PRINCIPAL PHONON SCATTERING SITES OF SINTERED ALUMINUM NITRIDE AND THERMAL CONDUCTION MECHANISM

Kozo ISHIZAKI

Department of Materials Science and Engineering

School of Mechanical Engineering

Nagaoka University of Technology

Nagaoka, Niigata 940-21, Japan

Koji WATARI

Government Industrial Research Institute Nagoya

Hirate, Kita, Nagoya 462, Japan

and

Takao FUJIKAWA

Technology Development Center

Engineering & Machinery Division

Kobe Steel, Ltd.

Wakinohama 1, Chuo, Kobe 651, Japan

ABSTRACT

AlN ceramics with extremely small and large grain size were produced without reducing the oxygen content by capsule and ultra-high temperature HIP sintering in order to examine experimentally which is the controlling factor on thermal conductivity either grain boundaries or internal defects of the grains. Though the grain size of capsule-HIPped AlN increased from 1 to 40mm by ultra-high temperature HIP sintering at 2773K for 1h under a nitrogen gas pressure of 100MPa, the room temperature thermal conductivity of capsule and ultra-high temperature HIPped AlN was almost the same (100W/(m×K)). Also the phonon mean free path of AlN specimens was about 10nm at room temperature, which is too small compared with the AlN grain size. Therefore it is concluded that the thermal conductivity of sintered AlN at room temperature is controlled by defects in the grains such as oxygen solute atoms. Furthermore it is shown that the thermal conduction of AlN ceramics (grain size; $\sim 10\mu m$) without defects in grains is controlled by the grain boundaries at low temperatures >60K.

I. INTRODUCTION

Aluminum nitride (AlN) ceramics have: (1) high thermal conductivity (which is predicted to be 320W/(m×K) for single crystal at room temperature [1,2]), (2) low thermal expansivity (which matches with that of silicon), (3) low dielectric constant and low energy loss at high frequencies, (4) high electric resistivity, and (5) high dielectric breakdown strength. Therefore AlN ceramics are better substrate materials for IC package than alumina [3,4].

The thermal conductivity of sintered AlN is decreased by impurities such as oxygen [1,2,5,6], silicon, iron and magnesium [6], as well as silicon dioxide [7]. Among them, oxygen is the most common impurity. It is reported that reduction of AlN thermal conductivity by oxygen impurity is due to crystalline defects such as solute atoms [1,2] and/or the oxide grain boundaries [5,8-10]. The former mechanism was found experimentally by Slack who measured the thermal conductivity of an AlN single crystal with various oxygen contents. This author concluded that the phonon scattering is caused by the aluminum vacancies such as $Al_{0.67}O$ in the AlN [1,2].

On the other hand, most reports have concluded that the reduction of the thermal conductivity for the sintered AlN was due to grain boundary oxide phases [5,8-10]. The AlN thermal conductivity increases with decreasing the number and the amount of grain boundary phases by sintering under reducing atmosphere at higher sintering temperatures, and for longer sintering periods [8]. But it is considered that in the case of normal-sintering and hot-pressing, the number and amount of grain boundary oxide phases decrease simultaneously with reducing the amount of oxygen impurity in the AlN lattice. Therefore the real mechanism has not yet been clarified from these experimental results. AlN ceramics with various grain sizes at constant oxygen impurity content are required to examine the real mechanism.

In a previous work, the authors produced extremely large grain size AlN ceramics without reducing the oxygen content, by ultra-high temperature HIP sintering (2773K, graphite heater) for 1h under a nitrogen gas pressure of 100MPa. The reasons why extremely large grain size AlN ceramics were obtained without reducing the oxygen content by HIP sintering at high temperature, are explained by the free energy change of the reactions under high total gas pressures as shown by the "HIP phase diagrams" proposed by the authors, and the increase of AlN thermodynamical stability by increasing the nitrogen gas pressure [11-14]. Furthermore the densified ceramics with extremely small grain size could be obtained maintaining the oxygen content by capsule-HIPping at lower sintering temperature [12]. Therefore by HIP sintering it is possible to control the grain size of sintered AlN without reducing the oxygen content.

In this research, AlN ceramics with extremely small and large grain sizes were produced maintaining the oxygen content by capsule and ultra-high temperature HIP sintering in order to examine experimentally which is the controlling factor on thermal conductivity either grain boundaries or crystalline defects. The AlN phonon mean free path was calculated and compared with the grain size and inter-defects distance. The temperature was calculated to have dominant phonon scattering at grain boundaries, if there is not any crystalline defects.

II. EXPERIMENTAL PROCEDURES

A commercial AlN powder (Tokuyama Soda, F series) with an average particle size of 0.6mm and a specific surface area of 3.2 m^2/g was used in this research. It contains 1wt% oxygen as impurity. An Y_2O_3 powder (supplied by Shin-Etsu Chemical) as sintering aid was added to 1mol% in the raw AlN powder. These powders were mixed by a ball mill. After drying, the mixed powder was formed into pellets of 14 mm diameter and 8mm height using a stainless steel die, and then cold isostatically pressed (CIPped) under 400MPa for 60s.

Capsule-HIP sintering

The CIPped bodies were coated by boron nitride powder, then sealed in a Vycor glass capsule, after it was degassed under vaccum (1Pa or less) for 1h at 1000K. They were HIPped at temperatures of 1973K for 1h under an argon gas pressure of 60MPa. The equipment and detailed procedures for capsule-HIP sintering have been reported elsewhere [12].

Ultra-high temperature HIP sintering

After removing the capsule, the AlN specimens obtained by capsule-HIP sintering were wrapped in carbon foils and then HIPped (Kobelco HIP model: System-20) at a temperature of 2773K with a graphite heater for 1h under a nitrogen gas pressure of 100MPa. The equipment and detailed procedures for the ultra-high temperature HIP sintering have been described elsewhere [11,15,16].

Evaluation of sintered AlN

The bulk density was measured by a displacement method in toluene and water. The oxygen content of sintered AlN was measured by a radioactive analysis. Thermal conductivity at room temperature was performed by the laser flash technique (Shinku-Riko, TC-3000H). Microstructure of the sintered AlN was examined by scanning electron microscope (SEM). The grain size of sintered AlN was measured from SEM fractographs.

III. RESULTS

Table 1 shows the characteristic data of the AlN specimens obtained by capsule and ultra-high temperature HIP sintering. The bulk density of capsule-HIPped AlN was 3315 kg/m^3, and reached the theoretical density (3310 kg/m^3) of AlN with 1mol% Y_2O_3. But, after ultra-high temperature HIP sintering, the bulk density was slightly decreased.

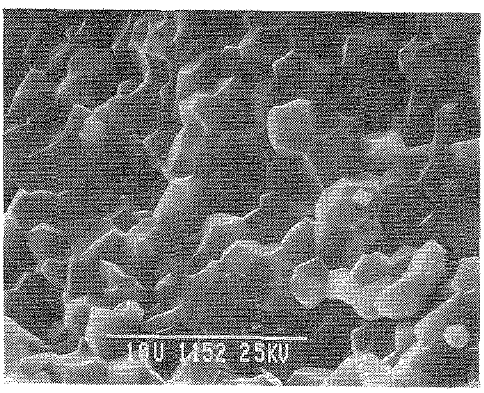
Table 1. Data on the AlN specimens obtained by capsule and ultra-high temperature HIP sintering.

	Capsule-HIP	Ultra-high temperature HIP
Bulk density (kg/m^3)	3315	3290
Oxygen content (wt%)	2.0	1.9
Thermal conductivity (W/(m×K))	100	105
Grain size (mm)	1	40

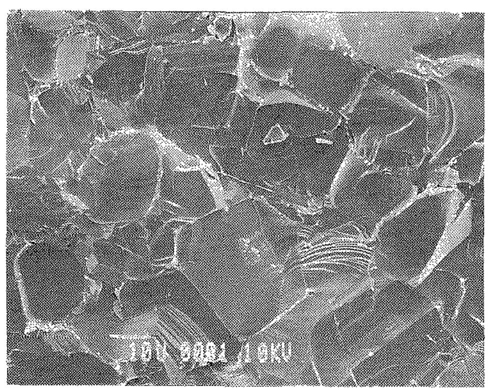
The oxygen content of capsule-HIPped AlN was almost the same as that of the ultra-high temperature HIPped one. The oxygen behavior in HIP sintered AlN was previously explained by the authors from the HIP phase diagram [12-14].

The thermal conductivity of capsule-HIPped AlN was about 100W/(m×K), and was almost equal to that of the ultra-high temperature HIPped one.

Figures 1 (a) and (b) are SEM micrographs of the fractured AlN surfaces. The AlN grain size increased from 1 to 40mm by HIP sintering at ultra-high temperature.



(a)



(b)

Figure 1. SEM micrographs of the fractured surfaces of sintered AlN. (a) Capsule-HIPped at 1973K for 1h under an argon gas pressure of 60MPa. (b) Capsule-free HIPped at 2773K for 1h under a nitrogen gas pressure of 100MPa. The bars indicate **10mm**.

IV. DISCUSSION

Most ceramic materials are composed of mixtures of one or more solid phases. The resulting thermal conductivity of the sintered body depends on the amount and arrangement of each phase present as well as their individual thermal conductivity [17]. Sintered AlN ceramics also exhibit a complex mixture of crystalline AlN grains and grain boundary phases such as $Al_2Y_4O_9$ and Y_2O_3. Indeed Y_2O_3 as grain boundary phase reached up to 3 to 8 weight percent in sintered AlN [8]. The thermal conductivity of Y_2O_3 at room temperature is about 16W/(m×K) [18], which is 20 times smaller than that of the AlN single crystal. Depending upon the configuration of these mixture phases, the grain boundary has a different kind of influence on the total thermal conductivity.

If the grain boundary phase has significant thickness, and phonons have to scatter few times in the grain boundary phase, the grain boundary phase thermal conductivity may play a dominant role in the final thermal conductivity. The thin enough grain boundaries, however, play the role of phonon scattering sites, i.e. a phonon may scatter only once at the grain boundary. The difference of the thickness of the grain boundaries for these two cases is that in the former case the thickness of the grain boundary is at least a few times larger that of the phonon mean free path. Most recently produced high thermal conducting AlN ceramics have grain boundary of the latter case.

To examine well the role of scattering sites, the phonon mean free path was estimated.

The phonon mean free path g is given by

$$g = 3k/(V\times C), \qquad (1)$$

where k is the thermal conductivity, V the group velocity, and C the specific heat capacity per unit volume. The group velocity is estimated to be the longitudinal sound velocity. From Eq.(1), the phonon mean free path of specimens obtained is calculated by using the thermal conductivity, longitudinal sound velocity (10^4 m/s) and specific heat capacity (0.735 J/(g×K)) measured by us [11,19]. The value obtained was about 10 nm at room temperature, which is too small to compare with the AlN grain size of 1 to 40mm.

The phonon mean free path of AlN single crystal without internal defects was calculated from the results of Slack [2], and was about 50nm at room temperature. This value is the possible phonon-phonon scattering distance. Therefore the thermal conductivity of sintered AlN at room temperature is independent of the AlN grain size and the grain boundary phase, and controlled by defects whose distance to each other is about 10nm.

It is well-known that thermal conductivity of sintered AlN increases with decreasing oxygen content. In previous work, the possible oxygen content dissolved in AlN grains was calculated, assuming that the dissolved oxygen atoms were distributed uniformly at distance of phonon mean free path at room temperature. The dissolved oxygen content should be about 0.05 to 0.005 wt%, which is enough to explain the reduction of AlN thermal conductivity by oxygen impurity in AlN grains [11]. Besides this amount is very small to detect by lattice constant change, because the impurity generates only short range order deformation unlike the case of metals of long range force due to the modification of free electron dispersion curve by impurities. Consequently it is concluded that the grain boundaries do not control AlN thermal conduction, but the internal defects of grains such as oxygen solute atoms.

At high temperatures, the phonon mean free path decreases because of phonon-phonon scattering. Thermal conductivity of a crystalline specimen without defects at low temperatures is limited by low specific heat capacity, and phonons will be scattered by grain boundaries. Then phonon mean free path will be saturated to the magnitude of AlN grain size.

It is important to calculate the phonon mean free path of AlN at low temperatures in order to investigate the phonon scattering by grain boundaries. But there are few data available on low temperature thermal conductivity for sintered AlN. In this research, the phonon mean free path was calculated from Eq. (1) using the low temperature thermal conductivity date of AlN single crystal [2]. The group velocity of 10^4 m/s for all temperatures was used, and the heat capacity was estimated by the Debye law using a Debye temperature of 950K.

The temperature dependence of the calculated phonon mean free path is shown in Fig. 2. The phonon mean free path is about 10μm at about 60K, and is about the grain size of AlN specimens obtained by conventional methods. The grain boundary scattering may become an important factor at lower temperatures than 60K for the AlN specimens with small amount of defects.

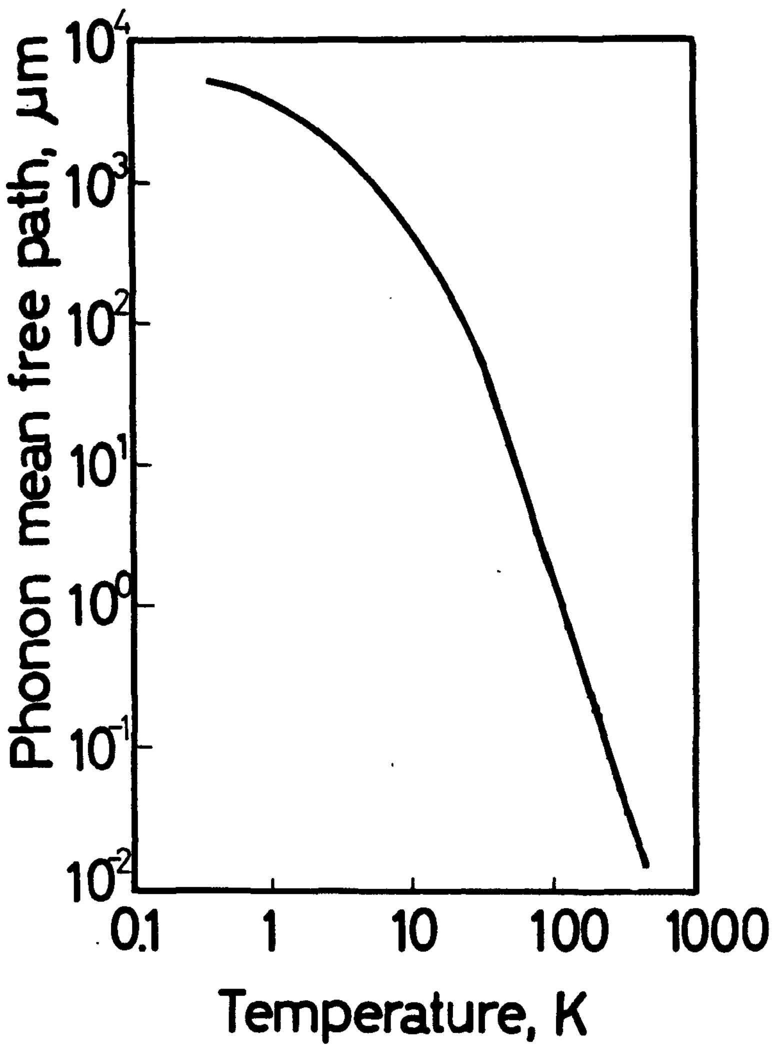


Figure 2. Calculated phonon mean free path for AlN single crystal.

From the experimental and theoretical results for high thermal conducting AlN ceramics(above 100w/(m×k)), it is concluded that the grain boundaries do not control the AlN thermal conduction at room temperature, but the internal defects of grains such as oxygen solute atoms. However the solute oxygen content relates closely to the oxygen activity, i.e. the oxygen content in grain boundaries of sintered AlN. Because the chemical reaction to improve AlN thermal conductivity by decreasing oxygen content occurs at grain boundaries [19]. Therefore it is important to decrease the grain boundary oxide phase to obtain the high thermal conductive AlN.

V CONCLUSION

Extremely small and large grain size AlN ceramics were synthesized maintaining the oxygen impurity content at a reasonably high level by capsule and ultra-high temperature HIP sintering to investigate the effects of microstructure on thermal conductivity. The oxygen content of capsule-HIPped AlN was almost equal to that of the ultra-high temperature HIPped one.

The grain size of AlN specimens obtained by capsule-HIP sintering increased from 1 to 40μm by ultra-high temperature HIPping at 2773K for 1h under a nitrogen gas pressure of 100MPa. However the room temperature thermal conductivity of both specimens were almost the same. Furthermore the calculated phonon mean free path of the obtained specimens at room temperature was about 10nm, which is too small compared with the grain size of sintered AlN. Also the possible phonon-phonon scattering distance of AlN was about 50nm at room temperature. Therefore it is concluded that the grain boundaries do not control the AlN thermal conduction, but the internal defects of grains, such as oxygen solute atoms, control the thermal conductivity for high thermal conducting AlN ceramics with thermal conductivity higher than about 100w/(m×k). Also the phonon scattering by grain boundaries may play a significant role on the thermal conductivity at temperatures below 60K, for AlN specimens without internal defects of grains.

REFERENCES

1 G.A.Slack, "Nonmetallic Crystals with High Thermal Conductivity," J. Phys. Chem. Solids, **34**, 321-35 (1973).

2 G.A.Slack, R.A.Tanzilli, R.O.Pohl and J.W.VanderSande, "The Intrinsic Thermal Conductivity of AlN," J. Phys. Chem. Solids, **48** [7], 641-47 (1987).

3 W.Wedecker and F.Aldinger, "Aluminum Nitride -An Alternative Ceramic Substrate for High Power Applications in Microcircuits," IEEE Trans. Compon., Hybrids, Manuf. Technol., **CHMT-7** [4] 399-404 (1984).

4 N.Kuramoto, H.Taniguchi and I.Aso, "Development of Translucent Aluminum Nitride Ceramics," Am. Ceram. Soc. Bull., **68** [4]883-87 (1989).

5 T.Sakai, M.Kuriyama, T.Inukai and T.Kijima, "Effect of the Oxygen Impurity on the Sintering and the Thermal Conductivity of AlN Polycrystal," Yogyo Kyokaishi (J. Ceram. Soc. Jpn.), **86** [4] 174-79 (1978).

6 N.Kuramoto, H.Taniguchi, Y.Numata and I.Aso, "Sintering Process of Translucent AlN and Effect of Impurities on Thermal

Conductivity of AlN ceramics," Yogyo Kyokaishi (J. Ceram. Soc. Jpn.), **93** [9] 517-22 (1985).

7 T.Yagi, K.Shinozaki, N.Mizutani, M.Kato and A.Tsuge, "Thermal Diffusivity of SiO_2- and Y_2O_3-Added AlN Ceramics," J. Mater. Sci., **24** 1332-36 (1989).

8 M.Okamoto, H.Arakawa, M.Oohashi and S.Ogihara, "Effect of Microstructure on Thermal Conductivity of AlN ceramics," Nippon Seramikkus Kyokai Gakujutsu Ronnbunshi (J. Ceram. Soc. Jpn.), **97** [12] 1478-85 (1989).

9 Y.Kurokawa, K.Utsumi and H.Takamizawa, "Development and Microstructure Characterization of High-Thermal-Conductivity Aluminum Nitride Ceramics," J. Am. Ceram Soc., **71** [7] 588-94 (1988)

10 A.V.Vikar, T.B.Jachson and R.A.Cutler, "Thermodynamics and Kinetic Effects of Oxygen Removal on the Thermal Conductivity of Aluminum Nitride," J. Am. Ceram. Soc., **72** [11], 2031-42 (1989).

11 K.Watari, K.Ishizaki and T.Fujikawa, "Thermal Conduction Mechanism of Aluminum Nitride Ceramics," J. Mater. Sci. in press.

12 K.Ishizaki and K.Watari, "Oxygen Behavior of Normal and HIP Sintered AlN," J. Phys. Chem. Solids, **50** 1009-12 (1989).

13 K.Ishizaki, "Oxygen Partial Pressure and HIPping of Ceramics-Proposed HIP Phase Diagrams"; pp.1.314-318, in "Euro-Ceramics Vol.1 Processing of Ceramics", Edited by G.D.With, R.A.Terpstra and R.Metselaar, Elsevier Applied Science, London and New York, 1989.

14 K.Ishizaki, "Phase Diagram under High Total Gas Pressures-Ellingham Diagrams for Hot Isostatic Press Processes", Acta Metall. Mater (in press)

15 K.Uehara and Y.Sakashita, "Recent Trends in HIP Equipment", pp.31-35 in Proc. of the 9th HIP seminar, Edited by Kobe Steel Ltd., Kobe Japan, 1989.

16 Y.Sakashita, C.Manabe, K.Muramatsu, S.Kofune, T.Fujikawa and T.Kanda, "Development and Application of Ultra-High-Temperature HIP by Means of an Optical Temperature Measurement System," in Proc. of the 2nd International Conference on Hot Isostatic Pressing -Theory and Application-, Edited by ASM International, Gaitherburg USA, in press, 1989.

17 W.D.Kingery, H.K.Bowen and D.R.Uhlmann, "Introduction to Ceramics", 2nd edition, Chapter 12, John Wiley and Sons, New York, 1975.

18 Y.S.Touloukian, "Thermophysical Properties of High Temperature Solid Materials", vol.4, The Macmillan Company, New York, 1967.

19 K.Watari, M.Kawamoto and K.Ishizaki, "Sintering Chemical Reaction to Increase Thermal Conductivity of Aluminum Nitride," J. Mater. Sci. in press.