

Relation between oxygen concentration in AlN lattice and thermal conductivity of AlN ceramics sintered with various sintering additives

Ryota KOBAYASHI, Yoshiaki MORIYA, Makoto IMAMURA,
Kazuhiro OOSAWA and Katsuyoshi OH-ISHI[†]

Department of Applied Chemistry, Faculty of Science and Engineering, Chuo University,
1-13-27 Kasuga, Bunkyo-ku, Tokyo 112-8551

Aluminum nitride (AlN) ceramics were fabricated by pressureless sintering with various sintering additives such as 5 mass % Y_2O_3 , 2 mass % Y_2O_3 –3 mass % Al_2O_3 , 3 mass % Y_2O_3 –1 mass % CaO –0.08 mass % B, and 6 mass % Y_2O_3 –2 mass % CaO –0.16 mass % B. The relative density, phases present, lattice parameter c , and thermal conductivity of the samples were evaluated. The oxygen concentration in AlN lattice was estimated from the lattice parameter c by using the relation between the oxygen concentration and the lattice parameter c of AlN. To analyze the effects on the thermal conductivity of the samples, we plotted the oxygen concentration in AlN lattice estimated from the lattice parameters c versus the thermal resistivity, which is inverse of the thermal conductivity measured in this work. The data of the samples sintered with 5 mass % Y_2O_3 and 3 mass % Y_2O_3 –1 mass % CaO –0.08 mass % B located on the plot of the relation between oxygen concentration in AlN lattice and thermal resistivity of AlN presented by Slack (Slack's line) or Harris et al. (Harris's line), respectively. In contrast, the data of the samples sintered with 2 mass % Y_2O_3 –3 mass % Al_2O_3 and 6 mass % Y_2O_3 –2 mass % CaO –0.16 mass % B, which contain excess grain boundary phases, located above the Harris's line. It was suggested that the thermal conductivity of the samples could be influenced by the density, the oxygen content in AlN lattice, and the presence of grain boundary phases.

©2011 The Ceramic Society of Japan. All rights reserved.

Key-words : Aluminum nitride, Thermal conductivity, Lattice parameter c , Sintering, Grain boundary

[Received January 12, 2011; Accepted January 28, 2011]

1. Introduction

Aluminum nitride (AlN) has high thermal conductivity (320 W/mK for a single crystal, comparable with Al) and excellent electrical insulation.¹⁾ AlN also has high corrosion resistances to halogens and plasma.²⁾ From these properties, AlN has been used for substrate materials in power electronics and semiconductor manufacturing parts.

AlN is a sintering resistance material because of its high covalence (57%), so that sintering additives are necessary for densification of AlN ceramics by pressureless sintering. In 1981, Komeya et al. developed dense AlN ceramics by pressureless sintering with Y_2O_3 as a sintering additive at 1800°C.³⁾ They stated that the added Y_2O_3 reacts with the oxide layer on the AlN particles and formed the liquid phase composed of Y–Al–O complex oxides at the sintering temperatures. The liquid phase would promote the densification of AlN ceramics by solution-precipitation mechanism.⁴⁾

Shinozaki and Tsuge,⁵⁾ and Virkar et al.⁶⁾ reported that the formation of Y–Al–O liquid phase restrains the diffusion of oxygen from the oxide layer into AlN particles, which is so-called oxygen trapping effect. The oxygen trapping effect contributes the purification of AlN particles and the enhancement of thermal conductivity of AlN. Subsequently, Ueno and Horiguchi⁷⁾ fabricated the dense AlN ceramics in a carbon crucible at 1930°C for 96 h and reported 260 W/mK of thermal conductivity, which is close to that of the single crystal.

These previous reports mentioned above^{3)–7)} are very important and useful to the fabrication of AlN ceramics with high thermal conductivity. However, it is pointed out that the main analyses on the AlN ceramics in the previous reports were measurements of shrinkage (mm), density (g/cm^3), and SEM observation (μm), except identifying phases in the AlN ceramics by XRD. Therefore, more fine analyses are necessary on the thermal conductivity of the AlN ceramics, e.g., lattice parameter of crystal lattice in the AlN particle.

It has been reported that the thermal conductivity of AlN ceramics is affected by oxygen concentration in AlN lattice.^{1),8)} In fact, the thermal conductivity of AlN ceramics is also affected by the presence of pores and grain boundary phases. Therefore, it is necessary to discuss the effects of them to obtain AlN ceramics with high thermal conductivity. In this work, we fabricated dense Aluminum nitride (AlN) ceramics with several types of sintering additives and estimated the oxygen concentration in AlN lattice from the lattice parameter c of AlN lattice. Moreover, we plotted the estimated oxygen concentration in AlN lattice versus the thermal resistivity, which is inverse of the thermal conductivity. Using this plot, we discuss the factors affecting on the thermal conductivity of AlN ceramics.

2. Experimental procedure

Commercial AlN powder (Tokuyama Corp., Grade-F) was used as a starting AlN raw powder. Y_2O_3 (Rare Metallic Corp., 99.99%), Al_2O_3 (Wako Pure Chemical Industries Ltd., Reagent grade), CaO fabricated by calcining of CaCO_3 (Rare Metallic Corp., 99.99%), and B (Furuuchi Chemical Corp., 99%) powders were added to the AlN raw powder as sintering additives. The

[†] Corresponding author: K. Oh-ishi; E-mail: oh-ishi@kc.chuo-u.ac.jp

Table 1. Starting composition of samples

Name	AlN (wt %)	Y ₂ O ₃ (wt %)	Al ₂ O ₃ (wt %)	CaO (wt %)	B (wt %)
5Y	95	5	0	0	0
2Y3A	95	2	3	0	0
1B	95.92	3	0	1	0.08
2B	91.84	6	0	2	0.16

compositions of the mixtures are listed in **Table 1**. The powder mixtures were ball-milled in butanol for 4 h using Al₂O₃ balls (ϕ 3 mm). The slurries were dried by using a rotary evaporator and sieved with a 212- μ m Nylon mesh to form granules. The granules were put into a steel mold (ϕ 12 mm) and uni-axially pressed at 82 MPa. The powder compacts in AlN sagger were sintered in a graphite heating furnace under an N₂ flow. The sintering temperatures were 1650–1800°C and the holding times were over for 1 h (see also Table 2).

The densities of the samples were measured at room temperature by the Archimedes method using pure water as solvent. The phases identification and measurement of lattice parameters c were carried out by X-ray diffractometer (XRD). For the measurement of the lattice parameters c , diffraction peaks (211), (114), (212), (105), (204), (300) of AlN, and diffraction peaks (440) and (531) of silicon powder (as internal standard) were used. The thermal conductivities of the samples were measured at room temperature by the laser flash method.

3. Results

Table 2 lists the relative densities, secondary phases presents, lattice parameters c , and thermal conductivities of the samples. The relative densities of the samples 5Y and 2Y3A were over 99% of theoretical densities, indicating the perfect densifications of the samples. In contrast, those of the samples 1B and 2B were 96–99% of theoretical densities, which is slightly lower than the other samples. All the samples contained AlN as the main phase and the Y–Al–O compounds as the grain boundary phases. Although the samples 2Y3A contained YAG (Y₃Al₅O₁₂), samples 5Y, 1B, and 2B contained YAM (Y₄Al₂O₉) as the secondary phases. The samples 2Y3A also contained Al₂O₃ and the samples 1B and 2B also contained CaYAl₃O₇ as the secondary grain boundary phases.

For all the samples, the lattice parameter c tended to increase with extending the holding times. The order of the length of lattice parameter c of the samples were 5Y > 1B and 2B > 2Y3A. The thermal conductivities of the samples 5Y were over 170 W/mK, but those of the other samples were below 120 W/mK. The samples 2Y3A had lower thermal conductivities than the samples 1B. The samples 2B also tended to have lower thermal conductivities than the samples 1B. The thermal conductivities of the samples increased with extending the holding times, which is similar with the variation of lattice parameter c .

4. Discussion

4.1 Estimation of oxygen concentration in AlN lattice from lattice parameter c

It has been reported by Slack that the variation of oxygen concentration in AlN lattice relates to lattice parameter c of AlN.¹⁾ The oxygen dissolution to AlN lattice shortens the lattice parameter c . Slack has also stated that the oxygen dissolution also degrades the thermal conductivity λ of AlN lattice.¹⁾ This is due to the formation of the Al vacancies in AlN lattice as shown in following equation,⁹⁾

Table 2. Relative density, secondary phases present, lattice parameter c , and thermal conductivity λ of samples

Name	Sintering	RD/%	Secondary phase	$c/\text{\AA}$	$\lambda/\text{W m}^{-1} \text{K}^{-1}$
5Y	1800°C 1.67 h	100	YAM	4.9799	170
	1800°C 5 h	100		4.9804	192
	1800°C 16.7 h	100		4.9806	210
2Y3A	1750°C 1 h	99.2	YAG, Al ₂ O ₃	4.9786	71.2
	1750°C 2 h	99.4		4.9784	76.1
	1750°C 3 h	99.6		4.9789	90.8
	1750°C 4 h	99.6		4.9792	94.3
1B	1650°C 2 h	96.8	YAM, CaYAl ₃ O ₇	4.9794	95.1
	1650°C 3 h	98.1		4.9798	112
	1650°C 4 h	98.4		4.9798	114
2B	1650°C 2 h	98.2	YAM, CaYAl ₃ O ₇	4.9794	106.1
	1650°C 3 h	97.7		4.9798	96.8
	1650°C 4 h	98.1		4.9798	106.0

RD = Relative densities, YAG = Yttrium Aluminum Garnet (Y₃Al₅O₁₂), YAM = Yttrium Aluminum Monoclinic (Y₄Al₂O₉).

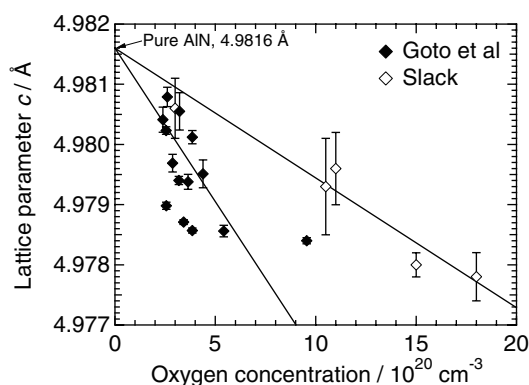
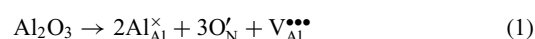


Fig. 1. Relation between oxygen concentration and lattice parameter c of AlN presented by Slack and Goto et al.



where $\text{Al}_{\text{Al}}^{\times}$, $\text{O}_{\text{N}}^{\bullet}$, and $\text{V}_{\text{Al}}^{\bullet\bullet\bullet}$ correspond to Aluminum atom at the Aluminum site, Oxygen atom at the Nitrogen site, and vacancies at the Aluminum site in the AlN crystal structure. After the Slack's report,¹⁾ Goto et al. also have reported the relation between oxygen concentrations and lattice parameter c of AlN.¹⁰⁾

Figure 1 shows the relation between the oxygen concentrations and the lattice parameter c of AlN reported by Slack¹⁾ and Goto et al.¹⁰⁾ The two lines in Fig. 1 were determined by using the weighted linear least square regression from Slack's and Goto's data. The relations determined from these lines are described as the Eqs. (2) and (3), respectively.

$$\Delta n = \frac{(c_0 - c) \times 10^{22}}{0.021} \quad (2)$$

$$\Delta n = \frac{(c_0 - c) \times 10^{22}}{0.051} \quad (3)$$

In these equations, Δn is the oxygen concentration (1/cm³), c and c_0 are the lattice parameter c of the sample and the theoretical value (= 4.9816 Å) for AlN without Al vacancy and dissolved oxygen, respectively.

4.2 Relation between oxygen concentration and thermal conductivity of samples

Slack has also reported that the oxygen concentration in the AlN lattice also correlates the thermal resistivity $1/\lambda$, which is inverse of the thermal conductivity.¹⁾ This correlation is shown as below,

$$\frac{1}{\lambda} = 0.9 \times 10^{-23} \cdot \Delta n + \frac{1}{\lambda_0} \quad (4)$$

where λ is the thermal conductivity (W/mK) and λ_0 is the theoretical thermal conductivity of AlN without Al vacancy and oxygen atom ($= 320$ W/mK). Equation (4) can be arranged if we assume $n = \Delta n/10^{20}$, and the Eq. (5) is obtained.

$$\frac{1}{\lambda} = 9.0 \times 10^{-4} \cdot n + \frac{1}{\lambda_0} \quad (5)$$

Equation (5) indicates that the oxygen dissolution into the AlN lattice degrades the thermal conductivity λ of AlN lattice. After the Slack's report,¹⁾ Harris et al. stated that the further oxygen dissolution into the AlN lattice causes the formation of AlO_6 octahedra in the AlN lattice instead of the Al vacancies,⁸⁾ based on the data of thermal conductivity λ and oxygen concentration n presented by Slack¹⁾ and Kurokawa et al.¹¹⁾ The critical oxygen concentration for this transition is estimated to be 0.75 at% ($= 3.59 \times 10^{20}/\text{cm}^3$) from the luminescence measurement. This correlation is shown in Eq. (6), which follows the same format as Eq. (5).

$$\frac{1}{\lambda} = 4.0 \times 10^{-4} \cdot n + \frac{1}{\lambda_0'} \quad (6)$$

Equation (6) indicates that the further oxygen dissolution ($> 3.59 \times 10^{20}/\text{cm}^3$) into the AlN lattice also degrades the thermal conductivity λ of AlN lattice. If the thermal conductivity λ and oxygen concentration n of the samples follow Eqs. (5) or (6), the thermal conductivity λ depends on only the oxygen concentration n in AlN lattice, and is not affected by the presence of pores and grain boundary phases.

Figure 2 shows the plot of the oxygen concentration n estimated by using Eqs. (2) and (3) along the x -axis and the thermal resistivities $1/\lambda$ along the y -axis of the samples 5Y. Slack's and Harris's line in Fig. 1 were theoretically plotted by using Eqs. (5) and (6) in this work, respectively. Using Goto's Eq. (3), the data of the oxygen concentrations and the thermal resistivities for the samples 5Y follow the Slack's line.¹⁾ In contrast, using Slack's Eq. (2), they do not follow both the Slack's line and the Harris's line. Therefore, we use Goto's Eq. (3) to estimate the oxygen concentration n in the following discussions.

4.3 Analyses of factors affecting on the thermal conductivity of samples

Figure 3 shows the plot of the oxygen concentration n estimated by using Goto's Eq. (3) along the x -axis and the thermal resistivities $1/\lambda$ along the y -axis of the samples 5Y, 2Y3A, 1B, and 2B. Using this plot, we can consider the effects on the thermal conductivity of dissolved oxygen in the AlN lattice and grain boundary phase as well as the porosity in the samples. In this plot, the effect of the porosity on the thermal conductivities of the samples were corrected by Kingery's equation,¹²⁾

$$\lambda_s = \frac{\lambda}{(100 - P)} \quad (7)$$

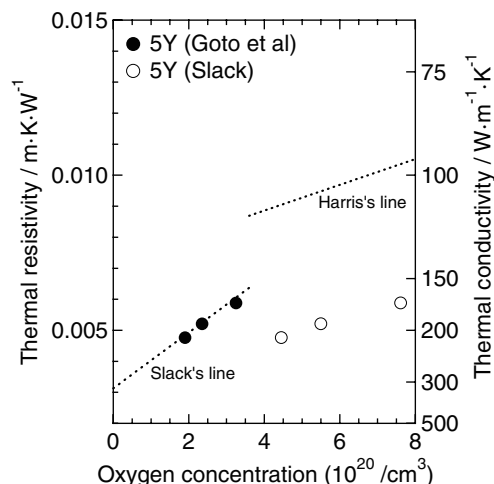


Fig. 2. Relation between oxygen concentration estimated by using Slack's or Goto's relations and thermal resistivity of sample 5Y.

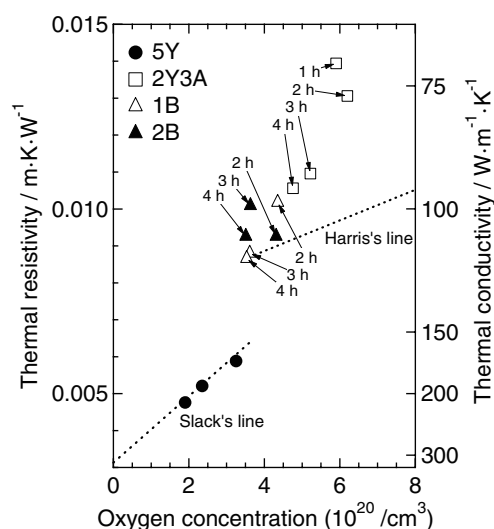


Fig. 3. Relation between oxygen concentration estimated by Goto's relations and thermal resistivity of all samples.

where λ_s are the thermal conductivity corrected to be zero porosity (W/mK), λ is the measured thermal conductivity (W/mK), and P is the porosity (%).

It is clearly shown that the data of the thermal resistivities and the oxygen concentrations for the samples 5Y without pores follow the Slack's line. This indicates that the thermal conductivities of the samples 5Y depend on only the oxygen concentration in the AlN lattice. In contrast, the samples 2Y3A, 1B, and 2B located out of the range of Slack's line and placed above the Harris's line. This means the thermal conductivities of these samples depend on not only the oxygen concentration in the AlN lattice but also the grain boundary phases. The thermal conductivities of the samples 2Y3A, 1B, and 2B were degraded by the grain boundary phases, because which have much lower thermal conductivities. The data of the samples 2Y3A tend to locate higher place than the samples 1B. This is because the samples 2Y3A contain Al_2O_3 in addition to YAG as grain boundary phases. The samples 2B sintered over for 3 h also tend to locate higher place than the samples 1B even the samples contained same compounds (YAM and CaYAl_3O_7) as grain boundary phases. The reason would be that the samples 2B

contained more sintering additives than the samples 1B, that is, thicker grain boundary phases in the samples 2B would decrease the thermal conductivity. The reason why the sample 2B sintered at 2 h had exceptionally higher thermal conductivity than the sample 1B sintered at 2 h is unknown at this time. The samples 2Y3A and 1B having lower oxygen concentrations (corresponding with longer sintering times) tend to locate near the Harris's line. In particular, the samples 1B shift toward the Harris's line with decreasing the oxygen concentration, and finally reach for the lower limit of the Harris's line. This indicates that the grain boundary phases were eliminated from the grain boundaries of the AlN ceramics by extending the sintering times.

5. Conclusions

In this work, we fabricated dense Aluminum nitride (AlN) ceramics by pressureless sintering with several types of sintering additives and evaluated relative densities, secondary phases present, lattice parameter c of AlN lattice, and thermal conductivities. Furthermore, we plotted the oxygen concentration in AlN lattice estimated from the lattice parameter c versus the thermal resistivity, which is inverse of the thermal conductivity. The samples 5Y follow the relation between oxygen concentration of AlN lattice and thermal resistivities presented by Slack (Slack's line), which indicates the thermal conductivity of the samples 5Y depend on only the oxygen concentration in the AlN lattice. In contrast, the samples 2Y3A, 1B, and 2B were located out of the range of Slack's line, and they were also located above the relation between oxygen concentration of AlN lattice and thermal resistivities presented by Harris et al. (Harris's line). Considering this result and the secondary phases present, the thermal conductivity of samples 2Y3A, 1B, and 2B depend on

not only the oxygen concentration in the AlN lattice but also the grain boundary phases. We suggested that the plot of the oxygen concentration in AlN lattice estimated from the lattice parameter c versus the thermal resistivities is useful to clarify the factors affecting on the thermal conductivities of AlN ceramics.

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 and A. Tsuge, *Yogyokyoikaishi*, **89**, 615–620 (1981).
- 4) W. D. Kingery, *Introduction to Ceramics*, John Wiley & Sons (1960).
- 5) K. Shinozaki and A. Tsuge, *Ceram. Japan*, **21**, 1130–1135 (1986).
- 6) A. V. Virkar, T. B. Jackson and R. A. Culter, *J. Am. Ceram. Soc.*, **72**, 2031–2042 (1989).
- 7) F. Ueno and A. Horiguchi, Grain Boundary Phase Elimination and Microstructure of Aluminum Nitride, Proc. 1st Eur. Ceram. Soc. Conf. (1989), pp. 383–387.
- 8) J. H. Harris, R. A. Youngman and R. G. Teller, *J. Mater. Res.*, **5**, 1763–1773 (1990).
- 9) G. A. Slack, R. A. Tanzilli, R. O. Pohl and J. W. Vandersande, *J. Phys. Chem. Solids*, **48**, 641–647 (1987).
- 10) Y. Goto, F. Ueno, M. Kasori and A. Horiguchi, The relation between oxygen content of aluminum nitride and its thermal conductivity, Proc. Annu. Meet. Ceram. Soc. Jpn. (1990), p. 10.
- 11) Y. Kurokawa, K. Utsumi and H. Takamizawa, *J. Am. Ceram. Soc.*, **71**, 588–594 (1988).
- 12) W. D. Kingery and M. C. McQuarrie, *J. Am. Ceram. Soc.*, **37**, 67–72 (1954).