Morphological Effect of Second Phase on the Thermal Conductivity of AlN Ceramics

Weon-Ju Kim, Do Kyung Kim, and Chong Hee Kim

Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, Taekon 305-701, Korea

The effect of the morphology of second phases in sintered microstructure on the thermal conductivity of AlN ceramics was investigated. When an Y$_2$O$_3$-doped AlN specimen was cooled down slowly at a rate of 3°C/min after sintering at 1850° or 1900°C, the second phases were concentrated in the corners of the AlN grains by an increase of dihedral angle during cooling. On the other hand, the fast-cooled specimen at a rate of 60°C/min showed a different structure of the second phases interconnected through the triple-grain junctions. The specimen with isolated second-phase morphology showed a higher thermal conductivity than those with interconnected second-phase morphology. The measured thermal conductivity of the specimens with different morphologies of the second phases agreed well with the calculated one derived from modeled microstructures. From the comparison of the measured and calculated thermal conductivity, it was shown that the thermal conductivity of the specimen with interconnected second-phase morphology decreased steeply with an increase of the amount of the second phases, assuming the content of lattice oxygen to be constant. However, the thermal conductivity of the specimen with isolated second-phase morphology was rather insensitive to an increase of the amount of the second phases.

I. Introduction

The high thermal conductivity of AlN, coupled with its high electrical resistivity and nontoxic nature, makes it a very promising material for electronic substrates. The thermal conductivity of pure AlN single crystal was calculated to be 319 W/(m·K) along the c-axis. Polycrystalline AlN, however, has been reported to have a thermal conductivity ranging from 100 to over 200 W/(m·K). The thermal conductivity of AlN ceramics is greatly affected by an impurity level, especially oxygen in the raw powder. Slack reported that oxygen is dissolved in the AlN grain and substitutes for the nitrogen atom. A single aluminum vacancy is formed by the substitution of three oxygen atoms to satisfy the charge neutrality condition. It is widely accepted that the aluminum vacancy mainly contributes to the scattering of phonons and hence lowers the thermal conductivity of dense AlN ceramics.

In order to enhance the densification of AlN ceramics, sintering aids are added; the most common additives are Y or Ca compounds. The sintering aids form liquid phases (yttrium aluminate in case of the Y compound) through the reaction with the oxide layer which inevitably exists on the surface of AlN powder. Formation of the eutectic phases between the additive and the surface oxide layer prevents the oxygen from diffusing into the AlN grains by trapping it in grain-boundary phases during sintering. Accordingly, the addition of sintering aids is essential to obtain highly thermal-conductive AlN ceramics, but it leads to residual grain-boundary phases which will adversely affect the thermal conductivity of polycrystalline AlN. Different microstructures of the grain-boundary phases have been presented, depending on the oxygen content of AlN raw powder, the additive content, the sintering condition, and so on. It is difficult to clarify the effect of the amount and morphology of the second phases on the thermal conductivity of AlN ceramics because the purification of the AlN lattice may occur simultaneously with the microstructural change.

The purpose of the present study was to examine the effect of second-phase morphology on the thermal conductivity of AlN ceramics. Specimens with interconnected or isolated second phases were obtained by control of the cooling rate after sintering. The measured thermal conductivity of the specimens with different second-phase microstructures was compared with the theoretical one calculated from modeled microstructures.

II. Experimental Procedure

1. Sample Preparation

The starting materials were commercially available AlN powder (Grade F, Tokuyama Soda, Tokyo, Japan) and Y$_2$O$_3$ powder (Grade Fine, Hermann C. Starck, Berlin, Germany) as a sintering aid. The Y$_2$O$_3$ powder was added to the AlN powder in amounts ranging between 2 and 8 wt% and the mixture was wet-mixed for 12 h in a ball mill using 2-propanol as a liquid medium. After mixing, the slurry was dried in a domestic microwave oven and dried completely in a vacuum oven at 60°C. The dried powder was shaped into 16 mm diameter by uniaxial pressing followed by cold isostatic pressing at 200 MPa. The compacts were placed in a covered BN crucible which contained a powder bed of BN. The specimens were then sintered at temperatures between 1800° and 1900°C for 2–4 h in a nitrogen atmosphere in a graphite resistance furnace (Astro, Thermal Technology, Santa Barbara, CA).

2. Characterization

Thermal diffusivity at room temperature was measured by the laser flash method with a glass-Nd laser and an InSb infrared sensor. The precision of this apparatus is believed to be ±3%. Typical sample dimensions were 12 mm diameter and 2–3 mm thickness, and both sides of the specimens were sputter-coated with gold to a thickness of 0.1 μm. A thin layer of colloidal carbon was spray-deposited onto the gold layers to enhance the absorption of the laser pulse and the emissivity of the rear surface of the specimen. The thermal conductivity was calculated from the equation \( K = C \cdot \rho \cdot d \), where \( C \) is the heat capacity (718 J/kg·K), \( \rho \) is the density, and \( d \) is the thermal diffusivity of the specimen. The reported thermal conductivity is an average of three measurements.
The crystalline phases present in the sintered samples were identified by X-ray diffractometry (XRD) with CuKα radiation. The microstructures were examined on the fracture surfaces of the sintered pellets using scanning electron microscopy (SEM). The volume fraction of the second phases was determined on the polished surfaces using an image analyzer attached to the SEM. The dihedral angle at the intersection of the second phase and the grain boundary was measured on several TEM micrographs. About 50 measurements were made to determine the dihedral angle. The TEM samples were prepared according to the general ceramographic technique.

Selective hot-gas extraction analysis (TC 436, Leco, St. Joseph, MI) was used to determine the oxygen concentration dissolved in the AlN lattice. The procedure was analogous with the method reported by Thomas and Müller. The sintered samples were crushed in a mortar and pestle, and the fragments were passed through a 325 mesh sieve. It has been reported that the quantitative analysis of the lattice oxygen was reproducible for fragment sizes smaller than 100 μm. The fragments were mixed with an equal amount of graphite powder (No. 501–073, Leco) in order to facilitate the carbothermal reduction of the surface oxide phases. The mixture was put in a tin capsule and heated to about 3000°C at a rate of 360°C/min in a graphite crucible. The oxygen released in the form of CO with a carrier gas of He was oxidized by CuO at 600°C to CO₂ and detected by an IR absorption cell. Three measurements were made to determine the concentration of the lattice oxygen, and the standard deviation was well within ±0.03 wt%.

III. Results and Discussion

1. Morphological Change of Second Phases during Cooling

Figure 1 shows the typical microstructures of the AlN specimens sintered at 1800°C to 1500°C for 2 h. The specimens were cooled at a rate of 25°C/min after sintering. When sintered at 1800°C, the secondary phases were isolated at the corners of the AlN grains and the AlN grains showed sharp grain edges. On the other hand, the second phases in the specimens sintered at 1850°C became more wetted and were present in elongated prisms along the triple-grain junctions. From the microstructural point of view, it is intuitively expected that the isolated second phase is less harmful in heat conduction than the interconnected second phase. However, a higher sintering temperature is expected to be more beneficial to the diffusional process for the purification of the AlN grains. In addition, the interconnected structure of the second phases as shown in Fig. 1(b) provides a shorter diffusion distance for the removal of oxygen.
within the AlN grains to the grain-boundary phases. In liquid-phase-sintered materials, one of the factors determining the morphology of the second phases is the ratio of the solid–solid interfacial energy to the solid–liquid one. If the microstructural difference shown in Fig. 1 was due to the difference in the ratio of the interfacial energies with temperature, the morphology of the second phase could be changed into an isolated structure by the control of the cooling rate after sintering.

The specimens doped with 4 wt% Y₂O₃ were cooled at different rates (Fig. 2) after sintering at 1850°C or 1900°C in order to explore the morphological dependence of the second phases on the cooling rates. Fast-cooled specimens with the thermal history of Fig. 2(a) had the interconnected second phases as shown in Figs. 3(a) and (b). Microstructures of the specimens heat-treated through the thermal history of Fig. 2(b) are shown in Figs. 3(c) and (d). The second phases were concentrated to the corners of the AlN grains and isolated from one another in the slow-cooled specimens.

The morphology of the grain-boundary phases is known to be a function of dihedral angle and volume fraction of the second phases. Figure 4 and Table I show the second phases present and their volume fractions, respectively, for the specimens cooled at different cooling rates after sintering at 1900°C. At the same sintering condition (1900°C, 2 h), different cooling rates did not result in a significant change of the composition of the second phase, although the peak intensity of the YAlO₃ phase was slightly lower in the case of the slowly cooled specimen (Figs. 4(a) and (b)). The second phase of the specimen fast-cooled after sintering at 1900°C for 2.5 h consisted of Y₃Al₂O₆ phase only. And the volume fractions of the second phases did not show any large difference with cooling rates, as depicted in Table I. It can be explained from these results that the morphological difference of the second phases between the slow-cooled and the fast-cooled specimens was not caused by the change of the composition or the volume fraction of the second phases.

Figure 5 shows TEM micrographs of the fast-cooled (Fig. 5(a)) and the slow-cooled (Fig. 5(b)) specimens after sintering at 1900°C for 2 h. The fast-cooled specimen had a smaller dihedral angle than the slow-cooled one. The dihedral angle measured on TEM micrographs were 70.0° (±18.6°) and 117.5° (±11.9°) for the fast-cooled and the slow-cooled specimens, respectively. It is well known that when the dihedral angle is greater than 120°, the second phase forms isolated pockets at the grain corners, and when the dihedral angle is between 60 and 120°, the second phase penetrates along the edges of three grains. If one assumes an isotropic interfacial energy, the dihedral angle, Ψ, can be expressed according to the familiar relation

\[
\cos \frac{\Psi}{2} = \frac{1}{2} \frac{\gamma_{ss}}{\gamma_{sl}}
\]

where \(\gamma_{ss}\) is the grain-boundary energy and \(\gamma_{sl}\) the solid–liquid interfacial energy. From Eq. (1) it can be seen that the dihedral angle increases as the ratio \(\gamma_{ss}/\gamma_{sl}\) decreases. And the interfacial energies are dependent on temperature by the following relations for an ideal case:

\[
\frac{\partial \gamma_{ss}}{\partial T} = -S_{ss}
\]

\[
\frac{\partial \gamma_{sl}}{\partial T} = -S_{sl}
\]

Fig. 3. SEM micrographs of the AlN–4 wt% Y₂O₃ specimens (a and b) fast-cooled and (c and d) slow-cooled after sintering at (a and c) 1850°C and (b and d) 1900°C for 2 h.
where $S_{ss}$ and $S_{sl}$ are the entropies of the solid–solid and the solid–liquid interfacial energies, respectively. The entropy of the solid–liquid interface is generally expected to be larger than that of the solid–solid one. Therefore, lowering the temperature will lead to the decrease of the ratio $\gamma_{ss}/\gamma_{sl}$, and hence the increase of the dihedral angle. On the basis of this relationship between the interfacial energy and the temperature, it can be explained that the isolated structure of the second phases in the slow-cooled specimens is attributed to the decrease of $\gamma_{ss}/\gamma_{sl}$ during cooling. In the case of the fast-cooled specimens, the morphological change of the second phases required to satisfy the equilibrium dihedral angle, which increases with lowering the temperature, might be kinetically limited due to the increase of the viscosity of the liquid phase. This will result in the frozen-in structure of second phases.

In order to verify above explanation, the fast-cooled and the slow-cooled specimens after sintering at 1900°C for 2 h were reheated to 1900°C with an isothermal holding period of 10 min and cooled at an inverse rate. The specimen, which had been sintered at 1900°C for 2 h and subsequently fast-cooled (60°C/min), was heat-treated again at 1900°C for 10 min and cooled at a rate of 3°C/min. The microstructure of this sample is depicted in Fig. 6(a). The interconnected second phase was retracted from the triple-grain junctions and concentrated in the corners of the AlN grains. In contrast, the isolated structure of the second phase in the slow-cooled specimen, which has been shown in Fig. 3(d), was changed into the interconnected structure (Fig. 6(b)) by fast cooling after reheating to 1900°C. It is concluded from these results that the morphological difference of the second phases was caused mainly by the alteration of the ratio of the solid–solid interfacial energy to the solid–liquid one during cooling. The wettability change of the liquid phase during cooling has also been reported in B$_2$O$_3$-doped ZnO and LiF-doped MgAl$_2$O$_4$ systems.

### Table I. Amount of Second Phases of Specimens with Different Morphologies of Second Phases

<table>
<thead>
<tr>
<th>Sintering condition</th>
<th>Amount of second phase (vol%)</th>
<th>Morphology of second phases</th>
</tr>
</thead>
<tbody>
<tr>
<td>1900°C, 2 h, fast cooling</td>
<td>4.84 (0.23)</td>
<td>Interconnected</td>
</tr>
<tr>
<td>1900°C, 2.5 h, fast cooling</td>
<td>4.53 (0.63)</td>
<td>Interconnected</td>
</tr>
<tr>
<td>1900°C, 2 h, slow cooling</td>
<td>4.81 (0.26)</td>
<td>Isolated</td>
</tr>
</tbody>
</table>

*Number in parentheses is one standard deviation for eight to ten measurements.

(2) Thermal Conductivity of Aluminum Nitride with Different Morphologies of Second Phases

Figure 7 shows the thermal conductivity of specimens with different morphologies of the second phases. It can be seen that the slow-cooled specimens have a higher thermal conductivity than the fast-cooled ones. There is a possibility that more purification of the AlN grain had taken place for the slow-cooled specimens, because the residence time at high temperature was longer in the case of the slow cooling. But the slow-cooled specimens still had a higher thermal conductivity than the specimens with a longer soaking period at sintering temperature. In order to elucidate the morphological effect of the second phase on the thermal conductivity of aluminum nitride, a comparison has to be made between the specimens having different second-phase morphologies but with the same purity of AlN grain. In practice, however, some grain purification is expected to occur at the region of high temperature during cooling, and thence the...
thermal conductivity was calculated from modeled microstructures that have interconnected and isolated second phases. The microstructure of the interconnected second phase was modeled as one proposed by Buhr and Müller. In this model, the AlN grains are simplified to a periodic stacking of cubes with beveled edges and secondary phases in the channels along the grain edges forming prisms. The thermal conductivity of this microstructural model is expressed as the following equation: \[ K = \frac{\chi^2}{2a^2}K_{SE} + \frac{(a-x)^2}{a^2}K_{AIN} + \frac{3\chi}{4a} \frac{K_{AIN} \cdot K_{SE}}{K_{AIN} + (3a/2x - 1) \cdot K_{SE}} + \frac{2\chi(a-x)}{a} \] Buhr and Müller model

where \( K \) is the overall thermal conductivity, \( K_{AIN} \) the thermal conductivity of the AlN grain itself, \( K_{SE} \) the thermal conductivity of the second phase, \( x \) the width of the second phase, and \( a \) the length of the cube edges. The original equation reported by Buhr and Müller was modified by neglecting a contribution of thin intergranular film to the overall thermal conductivity, because we did not find any evidence of the existence of the grain-boundary layer in our samples. The microstructure with isolated pockets of secondary phases is well suited for the application of the Maxwell model to calculate the overall thermal conductivity. The Maxwell model derived by Eucken in terms of thermal conductivity is given by:

\[ K = K_{AIN} \cdot \frac{1 + 2V_{SE} \left( \frac{1 - K_{AIN}/K_{SE}}{2K_{AIN}/K_{SE} + 1} \right)}{1 - V_{SE} \left( \frac{1 - K_{AIN}/K_{SE}}{2K_{AIN}/K_{SE} + 1} \right)} \]

Maxwell model

where \( V_{SE} \) is the volume fraction of the second phase.

Figure 8 shows the thermal conductivity calculated from Eqs. (4) and (5) as a function of the volume fraction of the second phase, assuming \( a = 5 \mu m \) and \( K_{SE} = 10 \text{ W/(m·K)} \). The dominant factor in determining the thermal conductivity of aluminum nitride appears to be the thermal conductivity of the AlN grain itself, \( K_{AIN} \), as has been reported by Virkar et al. The calculated thermal conductivity for a constant \( K_{AIN} \), however, decreases as the amount of the second phase increases for the interconnected microstructure, whereas it is rather insensitive to the amount of the second phase for the isolated microstructure. The morphological effect of the second phase on thermal conductivity becomes more significant as the volume fraction of the second phase increases.

In order to make a comparison of the measured thermal conductivity to the calculated one, the volume fraction of the second phase \( V_{SE} \) and the thermal conductivity of AlN grain \( (K_{AIN}) \) have to be known. \( V_{SE} \) was measured on the micrographs of the polished surfaces using an image analyzer, and \( K_{AIN} \) was calculated from the content of the lattice oxygen, which was measured by the selective hot-gas extraction method, through the following equation:

\[ K_{AIN} = K_{AIN, theor} + C \cdot \Delta n/n_0 \]

where \( K_{AIN, theor} \) is the theoretical thermal conductivity (= 319 W/(m·K)) of pure AlN single crystal, \( C \) a constant (=0.43), \( \Delta n \) the number density of the oxygen impurities (atoms/cm³), and \( n_0 \) the number density of the nitrogen atoms in AlN (= 4.79 × 10²³ atoms/cm³). The analysis of selective hot-gas extraction was made for the specimens fast-cooled after sintering at 1850°C for 4 h and for those slow-cooled after sintering at 1850°C for 2 h. The result is shown in Table II. For the specimens doped with 8 wt% yttria, it was difficult to measure the content of the lattice oxygen reproducibly, because of a significant overlap between the oxygen peaks generated from the surface oxide and the AlN lattice. It can be seen in Table II that the content of lattice oxygen decreases as the yttria content and the sintering time increase. This result is consistent with.
that of Virkar et al., who suggest that the purification of the AlN lattice is favored by the reduced Al₂O₃ activity in the second phase and is also related to kinetic factors. Another aspect that can be seen in Table II is that the slow-cooled specimens show higher thermal conductivity than the fast-cooled ones despite the higher content of the lattice oxygen. This clearly shows that the morphology of the second phase has an important effect on the thermal conductivity of aluminum nitride. The thermal conductivity calculated from the content of the lattice oxygen using Eqs. (4)–(6) was plotted as a function of the volume fraction of the second phase in Figs. 9 and 10. The measured thermal conductivities of the specimens with interconnected and isolated second phases were also included in Figs. 9 and 10, respectively. It can be seen that the measured and the calculated thermal conductivities are in good agreement. The symbols in Fig. 9, which were experimentally determined from the samples with interconnected second-phase structure, are close to the solid lines calculated from the Buhr and Muller model, but deviate significantly from the dashed lines calculated from the Maxwell model. In contrast, the measured thermal conductivity of the samples with isolated second-phase structure are close to the dashed lines in Fig. 10. The result in this study implies that the thermal conductivity of AlN ceramics, even those containing a large amount of second phase, can be improved by changing the morphology of the second phase into the isolated structure.

Table II. Amount of Second Phases, Oxygen Content in the AlN Lattice, and Thermal Conductivity of Specimens with Different Morphologies of Second Phases

<table>
<thead>
<tr>
<th>Sintering condition</th>
<th>Content of Y₂O₃ (wt%)</th>
<th>Amount of second phase (vol%)</th>
<th>Content of lattice oxygen (wt%)$^a$</th>
<th>Thermal conductivity (W/(m·K))$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1850°C, 4 h (fast cooling)</td>
<td>2</td>
<td>3.64 (0.32)</td>
<td>0.20 (0.03)</td>
<td>155.8 (4.7)</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>5.35 (0.36)</td>
<td>0.11 (0.03)</td>
<td>165.5 (5.0)</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>6.72 (0.32)</td>
<td>0.10 (0.02)</td>
<td>166.4 (5.0)</td>
</tr>
<tr>
<td>1850°C, 2 h (slow cooling)</td>
<td>2</td>
<td>3.34 (0.40)</td>
<td>0.25 (0.03)</td>
<td>159.1 (2.4)</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>5.27 (0.33)</td>
<td>0.19 (0.03)</td>
<td>173.1 (2.6)</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>6.47 (0.38)</td>
<td>0.19 (0.03)</td>
<td>174.9 (2.7)</td>
</tr>
</tbody>
</table>

$^a$Number in parentheses is one standard deviation. The amount of second phase was measured eight to ten times. The content of the lattice oxygen and the thermal conductivity were measured at least three times.
IV. Conclusions

Polycrystalline AlN ceramics with different morphologies of second phases were obtained by control of the cooling rate after sintering. In the case of the fast-cooled specimen, the second phases were interconnected through the edges of the AlN grains, whereas the slow-cooled specimen showed the isolated second phases concentrated in the corners of the AlN grains. The microstructural change of the second phases was attributed to the decrease of the ratio of the solid-solid interfacial energy to the solid-liquid one with lowering the temperature. The slow-cooled specimens showed higher thermal conductivity by 20–30 W/(m-K) than the fast-cooled samples. The experimentally measured thermal conductivity was consistent with the calculated values from the model microstructures. The oxygen content in the AlN lattice determined the thermal conductivity of AlN ceramics decisively, as generally accepted.\textsuperscript{1,2,17} If one assumed the thermal conductivity of the AlN grain to be constant, however, the overall thermal conductivity of the specimen with interconnected second phases decreased steeply as the amount of the second phases increased. On the other hand, for the specimen with isolated second phases, the thermal conductivity was rather insensitive to the volume fraction of the second phases. The implication of the present study is that morphological control of the second phases is especially effective to improve the thermal conductivity of AlN ceramics with large amounts of second phases.

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References


