Rapid Fabrication of Aluminum Nitride with High Thermal Conductivity by Millimeter-wave Heating Method

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Aluminum nitride has been interested for the usage of heat-sink substrate in the semiconductor device on account of its high thermal conductivity. But aluminum nitride is not so easily sintered similarly as other nitrides. Polycrystalline bulk aluminum nitride is generally sintered by adding some sintering aids. However, high sintering temperature around 2000°C is still required for attaining full densification with the conventional sintering method. Long time heat-treatment over 10 hr under reducing condition is also required in order to attain high thermal conductivity over 200 W/m·K. Further, appropriate selection of sintering aid is important to obtain aluminum nitride with high thermal conductivity. Thus, there are many problems to practically fabricate aluminum nitride with high thermal conductivity.

Instead of the conventional heating process, new electromagnetic process based on microwave energy is recently being expected for fabrication of ceramics. Microwave energy began to apply to industrial use such as drying of tealeaves since two decades ago. However, successful application to sintering of ceramics was not always obtained on account of various faults due to 2.45 GHz microwave such as heterogeneity of electromagnetic field and thermal runaway, which arises from strong temperature dependence of dielectric constant. These difficulties are now being solved by commercial use of millimeter-wave energy. Thus millimeter-wave heating method is now being expected as a candidate of environment-conscious and industrial fabrication process of ceramics. In the present study, we show millimeter-wave heating method is the rapid and low temperature process for producing aluminum nitride with high thermal conductivity. Importance in the selection of sintering aid is indicated in the millimeter-wave sintering of aluminum nitride. The relation between thermal conductivity and microstructure is also discussed.

AlN powder with the average size of 1μm (Mitsui Kagaku, MAN-2) was used as the starting raw material and Y2O3 or Yb2O3 (Shin-etsu Kagaku, average size; 0.25μm and 1.2μm, UU- and RU-grades, respectively) were used as sintering aids, respectively. After mixing AlN powder and sintering aid at a desired content, the mixed powder with 1-propanol and dispersant was milled for 20 hr with alumina balls in an alumina pot. The milled powder was shaped to the circular disk with 40 mm in diameter and 4~5 mm in thickness by slip-casting method. After drying enough, the slip-casted body was calcined at 600°C for 1 h in nitrogen atmosphere. The calcined body was sintered in nitrogen without hydrogen or with several % hydrogen by using millimeter-wave heating method. Millimeter-wave heating was performed in a multi-mode applicator (Fuji Denpa Kogyo, FGS-10-28) combined with a high power 28 GHz gyrotron generator.

Density of sintered body was calculated from measured size and weight, and when the relative density was over 90%, the precise density was measured by Archimedean method using oleic acid as immersion liquid. Thermal conductivity of sintered body was estimated from specific heat and thermal diffusivity, which were measured by laser-flash thermal constant analyzer (Sinku-Riko, TC-7000). Phase identification and microstructural observation were performed by XRD and SEM methods, respectively.

Temperature dependence of density for aluminum nitride with Y2O3 and Yb2O3 is shown in Fig.1. The contents of sintering aids for these aluminum nitrides were 5 wt% for Yb2O3 addition and 3 wt% for Y2O3 addition, respectively, so as to contain nearly the same volume fraction of the aid for aluminum nitride. For comparison, temperature dependence of density for conventionally sintered aluminum nitride with Y2O3 aid is also shown in Fig.1. Millimeter-wave sintered aluminum nitride with Y2O3 aid could be sintered at 1700°C, which was about 200°C lower than that for the same aluminum nitride sintered conventionally. By changing Y2O3 to Yb2O3 as the additive, sintering temperature of aluminum nitride could be lowered further from 1700°C to 1600°C in the millimeter-wave sintering. Full densification for millimeter-wave sintered aluminum nitrides was attained only for 20 min., while the conventional heating method needed 120 min. to obtain full densification in Y2O3 added aluminum nitride. Thus, rapid sintering of aluminum nitride can be attained by millimeter-wave heating method, and sintering temperature can be remarkably lowered by
using ytterbium oxide as the additive.

When aluminum nitride with Y$_2$O$_3$ or Yb$_2$O$_3$ was sintered in nitrogen atmosphere, maximum thermal conductivity was about 180 W/m·K and almost the same thermal conductivity was obtained in both millimeter-wave and conventional methods. The addition of hydrogen to nitrogen atmosphere in the millimeter-wave sintering showed remarkable effect on the improvement of thermal conductivity of Yb$_2$O$_3$-added aluminum nitride. With increasing hydrogen content up to 3% and the sintering time up to 3 hr, thermal conductivity of Yb$_2$O$_3$-added aluminum nitride was improved to be 210 W/m·K. On the other hand, the thermal conductivity of Y$_2$O$_3$-added aluminum nitride still remained to be about 180 W/m·K even when the aluminum nitride was sintered at nitrogen atmosphere for 3 hr in carbon heater furnace. Further, satisfactory thermal conductivity was not obtained from Yb$_2$O$_3$-added aluminum nitride because the aluminum nitride was not fully densified in the same sintering conditions. Because reducing condition (exactly oxygen potential) for N$_2$-3%H$_2$ mixed gas is not same to that for the conventional heating at nitrogen atmosphere with carbon heater, we can not simply compare the millimeter-wave sintering condition with that of the conventional sintering for the effect on the thermal conductivity of aluminum nitride. According to the previous papers, however, thermal conductivity of aluminum nitride higher than 200 W/m·K has been obtained at a sintering temperature higher than 1800°C and for a longer time than 10 hr. Accordingly, the thermal conductivity of conventionally-sintered aluminum nitride obtained in this study is judged to be reasonable. Therefore, it is concluded that millimeter-wave heating method enable to sinter aluminum nitride rapidly at a lower temperature than that in conventional method. Further, the selection of Yb$_2$O$_3$ as the sintering aid is quite important to obtain high thermal conductive aluminum nitride by the rapid fabricating process based on the millimeter-wave radiation. Details on these results are discussed in the presentation by connecting with microstructural results by SEM and XRD method.