

Effect of second phase after-heat treatment on the thermal conductivity of AlN Ceramics

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Abstract. The high thermal conductivity of Aluminum nitride, coupled with its high electrical resistivity and nontoxic nature, makes it a very promising material for electronic substrate. In this study, microstructural characterization on the thermal conductivity of AlN ceramics was investigated. An AlN ceramic was prepared with a dopant Y₂O₃ under a reducing nitrogen atmosphere with carbon. In order to obtain high thermal conductivity, cooling rate control and after-heat treatment was carried out. Morphology of the second phase was characterized using scanning electron microscopy (SEM). SEM studies showed that the microstructural change caused by after-heat treatment have a major influence on the thermal conductivity.

Introduction

The high thermal conductivity of AlN, coupled with its high electrical resistivity, thermal expansion coefficient which similar with Si and nontoxic nature, makes it a very promising material for electronic substrates.[1] In particular, the intrinsic thermal conductivity of pure AlN single crystal has been calculated to be 320 W/(mK) at room temperature[2]. However, because of the high degree of covalent bonding in AlN, complete densification of the material is difficult and liquid phase sintering is necessary. In order to enhance the densification of AlN ceramics, sintering aids are added; the most common additives are Y or Ca compounds.[1,3] Yttria (Y₂O₃) is the best additive for AlN sintering, and it has been shown that AlN densifies by a liquid phase sintering mechanism, where the surface oxide, Al₂O₃, reacts with other oxide additives, Y₂O₃, to form a Y-Al-O-N liquid that promotes particle rearrangement and densification.[4] Accordingly, the addition of sintering aids is essential to obtain highly thermal-conductive densified AlN ceramics, but it leads to residual grain-boundary phases which will adversely affect the thermal conductivity of polycrystalline AlN.[5,6]

The purpose of this study was to examine the effect of second phase after heat treatment on the thermal conductivity of AlN ceramics. Specimens with other second phase morphology were obtained by control of the cooling condition after sintering: slow cooling rate and after-heat treatment.

Experimental

Commercially available AlN powder (Grade F, Tokuyama Soda, Tokyo, Japan) was used as starting materials. Y₂O₃, as a sintering aid, powder (nanopowder, Aldrich, USA) was added to the AlN powder in amounts ranging between 1 and 7 wt%. These powders were mixed for 12 h in ethanol as a liquid medium using a ball mill. After ball milling, slurry was dried in an oven at 60 °C. The dried powder was made into pellets of 16 mm diameter by uniaxial pressing, followed by cold isostatic pressing at 200 MPa. The cold isostatic pressed compacts were placed in a carbon crucible which contained a powder bed of BN. The specimens were pressureless sintered at 1900 °C for 3h in a flowing nitrogen atmosphere in a graphite resistance furnace (Astro, Thermal Technology, Santa Barbara, CA). Following sintering, three different kinds of cooling schedules were performed as shown in Table.1.

The crystalline phase present in the sintered samples were identified by X-ray diffractometry

(XRD) with $\text{CuK}\alpha$ radiation. The fracture surfaces and polishing surfaces of the sintered pellets were observed by scanning electron microscopy (SEM). Thermal conductivity at room temperature was measured according to the laser flash technique. Typical sample dimensions were 12.7 mm diameter and 2 mm thickness, and both sides of the specimens were coated with carbon black.

Table 1 Cooling conditions

Sample number	Cooling rate	After-heat treatment
1	Fast (25 °C/min)	x
2	Slow (3 °C/min)	x
3	Slow (3 °C/min)	1800 °C, 2h

Result and discussion

The bulk density of AlN ceramics increased with the increase of the amount of Y_2O_3 . Theoretical density was estimated using the Rule of Mixture. Based on the calculating theoretical density of AlN ceramics, all AlN samples were almost fully densified to higher than 99 %. Yttrium-aluminum garnet (YAG) was found by XRD to be the major secondary phase in the bulk of all samples.

The microstructures of AlN with 5 wt% Y_2O_3 were investigated by SEM. Back-scattered SEM micrographs of fracture surface from three cooling condition sample are shown in Fig. 1. In fast-cooled specimen, the second phases are formed along the AlN grain boundaries. In slow-cooled specimen, although the small amounts of second phases move to the triple points, the most second phases are located along the grain boundaries. According to the study of Kim et al. about the relation between morphology of second phase and cooling rate, the second phases are formed at triple point when the cooling rate after sintering is slow.[7] It is explained that lowering the temperature will lead to decrease of the ratio between solid-solid interfacial energy and solid-liquid interfacial energy and hence the isolated structure of second phase by increasing of the dihedral angle. However, in this study the cooling rate of 3°C/min is not slow enough to induce a driving force for segregation of the secondary phase to the isolated triple points. In the specimen with slow cooling and after-heat treatment for 2h at 1800 °C, the second phases are primarily dispersed at the isolated AlN grain junction. In the previous study, pressureless sintered AlN specimen at 1800 °C with Y_2O_3 as a sintering additives have the second phase located at isolated triple points.[7] We controlled the morphology of second phase to the isolated shape at tripe points through slow cooling and after-heat treatment for 2h at 1800 °C in the specimen sintered at 1900 °C. There is no grain size difference in all cooling condition.

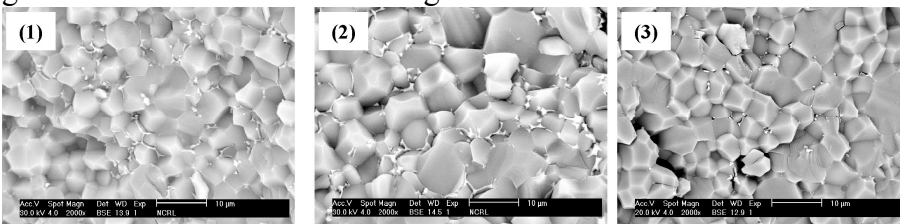


Fig. 1. SEM photographs of fracture surfaces of the AlN cermacis obtained by three kinds of cooling conditions as shown in Table 1.

Table 2 lists the measured thermal conductivity of each sample. Thermal conductivity increases as increase Y_2O_3 wt% in all cooling condition samples and shows the highest values with 5 wt% Y_2O_3 . Both fast-cooled sample and slow-cooled sample have similar thermal conductivity. In the specimen with slow cooling and after-heat treatment, thermal conductivity is increased by 4 ~ 10 %. It is investigated that the distribution of second phases was most likely the main reason for the observed difference in thermal conductivity since the lattice oxygen content, grain size, and total amount of secondary phase are fairly similar. Pezzotti et al. showed that the amounts of lattice oxygen did not change in case of extended annealing at 1800 °C.[8] It is seen that lattice oxygen contents of each sample with same Y_2O_3 wt% is almost same. Therefore we suggest that the

morphology of the second phases which are located at triple point, made by after-heat treatment during cooling process, was most likely the main reason for the observed increase in thermal conductivity

Table 2 Thermal conductivity of AlN samples

Sample number	Y ₂ O ₃ 1 wt%	Y ₂ O ₃ 3wt%	Y ₂ O ₃ 5wt%	Y ₂ O ₃ 7wt%
1	110	178	185	184
2	101	184	186	179
3	110	192	201	198

Conclusions

Polycrystalline AlN ceramics with different morphology of second phases were obtained by control of cooling condition after sintering. In the case of the fast-cooled and slow cooled specimen, the second phases were formed along grain boundaries, whereas the specimen with slow cooling and after-heat treatment showed the isolated second phases concentrated in triple points of AlN grains. The latter specimens showed higher thermal conductivity by 4 ~ 10 % than the former specimens.

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SiAlONs and Non-oxides

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