Fabrication of highly water-resistant AlN particles with hybrid α -Al₂O₃/organic layers

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The water resistance of AlN particles was improved by surface coating with hybrid α -Al₂O₃/organic layers. To maintain thermal conductivity, the higher-thermal-conductivity α -Al₂O₃ layer was designed to cover most of the AlN surface, and the lower-thermal-conductivity organic layer was formed on the remaining area. Scanning electron microscopy, energy dispersive X-ray spectrometry and thermogravimetric analyses of the particles revealed that the small amount of organic layer was filling the cracks in the α -Al₂O₃ layer. The water resistant property was evaluated by a water immersion test. The pH of water dispersing the particles with hybrid layers was less than that of water dispersing the particles coated only with α -Al₂O₃ or organic layers, which indicated that the particles with hybrid layers had improved water resistance. The particles have applications in polymer composites for insulation in electronic devices which require improved reliability.

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1. Introduction

Polymer composite materials consisting of ceramic particles and resins have been extensively investigated.^{1)–18)} The composite materials used for insulation in electronic devices are required to possess high thermal conductivity for heat dissipation.^{4),5)} Therefore, highly thermally conductive ceramic particles, such as alumina (Al₂O₃),^{3),6)–8)} boron nitride (BN),^{9)–14)} and aluminum nitride (AlN)^{14)–18)} have been widely used in these applications. Among these, AlN particles have been particularly studied because of their particularly high thermal conductivity.^{15),19)} Slack et al.¹⁹⁾ indicated that the intrinsic thermal conductivity of highly purified single AlN crystals was 319 W/(m·K), and Kume et al.¹⁵⁾ reported a value of 266 W/(m·K) for commercially available AlN particles measured with a thermal microscope.

However, AlN particles can be easily hydrolyzed in ambient conditions and immediately generate gaseous ammonia after being exposed to moisture.^{20)–22)} Therefore, water-resistant coatings are essential for AlN particles. It has been reported that these particles can be effectively protected from moisture by surface treatment with carboxylic acids, in particular, stearic acid.^{20),21)} However, the organic layers formed on the AlN surfaces by reacting with carboxylic acids may increase the thermal resistance because of their low thermal conductivities. As an alternative method to improve water-resistance, α -Al₂O₃ layers, which have higher thermal conductivity than that of the organic layers, can be formed on the AlN particle surfaces by oxidizing them at high temperatures. However, cracks and channels are often formed in the α -Al₂O₃ layers under thermal treatment because of the thermal expansion mismatch between α -Al₂O₃ and AlN.^{23),24)} As a result, the particles may be hydrolyzed due to the moisture passing through the cracks and channels.

In this work, we aimed to develop a method of applying a water-resistant coating to AlN particles, which retains their high thermal conductivity by forming hybrid α -Al₂O₃/organic layers on their surfaces. The hybrid α -Al₂O₃/organic layers were prepared by oxidizing the AlN particles to form α -Al₂O₃ layers and filling the cracks and channels formed in these layers with stearic acid, which selectively reacts with the AlN, but not with the α -Al₂O₃.

2. Experimental procedures

2.1 Sample preparation

Figure 1 is a schematic of the sample preparation processes of the AlN particles with α -Al₂O₃ layers, with organic layers, and with hybrid α -Al₂O₃/organic layers. Sintered AlN polycrystalline particles with an average diameter of 30 μ m, including a slight amount of yttria (Y₂O₃) to aid sintering (FAN-f30-TY, Furukawa Denshi Co. Ltd., Japan), were prepared (hereinafter, Particles 1). Particles 1 were then thermally treated using either a tube electric

Fig. 1. Sample preparation processes for AlN particles with α -Al₂O₃ layers, organic layers, and hybrid α -Al₂O₃/organic layers. The dashed and solid arrows indicate the thermal treating and refluxing with stearic acid, respectively. Particles 2–4 are fabricated using different equipment.

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furnace (KRM-22HH, Isuzu Seisakusho Co. Ltd., Japan) or a box electric furnace (KBF524N, Koyo Thermo Systems Co. Ltd., Japan) to form α -Al₂O₃ layers of different thicknesses. First, the tube furnace was used for the thermal treatment of the AlN particles. The AlN particles in an Al₂O₃ boat were set in the Al₂O₃ tube electric furnace, and heated up to 1200°C at 10°C/min and held at 1200°C for one hour in an air atmosphere. Consequently, α -Al₂O₃ layers were formed on the AlN particles surfaces. Hereinafter, the particles thus prepared are called Particles 2. Secondly, with the box furnace, the AlN particles were placed in two crucibles that were then put in the box electric furnace, one with a closed lid and another without a lid. Then, they were cured with the previously mentioned temperature program. As a result, two types of AlN particles with α -Al₂O₃ layers were fabricated. The particles made with a closed crucible and those with an open one are hereinafter called Particles 3 and Particles 4, respectively. After preparation, all particles (Particles 2–4) were characterized with an X-ray diffraction (XRD) apparatus (RINT 2500HL, Rigaku Co. Ltd., Japan) and observed by a scanning electron microscope (SEM, S900, Hitachi, Ltd., Japan).

Particles coated with α -Al₂O₃ layers (Particles 2, 3, and 4) were mixed with stearic acid at the weight ratio of particles/stearic acid = 50 g/1.5 g. Then, they were refluxed for three hours with dehydrated toluene in two-neck eggplant flasks while being stirred with magnetic stir bars. The resulting particles were filtered off and washed with toluene, and were dried at 120°C for two hours. The resulting particles with α -Al₂O₃/organic hybrid layers are called Particles 6, 7, and 8 (corresponding to Particles 2, 3, and 4, respectively). For reference, AlN particles coated only with organic layers (Particles 5) were also fabricated by treating Particles 1 with stearic acid applying same process conditions as previously mentioned. A thermogravimetry (TG) measurement was performed to determine the weight ratio of the organic layers. The atomic concentration of the resultant particle surfaces was analyzed using an energy dispersive X-ray (EDX) apparatus (Genesis XM2, Ametek Inc., USA).

2.2 Measurement of water-resistant property

The AlN particles were dispersed in water to examine their water-resistant properties at 60°C. The pH value of the water containing the particles was measured with a pH analyzer.

3. Results and discussion

3.1 Formation of α -Al₂O₃ layers on AlN particles

To form Al₂O₃ layers on AlN particles and to transit the layers to the α -phase, Particles 1 were thermally treated at 1200°C. Furthermore, to form α -Al₂O₃ layers of different thicknesses, Particles 2, 3, and 4 were fabricated using different furnaces and containers in anticipation that each particle would be supplied with different amount of oxygen. **Figure 2** shows the X-ray diffraction profile of the thermally treated particles (Particles 4). The diffraction peaks corresponding to AlN and α -Al₂O₃ were detected, which indicates the formation of Al₂O₃ layers on the surface of AlN particles and their transition to the α -phase under

the thermal treatment. The index to volume ratio of the oxidized α -Al₂O₃ layers and AlN cores can be estimated from the ratio between the integral intensities of the X-ray diffraction peaks corresponding to the (113) plane of the α -Al₂O₃ and the (100) plane of the AlN. **Table 1** lists the ratios between the integral intensities of the X-ray diffraction peaks corresponding to the (113) plane of α -Al₂O₃ and the (100) plane of AlN. It is obvious that the ratios were different among the particles fabricated by different methods. Thus, we concluded that α -Al₂O₃ layers with different thicknesses were successfully formed on the surfaces of the AlN particles. SEM observations were conducted to further characterize the AlN particles with α -Al₂O₃ layers fabricated using different methods. The SEM images presented in **Figs. 3(a)–3(d)** were observed at the same magnification. Figure 3(c') shows a digitally zoomed image of a part of Fig. 3(c). The facets of the un-oxidized AlN polycrystalline particles, Particles 1, seemed to be flat [Fig. 3(a)]. In comparison, the facets of all the thermally treated particles with α -Al₂O₃ layers became roundish with rough surfaces [Figs. 3(b)–3(d)]. Narrow traces (indicated by arrows) were also observed on the surfaces of Particles 2 (Fig. 2), which had the least amount of α -Al₂O₃ among the thermally treated particles. These traces may develop into cracks after additional oxidation in a more oxygen-rich atmosphere. In the particles with higher α -Al₂O₃ content (Particles 3 and 4), cracks and channels were found on the particle surfaces. The cracks in the surfaces of Particles 3 were quite narrow, and the channels were minor [Fig. 3(c')], although in Particles 4, relatively wide cracks and major channels were observed [Fig. 3(d)]. These results strongly suggest that the cracks and channels extended in the α -Al₂O₃ layers were developed by oxidation. The generation and development of cracks and channels were considered to be derived from the differences between the thermal expansion of the α -Al₂O₃ oxidized layers and that of the AlN.

The water-resistant properties of un-treated and thermally treated particles were examined. The pH values of the water dispersing Particles 1–4 were measured at 60°C while being stirred with a magnetic stir bar, are shown in **Fig. 4**. The pH of the water dispersing Particles 1 increased to over 10 after one hour, which is thought to be due to the reaction of the surfaces of the AlN particles with the water. Consequently, ammonium gas

Fig. 2. X-ray diffraction pattern of thermally treated particles (Particles 4).

Table 1. Equipment used for thermally treating the particles and the ratios between the integral intensities of the X-ray diffraction peaks corresponding to the (113) plane of α -Al₂O₃ and the (100) plane of AlN estimated from the X-ray diffraction patterns of Particles 2, 3, and 4

Particles	Equipment used	Ratio between integral intensities of X-ray diffraction peaks corresponding to the (113) plane of α -Al ₂ O ₃ and the (100) plane of AlN (α -Al ₂ O ₃ /AlN).
2	Al ₂ O ₃ boat in tube furnace	0.0057
3	Closed crucible in box furnace	0.030
4	Open crucible in box furnace	0.49

Fig. 3. SEM images of (a) un-oxidized particles (Particles 1), (b) particles oxidized using a tube furnace (Particles 2), (c) using a closed crucible in a box furnace (Particles 3), and (d) using an open crucible in a box furnace (Particles 4). Image (c') is a digitally zoomed section of (c). The arrows in (b) emphasize the traces.

Fig. 4. Variations in pH of water dispersing Particles 1–4 measured at 60°C while stirred with a magnetic stir bar. The filled circles stand for the pH of the water including un-oxidized particles (Particles 1). The open triangles and circles and squares stand for Particles 2, 3, and 4, respectively, which have α -Al₂O₃ layers.

was generated, and this gas increased the OH⁻ in the water dispersing the un-treated particles.^{20)–22)} The pH of the water dispersing Particles 2–4 increased to over 9 after two hours. The pH increment of the water dispersing Particles 2–4 was less than that of the water dispersing Particles 1, which may imply that the AlN outcrop area can be reduced by thermal treatment. However, the effect was not sufficient to prevent a reaction with the water. This indicates that the α -Al₂O₃ layers formed by the thermal treatment included cracks and channels that connected to the AlN.

3.2 Fabrication of particles with hybrid α -Al₂O₃/organic layers

The particles with hybrid α -Al₂O₃/organic layers (Particles 6, 7, and 8) were fabricated by the reaction between stearic acid and

Fig. 5. Thermogravimetric analysis curve for organic layers on Particles 7.

the AlN in the cracks and channels. The product of this reaction interrupts the reaction between the underlying AlN surface and moisture passing through the cracks and channels. **Figure 5** shows a TG chart, which shows mass depletion during the increase in temperature of the fabricated particles with hybrid α -Al₂O₃/organic layers. The weight of the particles decreased by approximately 0.05% in the temperature range between 200 and 400°C. This result indicates that 0.05 weight % of the whole particles was composed of the organic layer which was formed with stearic acid. Moreover, it was expected that the organic layers only existed on the AlN outcrop in the α -Al₂O₃ cracks because stearic acid can react only with the AlN but not with the α -Al₂O₃ and because stearic acid physically absorbed on the α -Al₂O₃ surface was removed by toluene rinse. The increase in particle weight was observed with a rise in temperature over 500°C, which may be derived from the formation of oxidation layers on the particle surfaces expanded into the AlN due to thermal agitation.

Fig. 6. EDX elemental analysis of the surface of Particles 7.

Table 2. Composition of the surface of Particles 7 estimated by the EDX spectrum

Elements	Weight%	Atom%
C	4.3	8.0
O	30.4	42.5
Al	57.5	47.6
Y	7.7	1.9

Figure 6 shows the result of the EDX measurement of Particles 7. Sharp peaks for oxygen at 525 eV, aluminum at 1484 eV, and yttrium at 2079 eV and a shoulder peak for carbon at 277 eV were detected. The detected oxygen is assumed to be derived from the oxidized α -Al₂O₃ layers on the particles, the aluminum from the AlN and oxidized α -Al₂O₃ layers, the yttrium from the sintering AlN grain boundaries near the particle surfaces, and the carbon from the organic layers in the cracks. Table 2 lists the compositions of the detected elements quantitatively estimated using the EDX spectra with a ZAF (atomic number, absorption, and fluorescence) correction method.²⁵⁾ It was revealed that the α -Al₂O₃ layers were occupying most of the area and that the sintering aids and the organic layers were slightly apparent on the particle surfaces, which suggests the organic layers existed only in the cracks and channels, not on all of the particle surfaces. This may indicate that the stearic acid reacted only with the AlN under-layers, and not with the α -Al₂O₃ layers, as we had previously speculated.

3.3 Results of water resistance analysis

Figure 7 shows the changes in the pH of the water dispersing AlN particles coated only with the organic layers (Particles 5) and AlN particles with the hybrid α -Al₂O₃/organic coating (Particles 6, 7, and 8) at 60°C. The pH of the water dispersing AlN particles with organic layers remained less than 7 after a one-hour immersion, but it increased to 7.7 after two hours. It is presumed that the organic layers on the particle surfaces may be removed from the AlN under-layers by thermal agitation and by particle collision during water immersion under stirring with a magnetic stir bar. The pH of the water dispersing the AlN particles with hybrid layers remained at a smaller value than that of the water dispersing the particles coated only with the organic layers.

Fig. 7. Variations in the pH of water dispersing Particles 5–8 measured at 60°C while being stirred with a magnetic stir bar. The filled circles stand for the pH of the water including for particles with organic layers only (Particles 5). The open triangles, circles, and squares stand for Particles 6, 7, and 8, respectively, which have hybrid α -Al₂O₃/organic layers.

Especially, the pH of the water dispersing Particles 7 and 8 remained below 7. These results suggest that the hybrid coating was much more stable than the coating composed only of the organic layers. The organic layers of the hybrid coating existed in the cracks and channels of the α -Al₂O₃ layers. Therefore, we believe that the organic regions in the hybrid coating were protected by the surrounding α -Al₂O₃ layer from possible damage and delamination, which may have been caused by agitation and collision during the water immersion process. The pH of the water dispersing Particles 6 increased to 7.5 after two hours, which may be caused by insufficient volume of the α -Al₂O₃ to protect the AlN from particle collisions.

Moreover, the AlN particles with hybrid α -Al₂O₃/organic layers can be expected to have a higher thermal conductivity than that of the AlN particles coated only with the organic layers because the α -Al₂O₃ layers have a higher thermal conductivity than that of the organic layers.

4. Summary

We aimed to improve the water resistance property of AlN particles while maintaining their high thermal conductivity. We fabricated the water resistant AlN particles with hybrid α -Al₂O₃/organic layers by means of thermal treatment and reflux with stearic acid. The resultant particles had higher water resistance than particles coated only with α -Al₂O₃ layers or only with organic layers. Moreover, for maintaining thermal conductivity, the particles were designed so that the α -Al₂O₃ layers, which have higher thermal conductivity than general organic materials, were formed on most of the AlN particles surface areas and the organic layers were formed in the cracks of the α -Al₂O₃ layers. Therefore, the resultant particles can be expected to have a higher thermal conductivity than the AlN particles with organic layers only.

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