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Low temperature sintering of aluminum nitride with millimeter-wave heating

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Rapid sintering of Yb_2O_3-added AlN was performed by applying the 28 GHz millimeter-wave heating method. It was found that full densification over 97%T.D. was attained by sintering at 1600°C for 20 min. The densification temperature was decreased by about 300°C, compared with those in the conventional method by an electric furnace. A high thermal conductivity over 180 W/(m · K) was obtained in the sample sintered at 1700°C for 40 min, even under non-reducing atmosphere. The main factor resulting in the rapid and low temperature sintering was attributed to efficient selective absorption of the millimeter-wave into Yb_2O_3 additive.

1. Introduction

Heat generation of the circuits in highly integrated semiconductor devices is one of the serious problems for their operation with high reliability [1], and a substrate material with high thermal conductivity is required to overcome this problem. Among various candidate materials, diamond and cubic boron nitride are expected to be the ones with the highest thermal conductivity and the next. However, they have not been available commercially, because of their expensiveness and difficulty of production [2]. As an another candidate, aluminum nitride (AlN) has also attracted considerable attention since last decade [3] by its thermal conductivity of 320 W/(m · K) [4, 5] and the coefficient of thermal expansion close to the value of silicon.

High density polycrystalline bulk AlN has been obtained by the hot pressing method [6, 7]. However, the necessity of a high sintering temperature over 1800°C is unfavorable in a commercially available production process, and its thermal conductivity is usually lower than the theoretical one. Lowering of the thermal conductivity is attributed to Al vacancy generated by dissolution of Al_2O_3 inherently existing on the outermost surface of AlN powders into AlN lattice during sintering [4, 5]. Generally, AlN can be densified by the addition of alkaline-earth or rare-earth oxides as sintering aids [8–10]. These sintering aids are not only effective for achieving densification, but also improve the thermal conductivity by the reacting with oxide on the outermost surface of AlN powders. It is also pointed out that a long time annealing under a reducing condition at high temperature around 1900°C is required for giving high thermal conductivity over 200 W/(m · K). Such a long time annealing at high temperatures is unfavorable for cost performance of industrial production.

A sintering method based on millimeter-wave energy has been much interested in the fields of ceramics and its composite processing because of their capability of rapid sintering at lower temperatures than by the conventional electric furnace [11–13]. It was demonstrated in our previous work that rapid sintering of silicon nitride was successfully performed by combining millimeter-wave heating with addition of ytterbia (Yb_2O_3) and alumina (Al_2O_3) as sintering aids [14].

In the present study, low temperature rapid sintering of AlN with Yb_2O_3 was examined, aiming at again clarifying the effectiveness of Yb_2O_3 as a sintering aid in the millimeter-wave sintering, in comparison with Y_2O_3-added.

2. Experimental procedures

AlN powder (Mitsui Chemical Industry Ltd., MAN-2, average grain size 1.1 μm), Y_2O_3 powder (Shin-Etsu Chemical Co., UU-grade, average grain size 0.25 μm) and Yb_2O_3 powder (Shin-Etsu Chemical Co., RU-grade, average grain size 1.2 μm) were used as the starting materials. Based on our previous result [15] on the sintering of AlN, the content of Y_2O_3 was fixed at 3 wt%, while that of Yb_2O_3 was fixed at 5 wt% which corresponded with the volume% of Y_2O_3. Powder compacts of AlN with Yb_2O_3 or Y_2O_3 were made by slip-casting method, after ball-milling of these mixed powders for 20 hr with a solvent and a dispersant. These compacts were calcined at 600°C for 1 hr in nitrogen after sufficient drying. These calcined compacts were sintered in nitrogen atmosphere of 0.1 MPa with the 28 GHz millimeter-wave heating method. A high power 28 GHz millimeter-wave generator combined with a multi-mode applicator (Fuji Denpa Kogyo, FGS-10-28) was used. 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 sintering temperature was varied in the range from 1500°C to 1750°C, and the holding time from 0 to 120 min. Alumina fiber and alumina board were used for thermal insulation of heated samples. Specimen temperatures were measured by direct contact of a Mo-sheathed thermocouple of W/Re to the sample surfaces.

The density of sintered AlN was determined by measuring the weight and the size in the range of below 90%T.D., over which the Archimedean method was applied using oleic acid. Thermal conductivity of the sintered AlN was estimated from the specific heat and thermal diffusivity measured with the laser flash method. In the measurement of specific heat, sintered specimens were coated with glassy carbon to keep the absorption of laser energy to be constant. For thermal diffusivity measurement, they were coated with deposited gold for preventing laser transmission. The crystalline phases in sintered specimens were identified by XRD method using Cu K_α radiation. Precise lattice constant of AlN phase was measured by XRD analysis, combined with step-scan method (step angle; 0.01 degree, step time 4 sec) by using Si powder as the internal standard. Microstructures of sintered specimens were observed with SEM using fracture surfaces of these specimens.

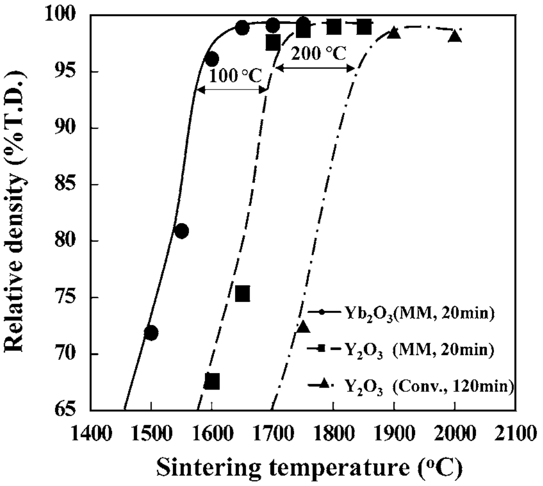

Figure 1 Dependence of relative density (%T.D.) on the sintering temperature in the Yb_2O_3-added AlNs sintered by millimeter-wave heating method. The data on Y_2O_3-added AlNs sintered by millimeter-wave and conventional methods are also shown for comparison. (MM and Conv. means sintered by millimeter-wave heating method and Conventional method, respectively.)

3. Results and discussion

3.1. Densification behavior

Fig. 1 shows the densification curve of AlN with 5 wt% Yb_2O_3 for various sintering temperatures for 20 min by the millimeter-wave heating. The densification curves of AlN sintered by millimeter-wave and conventional methods are also shown with a similar volume% of Y_2O_3 to that of Yb_2O_3. It is found that AlN with Yb_2O_3 can be fully densified up to 97%T.D. at a sintering temperature of 1600°C by the millimeter-wave heating. While, for Y_2O_3-added samples full densification is observed at about 1700°C for the millimeter-wave sintering and at about 1900°C for the conventional sintering. It is clear that the millimeter-wave sintering of Yb_2O_3-added AlN can decrease the sintering temperature by about 300°C, as compared with Y_2O_3-added AlN by the conventional method.

This feature was also found in our research of Si_3N_4 sintering [14]. It has been clarified that Yb_2O_3-Al_2O_3 binary oxide is an excellent aid for lowering the sintering temperature of Si_3N_4 on account of the better absorption character of Yb_2O_3 for millimeter-wave radiation.

3.2. XRD analysis

Fig. 2 shows XRD patterns of Yb_2O_3-added AlN for various sintering times at the temperature of 1700°C with the millimeter-wave heating method. As shown in this figure, intergranular phases were identified to be Yb_2O_3 (designated as Yb) and $Yb_3Al_5O_{12}$ (designated as 3Yb-5Al) and their peak intensities scarcely changed with the sintering time.

Fig. 3 shows XRD patterns obtained from Yb_2O_3-added AlN sintered at various sintering temperatures for 60 min with the millimeter-wave heating method. $Yb_3Al_5O_{12}$ and small amount of Yb_2O_3 were identified in all samples, and $Yb_4Al_2O_9$ (designated as 4Yb-2Al) phase was observed only at 1750°C. The existence of Yb_2O_3 and $Yb_4Al_2O_9$ phases is considered to be favorable for obtaining a high thermal conductivity.

According to Virkar *et al.* [8], from a thermodynamical standpoint the RE/Al ratio (RE; rare-earth atom in the sintering aid) in intergranular oxide phases of

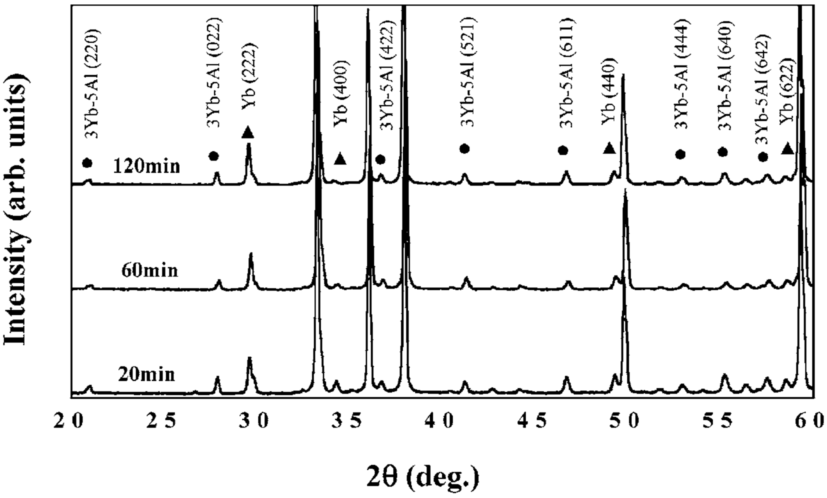

Figure 2 XRD patterns of Yb_2O_3-added AlNs sintered at 1700°C for 20 min, 60 min and 120 min by millimeter-wave heating. 3Yb-5Al and Yb means $Yb_3Al_5O_{12}$ and Yb_2O_3, respectively.

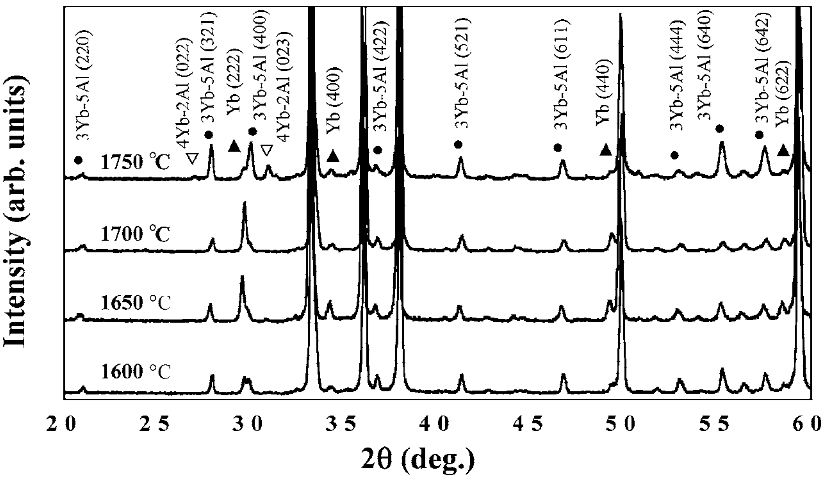

Figure 3 XRD patterns of Yb_2O_3-added AlNs sintered for 60 min by millimeter-wave heating. 3Yb-5Al, 4Yb-2Al and Yb means $Yb_3Al_5O_{12}$, $Yb_4Al_2O_9$ and Yb_2O_3, respectively.

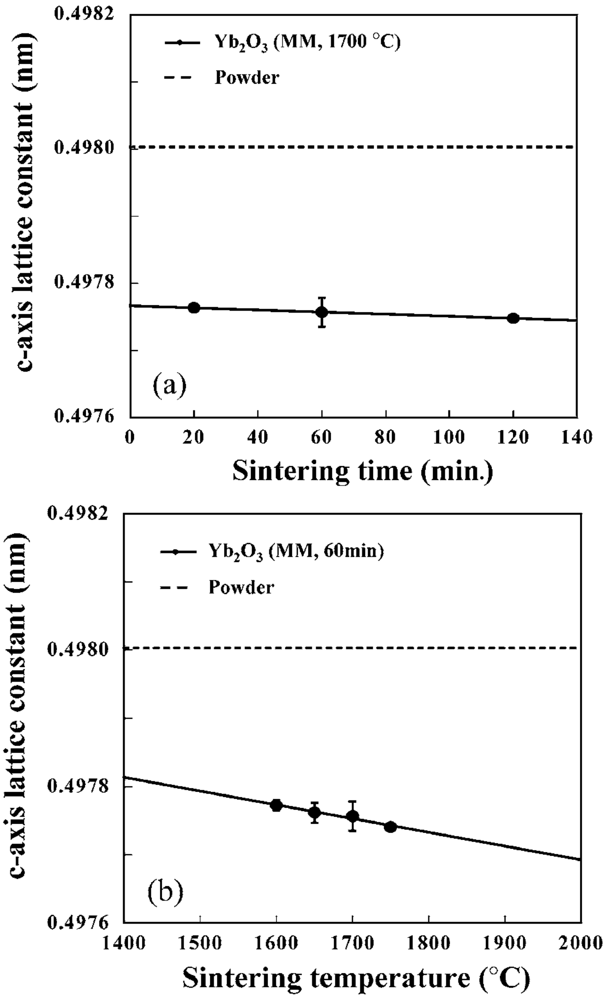

Figure 4 Dependence of *c*-axis lattice constant on (a) the sintering time and (b) sintering temperature in the Yb_2O_3-added AlNs sintered by millimeter-wave heating. (MM and Conv. means sintered by millimeter-wave heating method and Conventional method, respectively.)

sintered AlN reflects the tendency of dissolved oxygen into AlN lattice. The existence of rare-earth aluminates with high RE/Al ratio is important for obtaining a high thermal conductivity. According to our previous report [15], existence of Y_2O_3 and yttrium aluminates with high Y/Al ratio was an important factor to obtain a high thermal conductivity in Y_2O_3-added AlN. While, yttrium aluminates with low Y/Al ratio, such as $YAlO_3$ and $Y_3Al_5O_{12}$, have not been detected as the sintering was given under weak reducing conditions by both millimeter-wave and conventional heating methods. Thus we can expect similarly that the existence of high Yb/Al aluminates such as Yb_2O_3 and $Yb_4Al_2O_9$ phases in Fig. 3 is effective for obtaining a high thermal conductivity.

It has also been pointed out that the c-axis lattice constant of AlN decreases with the increase of dissolved oxygen amount into AlN lattice [4, 15, 16]. Dependence of the c-axis lattice constant of Yb_2O_3-added AlN on both the sintering temperature and time is shown in Fig. 4a and b. The lattice constant decreases with increasing both the sintering temperature and time and it is considered that the oxygen dissolution is enhanced by two parameters. Indeed, the content of dissolved impurity oxygen generally tends to increase with the sintering temperature and time, when the sintering is performed under a non-reducing atmosphere [15, 16]. Accordingly, it is considered that sintering at high temperature and for long time degrades the thermal conductivity of AlN.

3.3. SEM observation

Fig. 5 shows SEM photographs of fractured surface obtained from Yb_2O_3-added AlN sintered at 1700°C. For comparison, data of Y_2O_3-added AlN sintered at 1750°C are also shown. For both Yb_2O_3- and Y_2O_3-added AlN, the grain size increases with the sintering time. When the sintering time was 20 min, the average grain size grew scarcely (about 2 μm), but when the time was from 60 min and 120 min, the average grain size grew to 6 μm and 8 μm.

Fig. 6 shows SEM photographs of Yb_2O_3-added AlNs sintered for 60 min at various temperatures. The grain size does not so strongly depend on the sintering temperature. The average grain size in the AlN sintered at 1750°C was about twice at most to that at 1600°C. Furthermore, a trace of crack was observed in the AlN sintered at 1600°C and a weak grain boundary is suggested from this observation, although nearly full densification was obtained.

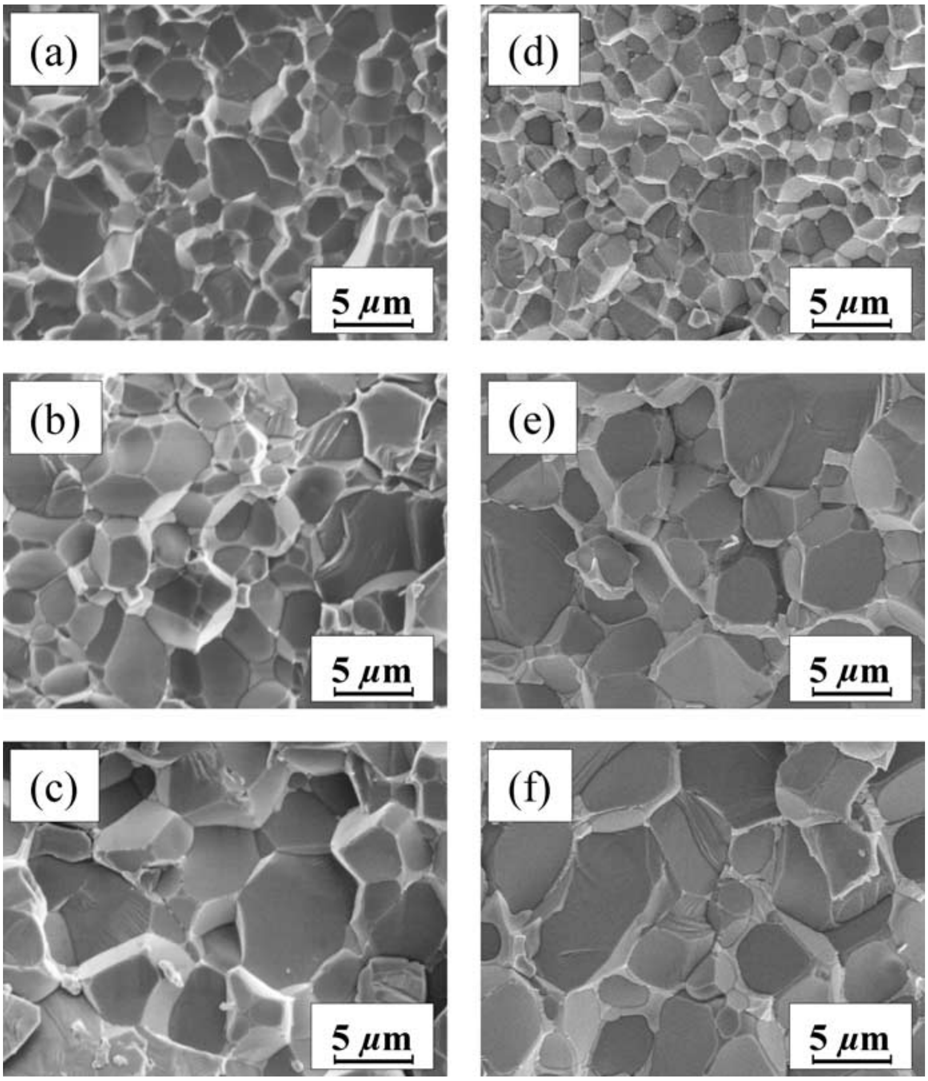

Figure 5 SEM photographs of Yb_2O_3- and Y_2O_3-added AlNs sintered by millimeter-wave heating. (a), (b) and (c); 20 min, 60 min and 120 min for Yb_2O_3-added AlNs sintered at 1700°C, (d), (e) and (f); 20 min, 60 min and 120 min for Y_2O_3-added AlNs sintered at 1750°C.

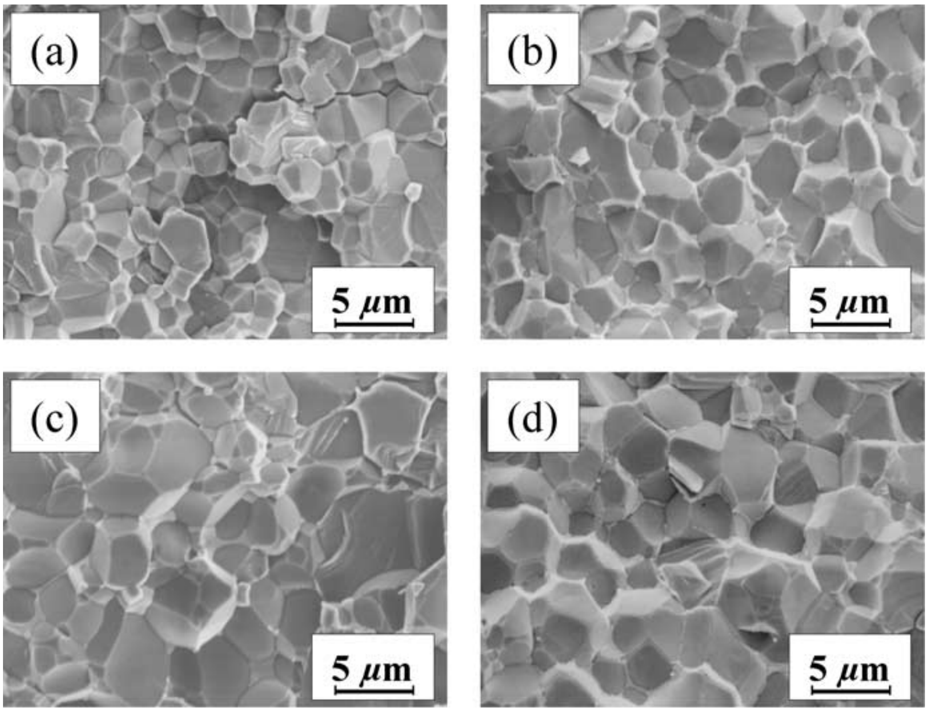

Figure 6 SEM photographs of Yb_2O_3-added AlNs sintered for 60 min by millimeter-wave heating (a) 1600°C, (b) 1650°C, (c) 1700°C and (d) 1750°C.

3.4. Thermal conductivity

Dependence of the thermal conductivity on the sintering time was examined for the Yb_2O_3-added AlN at 1700°C. The result is shown in Fig. 7 together with the result on Y_2O_3-added AlN sintered at 1750°C. As shown in the figure, the thermal conductivity increases with increasing the sintering time until 40 min, and decreases slightly with further increase of time. The rise of thermal conductivity up to 40 min can be explained by the evolution of sintering. From results in Figs 5 and 7 we can suggest that the grain growth in the early stage is effective for improving the thermal conductivity but further grain growth by the sintering for a long time is not favorable. Conclusively, a short sintering time of 40 min became to be an optimum one for obtaining a good thermal conductivity in Fig. 7. This result suggests no necessity of a long time sintering, as far as the condition of nearly full densification is satisfied.

Subsequently, dependence of the thermal conductivity of Yb_2O_3-added AlN on the sintering temperature was examined as shown in Fig. 8 together with the result of Y_2O_3-added sample. A fairly high thermal conductivity was obtained for Yb_2O_3-added AlN, even at a low sintering temperature of 1600°C. This result corresponds to the high densification of Yb_2O_3-added AlN at 1600°C as shown in Fig. 1. While clear decrease of thermal conductivity is observed in the Y_2O_3-added AlN sintered at 1700°C, irrespective of its relatively high density (around 97% T.D.).

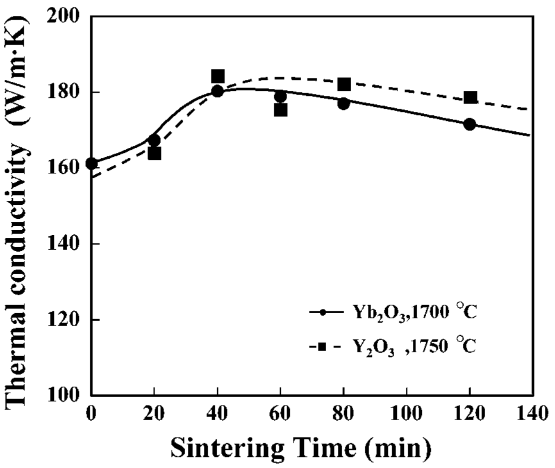

Figure 7 Dependence of thermal conductivity on the sintering time in the Yb_2O_3- and Y_2O_3-added AlNs sintered at 1700°C and 1750°C by millimeter-wave heating method, respectively.

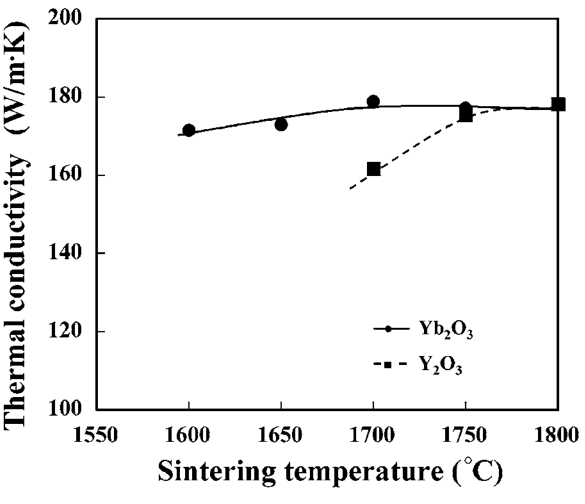

Figure 8 Dependence of thermal conductivity on the sintering temperature in the Yb_2O_3- and Y_2O_3-added AlNs sintered for 60 min by millimeter-wave heating method.

It has been reported [4, 8, 17, 18] that degradation of the thermal conductivity of sintered AlN is caused by the following two reasons. The first reason is based on the morphology of intergranular oxides existing on the AlN grain boundary [17, 18]. Immediately after reaching to nearly full densification state, AlN grains are isolated with each other by the thick intergranular layer of sintering aids with a low thermal conductivity, and this layer suppresses the evolution of the thermal conductivity. With further evolution of sintering, sintering aids in the intergranular layer react well with the Al_2O_3 layer existing on the surfaces of AlN grains, and the sintering aids are concentrated at the triple points between AlN grains forming complex aluminates, by which the intergranular region becomes very thin. At the same time, the thickness of the intergranular oxide layer decreases and the grains of AlN come into closer contact with another AlN grains through thin complex alumnates. Thus, the thermal conductivity is improved with the evolution of sintering through the change of morphology of AlN. We consider this tendency is observed up to the sintering time of 40 min in Fig. 7, and up to a temperature of 1700–1800°C in Fig. 8.

The second reason is attributed to impurity oxygen dissolved into AlN lattice [4, 8]. We have clarified that the dissolved oxygen tends to increase with both sintering temperature and sintering time, as described in the data of Fig. 4a and b, and this result corresponds to the decrease of the thermal conductivity over 60 min in Fig. 7. While, in Fig. 8 the lowering of the thermal conductivity with temperature is considered to appear over 1800°C.

We can conclude that owing to there two factors we have observed an optimum sintering time of 40 min in Fig. 7 and an optimum temperature of about 1700°C in Fig. 8 in the thermal conductivity of AlN.

4. Summary

Low temperature of sintering of AlN with a high thermal conductivity was successfully performed by combining 28 GHz millimeter-wave heating with the usage of Yb_2O_3 as sintering aid. Full densification of AlN was attained at a low sintering temperature of 1600°C with a short sintering time of only 20 min. The rapid sintering at low temperature is attributed to come from the efficient absorption of millimeter-wave in Yb_2O_3 additive. Irrespective of the rapid sintering in non-reduction atmosphere, a thermal conductivity higher than 180 W/(m · K) was obtained at a sintering temperature of 1700°C, and a sintering time of 40 min, for a sample of 5 wt% Yb_2O_3 addition. Rapid synthesis of AlN with a high thermal conductivity over 200 W/(m · K) is expected to be obtained by millimeter-wave sintering under reduction atmosphere.

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