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Properties and microstructure of aluminum nitride sintered by millimeter-wave heating

T. Yoshioka[a,*], Y. Makino[a], S. Miyake[a], H. Mori[b]

[a] Joining and Welding Research Institute, Osaka University, 11-1 Mihogaoka, Ibaraki, Osaka 567-0047, Japan
[b] Research Center for Ultra-High Voltage Electron Microscopy, Osaka University,
7-1 Mihogaoka, Ibaraki, Osaka 567-0047, Japan

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Abstract

Aluminum nitride is not so extensively applied because of low productivity and high cost due to necessity of high sintering temperature over 1900 °C and long sintering time around 10 h. In the present study, high thermal conductivity over 200 W/(m K) was attained by sintering with 28 GHz millimeter-wave heating at 1700 °C for 2 h under nitrogen/hydrogen mixed gas atmosphere. Attainment of such a high thermal conductivity of aluminum nitride sintered by millimeter-wave at low temperature for a short time is attributed to a characteristic microstructure induced by millimeter-wave heating. From the results of the observation by high resolution TEM, the intergranular film layer between aluminum nitride grains in the sintered body by millimeter-wave heating was as thin as difficult to be observed, resulting in remarkable enhancement of heat transfer at the thinner intergranular phase. Therefore, high thermal conductivity was attained in the millimeter-wave-sintered aluminum nitride in spite of short sintering time and low sintering temperature, compared with the conventional sintering method.

Keywords: Aluminum nitride; Grain boundary; Transmission electron microscopy; Thermal conductivity; Millimeter-wave heating

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1. Introduction

Aluminum nitride (AlN) has been much interested as a candidate of ceramic substrate materials for LSI and hybrid IC [1], because of its excellent properties such as a high thermal conductivity of 320 W/(m K), coefficient of thermal expansion close to silicon, and excellent electrical insulation and so on [1,2]. In the preparation of AlN by conventional sintering process, however, high temperature over 1900 °C is usually required for the densification of polycrystalline AlN even in the case of using a suitable sintering aid such as Y_2O_3 [3]. In addition, actual thermal conductivity of AlN is lower than its theoretical one, where a value of 180 W/(m K) is a limit to be obtained in ordinary sintering for 2 h or so [4]. According to previous reports, the thermal conductivity over 200 W/(m K) was obtained by a long time sintering for over 10 h at 1900 °C under reducing atmosphere [5]. A very high thermal conductivity of about 270 W/(m K) has also been obtained by the sintering for 100 h under reducing atmosphere [6]. However, such a long time sintering at high temperature is unfavorable for efficient productivity and cost performance. Thus, the sintering method to obtain over 200 W/(m K) at a shorter sintering time, is desired from manufacturing standpoint.

Since two decades ago, microwave heating has been applied to industrial uses such as drying tealeaves and vulcanization [7]. On account of inherent faults of centimeter-wave (2.45 GHz), however, application of millimeter-wave energy to sintering of ceramics is expected as an energy saving process in ceramics manufacturing. Millimeter-wave heating has various advantages such as easiness to make uniform distribution of electromagnetic field and small temperature dependence of dielectric loss [8]. Further, it is also demonstrated

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* Corresponding author. Tel.: +81 6 6879 8661; fax: +81 6 6879 8661.
E-mail address: yyosssy@yahoo.co.jp (T. Yoshioka).

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that a higher frequency microwaves such as millimeter-wave enable to decrease the sintering temperature of oxide ceramics by enhanced diffusion [9,10]. For example, it was found that Al_2O_3 with millimeter-wave heating method could be sintered at a lower temperature by 300 °C than that in the conventional method [9]. Further, Si_3N_4 with full densification was also obtained at a lower temperature by 250 °C than that in the conventional method, by selective heating of sintering aid due to the millimeter-wave heating [10].

In the present study, synthesis of high thermal conductivity AlN was performed using millimeter-wave heating under nitrogen atmosphere mixed with hydrogen. Further, the relation between thermal conductivity and oxygen contents or microstructure in the sintered AlN was investigated.

2. Experimental procedures

Commercial AlN powder (Mitsui Kagaku, MAN-2, average size: 1.1 μm) was used as starting material. The oxygen content and specific surface area were 0.4 wt.% and 2.0 m^2/g, respectively. Commercial Yb_2O_3 powder (Shin-Etsu Kagaku, RU-grade, average size: 1.2 μm) was used as sintering aid. Additive content of Yb_2O_3 was fixed at 5 wt.%. After ball-milling, powder mixture of AlN and Yb_2O_3 with 1-propanol and dispersant (Kyoeisha Kagaku, Flowren G-700) for 20 h, the mixture was shaped to the circular disk with 40 mm in diameter and 4–5 mm in thickness by slip-casting method. The shaped body was dried for 1 day and calcined at 600 °C for 1 h in nitrogen atmosphere. The calcined body was sintered at 1700 °C under nitrogen atmosphere without or with 3 wt.% hydrogen using a high power 28 GHz millimeter-wave generator combined with a multi-mode applicator (Fuji Denpa Kogyo, FGS-10-28). The heating rate was fixed at 20 °C/min in the temperature range below 1500 °C and it was lowered to 10 °C/min over 1500 °C. The cooling rate after the sintering was fixed at 30 °C/min down to the temperature of 1400 °C, after which the sample was kept at natural cooling in the applicator. The assembly for thermal insulations are written elsewhere [11].

Density of sintered body was measured by the Archimedean method using oleic acid. Thermal conductivity of sintered AlN was estimated from the specific heat and thermal diffusivity measured by laser-flash constant analyzer (Ulvac-Riko, TC-7000). Crystalline phases in sintered AlN were identified by XRD method using Cu Kα radiation (Rigaku, Miniflex). Oxygen contents in sintered AlN was measured by impulse fusion method (Horiba, EMGA-520). The sample was heated in carbon crucible under vacuum atmosphere, and the amount of oxygen was measured from the generated CO_2 gas. Microstructure of sintered AlN was observed with SEM using fractured surface of the sintered AlN (JOEL, JSM-840, electron gun was changed with TFE type). Further, microstructure between AlN grain was observed with high resolution (HR)-TEM using ion polished thin specimen (Hitachi, H-9000).

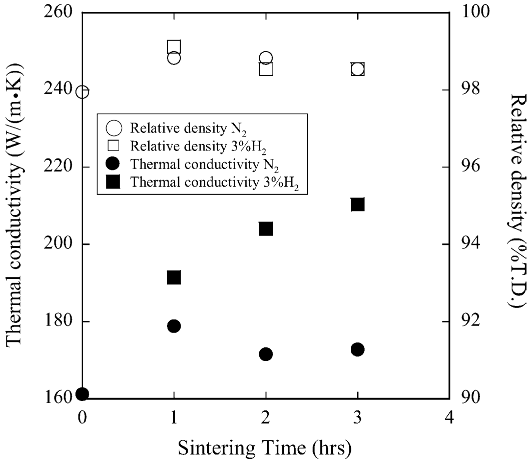

Fig. 1. Thermal conductivity and relative density of Yb_2O_3-added AlN sintered at 1700 °C under nitrogen atmosphere without hydrogen and with hydrogen.

3. Results and discussion

Fig. 1 shows the relative densities and thermal conductivities for AlN sintered by millimeter-wave heating under nitrogen or nitrogen/hydrogen mixed gas atmosphere. As shown in this figure, relative density over 97% T.D. was always attained regardless of the sintering condition. Thus, there is no harmful effect of the hydrogen on densification. Thermal conductivity of AlN sintered under nitrogen atmosphere decreased with sintering time except sintering time of 0 h. On the other hand, the thermal conductivity of AlN sintered under hydrogen/nitrogen atmosphere increased with sintering time. High thermal conductivity over 200 W/(m K) was attained by sintering at 1700 °C within 2 h and higher thermal conductivity of 210 W/(m K) was attained by prolonging sintering time up to 3 h. According to previous report, high temperature over 1900 °C and long time about 10 h has been required in order to obtain high thermal conductivity over 200 W/(m K) [5]. Thus, the millimeter-wave heating enable to shorten the sintering time drastically.

Fig. 2 shows the relation between total oxygen content in AlN and thermal conductivity. For comparison, the data of AlN sintered using carbon furnace in conventional method were also shown in this figure [2,12–14]. As shown in this figure, the oxygen contents of millimeter-wave-sintered AlN were higher than those of conventionally sintered AlN with similar thermal conductivity. The figure shows agreement with the result that the high thermal conductivity was attained despite of no change of intergranular oxide phase to nitride. This result also shows high thermal conductivity can be obtained easily irrespective of higher oxygen content in AlN grains. Accordingly, another reason of the increase of thermal conductivity should be considered. For example, the degradation of thermal conductivity can be suppressed with the decrease of the thickness of intergranular layer even when similar amount of intergranular phase is contained.

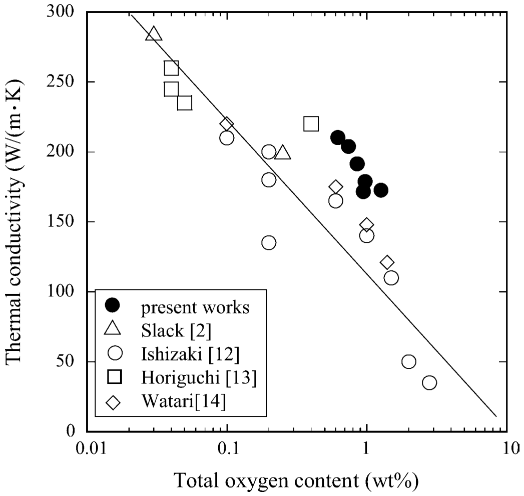

Fig. 2. Thermal conductivity plotted against oxygen content.

According to previous reports [12], the formation of a nitride such as YN was indicated in the conventionally sintered AlN with a high thermal conductivity over 200 W/(m K). This means the necessity of a strong reducing condition and long time sintering around 10 h in order to obtain high thermal conductivity. In the millimeter-wave heating, however, the AlN with about 210 W/(m K) was obtained by only 2–3 h sintering at a temperature without formation of nitride in the intergranular phase.

Fig. 3 shows microstructures of millimeter-wave-sintered Yb_2O_3-added AlNs observed with SEM. It is found that the grain size becomes finer by the addition of hydrogen in nitrogen. The grain size was less than about 5 μm at least and the size is fairly small, compared with the size in Y_2O_3-added AlN with 220 W/(m K) reported previously [15]. The finer grain structure has an advantage to improve mechanical strength of sintered AlN. However, it is suggested that the finer grain structure has disadvantage to improve thermal conductivity of sintered AlN [16].

Fig. 4 shows HR-TEM photograph of AlN sintered by millimeter-wave heating under hydrogen/nitrogen atmosphere at 1700 °C for 3 h. For comparison, the HR-TEM photograph of AlN with Y_2O_3 sintered by conventional method with similar thermal conductivity reported previously is also shown in this figure [15]. As shown in this figure, the intergranular film layer between AlN grains in the case of millimeter-wave sintering was as thin as difficult to be observable. On the other hand, the thickness of the intergranular layer was about 1.7 nm in the AlN sintered by conventional heating. Thus, millimeter-wave heating enables to attain the microstructure with very thin intergranular layer in spite of

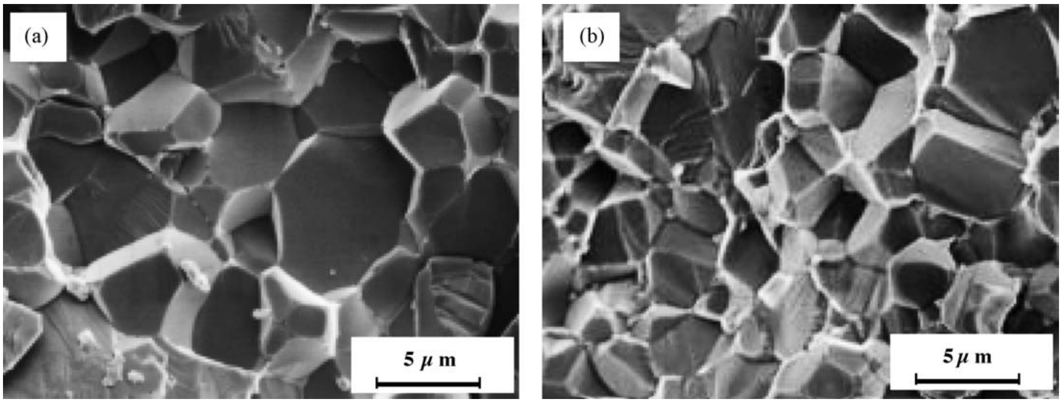

Fig. 3. SEM images of fracture surface of aluminum nitride sintered for 3 h under nitrogen atmosphere without 3 vol.% hydrogen (a) and with hydrogen (b).

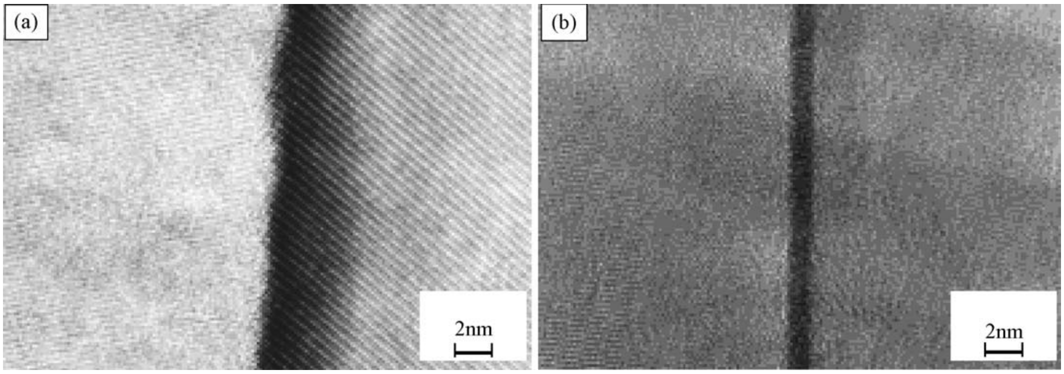

Fig. 4. HR-TEM images of aluminum nitride sintered for 3 h under nitrogen atmosphere with 3 vol.% hydrogen by millimeter-wave heating (a) or sintered for 20 h under nitrogen atmosphere in the carbon furnace by conventional method (b) [15].

Table 1
Calculated Hamaker constants and equilibrium thickness of AlN–Y_2O_3–AlN or AlN–Yb_2O_3–AlN intergranular layer

	ε_a	ε_b	n_a	n_b	$H_{\alpha\beta\alpha}$	ξ	h (nm, $P_{cap} = 0$)	h (nm, $P_{cap} = 1$)
AlN–Yb_2O_3	8.23	4.06	2.1	2.015	3.7×10^{-21}	0.42	7.1	3.9
AlN–Y_2O_3	8.23	4.4	2.1	1.8	1.9×10^{-20}	0.42	6.2	3.9

finer grain structure. It is suggested that such an extremely thin intergranular layer formed by millimeter-wave sintering scarcely inhibits heat transfer at the intergranular phase. Conclusively, millimetre-wave sintering can easily attain high thermal conductivity over 200 W/(m K) in spite of a short sintering time and low sintering temperature in comparison with conventional sintering method.

According to Clark [17], the thickness of intergranular layer is determined by a balance between attractive and repulsive forces. The attractive term, which draws the grains together is composed of van der Waals dispersion force, Π_{disp}, and capillary force, P_{cap}. During sintering of micrometer-size particles, the capillary force depends on the volume fraction of liquid phase, its magnitude is typically the order of 1 MPa. The repulsive term is the structure dispersion force, Π_{st}, contributed by the electrical double layer. The force balance was expressed by the following equation:

$$\Pi_{disp} + \Pi_{st} + P_{cap} = 0 \tag{1}$$

Here, the forces were expressed by the following equation as a function of intergranular layer thickness, h:

$$\Pi_{disp} = \frac{H_{\alpha\beta\alpha}}{6\pi h^3} \tag{2}$$

$$\Pi_{st} = -a\eta_0^2 \left[\sinh^2\left(\frac{h}{2\xi}\right)\right]^{-1} \tag{3}$$

Here, $H_{\alpha\beta\alpha}$ is the Hamaker constant of intergranular layer β between two AlN mother grain α, $a\eta_0^2$ the free energy difference between two states and ξ is the characteristic correlation length. $H_{\alpha\beta\alpha}$ is expressed by dielectric constant, ε, and refractive index, n:

$$H_{\alpha\beta\alpha} = \frac{3}{4}kT\left(\frac{\varepsilon_\alpha - \varepsilon_\beta}{\varepsilon_\alpha + \varepsilon_\beta}\right)^2 + \frac{3\pi\bar{h}\nu_e}{8\sqrt{2}}\frac{(n_\alpha^2 - n_\beta^2)^2}{(n_\alpha^2 + n_\beta^2)^{3/2}} \tag{4}$$

Here, h is the Planck's constant divided by 2π and ν_e is the absorption frequency = $3 \times 10^{15}\ s^{-1}$. The appropriate numerical a value is determined by free energy difference between two states, e.g. the heat of melting. The heat of melting of 87.4 kJ/mol was given in JANAF table, and this value corresponds to $a = 2.92 \times 10^9$ Pa for the constant. Here, if capillary force P_{cap} is assumed 0 or 1 MPa, the thickness h can be calculated. The dielectric constants, refractive indexes, Hamaker constants, and calculated equilibrium thickness of Y_2O_3 and Yb_2O_3 were shown in Table 1. As shown in this table, theoretically the thickness of intergranular phase should be thinner in Y_2O_3-added AlN. However, actually the thickness of intergranular phase was thinner in Yb_2O_3-added AlN. Therefore, something another force might be attracted to intergranular phase. The ponderomotive force, which arises from the second-order perturbed electric field induced by high frequency microwave, is considered as one of the forces attracted to intergranular phase. According to the results by Rebakov and Semenov, about 10 MPa of pressure is attracted to the boundary in the millimeter-wave [18]. Conclusively, the observation of very thin intergranular layer is considered to be a strong evidence of so-called microwave effect in the sintering.

4. Summary

Aluminum nitride doped with Yb_2O_3 was sintered by 28 GHz millimeter-wave heating under hydrogen/nitrogen mixed gas atmosphere. Thermal conductivity 200 W/(m K) was attained by sintering under reducing atmosphere for only 2 h at 1700 °C. The oxygen contents in millimeter-wave-sintered AlN were higher than those in the conventional sintered AlN with similar value of thermal conductivities. On the other hand, the thinner intergranular layer in millimeter-wave-sintered AlN was obtained than that in conventional sintered AlN. It is concluded that high thermal conductivity over 200 W(m K) in the millimeter-wave-sintered AlN is attained by the formation of the microstructure with very thin intergranular layer, which scarcely inhibits heat transfer at the intergranular phase. Formation of very thin intergranular layer is attributed to microwave effect in the sintering.

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