JOURNAL OF MATERIALS SCIENCE 28 (1993) 4725–4730

Sintering and characterization of fully dense aluminium nitride ceramics

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Aluminium nitride ceramics with no sintering additives could be densified to close to theoretical density (99.6% theoretical) by pressureless sintering of tape-cast green sheets at 1900 °C for 8 h. The thermal conductivity and bending strength of the specimens were 114 W m^{-1} K^{-1} and 240 MPa, respectively. The effect of Y_2O_3 additive on sinterability, thermal conductivity and microstructure of aluminium nitride ceramics was investigated. Thermal conductivity increased with increasing amount of Y_2O_3 additive, sintering temperature and holding time at the sintering temperature. Samples with a thermal conductivity up to 258 W m^{-1} K^{-1} were fabricated by elimination of the grain-boundary phase.

1. Introduction

Aluminium nitride (AlN) has a high thermal conductivity and good electrical insulation characteristics, and its thermal expansion coefficient is closely matched to that of silicon from room temperature to 200 °C (AlN 3.5×10^{-6} °C^{-1}, Si 3.4×10^{-6} °C^{-1}) [1, 2]. This explains why AlN is a promising material for passivation and dielectric layers in semiconductor devices, as well as for electronic substrates. The thermal conductivity of AlN is strongly influenced by its chemical purity and density, while the theoretical value was predicted to be 320 W m^{-1} K^{-1} at room temperature [1]. To densify pure AlN is difficult because of its high melting point and strong covalent bonding similar to other covalent materials, for example SiC. Therefore, experiments have been run in order to densify AlN with different additives. A variety of additives have been used [3–9] although much of the work has been with Y_2O_3 or CaO. Liquid phases, which promote densification, are formed between these additives and Al_2O_3 normally present on the surface of AlN powder as impurity. Because pressure sintering enhances densification faster than normal sintering, it has been reported that densification was performed by hot press (HP) sintering [8, 10] and hot isostatic press (HIP) sintering [11].

In the present study, pressureless sintering was carried out without sintering aids under a normal pressure of nitrogen. The conditions for sintering without additives in the fabrication of fully dense AlN ceramics have been studied, and the properties of the translucent body obtained with 99.6% theoretical density have been investigated. The additives are not only beneficial for achieving density, but also enhance the thermal conductivity of AlN. The effect of Y_2O_3 addition on thermal conductivity and densification in comparison with AlN ceramics without additives was also examined, as was the effect of elimination of the secondary phase formed at grain boundary on thermal conductivity.

2. Experimental procedure

2.1. Sample preparation

The starting material was AlN powder (Grade F, Tokuyama Soda, Tokyo, Japan) with a mean particle size of 1.3 μm, a specific surface area of 3.6 m^2 g^{-1}, and oxygen content of 0.8 wt %, as detailed in Table I. Fig. 1 shows the process of sample preparation. AlN powder was mixed in organic solvent with binder (methacrylic ester resin) and plasticizer for 20 h using a plastic bottle and plastic balls. The slurry prepared was formed into sheet by doctorblade casting. Furthermore, the AlN powder was formed preliminarily into a cylindrical compact under a pressure of 19.6 MPa by a stainless steel compaction die, and then cold isostatically pressed under 147 MPa.

The resultant green sheets after binder calcination at 400 °C and green compacts, were placed in highly pure and gas-tight AlN crucibles containing less sintering aids, and heated in a graphite resistance furnace at 1900 °C for 8 h under a pressure of 1 MPa (1 atm) nitrogen. A comparative study was made on the firing vessel, i.e. embedding in AlN powder or placing in a boron nitride (BN) crucible or in a BN-coated graphite crucible. The heating rate was 15 °C min^{-1} after 1000 °C.

In order to investigate the effect of addition of Y_2O_3 on thermal conductivity and sinterability, the specimens (green sheets and green compacts) containing Y_2O_3 additive were prepared by the process shown in Fig. 1. Setting conditions for firing of AlN green compact with Y_2O_3 additive were as follows. First of all, ring AlN green compacts containing the same amount of Y_2O_3 as the sample which was the firing vessel, were formed by cold isostatic pressing. AlN

TABLE I Analysis of AlN powder

Chemical composition (wt %)							Specific surface area ($m^2 g^{-1}$)	Average grain size (μm)
Al	N	O	C	Ca	Si	Fe		
65.8	33.5	0.82	0.024	0.008	0.002	0.001	3.6	1.3

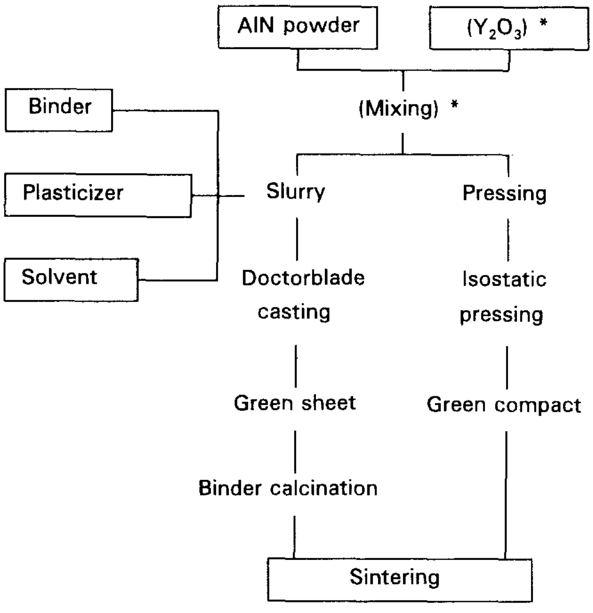

Figure 1 Flow diagram for the preparation of AlN ceramics. *Process for AlN ceramics containing Y_2O_3.

green compact sample containing Y_2O_3 additive, set inside the ring AlN green compact which was sandwiched by BN plates, was placed in a BN-coated graphite crucible. AlN green sheet containing Y_2O_3 additive was fired in a sintered AlN crucible without sintering aids. Sintering was performed in the range 1700–1900 °C in nitrogen gas at 1 MPa. To eliminate the yttrium aluminate formed at the secondary phase, sintered samples were placed in a carbon crucible, and reheated at 1900 °C for 8–50 h under a pressure of 1 MPa nitrogen.

2.2. Characterization

The bulk density was determined by the water displacement. The theoretical density of AlN was calculated to be 3.261 g cm^{-3}. The thermal diffusivity was measured by the laser-flash method using a ruby laser ($\lambda = 0.6943$ μm) and a liquid-nitrogen cooled InSb infrared detector (TC-3000, Shinku-Riko, Yokohama, Japan) at room temperature. Specimen discs, 10 mm diameter by 3 mm thick, cut from the sintered bodies were prepared for thermal conductivity, specific heat and thermal diffusivity measurements. The specimen surface on which the laser flash was incident was coated with gold, and both surfaces were coated with carbon to ensure complete absorption of the flash. Dielectric constant, ε, and volume resistivity were measured for the 50.8 × 50.8 mm substrate specimen of the 0.635 mm thick sintered body. The specimen was screen-printed with electrode paste, and then baked. Volumetric resistivity was measured by a high-resistance meter. Dielectric constant was measured by a multi-frequency LCR meter (YHP4275A, Yokogawa Howelett Packard Co., Tokyo, Japan). Fracture strength was measured in three-point bending on a universal testing machine (Instron, Canton, MA, USA), using a span of 30 mm and a crosshead speed of 0.5 mm min^{-1}. The microstructures of the sintered samples were observed by scanning electron microscopy (SEM). Crystalline phases were analysed by X-ray diffraction.

3. Results and discussion

3.1. Sintering without additives

The effect of the vessel and setting for firing on sintering of AlN without sintering aids is shown in Table II. From Table II (Experiments A, B), AlN powder with low oxygen content (0.8 wt %) was densified close to the theoretical density (99.6% theoretical) by pressureless sintering at 1900 °C for 8 h. The thermal conductivity of the dense AlN ceramics sintered without additives was in the range 90–115 $W m^{-1} K^{-1}$ at room temperature. The densities of AlN placed in a BN crucible (Experiment C) or in a BN-coated graphite crucible (Experiment D), were less than those of the sample placed in an AlN crucible (Experiment A) or embedded in AlN powder (Experiment B). The specimen placed in a graphite crucible without BN-coating was porous. The latter sintered bodies (Experiments A, B) were translucent but the former sintered bodies (Experiments C, D) were not uniform, and edge portions of the samples were whitish. The specimen placed in a BN crucible or BN-coated graphite crucible, showed a tendency for the inside of the body to be more dense than the surface layer. The portions of edge on the samples were found to be of lower density and to be loosely packed powder.

A study of the relationship between density and oxygen content of hot-pressed AlN has been reported [10], according to which, fully dense sintering requires an oxygen content of at least 2 wt %, and it is considered that the oxygen (Al_2O_3) as the impurity contained in AlN is important for sintering of AlN. Because graphite and BN crucibles are not gas-tight, Al_2O_3 contained in the surface region of the AlN green body is liable to evaporate under the carbon-reducing atmosphere in the graphite furnace. The obstacle to densification in the surface region of the AlN green body in the case of Experiments C and D, was considered to be caused by lowering the sinterability due to the evaporation of Al_2O_3 in the grain boundary of the AlN green body.

As-fired translucent AlN ceramics without sintering aids were fabricated by pressureless sintering at

TABLE II Effect of firing vessel and setting on the density of AlN ceramics

Firing Vessel and setting	Bulk density (g cm^{-3})	Thermal conductivity (W m^{-1} K^{-1})
A Placed in an AlN crucible[a]	3.25	114
B Embedded in AlN powder	3.25	91
C Placed in a BN crucible	≤ 3.00	–
D Placed in a BN-coated graphite crucible	≤ 3.00	–

[a] Gas-tight AlN crucible containing less sintering additives.

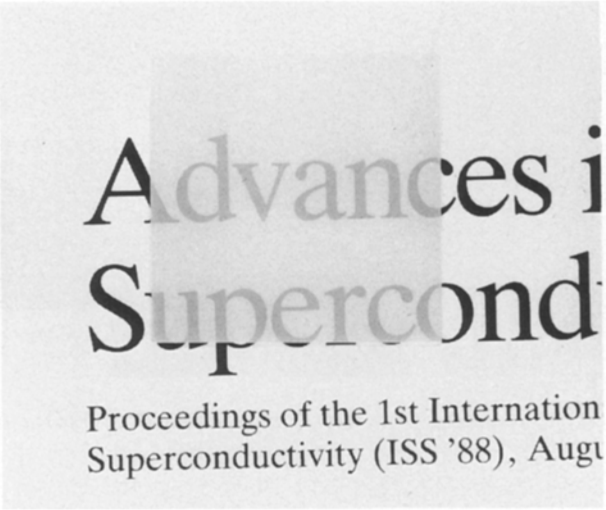

Figure 2 As-fired translucent AlN ceramics pressureless sintered at 1900 °C for 8 h without sintering aids (40 mm × 40 mm, 0.5 mm thick).

1900 °C for 8 h from green sheets (Fig. 2). The fracture surface of the sintered AlN without sintering aids is shown in Fig. 3. It is clear that this ceramic shows relatively uniform microstructure and high density. AlN grains were about 10–15 µm in size, and some spherical micropores about 0.2–0.5 µm located at grain boundaries, could be found in the higher magnification fractograph. The density of the sample was close to theoretical and the porosity was less than 0.4%. It has been reported that densification of AlN to the theoretical density requires an oxygen content of at least 2 wt % [10, 12]. In the present study and elsewhere [13, 14], using AlN powder containing approximately less than 1 wt % oxygen prepared by carbothermal reduction of Al_2O_3, dense AlN ceramics could be fabricated by pressureless sintering without sintering aids. To fabricate dense AlN ceramics by pressureless sintering without additives, requires AlN powder with high sinterability which is determined by purity, specific surface area, particle size and particle-size distribution. When the sintering is performed, it is important to place the green sample in an AlN crucible or to embed it in AlN powder.

3.2. Sintering with Y_2O_3

Fig. 4 shows the sintering behaviour for AlN green sheets containing 3.5 and 5 wt % Y_2O_3. There is a tendency that the higher the content of Y_2O_3 additive, the more sintering proceeded at lower sintering temperature. The densities of the specimens containing 3.5 and 5 wt % Y_2O_3 reached maximum densities of 3.321 and 3.353 g cm^{-3} at 1775 °C, respectively. These samples were fully dense. Because of the presence of the secondary phase with higher specific gravity, the theoretical densities of these specimens were bigger than that of pure AlN (3.261 g cm^{-3}).

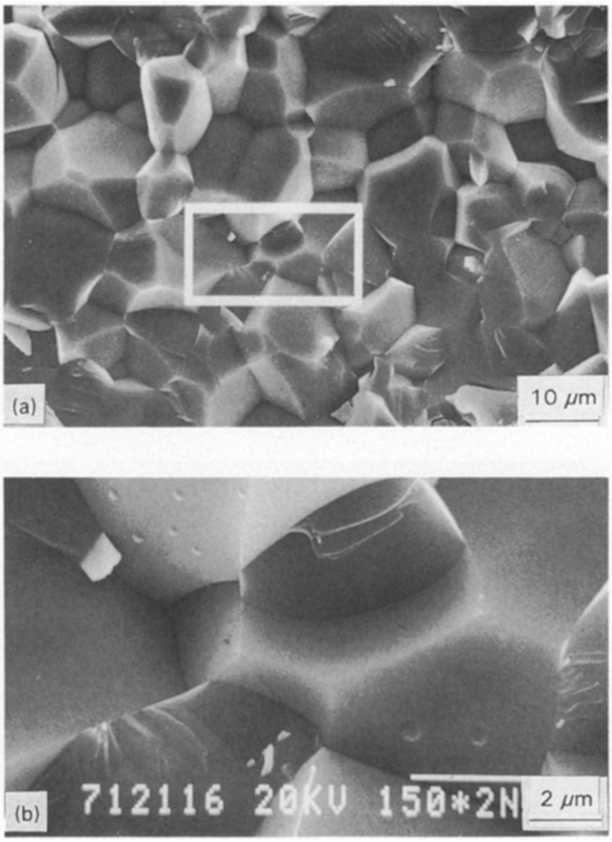

Figure 3 Scanning electron micrographs of the fracture surface of AlN sintered at 1900 °C for 8 h without sintering aids.

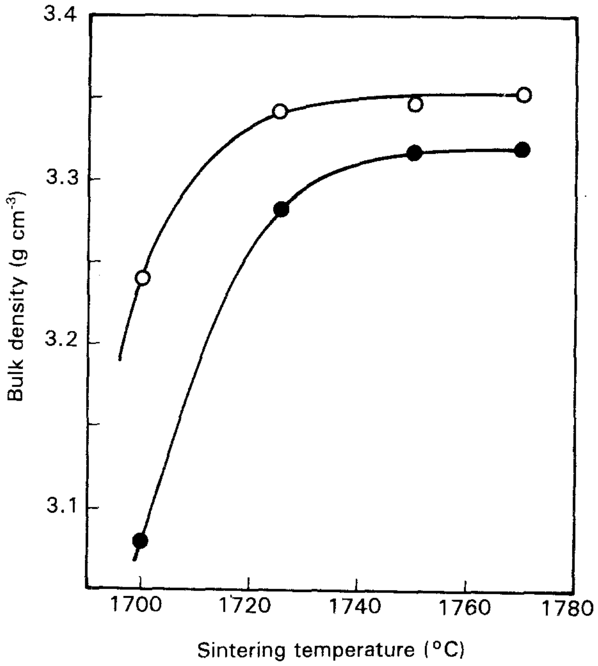

Figure 4 Bulk density as a function of sintering temperature for AlN substrates containing (●) 3.5 and (○) 5 wt % Y_2O_3.

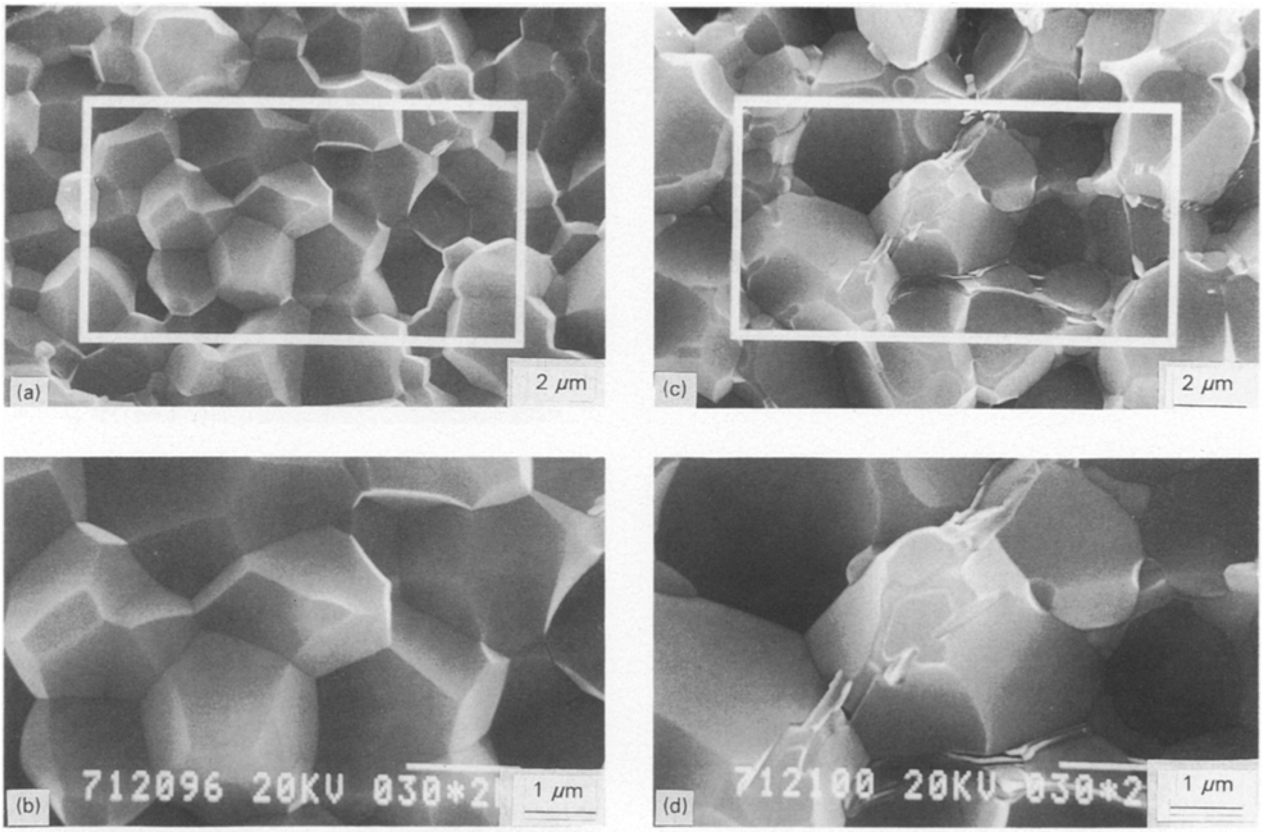

Figure 5 Scanning electron micrographs of the fracture surface of AlN substrates containing 4 wt % Y_2O_3 sintered at (a, b) 1725 °C and (c, d) 1775 °C for 2 h.

Investigations have been reported on the sintering behaviour and mechanism of AlN with sintering additives such as Y_2O_3, CaO, CaC_2, and $3CaO \cdot Al_2O_3$ [3, 8, 9, 15]. The role of Y_2O_3 as a sintering additive can be summarized as follows. The sintering additive Y_2O_3 reacted with Al_2O_3 on the surface of AlN powder to form liquid phases, which promoted sintering. The densification of these samples occurred rapidly and at a lower sintering temperature, owing to the presence of liquid phases, compared to the sample without additives.

Fig. 5 shows fracture surfaces of AlN substrates containing 4 wt % Y_2O_3 sintered at 1725 and 1775 °C for 2 h. The microstructures of these samples are uniform, and had a uniform grain size of about 2.5 m and 4.0 μm, respectively. As shown in the fractographs, the presence of the secondary phase at the grain boundary is clearly seen on increasing the sintering temperature from 1725 °C to 1775 °C. The observed fracture mode was intergranular rather than intragranular.

The effect of Y_2O_3 additive on density and thermal conductivity for AlN ceramics sintered at 1750 °C for 2 h and 1900 °C for 8 h is shown in Fig. 6. The specimen with 1.5 wt % Y_2O_3 sintered at 1750 °C did not reach its full density. The addition of nearly 3 wt % Y_2O_3 was required to obtain fully densified body by sintering at 1750 °C. The addition of Y_2O_3 is not only effective for densification, but also enhances the thermal conductivity of AlN. Thermal conductivity in excess of 180 W m^{-1} K^{-1} could be achieved by sintering AlN containing > 3 wt % Y_2O_3 at 1750 °C.

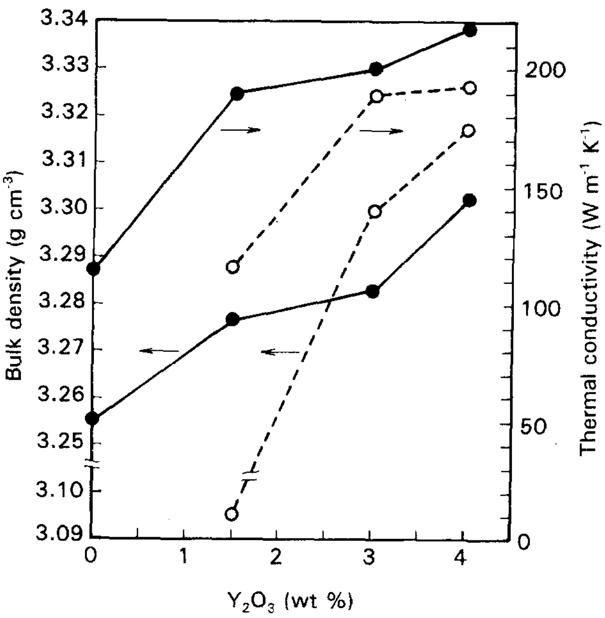

Figure 6 Effect of Y_2O_3 content on density and thermal conductivity of AlN ceramics sintered at (○) 1750 °C for 2 h and (●) 1900 °C for 8 h.

The density of the specimen containing 3 and 4 wt % Y_2O_3 decreased with increasing sintering temperature and holding time from 1750 °C for 2 h to 1900 °C for 8 h. Thermal conductivity of AlN sintered at 1900 °C for 8 h, was enhanced from 113 W m^{-1} K^{-1} for AlN without additives, to 188, 200 and 218 W m^{-1} K^{-1} by the addition of 1.5, 3 and 4 wt % Y_2O_3, respectively.

Thermal conductivity increased with increasing amount of additive and sintering temperature. Y_2O_3

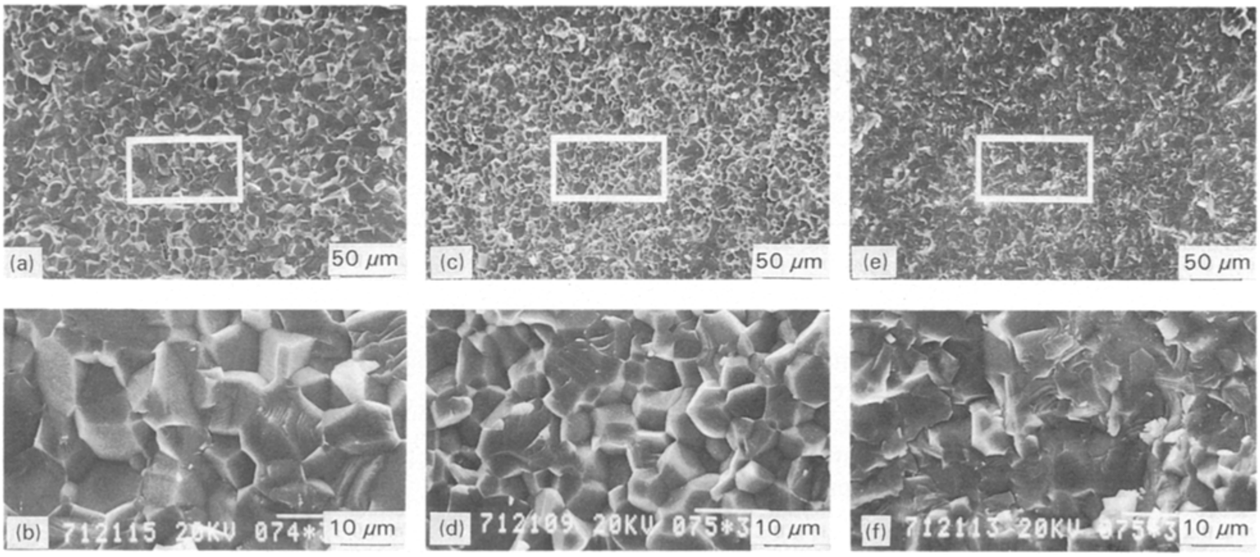

Figure 7 Scanning electron micrographs of the fracture surface of AlN ceramics (a, b) without additives, (c, d) with 2 wt % Y_2O_3 and (e, f) with 4 wt % Y_2O_3 sintered at 1900 °C for 8 h.

TABLE III Density and thermal conductivity of AlN specimen sintered at 1800 °C for 2 h in an AlN crucible and then reheated in a carbon crucible at 1900 °C for 8 h

Y_2O_3 composition (wt %)	Bulk density ($g\ cm^{-3}$)	Thermal conductivity ($W\ m^{-1}\ K^{-1}$)
2	3.258	221
3	3.258	218
4	3.265	225

additive reacted with Al_2O_3 on the surface of AlN powder, to form yttrium aluminates ($Y_3Al_5O_{12}$, $Y_4Al_2O_9$) as the secondary phase, as well as Y_2O_3, which were along three grain junctions and along grain facets. In this way, the AlN lattice was purified, and then thermal conductivity was enhanced by removing dissolved oxygen. Thermal conductivity was also enhanced by increasing the AlN grain size with increasing sintering temperature and holding time.

Table III shows the density and thermal conductivity of an AlN specimen, sintered in an AlN crucible at 1800 °C for 2 h and then reheated in a carbon crucible at 1900 °C for 8 h. The density of specimen containing 2, 3 and 4 wt % Y_2O_3 decreased from 3.290, 3.312 and 3.331 $g\ cm^{-3}$ to 3.258, 3.258 and 3.265 $g\,cm^{-3}$, respectively. The density of these specimens reached close to the theoretical density of AlN (3.261 $g\,cm^{-3}$). Thermal conductivity also reached about 220 $W\,m^{-1}\,K^{-1}$, unrelated to the Y_2O_3 content.

Microstructures of fracture surfaces of AlN sintered at 1900 °C for 8 h are shown in Fig. 7. The grain size of AlN without additives was larger than that of AlN with Y_2O_3. Although the observed fracture mode of AlN without additives and with 2 wt % Y_2O_3 was intergranular, AlN with 4 wt % Y_2O_3 was intragranular. The density of AlN with 2 wt % Y_2O_3 is close to the theoretical density of pure AlN, as given in Table III. In contrast, the density of AlN with 4 wt % Y_2O_3 is still larger than the theoretical density of pure AlN, and it is considered that the secondary phase remains. Microstructural differences between AlN with 2 wt % Y_2O_3 and AlN with 4 wt % Y_2O_3 are due to the existence of the secondary phase still remaining.

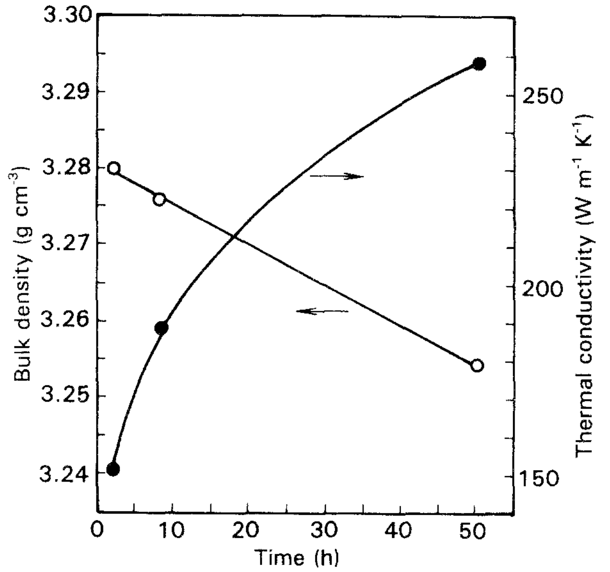

Figure 8 Effect of reheating at 1900 °C for 50 h in a carbon crucible on (○) density and (●) thermal conductivity of AlN with 1.5 wt % Y_2O_3 sintered in 1900 °C for 2 h and 8 h.

Fig. 8 shows the effect of holding time at the reheating temperature (1900 °C) on density and thermal conductivity of a sintered AlN specimen with 1.5 wt % Y_2O_3. The density decreased from 3.283 $g\,cm^{-3}$ to 3.255 $g\,cm^{-3}$ and the thermal conductivity increased from 150 $W\,m^{-1}\,K^{-1}$ to 258 $W\,m^{-1}\,K^{-1}$. Because reheating was conducted in a graphite crucible and graphite resistance furnace, yttrium aluminate as a secondary phase was reduced, nitrified and removed under a reducing gaseous atmosphere. It is considered that the elimination of the aluminate as the secondary phase and grain growth further enhanced the thermal conductivity.

Properties of fully dense AlN substrates without and with Y_2O_3 fabricated in this study are listed in

TABLE IV Properties of fully dense AlN ceramics

Additives	Bulk density ($g\ cm^{-3}$)	Thermal conductivity ($W\ m^{-1}\ K^{-1}$)	Resistivity at 500 °C (Ω cm)	Dielectric constant	Grain size (μm)	Bending strength (MPa)
No addition[a]	3.25	114	1.0×10^9	8.7	12.5	240
4 wt % Y_2O_3[b]	3.32	194	4.4×10^9	8.9	3.5	353

[a] Sintered at 1900 °C for 8 h.
[b] Sintered at 1770 °C for 2 h.

Table IV. As the grain size of AlN without additives is larger than that of AlN with Y_2O_3, the bending strength of AlN without additives was relatively low. From these data, it is demonstrated that AlN is attractive and useful for electronic materials.

4. Conclusions

1. AlN substrates were fabricated by pressureless sintering of tape-cast green sheets with and without Y_2O_3 additive.

2. Translucent AlN ceramics with uniform microstructure, high sintered density of 3.25 $g\,cm^{-3}$ (99.6% theoretical) and a thermal conductivity of 114 $W\,m^{-1}\,K^{-1}$ were obtained by sintering without additives at 1900 °C for 8 h in nitrogen gas at 1 MPa.

3. The thermal conductivity of the specimen with Y_2O_3 depended on sintering conditions (temperature and holding time) and the amount of addition, and it was enhanced up to 258 $W\,m^{-1}\,K^{-1}$ by long-period reheating under a reducing gaseous atmosphere.

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Received 30 April 1992
and accepted 3 February 1993