Effect of amounts and types of silicon nitride on thermal conductivity of $\text{Si}_3\text{N}_4$/epoxy resin composite

Akihiro SHIMAMURA, Yuji HOTTA, Hideki HYUGA, Naoki KONDO and Kiyoshi HIRAO

National Institute of Advanced Industrial Science and Technology (AIST), 2266–98 Shimo-Shidami, Moriyama-ku, Nagoya 463–8560, Japan

Thermal conductive ceramic/resin composites are necessary for thermal management in order to improve the reliability of high-performance products in various industrial fields. The present study created composites consisting of silicon nitride ($\text{Si}_3\text{N}_4$) particles and epoxy resin by imbedding the particles into the resin matrix. Two common types of $\text{Si}_3\text{N}_4$ were applied in this work. $\alpha$ phase ($\alpha$-Si$_3$N$_4$) and $\beta$ phase ($\beta$-Si$_3$N$_4$) silicon nitride were loaded with epoxy resin. The effect of $\text{Si}_3\text{N}_4$ type on the thermal conductivity of composites was investigated by varying the $\text{Si}_3\text{N}_4$ particle content. For composites below 50 vol.-% $\text{Si}_3\text{N}_4$, there was almost no difference in thermal conductivity between equivalently loaded $\alpha$-Si$_3$N$_4$ or $\beta$-Si$_3$N$_4$/epoxy composites. However, for $\text{Si}_3\text{N}_4$ contents exceeding 50 vol.-%, the $\beta$-Si$_3$N$_4$/epoxy composites showed higher thermal conductivities relative to the $\alpha$-Si$_3$N$_4$/epoxy composite. The relative difference in thermal conductivities between the $\beta$-Si$_3$N$_4$ and $\alpha$-Si$_3$N$_4$ epoxy composites ($\beta$-Si$_3$N$_4$/ $\alpha$-Si$_3$N$_4$) increased to 1.6 times at 68 vol.-% of $\text{Si}_3\text{N}_4$ content.

Key-words : Silicon nitride, Composite, Thermal conductivity, Epoxy resin

1. Introduction

Thermally conductive ceramic/polymer composites are expected to open up new possibilities in various industrial fields as they are light weight and have superior heat dissipation capabilities, corrosion resistance, and flexibility. In particular, heat dissipation in electronic devices has been becoming increasingly important because packing densities of these devices are increasing year by year, resulting in the generation of great deal of heat in a small space. To deal with the heat, the primary requirement are to use electrically insulating materials that have high thermal conductivities necessary for heat dissipation. Epoxy resin is generally used as an insulating material for general electronic devices. The thermal conductivity of epoxy resin is very low [about 0.20 W/(m·K)]. It is known that the thermal conductivity of resins can be enhanced by adding ceramic fillers, and many reports have been published with the aim of enhancing the thermal conductivity of resins by adding of alumina ($\text{Al}_2\text{O}_3$), carbon fibers, nanotubes, silicon carbide, and nitride fillers. Among them aluminum nitride (AIN) and boron nitride (BN) have proven to be very effective for the improving thermal conductivity. However, in case of AIN fillers, drawbacks such as high reactivity with moisture cannot be disregarded for producing composites with high thermal conductivity. The BN filler has great potential for filler material with polymer material because of their high thermal conductivity and excellent resistance to oxidation and chemical corrosion. The BN is commercially available in amorphous (a-BN) and crystalline forms (hexagonal and cubic). The most stable crystalline form is hexagonal BN (h-BN), which has a layered structure like graphite. The dispersion of the h-BN fillers into the polymer matrix is an important issue for the composite fabrication. This issue has been sorted out by functionalized the surface of the h-BN with organic surfactants. Moreover, Sato et al. reported that uniform dispersion of h-BN was achieved by using low-aspect ratio h-BN and the composite material showed high thermal conductivity and flexibility. Thus, the h-BN has been studied as filler material by many researchers. On the other hands, silicon nitride filler has not been studied as much as h-BN filler even though silicon nitride also has high thermal conductivity and chemical stability. Silicon nitride ($\text{Si}_3\text{N}_4$) ceramic is well-known as structural ceramic because of its high strength, high fracture toughness, chemical stability, and high refractoriness. Recently, silicon nitride ceramic has attracted a great deal of attention as high thermal conductivity substrate due to its unique combination of excellent mechanical properties and high thermal conductivity. There are two crystalline phases in $\text{Si}_3\text{N}_4$; $\alpha$ and $\beta$, which are considered to be low- and high-temperature phases, respectively. Theoretical thermal conductivities of $\alpha$- and $\beta$-Si$_3$N$_4$ single crystals were estimated by Hirotsuki et al. In their estimation thermal conductivities of $\alpha$- and $\beta$-Si$_3$N$_4$ single crystal along the $a$ and $c$ axes are 105 W/(m·K) and 225 W/(m·K) for $\alpha$-phase, and 170 W/(m·K) and 450 W/(m·K) for $\beta$-phase, indicating that $\beta$-Si$_3$N$_4$ has higher thermal conductivity than $\alpha$-Si$_3$N$_4$. Thermal conductivity of $\beta$-Si$_3$N$_4$ crystals is high, at about 260 W/(m·K), calculated from a simple arithmetic mean in the three axis directions.

Intensive research has been undertaken for improving the thermal conductivity of sintered silicon nitrides. Recently, Zhou et al., have succeeded in fabricating $\beta$-Si$_3$N$_4$ silicon nitride ceramic with high thermal conductivity of 177 W/(m·K) by post-sintering of reaction bonded silicon nitride. However, there have been smaller number of report on the application of Si$_3$N$_4$ as a filler material for ceramic/resin composites compared with other ceramics filler. Furthermore, it has not known how the silicon nitride types with different thermal conductivity affect to thermal conductivity of composite material. In this investigation, we examined the effects of the types of $\text{Si}_3\text{N}_4$ and the loading amounts of $\text{Si}_3\text{N}_4$ on the thermal conductivities of resulting composites with epoxy resin.
2. Experimental procedures

α-Si₃N₄ (SN-9, α-phase > 90%, Denki Kagaku Kogyou Co. Ltd., Japan) and β-Si₃N₄ (SN-F1, β-phase > 95%, Denki Kagaku Kogyou Co. Ltd., Japan) powders were used as a ceramic filler in the present work. The lattice oxygen content of the α-Si₃N₄ and β-Si₃N₄ filler were 0.59 ± 0.02 and 0.39 ± 0.02 wt %, respectively. The average particle size (D₅₀) of these commercial α- and β-Si₃N₄ powders measured by a laser-diffraction particle size analyzer (Horiba LA-920, Horiba Ltd., Japan) were 5.9 and 3.5 μm, respectively.

It is well known that the filler size is an important factor that affects the thermal conductivity of ceramics/resin composites. In order to exclude the effect of particle size, the α-Si₃N₄ powder was ball-milled in ethanol for 2 h using Si₃N₄ balls (10 mm diameter) and a Si₃N₄ pot. The β-Si₃N₄ filler was used as received. The milled α-Si₃N₄ is hereafter referred to as "α-SN filler" and the as-received β-Si₃N₄ is hereafter referred to as "β-SN filler". Mixtures were prepared by mixing the Si₃N₄ fillers with an epoxy resin of bisphenol-A (EPICRON855, DIC Co. Ltd., Japan) and a curing agent [JER CURE ST12 (aliphatic poly amine), Mitsubishi Chemical Co. Ltd., Japan]. The resultant mixtures were cured at 120°C for 2 h in a metal mold under 47.8 MPa in order to fabricate composites. The Si₃N₄ filler contents were varied from 20 to 70 vol.%.

Crystal phases of the Si₃N₄ fillers were determined by X-ray diffraction (XRD: RINT-2500, Rigaku Co. Ltd., Japan). The morphology of the fillers and composite were evaluated by scanning electron microscopy (SEM: JSM-5600, JEOL Ltd., Japan). SEM images of the filler were obtained with secondary electron. SEM images of the composite material were obtained by background-scatter electron (BSE). The amount of oxygen impurities dissolved in the Si₃N₄ particles, or lattice oxygen content, was determined by the method reported by Kitayama et al. using a hot-gas extraction analyzer (Model TC-436 and EF-400, LECO Co., USA). In this method, the sample was placed in a graphite crucible, followed by heating to 2500°C in 5 min in a flowing argon atmosphere. The amount of released oxygen from the specimen was recorded as a function of temperature. Oxygen released as a function of temperature exhibited two peaks. The first peak at a lower temperature was ascribed to oxygen released from the oxidized surface of Si₃N₄ particles, and the second peak at a higher temperature was ascribed to oxygen released from the Si₃N₄ crystal lattice. The lattice oxygen content was determined by Gaussian analysis. Three measurements were performed for each sample.

The relative densities of the composites were measured by Archimedes’ method. Thermal conductivity measurements of the composites (sample size, diameter: 40 mm, thickness: 3 mm) were performed by the heat flow method (EKO HC-110, Eikoseiki, Japan). Thermogravimetric (TG) analyses of the composites (TG, TG8120, Rigaku Co., Japan) were carried out under air with a heating rate of 10°C per minute from room temperature to 1000°C in order to determine the precise amount of Si₃N₄ filler. Weight loss in the composite owing to burn-out of the resin was observed until 600°C. The content of Si₃N₄ filler was calculated from the residual weight at 1000°C

3. Results and discussion

3.1 Characteristics of Si₃N₄ fillers

Figure 1 shows XRD patterns of the α-SN filler and the β-SN filler. The XRD patterns of α-SN and β-SN filler show the α-Si₃N₄ and β-Si₃N₄ as a major phase, respectively. A very small amount of β-Si₃N₄ and α-Si₃N₄ phase can be observed in the α-Si₃N₄ filler and β-Si₃N₄ fillers, respectively. Figure 2 shows the particle size distribution of the SN fillers. The particle size distribution of the as-received α-Si₃N₄ powder ranged from 0.5 to 60 μm, with a mean particle size, D₅₀, of 5.9 μm. After milling the range shifted to smaller sizes, ranging from 0.2 to 20 μm, with a D₅₀ of 3.5 μm. The particle size of the β-SN filler ranged from 0.2 to 20 μm, with a D₅₀ of 3.6 μm. Thus the particle size distribution and average particle size of the α-SN filler was adjusted to match that of the β-SN filler. Figure 3 represents SEM images of the as-received α-Si₃N₄ powder (A), the α-SN filler (B), and the β-SN filler (C). The larger particles observed in the as-received α-Si₃N₄ powder were crushed into smaller particles on image (B). Comparing particles on image (B) and (C), both particles also have random shape and similar particle sizes.

3.2 Characteristics of composites

Figure 4 shows the relative density of the α-SN and β-SN filler-loaded composites as a function of the Si₃N₄ content. The relative density of the α- and β-SN filler-loaded composites at
A decrease of relative density was due to incomplete molding of the composite, ascribed to the higher loading of SN fillers. Therefore, only the composites with SN filler content lower than 68 vol.% were discussed in terms of thermal conductivity.

Figure 5 shows the thermal conductivities of the α- or β-SN filler-loaded composites as a function of the filler content from 20 to 68 vol.%. Thermal conductivities of the as-received α-Si3N4 loaded composites with loading above 50 vol.% are also shown in the Fig. 5. The thermal conductivity of the α- and β-SN filler-loaded composite gradually increased until 50 vol.%. The thermal conductivity of the α- and β-SN filler-loaded composite at 50 vol.% was 1.38 and 1.41 W/(m·K), respectively. Both composites type showed similar thermal conductivity until 50 vol.%. The thermal conductivity increased rapidly at loadings above 50 vol.% Notably, the β-SN filler-loaded composite showed a significant increase in thermal conductivity compared with the α-SN filler-loaded composite. The thermal conductivities of β-SN filler loaded composites were 3.2 W/(m·K) at 60 vol.%, 5.1 W/(m·K) at 65 vol.% and 6.0 W/(m·K) at 68 vol.%. In contrast, the thermal conductivity of the α-SN filler loaded composite were 2.6 W/(m·K) at 60 vol.%, 3.5 W/(m·K) at 65 vol.% and 3.8 W/(m·K) at 68 vol.%, indicating less pronounced increase, compared with the β-SN filler-loaded composites. The as-received α-Si3N4 filler-loaded composites showed similar thermal conductivities to the α-SN filler loaded composite despite the large size of the as-received α-Si3N4. Therefore, it was concluded that particle size of the α-Si3N4 filler did not have a significant effect on the thermal conductivity of composite materials.

The thermally conductive behavior of both composite types can be divided into two regions: above and below 50 vol.% of SN filler content. In the region below 50 vol.% filler content (1st Region), the thermal conductivity of both composites types were similar to each other and exhibited relatively low values. Those thermal conductive values were nearly in line with the estimated curve of Bruggeman’s model. (inset of Fig. 5). The Bruggeman model was based on the hypothesis that spherical particles homogeneously distribute in a matrix without contact between particles inside the matrix. In this model, thermal conductivity of a composite is described by the following equation

\[ 1 - \left( \frac{\varphi}{100} \right) = \left[ (\lambda_c - \lambda_1) / (\lambda_1 - \lambda_2) \right] \times (\lambda_1 / \lambda_c)^{1/3} \]
where $\lambda_f$ is the thermal conductivity of the filler [W/(m·K)], $\lambda_r$ is the thermal conductivity of the resin [W/(m·K)], $\lambda_c$ is the thermal conductivity of the composite [W/(m·K)], and $\varphi$ is the content of the filler (vol.%). Thermal conductivity of the epoxy resin, $\lambda_r$, is per as a simple arithmetic mean in the three axis directions based on the report by Hiroasaki et al.$^{15}$ The good agreement between the thermal conductivities between both 50 vol.% indicates that the Si$_3$N$_4$ fillers are mostly homogeneously distributed. The thermal conductivity of the resulting composite materials was minimally affected by the SN filler. Since the epoxy resin has low thermal conductivity [about 0.2 W/(m·K)] compared with the SN fillers, the heat flow through SN filler was hindered by the epoxy resin below 50 vol.%, which the SN fillers were dispersed in epoxy resin matrix. Similar results were also reported in other filler-material/epoxy composites, including alumina, silica, and aluminum nitride.$^{25}$ For example, Bujard et al. reported an alumina/epoxy resin composite with 50 vol.% alumina content with thermal conductivity of around 1.5 W/(m·K),$^{22}$ while Hsieh et al. reported an AlN/epoxy composite at 45 vol.% of AlN content with a thermal conductivity of around 1.3 W/(m·K).$^{25}$

Differences in thermal conductivity were clearly observed in the region above 50 vol.% (2nd region). Both the $\alpha$- and $\beta$-SN filler-loaded composites showed a rapid increase in thermal conductivity in the 2nd region. This rapid increase in thermal conductivity between $\alpha$- and $\beta$-SN filler-loaded composites was caused by formation of Si$_3$N$_4$ percolation networks of particles. A percolation network is a phenomenon in which the percolation network of the SN composite. Since heavy atom with high atomic number scatters electron stronger than the light ones, it is well known that back-scatter electron’s image provides information of composition. The $\beta$-SN filler and epoxy resin were represented as whitish and blackish color on the SEM image with BSE. Particle size of the whitish particle at 40 and 60 vol.% were less than 10 μm, which agreed with particle size distribution result. The $\beta$-SN fillers were dispersed in the matrix at 40 vol.%. By contrast, the $\beta$-SN fillers were continually contacted with each other in the matrix at 60 vol.%, indicating formation of thermally conductive network between the $\beta$-SN fillers. Thus, the backscatter SEM results also explained that the percolation network of the SN fillers was formed in the 2nd region. In comparing the thermal conductivity between both composite types, a difference in thermal conductivity was clearly observed, which increased with increasing SN filler content. The ratios between the thermal conductivities of composites ($\beta$-Si$_3$N$_4$/$\alpha$-Si$_3$N$_4$) were 1.0 (at 50 vol.%), 1.2 (at 60 vol.%), 1.4 (at 65 vol.%) and 1.6 (at 68 vol.%). The thermal conductivity of the composite materials was strongly affected by the thermal conductivity of the Si$_3$N$_4$ filler type because the heat flows preferentially through the Si$_3$N$_4$ particles percolated network form. Since single crystalline $\beta$-Si$_3$N$_4$ has a higher intrinsic thermal conductivity than single crystalline $\alpha$-Si$_3$N$_4$, it is practically observed that the composites with $\beta$-SN filler have higher thermal conductivity than those with $\alpha$-SN filler.

It has been reported that thermal conductivity of crystalline silicon nitride is influenced by the lattice oxygen content.$^{19}$ Kitayama et al. reported a correlation between lattice oxygen content and thermal resistivity (the inverse of thermal conductivity) of crystalline $\beta$-Si$_3$N$_4.$$^{20}$ The lattice oxygen content of the $\beta$-Si$_3$N$_4$ filler is $0.39 \pm 0.03$ wt.%. Comparing this value with Kitayama’s results, it is speculated that the thermal conductivity of the $\beta$-SN composite is around $100$ W/(m·K). Lattice oxygen of the $\alpha$-SN filler was $0.59 \pm 0.02$ which is slightly higher than the lattice oxygen of the $\beta$-SN filler. The higher content of lattice oxygen in the $\alpha$-SN filler may be another reason why the $\alpha$-SN filler-loaded composites had lower thermal conductivities than the $\beta$-SN filler-loaded composite. Thus, the lattice oxygen content could also be a factor of improving thermal conductivity of SN filler-loaded composite, especially above 50 vol.% of SN-filler content. Based on this, it would be expected that reducing the content of lattice oxygen in $\beta$-SN fillers could further increase the thermal conductivity of the $\beta$-SN filler-loaded composite in the high SN-filler content region.

4. Conclusion

In this study, we demonstrated how $\alpha$- and $\beta$-SN fillers affect the thermal conductivity of composite materials. The behavior of thermal conductivity of the $\alpha$- and $\beta$-SN loaded composites can be divided into two regions above and below 50 vol.%. Below 50 vol.% Si$_3$N$_4$ filler content, there is almost no difference in thermal conductivities between the $\alpha$- and $\beta$-SN loaded composites. This is because epoxy resin interrupted the heat flow between the SN filler particles in the composite material. Above 50 vol.%, the thermal conductivity of both SN composites showed rapid increase due to formation of percolation network of the SN filler in the composite. The $\beta$-SN loaded composite exhibits a maximum of 1.6 times higher thermal conductivity than its $\alpha$-SN loaded counterpart. This significant enhancement in thermal conductivity of the $\beta$-SN loaded composite is because the $\beta$-Si$_3$N$_4$ has higher theoretical thermal conductivity than the $\alpha$-Si$_3$N$_4$ and this thermal conductivity difference between the $\alpha$-SN and the $\beta$-SN is clearly appeared on the composite by rapid
increase of thermal conductivity above 50 vol.%. For further improvement of thermal conductivity of the composite, it would be expected that reducing the lattice oxygen in β-SN filler also improve thermal conductivity of the composite, especially above 50 vol.% of SN-filler content.

References
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