NOTE

Thermal conductivity and mechanical strength of low-temperature-sintered aluminum nitride ceramics containing aluminum nitride whiskers

Hiroya OKAZAKI¹, Ryota KOBAYASHI¹, Rei HASHIMOTO¹, Emiko FUKUSHI¹ and Junichi TATAMI²

¹Department of Chemistry and Energy Engineering, Faculty of Engineering, Tokyo City University, 1–28–1 Tamazutsumi, Setagaya-ku, Tokyo 158–8557, Japan
²Graduate School of Environmental and Information Sciences, Yokohama National University, 79–7 Tokiwadai, Hodogaya-ku, Yokohama 240–8501, Japan

We successfully fabricated dense aluminum nitride (AlN) ceramics containing AlN whiskers by low-temperature pressureless sintering and evaluated their microstructures, thermal conductivities, and mechanical strengths. Furthermore, the anisotropy of thermal conductivities caused by the orientation of AlN whiskers was also evaluated. The thermal conductivities of the samples measured in parallel and perpendicular to the longer direction of AlN whiskers were 98 and 67 W m⁻¹ K⁻¹, respectively. The bending strengths of the samples without and with AlN whiskers were 147 and 235 MPa, respectively. From the observation of the fracture surface of the samples, AlN whiskers in the samples probably withstand the fracture originating from weak grain boundaries.

Key-words : Aluminum nitride, Sintering, Whiskers, Strength, Thermal conductivity

Aluminum nitride (AlN) is a ceramic material that has a high thermal conductivity, electrical insulation, and corrosion resistance to halogens and plasma.¹,² Therefore, AlN has been used for substrate materials for power devices such as superluminosity LED lights, control boards for electronic vehicles, and railcars. Owing to its high covalent bonding, AlN is a sintering-resistant ceramic. A high temperature and long sintering time with sintering additives such as Y₂O₃ and CaO are required to obtain dense AlN ceramics through conventional pressureless sintering (PLS).³ Typically, the sintering temperature of AlN ceramics is 1800 °C or higher. We successfully obtained dense AlN ceramics by PLS at 1650 °C for 2 h with Y₂O₃–CaO–B (Boron: Rare Metallic Corp., 97 %) as low-temperature sintering additives.⁴ However, these low-temperature-sintered AlN ceramics did not exhibit high thermal conductivity owing to the increase in the grain boundary caused by the restrained grain growth.

To solve these problems, we believe that controlling the grain shape and orientation of AlN are necessary, as are adjustments of sintering conditions and additives. Increasing the thermal conductivity by using the orientation control of columnar grains has been reported in the fabrication process of silicon nitride (Si₃N₄) ceramics, which is one of the competitive thermal conductive materials.⁵ Furthermore, Si₃N₄ ceramics containing orientation-controlled columnar grains have a high mechanical strength and fracture toughness.⁶ However, the texture controls adopted in the fabrication of Si₃N₄ ceramics have not been considered so far in the fabrication of AlN ceramics. We aim to impart both a high thermal conductivity and mechanical strength to AlN ceramics by the addition and orientation control of AlN whiskers, which are needlelike AlN crystals with high aspect ratios. In this letter, we report the microstructures, thermal conductivities, and strengths of AlN ceramics containing AlN whiskers processed by using low-temperature pressureless sintering. In addition, we discuss the anisotropy of the thermal conductivity caused by the orientation of AlN whiskers in the sintered samples.

Commercially available AlN powder (Tokuyama Corp., Grade-E, D₅₀ = 0.8 μm) was used as the raw material. Y₂O₃ (Rare Metallic Corp., 99.99 %), CaO produced by calcining CaCO₃ (Rare Metallic Corp., 99.99 %), and B (Boron: Rare Metallic Corp., 97 %) powders were added as sintering additives to the AlN powder. The composition of the mixture was 95.92 % AlN, 3 % Y₂O₃, 1 % CaO, 0.08 % B (named 0.08B) by mass. The mixture was ball milled in ethanol for 4 h by using ZrO₂ balls (φ 5 mm). The slurry was dried with the help of a rotary evaporator. The powder mixture was mixed with 1 % (by mass) of acrylic binder and 1 % (by mass) of bis (2-ethylhexyl) phthalate dissolved in cyclohexane and sieved to form granules. The granules were carefully mixed with 5 % (by
volume) of AlN whiskers synthesized by direct nitridation of the Al melt by using alumina mortar. The synthesized AlN whiskers were between 20 and 30 μm in diameter and between 500 and 2000 μm in length.

The granules containing AlN whiskers were uniaxially pressed at 80 MPa into thin cylindrical pellets (φ12 mm × 4 mm, named as whisker0 or whisker5), thick cylindrical pellets (φ12 mm × 8 mm), or rectangular bars (5 mm × 4 mm × 30 mm, named as whisker0-b or whisker5-b). Furthermore, the thick cylindrical pellets were longitudinally cut into square prisms (8 mm × 3 mm, named as whisker5||) to evaluate the effect of the orientation of AlN whiskers on the texture and thermal conductivity of the sample. These green bodies were placed in a carbon crucible with an infill of coarse AlN powder (Takion Corp, D50 = 7 μm) and pressurelessly sintered at 1650 °C for 2 h under 1 atm of N2 atmosphere.

The sintered pellet and square prism samples (whisker5|| and whisker5||) were grinding to 2 mm thickness to measure their thermal conductivities. Furthermore, the sintered bar samples were machined to 3 mm thickness, 4 mm width, 25 mm length for the three-point bending test. The densities of the sintered samples were measured by Archimedes’ method. The thermal conductivities of the samples were calculated from the thermal diffusivities measured at room temperature by using the laser flash method. The bending strengths of the samples were measured by the three-point bending test (n = 5). Subsequently, the microstructures of the samples were evaluated through the scanning electron microscopy (SEM). Figure 1 depicts the sample shapes and the evaluation models of AlN ceramics containing orientation-controlled AlN whiskers.

Table 1 lists the densities and relative densities of the samples containing 0 and 5% AlN whisker by volume (whisker0, whisker5). The relative densities of whisker0 and whisker5 were higher than 95%, indicating that these samples were sintered densely. However, the relative density of whisker5 was slightly lower than that of whisker0. The relative density of both green body was about 55%.

Therefore, it is considered that the decrease in density occurred at the time of sintering. AlN whiskers have larger sizes and smaller specific surface areas than that of AlN grains. Therefore, the addition of AlN whiskers possibly inhibits the densification of AlN ceramics.

Figure 2 shows the SEM images of the surfaces of whisker0, whisker5||, and whisker5|| in which the orientation of AlN whiskers was controlled. The whisker0 sample did not contain voids and had a dense texture composed of small-sized AlN grains. The whisker5|| sample had voids around AlN whiskers. However, the sample had a dense texture, except around AlN whiskers, similar to the whisker0 sample. This is the reason the density of the whisker5 sample was found to be decreased. Then, it was confirmed that the size of the AlN whisker was as small as 100 μm. It can be considered that the whiskers broke when mixing the whiskers with the powder. On the other hand, AlN whiskers in contact with AlN grains tend to incorporate AlN grains and the growth of AlN whiskers seemed to occur (see also the inset enlarged images in Fig. 2 indicated by the arrow).

From the SEM image of the surface of the whisker5|| sample, it was confirmed that AlN whiskers existed directly parallel to the surface of the sample. In contrast, from the SEM image of the surface of the whisker5|| sample, it was confirmed that the AlN whiskers oriented perpendicular to the surface of the samples. The structures of whisker5|| and whisker5|| are considered to be similar to the AlN whisker orientation-controlled model as shown Fig. 1. Figure 3 shows the distribution of the orientation angles of AlN whiskers to the top surface of the pellet measured from the SEM images of the side surface of the pellet. Since most of

---

Table 1. Densities and relative densities of AlN ceramics containing AlN whiskers

| Whisker  | Density (g cm⁻³) | Relative density (%) |
|----------|------------------|----------------------|
| whisker0 | 3.27             | 99.1                 |
| whisker5 | 3.19             | 97.0                 |

---

Fig. 1. Evaluation models of AlN ceramics containing orientation-controlled AlN whiskers.

Fig. 2. SEM images of the surfaces of whisker0, whisker5||, and whisker5|| in which the orientation of AlN whiskers was controlled.
the orientation angles are below 45 degrees, the whiskers found to be oriented by the uniaxial pressing during the pelletizing. Table 2 shows the densities and thermal conductivities of whisker0, whisker5⊥, and whisker5∥ samples. The thermal conductivity of whisker0 was 103 W m⁻¹ K⁻¹, without the anisotropy in the measuring direction. The thermal conductivity of whisker5⊥, in which AlN whiskers are oriented parallel to the surface, was 67 W m⁻¹ K⁻¹. On the other hand, the thermal conductivity of whisker5∥, in which AlN whiskers are oriented perpendicular to the surface, increased to 96 W m⁻¹ K⁻¹. Therefore, it is assumed that the orientation of AlN whiskers in whisker5∥ reduced the passage of the grain boundary phase with a low thermal conductivity and promoted the transfer of heat in AlN ceramics. Therefore, oriented AlN whiskers in AlN ceramics are predictably effective in enhancing the thermal conductivity of AlN ceramics.

However, the whisker5 sample did not have a high thermal conductivity compared to the whisker0 sample. This finding is attributed to the fact that heat transfer could not be sufficiently achieved in voids increased by the addition of AlN whiskers. Moreover, the volume of AlN whiskers added was only 5%, which was not enough to form the heat transfer path by connecting AlN whiskers to each other.

Table 3 shows the densities and bending strengths, measured by using the three-point bending test, of whisker0 and whisker5 samples. The bending strength of whisker5 was 235 MPa, which was better than that of whisker0.
Generally, the bending strength tends to increase when the grain size of ceramic particles becomes smaller. The grain sizes of low-temperature-sintered AlN ceramics were smaller than that of the general AlN ceramics. Therefore, the low-temperature-sintered AlN ceramics were thought to show higher bending strengths. In fact, the bending strength of whisker0 (147 MPa) was lower than that of the general AlN ceramics (300 MPa). Figure 4 shows the SEM images of the fracture surfaces of whisker0 and whisker5. The fracture surface of whisker0 showed a grain boundary fracture, and the grain boundary phase originating from the sintering additives was confirmed. Therefore, the fracture of whisker0 was induced by the low strength grain boundary phases. The fracture surface of whisker5 showed a grain boundary fracture like whisker0. Additionally, the fractures of AlN whiskers themselves were also confirmed. These results indicate that the AlN whiskers withstand fractures induced by the grain boundary in the samples. Although the detailed mechanism of strength enhancement by AlN whiskers is not obvious at this time, the addition of AlN whiskers may be effective in enhancing the bending strength of low-temperature-sintered AlN ceramics.

The thermal conductivity and bending strength of the low-temperature (1650 °C) sintered AlN ceramics admixed with 5% AlN whiskers by volume were measured. The samples mixed with AlN whiskers showed an increase in the thermal conductivity from 67 to 96 W m⁻¹ K⁻¹ depending on the orientation of AlN whiskers. Furthermore, the bending strength of the admixed samples (235 MPa) was better than that of AlN ceramics without AlN whiskers (147 MPa). The addition of AlN whiskers, in some measure, to low-temperature-sintered AlN ceramics was shown to be of benefit.

References
1) G. A. Slack, *J. Phys. Chem. Solids*, 34, 321–335 (1973).
2) G. Long and L. M. Foster, *J. Am. Ceram. Soc.*, 42, 53–59 (1959).
3) K. Komeya, H. Inoue and A. Tsuge, *Yogyo-Kyokai-shi*, 89, 330–336 (1981).
4) R. Kobayashi, Y. Moriya, M. Imamura, K. Oosawa and K. Oh-ishi, *J. Ceram. Soc. Jpn.*, 119, 291–294 (2011).
5) N. Hirosaki, M. Ando, Y. Okamoto, F. Munakata, Y. Akimune, K. Hirao, K. Watari, M. E. Brito, M. Toriyama and S. Kanzaki, *J. Ceram. Soc. Jpn.*, 104, 1171–1173 (1996).
6) H. M. Lee, J. Tatami and D. K. Kim, *J. Ceram. Soc. Jpn.*, 124, 800–807 (2016).
7) R. Kobayashi, Y. Fukui and T. Takagi, *J. Ceram. Soc. Jpn.*, 124, 1161–1163 (2016).