# Thermal conduction mechanism of aluminium nitride ceramics

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Extremely large grain size AlN ceramics were produced by HIP sintering at an ultra-high temperature of 2773 K without reducing the oxygen content in order to determine experimentally whether the factor controlling thermal conductivity is either grain boundaries or the internal structure of the grains. The room-temperature thermal conductivity of the HIPed AlN with a grain size of $\sim 40$ µm was $155\,W\,m^{-1}\,K^{-1}$, and was almost equal to that of the normally sintered AlN with a grain size of 4 µm. Therefore, thermal conductivity at room temperature is independent of AlN grain size, or the number and amount of grain-boundary phase for reasonably well-sintered AlN ceramics. The calculated phonon mean free path of sintered bodies was 10–30 nm at room temperature, which is too small to compare with the AlN grain size. Consequently, it is shown that the thermal conductivity of sintered AlN is controlled by the internal structure of the grains, such as oxygen solute atoms.

## 1. Introduction

Aluminium nitride (AlN) ceramics exhibit excellent thermal conductivity and are being considered as a future substrate material instead of $Al_2O_3$ [1]. The theoretical thermal conductivity of an AlN single crystal is predicted to be $320\ W\,m^{-1}\,K^{-1}$ at room temperature [2], and is about ten times larger than that of $Al_2O_3$. However, the thermal conductivity of AlN decreases with increasing oxygen impurity content [2–4].

Two possible mechanisms by which the AlN thermal conductivity is reduced by the oxygen impurity have been considered. The first is due to the internal structure of grains, i.e. oxygen atoms dissolved in the AlN lattice create aluminium vacancies which scatter phonons [2, 3]. The second is phonon scattering on grain boundaries [5–7]. The possibility of the former mechanism was shown by thermal conductivity measurements on single crystals with various oxygen contents [2, 3]. However, the latter mechanism has not been clarified from experimental results because, in the case of conventional sintering methods, such as normal sintering and hot-pressing, AlN grains grow, and the number and amount of grain-boundary phase decrease simultaneously with reducing oxygen content, while densifying AlN.

We reported the oxygen behaviour in normally sintered and hot isostatically pressed (HIPed) AlN, and found that the oxygen content in normally sintered AlN decreased with increasing sintering temperatures. However, the oxygen content of HIPed AlN was almost constant, due to the fact that the threshold reaction temperatures to decrease the oxygen content of sintered AlN increase with higher applied gas pressures. This could be explained by the free energy change of the reactions under high gas total pressures as shown by the "HIP phase diagrams" proposed earlier [8–10]. Also it is reported that the thermal stability of nitride ceramics such as $Si_3N_4$ increases with increasing nitrogen gas pressure [11]. Therefore, it is possible to enlarge AlN grain size at higher temperatures under certain HIPing conditions without reducing the oxygen content of the raw material.

In this research, extremely large grain size AlN ceramics were synthesized, maintaining the oxygen impurity content at a reasonably high level, by ultra-high temperature HIPing process. The phonon mean free path of sintered AlN was also calculated and compared with the experimental results. These theoretical and experimental results allow evaluation of whether the factor controlling the thermal conductivity of AlN ceramics is either grain boundaries or the internal structure of the grains.

## 2. Experimental procedure

A commercial AlN powder (Tokuyama Soda) with an average particle size of 0.6 µm and a specific surface area of $3.2\ m^2\,g^{-1}$ was used as a raw material. This powder contained about 1 wt % oxygen impurity. Up to 1 mol % $Y_2O_3$ powder (average particle size 1.6 µm, specific surface area $8.4\ m^2\,g^{-1}$) was added as a sintering aid to the raw AlN powder (supplied by Shin Etso Chemicals).

These powders were mixed by a ball-mill. After drying, the mixtures were pressed into circular cylinders of 14 mm diameter and 8 mm height using a stainless steel die, and then cold isostatically pressed (CIPed) under 400 MPa for 60 s. The CIPed bodies were sintered in a graphite crucible at 2073 K for 4 h under 0.1 MPa nitrogen gas atmosphere. These samples are termed "normally sintered AlN".

The normally sintered bodies were wrapped in carbon foils, and then HIPed at 2773 K under a nitrogen gas pressure of 100 MPa for 1 h (Kobelco HIP, model System-20). The heating rate was 100 K h$^{-1}$. A high-purity graphite heater was used in the present HIP experiment. The temperature in the furnace was measured with a two-colour optical pyrometer. The specific details of the HIP equipment used were described elsewhere [12, 13].

The bulk density was measured by a displacement method in water. The oxygen and yttrium contents of sintered AlN were measured by radioactive analysis and inductively coupled plasma (ICP) methods, respectively. Crystalline phases were determined by X-ray diffraction.

Thermal conductivity was calculated from thermal diffusivity and specific heat measured by a laser flash technique and the bulk density. The obtained thermal conductivity was calibrated by the total porosity of the sintered AlN. The equipment and detailed procedures for thermal coefficient measurements were described elsewhere [14, 15].

Microstructure was analysed using a scanning electron microscope (SEM). The grain size of sintered AlN was measured from scanning electron micrographs of fractured surfaces.

## 3. Results

Table I shows the characteristic data of the normally sintered and the HIP sintered AlN. The bulk density of the HIPed AlN was lower than that of the normally sintered one, and also was lower than the theoretical value of AlN with 1 mol % $Y_2O_3$ (3310 kg m$^{-3}$).

As shown in Table I, the oxygen and yttrium contents of the HIP sintered AlN are almost the same as those of the normally sintered one. We reported previously that in the case of normal sintering in a reducing atmosphere, the oxygen content decreased from 2.8–0.6 wt % on increasing the sintering temperature from 1773–2173 K for 1 h under 0.1 MPa nitrogen gas pressure [8]. Udagawa et al. studied the influence of nitrogen gas pressure between 0.1 and 1 MPa on the

oxygen and calcium contents of sintered AlN, and found that the oxygen and calcium contents decreased with lower nitrogen gas pressures [16]. In this work the gas pressure during HIP sintering was 100 MPa, which is very large compared to those used in normal sintering. For high gas pressure, the oxygen content of the HIPed AlN decreases slightly, compared to that of the normal sintered AlN. The oxygen behaviour in normal and HIP sintered AlN ceramics was previously explained using Gibbs' energy change of reactions under normal and high pressures by Authors [9].

It is well known that the oxygen content in the sintered AlN influences the thermal conductivity. Although the oxygen content of the HIPed AlN is slightly lower than that of the normally sintered one, the thermal conductivities of the normally sintered and HIPed AlN were almost the same (about 160 W m$^{-1}$ K$^{-1}$).

Fig. 1a and b show, respectively, the fractured surfaces of the normal and HIP sintered AlN. The grain size of the normally sintered AlN was about 4 μm. On the other hand, a grain size of about 40 μm and some pores were observed in the HIP sintered AlN. Also the number of grain-boundary phases of the HIPed body decreased more markedly than that of the normally sintered ones, as shown in Fig. 1. HIP sintering is thus an adequate method to control grain size without reducing oxygen content.

## 4. Discussion

It is reported that the reduction of the AlN thermal conductivity is due to the internal structure of grains such as oxygen solute atoms [2, 3] and/or the oxide grain-boundary structure [5–7]. However, in this work, the thermal conductivity of HIPed AlN with a grain size of about 40 μm was almost equal to that of the normally sintered AlN with about a ten times smaller grain size than the HIPed sample. Therefore, the thermal conductivity of AlN at room temperature is not controlled by grain size or grain-boundary phases.

The reason why grain size or grain-boundary phases is not the main controlling factor of AlN thermal conduction, may be shown from the calculated phonon mean free path of sintered bodies. The phonon mean free path, $l$, is given by

$$l = 3\kappa/VC \qquad (1)$$

where $\kappa$ is the thermal conductivity, $V$ the group velocity of phonons, and $C$ the specific heat. Usually the group velocity is estimated to be the longitudinal sound velocity for this case of thermal conduction. From Equation 1 the phonon mean free path of the specimens obtained is calculated by using the thermal conductivity, longitudinal sound velocity and specific heat. In this work, the measurement of the longitudinal sound velocity was performed by the ultrasonic pulse method [17], and the experimental details for measuring sound velocity are described elsewhere [14].

Table II shows the phonon mean free path, thermal conductivity and grain size of the AlN specimens

TABLE I Data on the normal and HIP sintered AlN

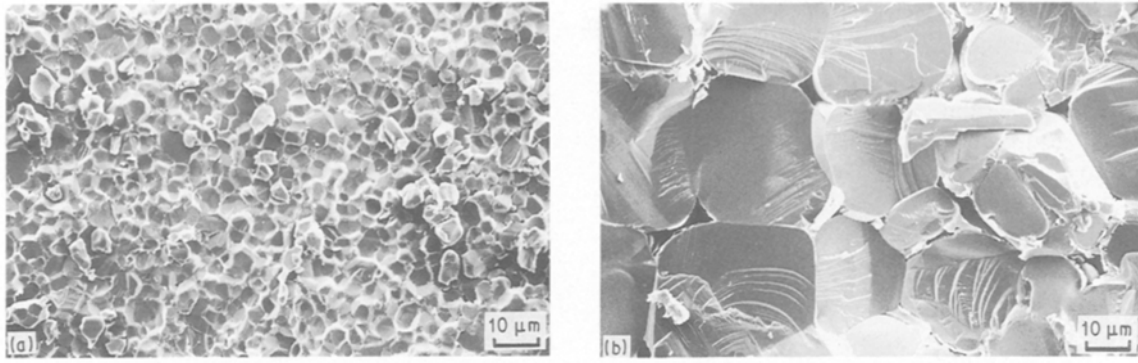| | Normally sintered AlN | HIP sintered AlN |
|---|---|---|
| Bulk density (kg m$^{-3}$) | 3300 | 3240 |
| Oxygen content (wt %) | 1.04 | 0.91 |
| Yttrium content (wt %) | 3.86 | 3.38 |
| Grain-boundary phase | $Al_2Y_4O_9$ | $Y_2O_3$ |
| Thermal conductivity (W m$^{-1}$ K$^{-1}$) | 160 | 155 |
| Grain size (μm) | 4 | 40 |

*Figure 1* Scanning electron micrographs of the fractured surface of (a) normal and (b) HIP sintered AlN. Normal sintering: 2073 K for 4 h under a nitrogen gas pressure of 0.1 MPa. HIP sintering: 2773 K for 1 h under a nitrogen gas pressure of 100 MPa.

TABLE II Phonon mean free path, thermal conductivity and grain size of sintered AlN

| Method | Phonon mean free path (nm) | Thermal conductivity $(W\,m^{-1}\,K^{-1})$ | Grain size $(\mu m)$ | Reference |
|---|---|---|---|---|
| Normal sintering | 20 | 160 | 4 | This work |
| HIP | 21 | 155 | 40 | This work |
| Capsule-HIP | 10 | 100 | 1 | [9] |
| Normal sintering | 26 | 180 | 6 | [8] |
| Normal sintering | 30 | 220 | 10 | [8] |

obtained. The results for AlN ceramics obtained by capsule-HIP and normal sintering are also shown in Table II.

It is known that phonons are scattered by lattice defects, impurities, secondary phases, pores, grain boundaries, etc. If phonons are scattered at grain boundaries, the phonon mean free path must be equal to the magnitude of the AlN grain size. However, as shown in Table II, the phonon mean free path of sintered bodies, including highly thermally conductive AlN ( > 200 W m$^{-1}$ K$^{-1}$) was about 10 ~ 30 nm at room temperature, which is too small to compare with the AlN grain size of 1–40 μm. Therefore, thermal conductivity at room temperature is independent of AlN grain size and grain-boundary phases.

The possible oxygen content dissolved in AlN grains is calculated from the number of oxygen atoms present in AlN, assuming that the dissolved oxygen atoms are distributed uniformly at distances of 10–30 nm from each other, which is equal to the calculated phonon mean free path. The dissolved oxygen content should be about 0.05–0.005 wt %. This is the minimum oxygen amount required to explain the thermal conductivity. There are sufficient oxygen atoms in most sintered AlN samples. Therefore, we may conclude that the main controlling factor of thermal conduction in sintered AlN is not the grain boundaries, but is the internal structure of the grains, such as the oxygen solute atoms.

Many authors related solute oxygen contents and the lattice constant. For example, Okamoto *et al.* [5] investigated the thermal conductivity, oxygen content and c-axis lattice parameter of AlN specimens sintered at temperatures from 2123–2273 K for 1 h, and found that the thermal conductivity increased, the number and amount of grain-boundary phases decreased with increasing sintering temperature, and then the

c-axis lattice parameter had constant values of 0.497 45–0.497 58 nm. These authors also concluded that thermal conduction of sintered AlN was controlled by grain-boundary phases, because of the constant c-axis lattice parameter. The lowest oxygen content of the specimens obtained was about 1 wt % [5].

However, as described earlier, the thermal conduction of AlN grains was influenced by an oxygen content of about 0.05–0.005 wt %. The impurity oxygen atoms have a lattice distortion which changes the over-all lattice parameter. However, this elastic deformation is a short-range ordered force. Therefore, it is not possible to detect the difference in this range of order using the lattice parameter. Slack [2] found experimentally that there is no change in the AlN c-axis lattice parameter over this range of oxygen impurity. Consequently, it is not possible to discuss from the results of the c-axis lattice parameter, whether the most effective factor controlling thermal conductivity is either grain boundaries or the internal structure of the grains, such as the oxygen solute atoms.

The phonon mean free path of the HIPed AlN was about 20 nm, and was almost equal to that of the normally sintered AlN. Therefore, the thermal conductivities of the normally and HIP sintered samples were almost the same.

Slack [3] reported that above 150 K the phonon mean free path of high-purity single-crystal AlN was determined by phonon–phonon scattering. Furthermore, it may be considered that the phonon–phonon scattering influences the thermal conduction of highly thermally conductive AlN ( > 200 W m$^{-1}$ K$^{-1}$).

It is considered that the dissolved oxygen content is closely related to the oxygen content in grain boundaries of sintered AlN, because the chemical reactions

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to improve AlN thermal conductivity by decreasing the oxygen content occur at the grain boundaries [8]. Therefore, it is believed that the oxygen content dissolved in AlN grains is a function of the oxygen content in the grain boundaries. Consequently, it is important to decrease the grain-boundary oxide phases to obtain highly thermally conductive AlN.

## 5. Conclusion

Large grain size AlN ceramics, with no reduction in oxygen content, were produced by HIP sintering at a temperature of 2773 K under a nitrogen gas pressure of 100 MPa for 1 h, to investigate the effects of microstructure on thermal conductivity. The grain size of the HIPed AlN was about 40 μm, which was about ten times larger than that of the normally sintered AlN. The number of grain-boundary phases of HIPed AlN decreased more markedly than those of the normally sintered sample. However, the thermal conductivities of the HIPed and the normally sintered AlN were almost the same (about $160 \, \mathrm{W \, m^{-1} \, K^{-1}}$). The phonon mean free path of AlN ceramics with thermal conductivities of $100-220 \, \mathrm{W \, m^{-1} \, K^{-1}}$, calculated using the experimental values of ultrasonic velocities, was found to be about 10–30 nm at room temperature, which is too small to compare with the AlN grain size of 1–40 μm. Therefore, it is concluded that the thermal conduction of AlN is not controlled in the grain boundaries, but rather the internal structure of the grains, such as oxygen solute atoms. The reason for the HIPed and normally sintered AlN having the same thermal conductivities must be due to their having equal phonon mean free paths, of about 20 nm.

## References

1. W. WERDECKER and F. ALDINGER, *IEEE Trans. Compon. Hybrids Manuf. Technol.* **7** (1984) 399.
2. G. A. SLACK, *J. Phys. Chem. Solids* **34** (1973) 321.
3. G. A. SLACK, R. A. TANZILLI, R. O. POHL and J. W. VANDERSANDE, *ibid.* **48** (1987) 641.
4. N. KURAMOTO, H. TANIGUCHI, Y. NUMATA and I. ASO, *J. Ceram. Soc. Jpn* **93** (1985) 517.
5. M. OKAMOTO, H. ARAKAWA, M. OOHASHI and S. OGIHARA, *ibid.* **97** (1989) 1478.
6. Y. KUROKAWA, K. UTSUMI and H. TAKAMIZAWA, *J. Amer. Ceram. Soc.* **71** (1988) 588.
7. A. V. VIRKAR, T. B. JACKSON and R. A. CUTTER, *ibid.* **72** (1989) 2013.
8. K. WATARI, M. KAWAMOTO and K. ISHIZAKI, *J. Mater. Sci.* **26** (1991) 4727.
9. K. ISHIZAKI and K. WATARI, *J. Phys. Chem. Solids* **50** (1989) 1009.
10. K. ISHIZAKI, in "Euro-ceramics, Vol. 1, Processing of Ceramics", edited by G. D. With, R. A. Terpstra and R. Metselaar (Elsevier Applied Science, London, New York, 1989) p. 1.314.
11. C. GRESKOVICH and S. PROCHAZKA, *J. Amer. Ceram. Soc.* **64** (1981) C-96.
12. K. UEHARA and Y. SAKASHITA, in "Proceedings of the 9th HIP Seminar" (Kobe Steel Ltd, Kobe, Japan, 1989) p. 31.
13. Y. SAKASHITA, C. MANABE, K. MURAMATSU, S. KOFUNE, T. FUJIKAWA and T. KANDA, in "Proceedings of the 2nd International Conference on Hot Isostatic Pressing – Theory and Application" (ASM International, Gaithersburg, USA, 1989) in press.
14. K. WATARI, Y. SEKI and K. ISHIZAKI, *J. Ceram. Soc. Jpn* **97** (1989) 174.
15. *Idem.*, *J. Ceram. Soc. Jpn Int. Ed.* **97** (1989) 170.
16. E. UDAGAWA, N. MAKIHARA, N. KAMEHARA and K. NIWA, in "Proceedings of the 1st Fall Meeting of the Ceramic Society of Japan", Nagaoka, Japan (1987) p. 241.
17. K. ISHIZAKI, I. L. SPAIN and P. BOLSAITIS, *J. Acoust. Soc. Amer.* **59** (1976) 716.