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Thermal diffusivity of SiO_2 and Y_2O_3 added AlN ceramics

TAKESHI YAGI, KAZUO SHINOZAKI, NOBUYASU MIZUTANI,
MASANORI KATO
Department of Inorganic Materials, Faculty of Engineering, Tokyo Institute of Technology, O-Okayama, Meguro-ku, Tokyo 152, Japan

AKIHIKO TSUGE
Research and Development Center, Toshiba Corporation, Komukai, Saiwai-ku, Kawasaki-shi, Kanagawa 210, Japan

The addition of both SiO_2 and Y_2O_3 to AlN led to decrease of 27R polytype in specimens sintered above 1600° C and also to an increase of thermal diffusivity of AlN ceramics. Furthermore, SiO_2 and Y_2O_3 added AlN ceramics were fully densified by liquid-phase sintering, and resulted in higher thermal diffusivity. The formation temperature of the liquid phase was lowered more by the addition of both SiO_2 and Y_2O_3 than only Y_2O_3 to AlN ceramics.

1. Introduction

It is difficult to obtain fully densified AlN ceramics by pressureless sintering [1, 2]. Additives for densification of AlN ceramics have been investigated [3, 4]. The effect of thirty kinds of additives on pressureless sintering of AlN was examined systematically by Komeya *et al.* [5], who suggested that alkali earth and rare earth oxides had a great effect on the densification of AlN ceramics.

The thermal conductivity of AlN has been investigated. AlN essentially has high thermal conductivity ($320\,W\,m^{-1}\,K^{-1}$ is expected for a single crystal [6]), but it is known that impurities, oxygen in particular, are responsible for the decrease of thermal conductivity [7–9]. Recently, it was found that some additives (e.g. Y_2O_3, CaO and $Ca(NO_3)_2$), which densified AlN to nearly theoretical density, were very effective for the increase of thermal conductivity of AlN ceramics [9, 10].

In our previous work [11], the thermal diffusivity of AlN ceramics decreased significantly by addition of SiO_2. The AlN ceramics with 4 wt % SiO_2 could not be densified by pressureless sintering in the temperature range from 1400 to 1800° C, because of the absence of a liquid phase. The thermal diffusivity of these samples was very low, because of their porous structure. The AlN ceramics containing 2, 4 and 8 wt % SiO_2 were densified by hot-pressing, but also had low thermal diffusivity. In these samples, the grains of 27R polytype formed by the reaction between AlN and SiO_2 were dispersed and obstructed the conduction of heat.

In this study, the sinterability and the thermal diffusivity of AlN ceramics with both SiO_2 and Y_2O_3 added were investigated.

2. Experiment

2.1. Simultaneous addition of SiO_2 and Y_2O_3

3 wt % SiO_2 (Wako-Junyaku Co Ltd) and 8 wt % Y_2O_3 (Shin'etsukagaku Ltd) were added to the AlN powder (Toshiba Corporation Research and Development Center), which was prepared by reduction process of Al_2O_3, and mixed in butyl alcohol. After drying, the mixture was formed into pellets by isostatic-pressing at $1000\,kg\,cm^{-2}$. The compact bodies were sintered in an AlN crucible at 1400, 1500, 1600, 1700 and 1800° C for 2 h in 1 atm of nitrogen.

2.2. Two-step addition of SiO_2 and Y_2O_3

In the first step, SiO_2 was added to AlN powder. The mixture was compacted and sintered at 1800° C for 2 h in 1 atm of nitrogen. In the second step, sintered AlN bodies with SiO_2 were ground in an agate mortar, and then Y_2O_3 was added to this ground AlN powder. The mixture was compacted and sintered again at 1400, 1600, 1700 and 1800° C for 2 h in 1 atm of nitrogen. The composition of final products was 3 wt % SiO_2 and 8 wt % Y_2O_3 as same as in experiment 2.1.

Thermal diffusivity was measured by a laser-flash method using a ruby laser ($\lambda = 0.6943\,\mu m$) and the liquid nitrogen-cooled InSb infrared detector (TC-3000-NCA, Shinkuriko Co., Ltd) at room temperature. The specimen discs were ≈ 10 mm in diameter and 3 mm thick.

The powder X-ray diffraction data were obtained by a diffractometer (Philips PW1700, Nippon Philips Corporation) using graphite-monochromated Cu*Kα* radiation.

Microstructural analysis was carried out using an analytical electron microscope (AEM: JEOL 200CX, JEOL Ltd with EDAX PV9100, Nippon Philips Corporation) and a scanning electron microscope (SEM: JEOL T-200, JEOL Ltd). Samples for AEM were sliced from the sintered bodies by a diamond cutter, thinned by hand to $\approx 20\,\mu m$ thick and finally by an ion beam milling machine (Edwards IBT-200, Nissan-Edwards Co., Ltd).

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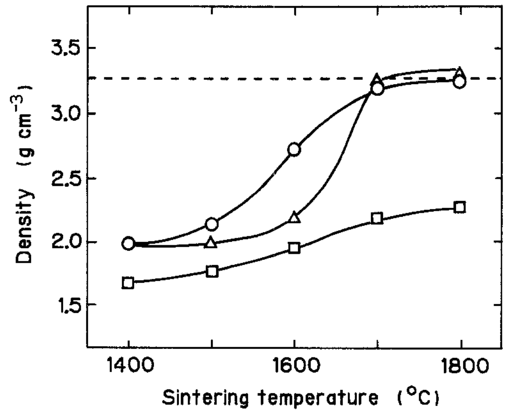

Figure 1 The effect of sintering temperature on the density of AlN ceramics for various additives. The dotted line indicates the theoretical density of AlN (3.26 g cm^{-3}) (○ $SiO_2 + Y_2O_3$, △ Y_2O_3, □ SiO_2).

The density of the sintered body was calculated using diameter, thickness and weight of specimens.

3. Result and discussion

3.1. Simultaneous addition of SiO_2 and Y_2O_3

3.1.1. Densification

Figure 1 shows the change of density with sintering temperature for AlN ceramics with 3 wt % SiO_2 and 8 wt % Y_2O_3. The results for AlN ceramics with 7 wt % Y_2O_3 and with 4 wt % SiO_2 [11] are also plotted for reference. The density of AlN ceramics with SiO_2 and Y_2O_3 increased with sintering temperature, and finally this sample was fully densified at 1800° C. Particularly, in the temperature range from 1500 to 1700° C, the increase in density was large. Similarly, for AlN ceramics containing Y_2O_3, the density increased rapidly in the temperature range from 1600 to 1700° C and then reached the theoretical value. The addition of alkali earth and rare earth oxides gave fully densified AlN by sintering with liquid phase aluminate in the system of AlN–alkali earth oxides or rare earth oxides [5, 10]. The effect of Y_2O_3 in this work agreed with previous results [5, 10]. In addition, the result of AlN ceramics with SiO_2 and Y_2O_3 suggested that even in the case of coexistence of SiO_2, Y_2O_3 was effective on the densification of AlN. The following microstructure observation shows that the sintering with liquid phase also occurred in AlN ceramics containing SiO_2 and Y_2O_3 in the temperature range from 1500 to 1800° C. In this temperature range, the rapid densification occurred as shown in Fig. 1.

Furthermore, the comparison of densification curves of AlN ceramics containing only Y_2O_3 and containing both SiO_2 and Y_2O_3 suggested that the temperature at which densification started, i.e. liquid phase began to form, in AlN ceramics with both SiO_2 and Y_2O_3 was lower than that for AlN ceramics with Y_2O_3. Thus, there may be the possibility of sintering at lower temperature by addition of the Y_2O_3 and SiO_2.

3.1.2. Identification of phases

Figure 2 shows the powder X-ray diffraction patterns of AlN ceramics containing 3 wt % SiO_2 and 8 wt % Y_2O_3 sintered at various temperatures. The specimen sintered at 1400° C consisted of AlN and $Y_4Al_2O_9$ as major phases, 27R polytype of AlN [12] as minor and trace of α-Al_2O_3. α-Al_2O_3, present in the surface layer of AlN particles of the starting powder [8], did not exist in the specimens sintered above 1600° C. This might be due to the formation of compounds in the system of Al_2O_3–Y_2O_3 and/or the the diffusion of oxygen from Al_2O_3 layer into AlN grain. $Y_4Al_2O_9$ and $Y_3Al_5O_{12}$ were formed by the reaction of Al_2O_3 and Y_2O_3 as mentioned above. At lower sintering temperature (1400° C), $Y_4Al_2O_9$ was formed in the specimen, then $Y_3Al_5O_{12}$ appeared. However $Y_4Al_2O_9$ decreased above 1500° C and finally disappeared above 1700° C.

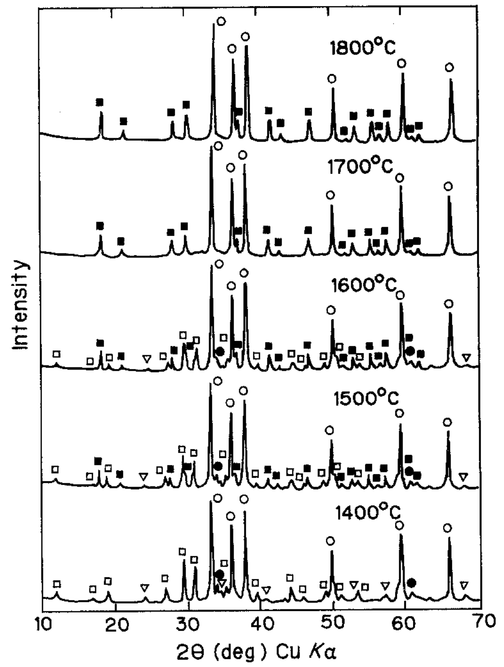

Figure 2 The powder X-ray diffraction patterns of SiO_2 and Y_2O_3 added AlN ceramics sintered at various temperatures (○ AlN, ● 27R, ▽ Al_2O_3, □ $Y_4Al_2O_9$, ■ $Y_3Al_5O_{12}$).

The 27R polytype of AlN, which already existed in the specimen sintered at 1400° C, decreased with increasing sintering temperature. As reported in the previous paper [11], in the case of the pressureless sintered AlN ceramics with SiO_2, 27R polytype was present in all specimens sintered in the temperature range from 1400 to 1800° C. However, in AlN ceramics containing both SiO_2 and Y_2O_3, the 27R polytype was not detected in the specimen sintered at 1700 and 1800° C.

3.1.3 Microstructure

Figure 3 shows the scanning electron micrographs of fracture surfaces of AlN ceramics containing SiO_2 and Y_2O_3 sintered at various temperatures.

The grains in the sample sintered at 1400° C were about 0.5 μm in diameter which were comparable to starting AlN powders. The sample sintered at 1500° C had little change of microstructure. However in the sample sintered at 1600° C, AlN grains were wetted by a liquid phase and the size of grains slightly increased. Furthermore, outlines of several grains in this sample were indistinct, owing to dissolving in the liquid phase. AlN grains rapidly and drastically grew between 1600 and 1700° C. The size of grains of the sample sintered at 1800° C was about 5 μm which was 10 times larger than that of the starting powder. This shows that this

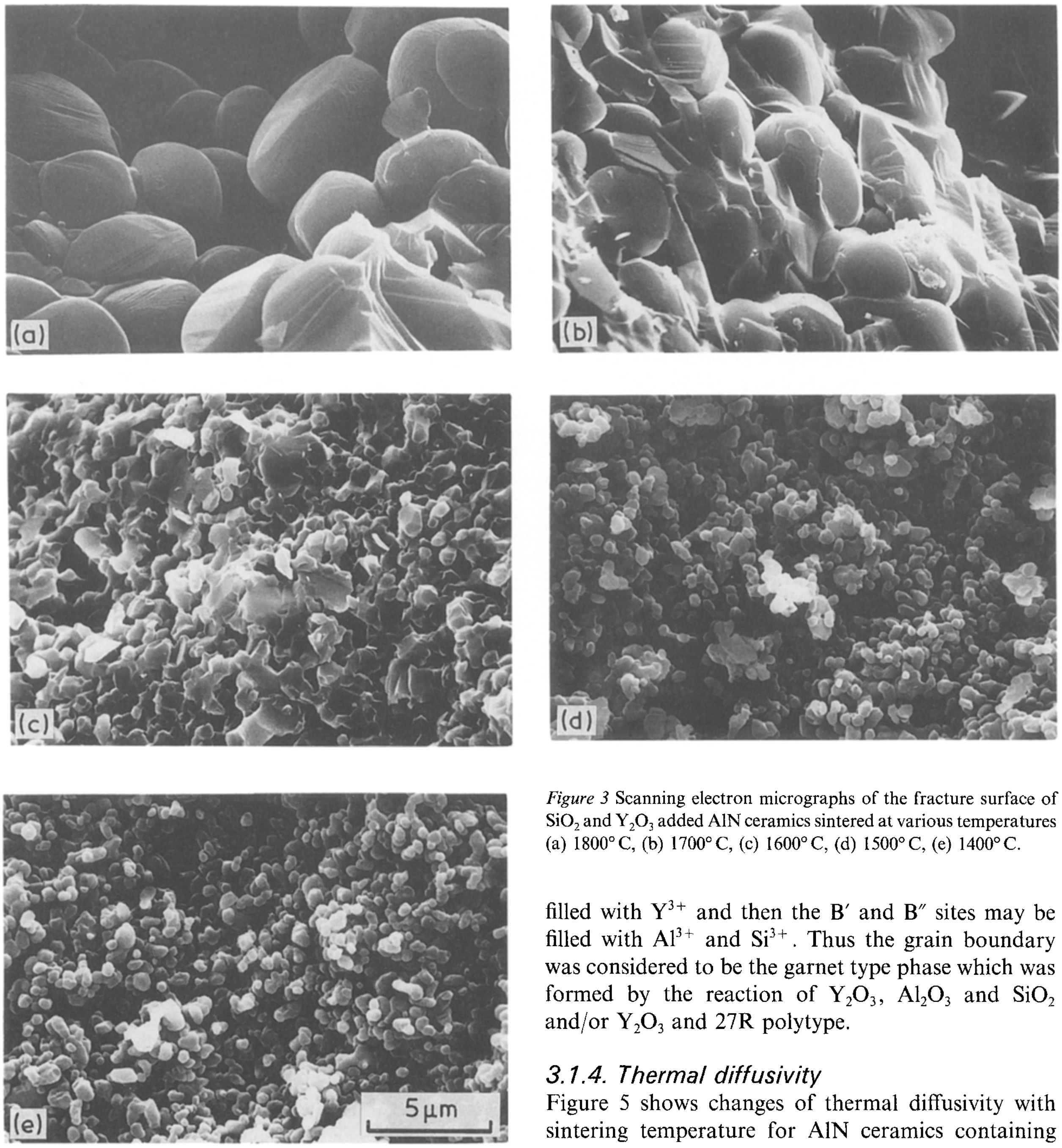

Figure 3 Scanning electron micrographs of the fracture surface of SiO_2 and Y_2O_3 added AlN ceramics sintered at various temperatures (a) 1800° C, (b) 1700° C, (c) 1600° C, (d) 1500° C, (e) 1400° C.

sintering occurred with the liquid phase. The relation of density (Fig. 1) and microstructure changes (Fig. 3) suggested that the density began to increase at 1500° C, owing to formation of liquid phase.

The bright-field transmission electron micrograph (Fig. 4a) shows that the texture of AlN ceramics with SiO_2 and Y_2O_3 consists of spherical grains (5 to 10 μm in diameter) and grain boundary. The selected-area electron diffraction from the grain boundary (Fig. 4e) can be indexed as [3 1 3] for $Y_3Al_5O_{12}$. As shown in Figs 4b, 4c and 4d, Al*Kα*, Si*Kα* and YL*α* lines were detected from the grain boundary. Therefore, the grain boundary had garnet structure and consisted of aluminium, yttrium, silicon and oxygen.

The cubic unit cell of garnet structure contains eight units of $A_3B'_2B''_3O_{12}$, where A is dodecahedrally coordinated site, B′ is a tetrahedrally coordinated site, B″ is an octahedrally coordinated site and 0 is an oxygen ion [13]. In this grain boundary, the A site is filled with Y^{3+} and then the B′ and B″ sites may be filled with Al^{3+} and Si^{3+}. Thus the grain boundary was considered to be the garnet type phase which was formed by the reaction of Y_2O_3, Al_2O_3 and SiO_2 and/or Y_2O_3 and 27R polytype.

3.1.4. Thermal diffusivity

Figure 5 shows changes of thermal diffusivity with sintering temperature for AlN ceramics containing each additive. In the case of SiO_2 addition, the thermal diffusivity was very low and independent of sintering temperature as reported in the previous paper [11]. On the other hand, in the case of Y_2O_3 addition with and without SiO_2, the thermal diffusivity increased with sintering temperature. Especially, from the combination of Figs 1 and 5, large increase of the thermal diffusivity occurred in the temperature range in which the increase of density was large. Thus, the densification leads to the increase of thermal diffusivity of AlN ceramics containing Y_2O_3 with and without SiO_2.

The thermal diffusivity of both SiO_2 and Y_2O_3 added AlN ceramics, however, was much lower than that of Y_2O_3 added AlN ceramics at 1700 and 1800° C.

The addition of SiO_2 gave poor densification and the formation of 27R polytype to result in the decrease of thermal diffusivity of AlN ceramics [11]. When Y_2O_3 was added together with SiO_2, AlN ceramics were fully densified and the amount of 27R polytype decreased. Thus, the thermal diffusivity of both SiO_2

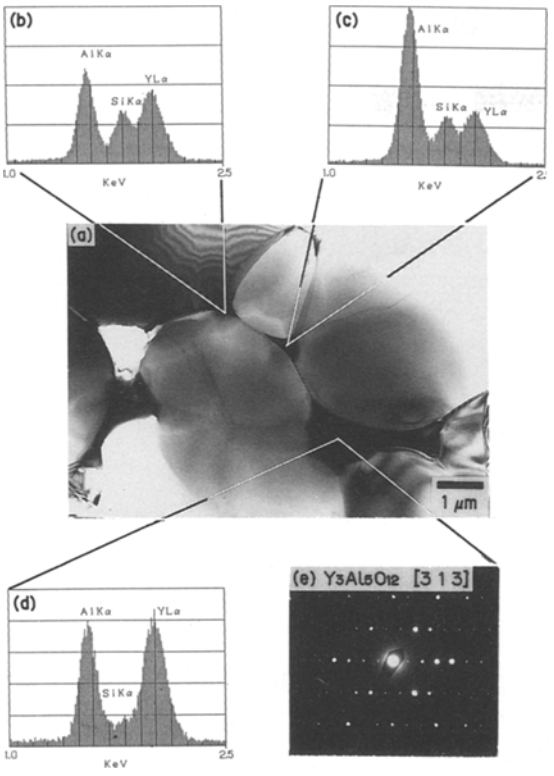

Figure 4 (a): Bright field micrograph of SiO_2 and Y_2O_3 added AlN ceramics, (b), (c) and (d): energy dispersive X-ray spectra and (e): electron diffraction pattern of grain boundary.

and Y_2O_3 added AlN ceramics was higher than that of SiO_2 added AlN ceramics. The reaction of Y_2O_3 and Al_2O_3, i.e. oxygen trapping effect [10], was considered to be obstructed by the reaction of Y_2O_3 and SiO_2. Thus the oxygen diffused into AlN grains, so that the thermal diffusivity of this sample was much lower than that of only Y_2O_3 added AlN ceramics. Furthermore, not only oxygen but also SiO_2 and/or silicon were considered to diffuse into AlN grains, resulting in a decrease of thermal diffusivity. This, however, could not be detected within the limit of measurement by the analytical electron microscope.

3.2. Two-step addition of SiO_2 and Y_2O_3

3.2.1. *Elimination of 27R polytype*

Figure 6 shows X-ray powder diffractograms of samples for stepwise addition. Starting powder, obtained by the reaction of AlN and SiO_2, consisted of AlN and 27R polytype. The mixture of this powder and Y_2O_3 was sintered at 1400° C, and formed AlN, $Y_4Al_2O_9$, α-Al_2O_3 and 27R polytype. However, the amount of 27R polytype decreased with increasing sintering temperature. This suggests that 27R polytype reacted with Y_2O_3 and/or dissolved into liquid phase formed by Y_2O_3–Al_2O_3, resulting in elimination of 27R polytype. Therefore, it is considered that the same reaction occurred in the case of coexistence of Y_2O_3 and SiO_2 as described above. However, it is not clear which Y_2O_3, the liquid phase or both of them reacted with 27R polytype.

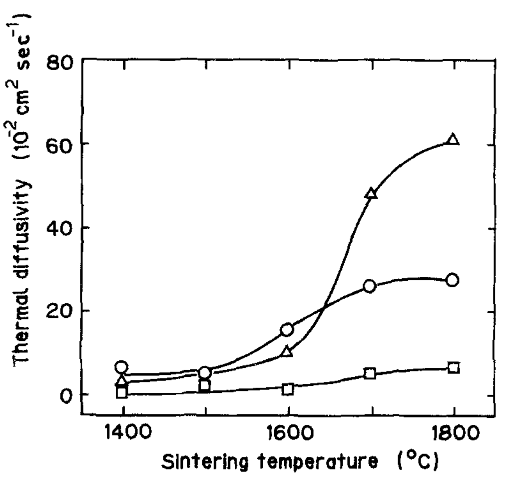

Figure 5 The effect of sintering temperature on thermal diffusivity of AlN ceramics for various additives (○ SiO_2 + Y_2O_3, △ Y_2O_3, □ SiO_2).

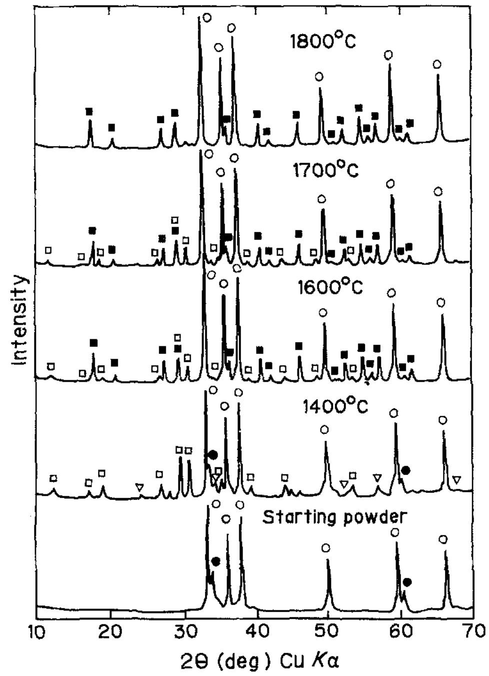

Figure 6 The powder X-ray diffraction patterns of AlN powder pre-reacted with SiO_2 (starting powder) and Y_2O_3 added starting powder sintered at various temperatures (○ AlN, ● 27R, ▽ Al_2O_3, □ $Y_4Al_2O_9$, ■ $Y_3Al_5O_{12}$).

3.2.2. *Densification and thermal diffusivity*

Figure 7 shows the change of density against sintering temperatures for samples of stepwise addition. Specimens densified in the temperature range from 1600 to 1700° C and fully densified at 1800° C. From the microstructure observation, a liquid phase was formed in the temperature range from 1600 and 1700° C. Thus, a liquid-phase sintering occurred in these specimens, by addition of Y_2O_3. In comparison with the experiment 2.1, the formation temperature of liquid phase of this specimen was nearly equal to that of Y_2O_3 added AlN ceramics, in spite of the coaddition of SiO_2 and Y_2O_3.

Since SiO_2 reacted with AlN completely in the first step, there was no reaction of Y_2O_3-Al_2O_3 and SiO_2 in the second step. Therefore, the decrease of formation temperature of liquid phase in the experiment I might be due to the reaction of Y_2O_3-Al_2O_3 and SiO_2.

Fig. 7a shows the thermal diffusivity of these samples. The thermal diffusivity of these samples increased, though density of them did not increase in the temperature range from 1400 to 1600° C. From the

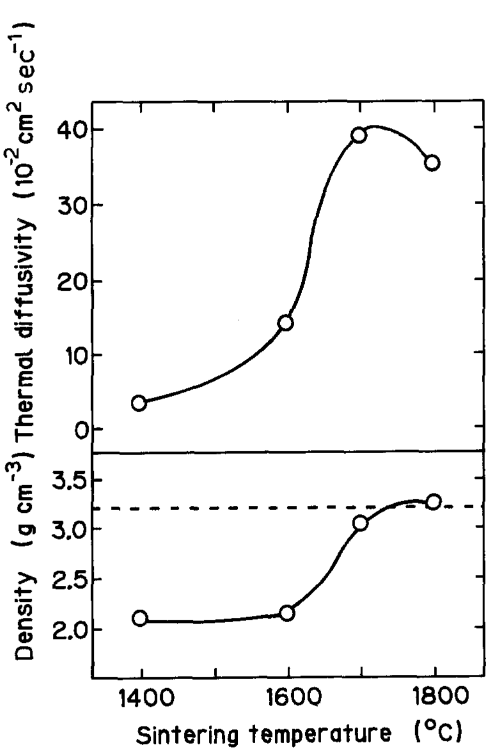

Figure 7 The effect of the sintering temperature on (a) the thermal diffusivity and (b) the density of AlN ceramics for two-step addition of SiO_2 and Y_2O_3. The dotted line indicates the theoretical density of AlN (3.26 g cm^{-3}).

results of powder X-ray analysis described in Section 3.2.1. (Fig. 6), 27R polytype decreased in this temperature range. Thus the increase of thermal diffusivity is considered to be due to the elimination of 27R polytype. In the temperature range from 1600 to 1800° C, the increase of thermal diffusivity was dominated by densification. However, it is not clear why the thermal diffusivity of the specimen sintered at 1800° C was lowered.

4. Conclusion

The addition of SiO_2 and Y_2O_3 to AlN ceramics resulted in the following

(1) specimens densified by liquid-phase sintering,

(2) the formation temperature of liquid phase was lower than the Y_2O_3 added AlN ceramics,

(3) SiO_2 and 27R polytype decreased, and silicon was contained in grain boundary and

(4) thermal diffusivity was higher than SiO_2 added AlN ceramics by the effect of (1) and (2).

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