemical stability. However, its thermal conductivity (29 W/m·K)⁷⁾ is relatively low compared to that of AlN (320 W/m·K).²⁾ Thus, AlN is a potentially attractive material for use as a thermally conductive filler.

The thermal conductivities of such composites are largely affected by the morphology of the filler. One-dimensional (1D)-structured AlN fibers are considered to be better heat-dissipation fillers than AlN particles because the fibers interconnect to form a network through which heat can be transferred efficiently and easily.^{8),9)} Furthermore, hybrid fillers comprising both spherical AlN parti-

cles and AlN fibers have been demonstrated to improve the thermal conductivity of their host composite materials.¹⁰⁾

AlN powders are synthesized by various methods, such as direct nitridation,^{11)–13)} carbothermal reduction-nitridation,¹⁴⁾ and vapor-phase reactions.¹⁵⁾ Among the various methods available, carbothermal reduction-nitridation and direct nitridation are most commonly used in industry. For synthesis of AlN by direct nitridation, Al powder is reacted with N₂ gas. The nitridation reaction is exothermic ($\Delta H = -318$ kJ/mol), so once it is initiated with a small input of energy, the reaction proceeds without the need for additional energy from an external source. Thus, direct nitridation including combustion synthesis is a very fast and energy-efficient method for AlN synthesis.^{16),17)} However, the heat generated by the reaction melts the Al powder used as the raw material, and the resulting Al agglomerates prevent the nitridation reaction from reaching completion. In addition, the high reaction heat causes sintering and growth of AlN grains. Consequently, a pulverization step is required before using as AlN a raw material for sintered bodies and thermally conductive fillers, and this step often introduces impurities.

A drop tube furnace (DTF) consists of a feeder for the introduction of raw materials, a vertical electric furnace, a reaction tube, and a sample collection device. In DTF

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Fig. 1. (a) SEM image and (b) particle-size distribution of the Al powder used as raw material.

processes, the raw materials are continuously supplied through the top of the DTF and are heated as they drop. DTF processes are continuous and thus allow high productivity. Accordingly, DTFs have been used for biomass pyrolysis,^{18),19)} destruction of tar,²⁰⁾ coke formation,²⁰⁾ and gasification of coal char.²¹⁾

DTF processes also have attractive features for AlN production. When Al powder is fed into a N₂-filled DTF, direct nitridation occurs without agglomeration, resulting in the formation of fine AlN particles. Furthermore, because the sintering and growth of AlN grains are suppressed, no pulverization step is required. In addition, the Al powder does not come into contact with the reaction chamber as it drops, so the resulting product is typically of high purity.

In this study, we explored the possibility of AlN synthesis by direct nitridation in a DTF. We used a mullite (Al₂O₃–SiO₂, 1200–1400°C) or an alumina tube (1800°C) as the reactor tube. To evaluate the potential of DTF methodology for AlN production, we investigated how the reaction-tube material and N₂ flow rate affected the synthesized AlN. The products were collected in a crucible placed at the bottom of the furnace and on a filter in the dust collector. Finally, the mechanism of formation for each reaction product was considered based on observation, phase analysis, and particle size analysis.

2. Materials and methods

Atomized Al powder (99.9%, Fe 0.08 mass%, Si 0.02 mass%, 3 μm) was purchased from Kojundo Chemical Laboratory Co., Ltd. (Saitama, Japan) and used as the raw material. The heterogeneous powder was comprised of spherical and non-spherical particles, as shown by the scanning electron microscopy (SEM) image and particle-size distribution in Fig. 1. A schematic diagram of the DTF is shown in Fig. 2. The reactor consisted of a micron feeder, an ejector, a reaction tube, a filter, and a crucible. The quantity of Al powder fed into the furnace was controlled with a Micron TF-70-CT rotary valve feeder (Aisin Nano Technologies Co., Ltd., Japan). The Al powder was supplied to the reaction apparatus through an upward-facing nozzle. The powder was ejected through the nozzle

Fig. 2. Schematic illustration of the DTF.

towards the top end of the furnace before introduction into the reactor to decrease its falling velocity. The HB mullite tube (56 mass% Al₂O₃ and 40 mass% SiO₂, Nikkato Corp., Japan) and SSA-S alumina tube (99.6 mass% Al₂O₃, Nikkato Corp., Japan) had an inner diameter of 70 mm, an outer diameter of 80 mm, and a height of 1,500 mm. The temperature of the tube was controlled with an RHTV 120/600/18 vertical tubular electric furnace (Nabertherm GmbH, Germany). The height of the furnace was 960 mm, and the length of the heating zone was 600 mm. The uniform temperature zone was 170 mm in length and the temperature therein could be controlled to within ±5 K. A VF-5N filter (Amano Corp., Japan) was installed to collect samples and discharge gases.

Fig. 3. (a) XRD patterns and (b) an enlargement of the 25–40° region of products synthesized using a DTF equipped with a mullite reactor tube and under a N_2 flow rate of 4 L min^{-1} . The products were sieved to a particle size of less than $75\text{ }\mu\text{m}$.

The feeder was filled with Al powder prior to each DTF experiment. N_2 (99.99%, Hokkaido Air Water Inc., Japan) was supplied as the carrier gas at a flow rate of 2 or 4 L min^{-1} . When the mullite tube was used, the temperature was increased from 1200 to 1400°C . For the alumina tube, the DTF was heated to 1800°C . The Al powder was dropped continuously into the pre-heated DTF at a supply rate of 0.108 g min^{-1} . N_2 cooling gas (10 L min^{-1}) was circulated at the bottom of the furnace to cool the reaction products and the carrier gas. The products were then collected in the crucible and the filter.

The compositions of the products were determined by X-ray diffraction (XRD) analysis with a MiniFlex 600 diffractometer (Rigaku Corp., Japan). The morphologies of the products were investigated using SEM with a JSM-7001FA field-emission SEM (JEOL, Japan). The elemental composition of the products was determined using an SEM apparatus equipped with an energy dispersive spectroscopy (EDS) detector. The particle-size distributions were analyzed with a Partica LA-950 laser diffraction particle-size distribution analyzer (Horiba Scientific, Japan). The nanofibers were observed using a field-emission transmission electron microscope (TEM, JEM-2010F, JEOL) equipped with an EDS detector and an electron energy-loss spectroscopy (EELS) detector.

3. Results and discussion

3.1 Results obtained using the mullite reactor tube (1400°C)

The mullite tube was heated continuously from 1200 to 1400°C and the products were collected in the crucible. The flow rate of the N_2 gas was fixed at 4 L min^{-1} . **Figure 3(a)** shows the XRD patterns of the collected products, which were sieved to a particle size of less than $75\text{ }\mu\text{m}$. Most of the particles were found to be unreacted Al. **Figure 3(b)** shows an enlargement of the 25–40° region of the XRD

pattern in **Fig. 3(a)**, where the peaks are normalized by the maximum intensity of the Al peak. A small amount of AlN was detected following reaction at 1250°C , and the relative intensity of the AlN peak against that of the Al peak increases with an increase in temperature. At 1400°C , some metallic Si is also observed. **Figure 4** shows the AlN weight ratios for the products obtained at different temperatures as calculated by the reference intensity ratio (RIR) method based on the XRD results. Clearly, a high reaction temperature enhances nitridation.

Figure 5 shows the SEM images of the products produced at different temperatures. When the temperature is below 1250°C [Figs. 5(a)–5(c)], the product morphologies are largely similar to those of the raw materials shown in **Fig. 1(a)**. However, for reactions preformed at 1200– 1250°C [Fig. 5(c)], coarse spherical particles, which may be formed via agglomeration of liquid Al, are observed. For reactions performed at temperatures over 1250°C , spherical particles with radially grown fibers appear, as indicated by the arrows in **Fig. 5(d)**. The formation of these radially grown fibers increases with increasing temperature, as shown in Figs. 5(d)–5(g). **Figure 5(h)** shows an enlarged SEM image of these unique radially-grown fibers.

The effect of N_2 flow rate was investigated while keeping the reactor temperature constant (1400°C) and sieving the products to different sizes. **Figure 6** shows how the AlN weight ratio changes with particle size. Decreasing the flow rate from 4 to 2 L min^{-1} increases AlN formation. In addition, the smaller particles were found to have higher AlN contents. These results indicate that the residence time of the falling particles in the heating zone relates to the degree of nitridation, with a lower flow rate and a smaller particle size resulting in the production of larger quantities of AlN.

To evaluate how the particle size and carrier gas flow rate affect the AlN content of the product, the residence

Fig. 4. AlN weight ratios of products synthesized at different temperatures using a DTF equipped with a mullite reactor tube, as calculated using the RIR method based on the XRD results.

Fig. 5. SEM images of products synthesized using a DTF equipped with a mullite reactor tube and performed reaction temperatures of (a) 1100–1150°C, (b) 1150–1200°C, (c) 1200–1250°C, (d) 1250–1300°C, (e) 1300–1350°C, (f) 1350–1400°C, and (g, h) 1400°C. Arrows indicate radially-grown fibers.

time of the Al particles in the uniform temperature zone of the DTF was calculated assuming that the Al particles are added to the DTF at room temperature. We defined the residence time, t_p (s), as the residence time of Al particles in the uniform temperature zone and calculated it using Eqs. (1)–(4).²²⁾

$$U_p = U_g + U_s \quad (1)$$

$$U_g = Q/S \quad (2)$$

$$U_s = 2(\rho_p - \rho_g)gr_0^2/9\mu \quad (3)$$

$$t_p = L/U_p \quad (4)$$

where U_p is the particle velocity (m s^{-1}), U_g is the gas flow velocity (m s^{-1}), U_s is the particle terminal velocity (m s^{-1}), Q is the gas flow rate ($\text{m}^3 \text{s}^{-1}$), S is the cross-

sectional area of the reaction tube (m^2), ρ_p is the particle density (kg m^{-3}), ρ_g is the gas density (kg m^{-3}), g is acceleration due to gravity (9.8 m s^{-2}),²³⁾ r_0 is the mean particle radius (m), μ is the viscosity of the carrier gas (Pa s), and L is the length of the uniform temperature zone (m). For these calculations, the Al particle density (ρ_p) was assumed to be $2,700 \text{ kg m}^{-3}$, the N_2 gas density (ρ_g) 1.25 kg m^{-3} , and the N_2 gas viscosity (μ) $17.6 \times 10^{-6} \text{ Pa s}$. The calculated residence times of the Al particles in the uniform temperature zone of the DTF are plotted against particle size in Fig. 7. Smaller particles fall much more slowly than larger particles. Thus, the residence time of smaller particles in the uniform temperature zone is longer, enhancing nitridation. Conversely, larger particles fall at

Fig. 6. AlN weight ratios for DTF products with different particle sizes and that were prepared under different N_2 flow rates. The weight ratios were calculated using the RIR method based on the XRD results.

Fig. 7. Calculated particle residence times in the soaking zone of the DTF. Smaller particles have longer residence times and are strongly affected by the N_2 flow rate. However, larger particles pass through the soaking zone within a very short time.

higher speeds and thus spend less time in the uniform temperature zone, resulting in inadequate heating and unreacted raw Al powder.

To investigate the composition of the radially-grown fibers, SEM-EDS analysis was performed. **Figure 8** shows the SEM image of the product produced at 1400°C with a N_2 flow rate of 2 L min^{-1} (the regions analyzed using EDS are indicated by black lettered squares). The results of quantitative EDS analysis are summarized in **Table 1**. The particles with smooth surfaces mainly consist of Al, as shown in Figs. 8(a), 8(c). In contrast, the particles with radially grown fibers contain Si, N, and O [Figs. 8(b), 8(d)]. **Figure 9(a)** shows a TEM image of these fibers, revealing the presence of spherical particles attached to their tips. The fibers have either a straight or bellows-like

Fig. 8. SEM image of the product synthesized using the mullite reactor tube at 1400°C and a N_2 flow rate of 2 L min^{-1} . The square-highlighted regions are those analyzed by EDS, where (a) and (c) are particles without fibers and (b) and (d) are particles with fibers.

Table 1. Results of quantitative EDS analysis of the DTF products

Sample name	Composition/mass %			
	Al	N	O	Si
(a)	86	9	4	1
(b)	61	18	15	6
(c)	83	15	1	1
(d)	62	15	8	15

morphology. **Figure 9(b)** shows a high-resolution TEM image of some representative bellows-like fibers, revealing that the fibers are single crystalline and that no grain boundaries are present in the necks of the bellows. **Figures 9(c) and 9(d)** show a TEM image and a corresponding electron diffraction patterns, respectively. We confirmed that the fibers have a wurtzite AlN structure and grow in the $[001]$ direction, which is the typical growth direction for AlN fibers.

Subsequently, we focused on the spherical particles attached to the tips of the AlN fibers. **Figure 10(a)** shows a TEM image of the fibers. The spherical particles are attached to both straight and bellows-like AlN fibers. The EEL spectra were acquired from the selected areas shown in Fig. 10(a). **Figures 10(b) and 10(c)** show the EEL spectra for Al, Si, N, and O. Al and Si, but not N, were detected in the tip particles. EDS analysis also revealed a similar result. The features of the Si-K edge indicate the presence of metallic Si. Based on these results, we concluded that the spherical tip particles are composed of a eutectic Al-Si alloy. In Fig. 10(a), the spherical particles on the tips consist of two distinct areas that relate to Si and Al phases. In contrast, Al and N, but not Si, were detected in the fibers, indicating that they are AlN fibers. It has been

reported that metallic particles can act as metallic catalysts for the vapor–liquid–solid (VLS) growth of fibers. In the case of AlN, Au can act as a catalyst for VLS growth.²⁴⁾ It

has also been previously reported that when MgO is added to the raw materials for the combustion synthesis of AlN, AlN nanowires with Mg–Al–O–N droplets on the tips are formed, suggesting VLS growth.²⁵⁾

Similarly to these previous studies, VLS growth of AlN occurred in our DTF experiments. Figure 10(d) shows the proposed formation mechanism for radially grown AlN fibers obtained in a DTF using a mullite tube. Si is attached to the surface of Al particles and diffuses into Al to form eutectic Al–Si droplets. However, the vaporization of Al also occurs at high temperature. Because eutectic Al–Si droplets have a lower melting temperature than that of Al and Si alone, they exist as melted droplets, which act as catalysts for VLS growth of AlN fibers. Although Si is an unexpected contamination, it was found that the Si acts as an effective catalyst of AlN growth during DTF processes.

3.2 Results obtained using the alumina tube (1800°C)

When the mullite reactor tube was used, the maximum heating temperature was limited to 1500°C and contamination by Si occurred. Thus, to improve nitridation and product purity, we used an alumina reactor tube. In these experiments, the furnace temperature was set at 1800°C and products formed under different flow rate conditions were collected in the crucible and the filter at the exhaust port, as shown in Fig. 2. Due to technical reasons, the material collected from the filter contained products formed at both 4 and 2 L min^{−1} flow rates.

Figure 11(a) shows the XRD patterns of the products collected from the crucible and the filter. The products collected from the crucible were macroscopic grayish powders. Strong Al peaks and weak AlN peaks are present

Fig. 9. TEM images of the product synthesized at 1400°C and a N₂ gas flow rate of 2 L min^{−1}. (a) TEM image of the fibers; (b) high-resolution TEM image of bellows-like fibers; (c) TEM image of one single fiber; and (d) selected area electron diffraction pattern from Fig. 9(c). The incident direction of the electron beam was [100].

Fig. 10. (a) TEM image of AlN fibers; (b, c) EEL spectra taken from areas A, B, C, and D in Fig. 10(a). (d) Proposed formation mechanism of radially grown AlN fibers in a mullite tube.

Fig. 11. (a) XRD patterns of products formed using the alumina reaction tube collected from the crucible and filter. AlN is produced under all experimental conditions. (b) The AlN weight ratios for each DTF product as calculated using the RIR method based on the XRD results.

Fig. 12. SEM images of DTF products synthesized using the alumina reactor tube at 1800°C. (a-1) and (b-1) show the particle morphologies for samples collected from the crucible at different N_2 flow rates. The surfaces of the particles are shown at higher magnification in (a-2) and (b-2). (c-1) shows the sample collected from the filter, and (c-2) is an enlarged image of the radially aligned AlN nanofibers.

in the XRD patterns of these powders, indicating that nitridation of the Al raw material does not complete under the conditions employed. However, upon decreasing the flow rate of the N_2 carrier gas from 4 to 2 L min⁻¹, the AlN peaks for the synthesized product increase in intensity. The product obtained from the filter in the dust collector was grayish in color and had a cotton-ball morphology. In the XRD pattern of this sample, intense AlN peaks are apparent. This material is clearly different from the product collected in the crucible.

Figure 11(b) shows the AlN weight ratio for each DTF product as calculated using the RIR method based on the XRD results. The product ratio of AlN is higher at the lower carrier gas flow rate. As discussed in Section 3.1, the dropping speed is slower for the lower N_2 flow rate, allow-

ing the Al powder to be maintained at a high temperature for a longer period of time. The sample collected from the filter had the highest AlN content of 72% by mass.

SEM images of the DTF products synthesized at 1800°C with N_2 flow rates of 2 and 4 L min⁻¹ are shown in Fig. 12. The particles collected in the crucible [shown in Figs. 12(a-1)–12(b-1)] are relatively large (>50 μm in diameter), whereas the raw Al powder particles were 3 μm in diameter. In addition, all of these coarse particles are spherical, while the Al particulates in the raw material were non-spherical. This indicates that the Al powder supplied through the top of the DTF melts in the heating zone, resulting in aggregation and coarsening. Furthermore, these agglomerated particles melt at high temperature to form coarse spheres.

We subsequently focused on the surfaces of these particles, which are shown in Figs. 12(a-2)–12(b-2). Hexagonal crystals less than 5 μm in size are observed on the particle surfaces. AlN has a hexagonal crystal structure, indicating that these particles are AlN crystals. Owing to the short reaction time, this AlN does not grow into fibers. Conversely, the product particles collected from the filter are smaller than those collected from the crucible, as shown in Fig. 12(c-1). Because the crucible was located at the bottom of the furnace (Fig. 2), the coarse particles fall directly into the crucible. In contrast, smaller particles can be transported by the cooling gas. This is why the smaller particles collect on the filter. The radially aligned nanofibers are found mainly in the products collected from the filter. The cotton-like morphology of the product collected from the filter is a consequence of their fibrous structure.

An enlarged SEM image of the radially aligned nanofibers is shown in Fig. 12(c-2). The numerous fibers grow radially to form spheres. However, no droplets are observed on the tips of the fibers. According to the EDS analysis, Si is not detected. Therefore, the mechanism for formation of AlN fibers in the alumina tube is different from that in the mullite tube. The surface of an Al particle is covered with a native oxide film, and heating causes the Al within to melt, subsequently expanding and disrupting the native oxide film. Al vapor is released from cracks on the particle surface, which reacts with N_2 , and AlN fibers are formed by vapor–solid growth. We believe that this is a rational mechanism for the formation of these fibers.

4. Conclusions

In this study, Al powder and N_2 gas were used as raw materials for the synthesis of AlN fine powders in a DTF. A lower N_2 flow rate and smaller particle size increase the residence time of the Al particles in the heated zone of the furnace, enhancing the nitridation of the Al powder. The mechanism of AlN synthesis depends on the material from which the reaction tube of the DTF is fabricated. In the case of the mullite tube, radially-aligned nanofibers with droplets on their tips are formed at 1400°C. TEM investigation revealed that Si from the mullite tube reacts with Al to form eutectic Al–Si droplets on the Al surface, which act as a catalyst for VLS growth of AlN fibers. When an alumina reactor tube is employed at 1800°C, a predominance of coarse Al particles is collected from the crucible. When Al particles agglomerate as they drop, they melt and form coarse particles. Radially aligned AlN nanofibers with no droplets on their tips are thought to form via vapor–solid growth and are easily carried along with the N_2 gas flow, resulting in their collection on the filter. This seems to suggest that the suppression of Al particle agglomeration is needed to realize the synthesis of high-purity fine AlN powders.

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