

Development of as-fired aluminium nitride substrates with smooth surface and high thermal conductivity

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As-fired aluminium nitride (AlN) substrates with smooth and uniform surface have been developed by green sheet and firing technology. The effect of setting for firing on surface roughness was investigated. AlN substrates were fabricated by pressureless sintering of green sheets piled up and sandwiched between AlN plates in an AlN crucible. The thermal conductivity, surface roughness and bending strength of the substrate sintered at 1770 °C for 2 h under a pressure of 1 MPa nitrogen were 194 W m⁻¹ K⁻¹, 0.15 μm and 353 MPa, respectively.

1. Introduction

The increase in the amount of heat generated in electronic packages results in an increasing circuit density and power on silicon chips. Highly thermally conductive substrates are required to dissipate the heat generated in these packages. AlN has excellent 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 $3.5 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$, Si $3.4 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$) [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]. The primary heat transport mechanism of AlN is phonon propagation [3]. Oxygen impurities scatter phonons mostly from the mass defects caused by aluminium vacancies in the AlN lattice and thus lower the thermal conductivity.

Densification of pure AlN is difficult because of its high melting point and strong covalent bonding. Because pressure sintering enhances densification faster than normal sintering, it has been reported that densification was performed by hot press (HP) [4, 5] and hot isostatic press (HIP) [6] sintering. Dense AlN bodies were achieved by pressureless sintering with a variety of additives such as alkali earth or rare earth oxide [7-15] although much of the work has been with Y₂O₃ or CaO. Liquid phases which promote densification are formed between these additives and Al₂O₃ normally present on the surface of AlN powder as an impurity. We have studied the sintering of AlN with or without Y₂O₃ additive, and have fabricated AlN ceramics with a thermal conductivity up to 258 W m⁻¹ K⁻¹ by a pressureless sintering and

reheating process [16]. Sintering temperature, sintering time and sample setting condition affect the thermal conductivity, microstructure and density of AlN ceramics as well as the amount of additives. Usually, the standard AlN substrates are lapped to 0.4-0.6 μm R_a surface roughness to be desirable for thick-film metallization [17]. For the purpose and the first stage of fabricating the multilayer substrates and packages by the co-firing process for AlN substrate with a tungsten conductor, it is necessary to develop the technique for fabrication of as-fired substrates with smooth and uniform surface and high thermal conductivity. Kurokawa *et al.* [18] have reported as-fired AlN substrate with a surface roughness R_a = 0.5 μm. Generally, the surface roughness of the substrate mainly depends on the grain size and defect size on the surface, which is related to starting raw materials, properties of green sheet, firing technique and sintering conditions and so on.

In the present study, the effects of sintering conditions and additive on the surface roughness as well as densification, microstructure and thermal conductivity of AlN substrates, were investigated.

2. Experimental procedure

2.1. Processing

The process for AlN substrate fabrication is shown in Fig. 1. Commercial AlN powder (Grade F, Tokuyama Soda, Tokyo, Japan) with a specific surface area of 3.6 m² g⁻¹, and oxygen content of 0.9%, was used. Chemical analyses and size characteristics are given in Table I. The average particle size of the sintering additive Y₂O₃ is 1.1 μm and the purity is higher than 99.9%. AlN and Y₂O₃ powders were mixed in organic solvent with a binder (methacrylic ester resin) and plasticizer for 20 h using a plastic bottle and plastic

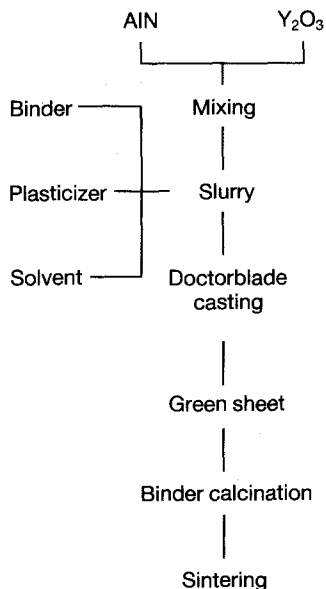


Figure 1 Flow diagram for the preparation of AlN ceramics.

balls. The slurry was formed into a thin ceramic green sheet by the doctor blade casting process. A uniform green sheet ($\sim 1000 \mu\text{m}$) with high tensile strength and without pin holes or cracks was obtained. The green sheets which were piled up and sandwiched between AlN plates were heated to 400°C at a slow heating rate in nitrogen gas to burn out the binder. The resultant sheets were placed in an AlN crucible which was highly pure, gas-tight and contained less sintering aids, and then heated in a graphite resistance furnace at temperatures ranging from $1700\text{--}1800^\circ\text{C}$ for 2 h under a pressure of 1 MPa (1 atm) nitrogen. Fig. 2 shows the sample arrangement for firing. A comparative study has been made of setting conditions for firing in an AlN crucible using BN particles instead of AlN plates. The standard size of AlN substrates after sintering was about $50.8 \text{ mm} \times 50.8 \text{ mm}$ and 0.635 mm thick.

2.2. Characterization

The bulk density was determined by water displacement; the theoretical density of AlN was calculated to be 3.261 g cm^{-3} . The thermal conductivity was measured by the laser-flash method using a ruby laser ($\lambda = 0.6943 \mu\text{m}$) 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 obtained from laminated green sheets, 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. Surface roughness was measured by a probe-type surface roughness meter (Talysurf-10, Taylor-Hobson, Leicester, England) for the centre-line average roughness, R_a . Dielectric constant, ϵ , dielectric loss, $\tan \delta$, and

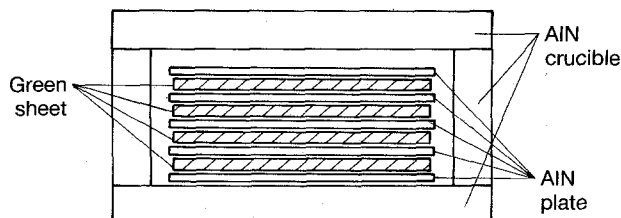


Figure 2 Sample set-up for firing.

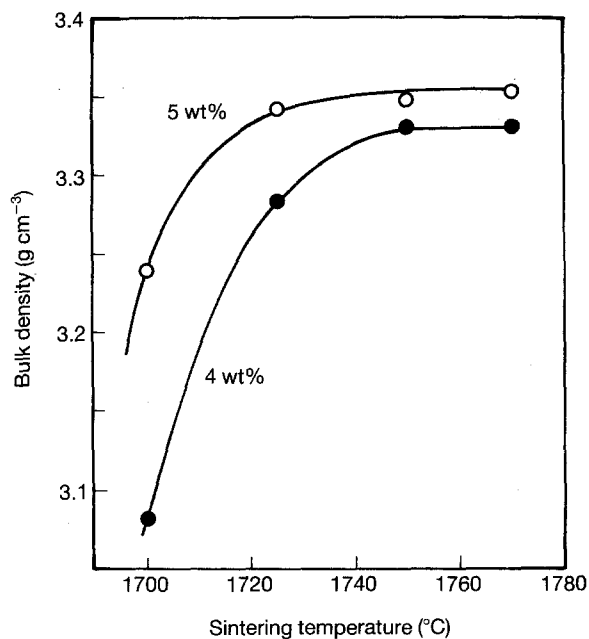


Figure 3 Bulk density as a function of sintering temperature for AlN substrates containing 4 and 5 wt % Y_2O_3 .

TABLE I Analysis of AlN powder

Chemical composition (wt %)							Specific surface area ($\text{m}^2 \text{g}^{-1}$)
Al	N	O	C	Ca	Si	Fe	
65.8	33.5	0.91	0.031	0.009	0.003	0.001	3.6

volume resistivity were measured for the $50.8 \text{ mm} \times 50.8 \text{ mm}$ 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 and dielectric loss was measured by a multi-frequency LCR meter (YHP4275A, Yokogawa Howeleet Packard, Tokyo, Japan). Fracture strength was measured in three-point bending on a universal testing machine (Instron, Canton, MA), using a span of 30 mm and a crosshead speed of 0.5 mm min^{-1} . The microstructure 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. Firing conditions and surface properties

The sintering behaviour for AlN green sheets containing 4 and 5 wt % Y_2O_3 is shown in Fig. 3. It had the

tendency for which the higher the content of Y_2O_3 , additive the more the sintering proceeded at lower sintering temperature in the range of the present experiment. The densities of the specimens containing 4 and 5 wt % Y_2O_3 reached maximum densities of 3.331 and 3.353 $g\ cm^{-3}$ at 1775 °C, respectively, and these samples were fully dense. The bulk densities of these samples were higher than the theoretical density of pure AlN (3.261 $g\ cm^{-3}$). The higher density in these samples containing Y_2O_3 are related to the presence of the denser grain-boundary phase. A variety of additives has been used for sintering aids [7–15]. The additives reacted with Al_2O_3 normally present on the surface of AlN powder as an impurity, and formed liquid phases. The densification was promoted by the presence of liquid phases. When the sintering temperature and time increased above 1775 °C and 2 h, it showed the tendency for the densities of the specimens to decrease from maximum values and reach a value close to the theoretical density of pure AlN.

Fig. 4 shows a scanning electron micrograph of AlN substrate fabricated by pressureless sintering with 4 wt % Y_2O_3 . Linear shrinkage of the AlN substrate was 20.1%. Sintered density and uniformity in macrostructure and microstructure depend on firing conditions [14, 16]. The specimens placed in a graphite crucible and heated in a graphite furnace were not uniform and had lower densities. The edge on the sample was white and found to be loosely packed powder. When using Y_2O_3 additive, the colour of the sample changed to black, which was due to the presence of YN, because of heating under a carbon-

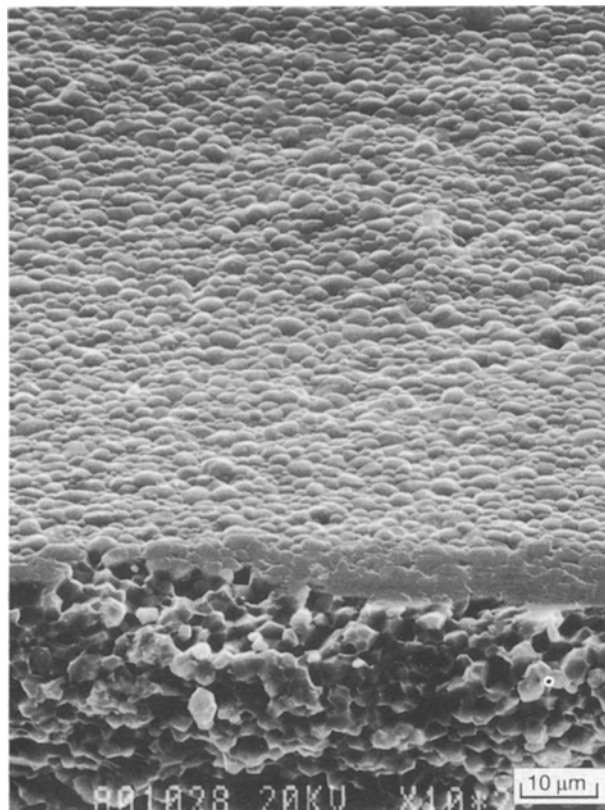


Figure 4 Scanning electron micrograph of the section of AlN substrate containing 4 wt % Y_2O_3 .

reducing atmosphere in the graphite furnace. Therefore, sintering of AlN was performed with the samples embedded in AlN [14, 16, 19] or Y_2O_3 powder [19] or by placing them in a BN [14] or AlN crucible [16] or BN-coated graphite crucible [12].

To obtain uniform AlN substrate with a smooth surface, the firing conditions are the key factor. In the case of the green body embedded and heated in AlN or Y_2O_3 powder, the surface of the sample is apt to react with those packing powders. In the present study, two different firing conditions were employed: (1) green sheets were piled up using BN particles between them, and then placed in an AlN crucible, (2) green sheets were piled up and sandwiched between AlN plates, and then placed in an AlN crucible, as illustrated in Fig. 2. In both cases, specimens were sintered at 1770 °C for 2 h in a graphite furnace.

Fig. 5 and Table II show the results of surface roughness of the substrates fabricated by the former firing condition 1. Except for the upper side of the top substrate, surface roughness, R_a , was in the range 0.3–0.5 μm . The results in the present study were on the same level with the value in the Kurokawa's *et al.*'s report [18]. These values of surface roughness are almost the same as those of 96 % Al_2O_3 substrates. Because the upper side of the top substrate did not come into contact with BN particles, it was not affected by them, so that the surface roughness of the upper side of the top substrate was a good value.

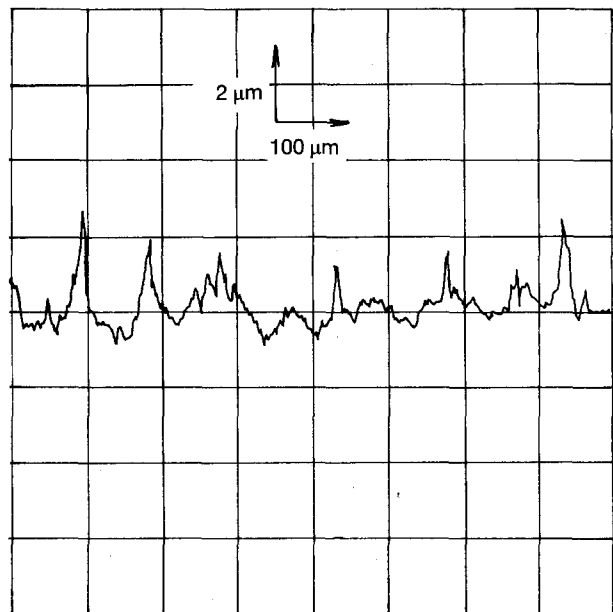


Figure 5 Surface roughness of as-fired AlN substrate fabricated by using BN particles between green sheets.

TABLE II Surface roughness, R_a , of as-fired AlN substrates fabricated by using BN particles between green sheets

Sample position	Side	R_a (μm)
Top	Upper	0.16
	Lower	0.48
Bottom	Upper	0.36
	Lower	0.34

TABLE III Surface roughness, R_a , of as-fired AlN substrates fabricated by using AlN plates between green sheets

Sample position	Side	R_a (μm)
Top	Upper	0.20
	Lower	0.13
Second	Upper	0.18
	Lower	0.13
Third	Upper	0.18
	Lower	0.12
Bottom	Upper	0.19
	Lower	0.13

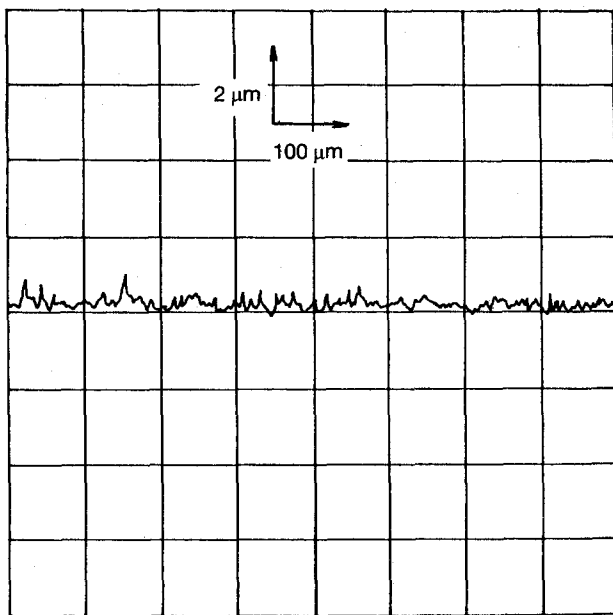


Figure 6 Surface roughness of as-fired AlN substrate fabricated by using AlN plates between green sheets.

Fig. 6 and Table III show the results of surface roughness of the substrates, which were sandwiched between AlN plates (firing condition 2). The surface roughness, R_a , of the upper side of the substrates was in the range 0.18–0.20 μm and that of the lower side of the substrates was in the range 0.12–0.13 μm , respectively. There was a tendency for the surface of the upper side to be rougher than that of lower side. Usually, it is desirable for the standard AlN substrates to be used lapped for thick-film metallization, and the surface roughness, R_a , of standard AlN substrate is 0.4–0.6 μm [17]. The surface roughness of as-fired substrate obtained in this study was superior to the standard AlN substrates lapped.

Fig. 7 shows the camber of as-fired AlN substrate fabricated by firing condition 2. The camber of as-fired AlN substrate was below 30 $\mu\text{m}/50\text{mm}$. In the case of Al_2O_3 substrates, usually they are reheated with weights to reform the camber of as-fired substrates. Because the camber of as-fired AlN substrates was small, there was no need to reform them.

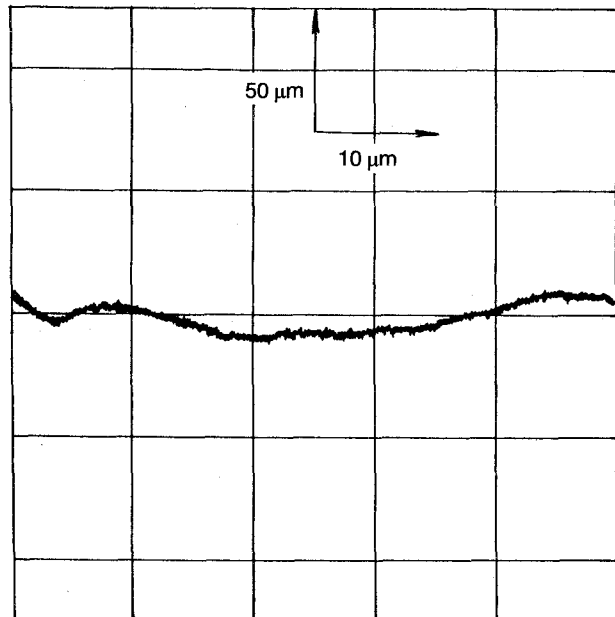


Figure 7 Camber of as-fired AlN substrate.

3.2. Microstructure and substrate properties

Fig. 8 shows fracture surfaces of AlN substrates with 4 wt % Y_2O_3 sintered at 1700, 1750 and 1775 $^\circ\text{C}$ for 2 h. The microstructures of these samples are uniform with grain sizes of about 1.5, 3.5 and 4.0 μm , respectively. As the density of the specimen sintered at 1700 $^\circ\text{C}$ was 3.08 g cm^{-3} and did not reach full density, some pores were observed in Fig. 8a. The microstructure of the sample sintered at 1775 $^\circ\text{C}$ shows the presence of the grain-boundary phase clearly.

Fig. 9a shows the surface of one of the as-fired AlN specimens. There are crystallites uniformly distributed over the surface. Fig. 9b is the EPMA photograph. The crystallites shown in the photograph were distinguished from others by the distribution of yttrium. More yttrium was found in these crystallites. From analysis by X-ray diffraction and the EPMA photograph, it was surmised that yttrium aluminates as the liquid phase was crystallized on the surface by cooling.

Fig. 10 shows photographs of the surface of green sheet after binder burn-out. From Fig. 10b, yttrium was seen to be distributed uniformly in the green sheet. It may be clear that yttrium is concentrated during the firing process. It is considered that the yttrium aluminates liquid phase contents, which are formed in the sintering process, is apt to increase with increasing oxygen content in the AlN green body. To improve surface roughness of as-fired AlN substrate, it is necessary to decrease the oxygen content in the AlN green body.

The addition of Y_2O_3 is not only effective for densification, but also enhances the thermal conductivity of AlN ceramics. The thermal conductivity of the substrate was measured using the sample obtained from laminated green sheets. Some characteristics of the AlN substrate are listed in Table IV. The thermal conductivity of AlN substrates with 4 wt % Y_2O_3 was

TABLE IV Properties of AlN substrate with 4 wt % Y_2O_3 fabricated by sintering at 1770°C for 2 h

Bulk density ($g\ cm^{-3}$)	Thermal conductivity ($W\ m^{-1}\ K^{-1}$)	Bending strength (MPa)	Resistivity at 500°C ($\Omega\ cm$)	Dielectric constant at 1 MHz	Dielectric loss ($\tan\ \delta$) at 1 MHz
3.32	194	353	4.4×10^9	8.9	0.00065

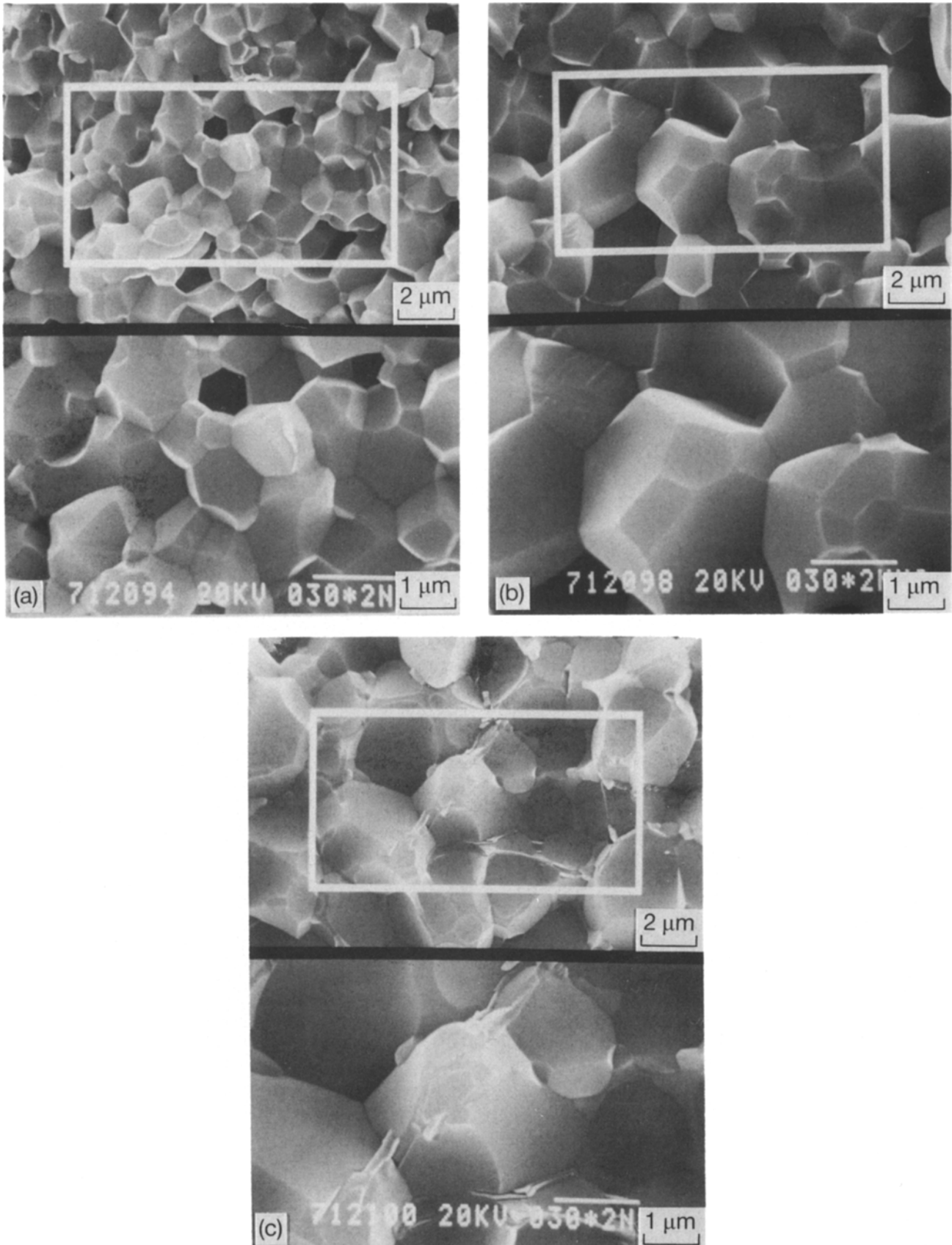


Figure 8 Scanning electron micrographs of the fracture surface of AlN substrates containing 4 wt % Y_2O_3 sintered at (a) 1700°C, (b) 1750°C and (c) 1775°C for 2 h.

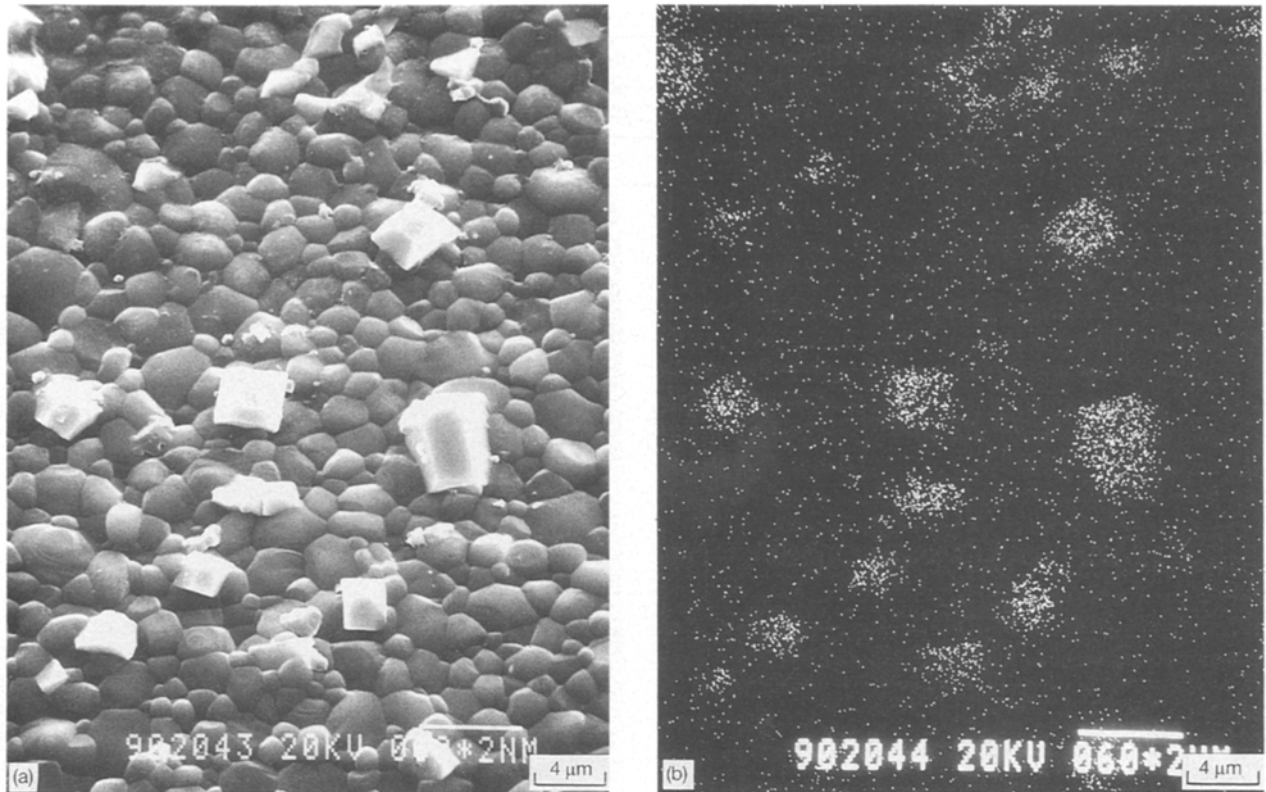


Figure 9 Scanning electron micrograph of (a) the surface of as-fired AlN substrate, and (b) the yttrium X-ray image of (a).

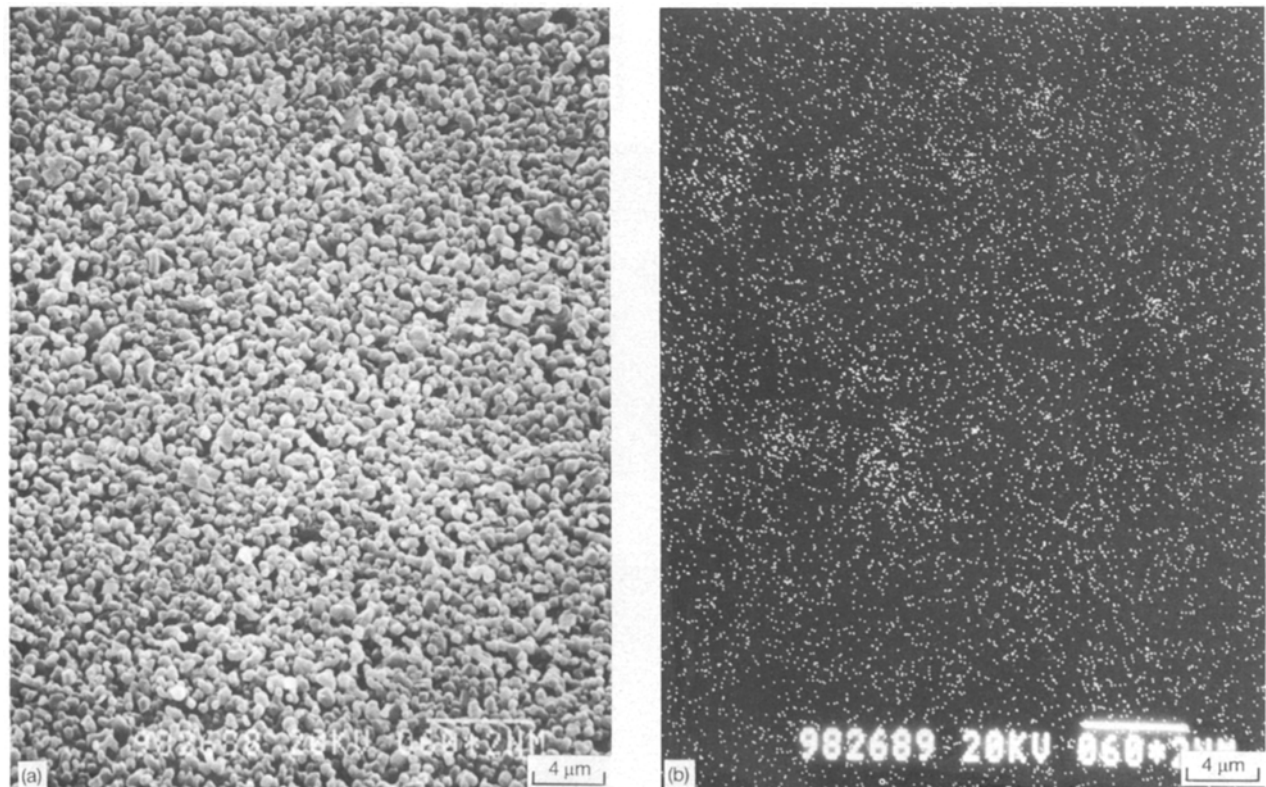


Figure 10 Scanning electron micrograph of (a) the surface of AlN green sheet, and (b) the yttrium X-ray image of (a).

$194 \text{ W m}^{-1} \text{ K}^{-1}$ although that of AlN ceramics sintered without sintering additives at 1900°C was $114 \text{ W m}^{-1} \text{ K}^{-1}$ [16]. The fabricated AlN substrate with a smooth and uniform surface showed excellent thermal conductivity, low dielectric loss and high mechanical property.

4. Conclusions

1. As-fired substrates with a smooth and uniform surface were developed by firing the green sheets piled up and sandwiched between AlN plates in an AlN crucible.

2. Crystallites distributed over the surface were found in as-fired AlN substrates, and it was surmised that yttrium aluminates as the liquid phase was crystallized on the surface by cooling.

3. Surface roughness, camber and thermal conductivity of the as-fired substrates fabricated were 0.15 μm , 30 $\mu\text{m}/50\text{ mm}$ and 194 $\text{W m}^{-1} \text{K}^{-1}$, respectively.

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