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Diffusion of oxygen out of AlN polytypoid grains

N.K. Kim[1], M. Mitomo*, T. Mitsuhashi, G.D. Zhan, M. Tsutsumi

National Institute for Research in Inorganic Materials, 1-1, Namiki, Tsukuba-shi, Ibaraki, 305-0044, Japan

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Abstract

The phase change from 27R AlN polytypoid to AlN in the presence of oxide has been investigated in order to determine the qualitative behavior of oxygen release from AlN grains. The 27R polytypoid ($Al_9O_3N_7$) powders were mixed with a stoichiometric amount of Y_2O_3 and, then hot-pressed at 20 MPa. X-ray diffraction analysis revealed that the phase change from 27R to AlN started at about 1350°C in the absence of a liquid phase, since the lowest liquidus temperature in the system AlN–Al_2O_3–Y_2O_3 is reported to be about 1690°C. The result revealed that the diffusion of oxygen out of 27R grains can progress in part through solid-state reaction at low temperatures. However, the reaction was complete at temperatures exceeding 1700°C in the presence of liquid phase. Thermal conductivity of the hot-pressed samples was also measured and discussed in terms of the phase change as well as microstructural evolution.

Keywords: AlN; C. Diffusion

1. Introduction

The amount of oxygen impurity in AlN grains significantly influences the thermal conductivity of AlN ceramics [1–5]. When AlN powders are densified without additives, the thermal conductivity of sintered material decreases sharply with the increase of oxygen content in AlN powders [1,6]. The decrease is mainly attributed to the formation of Al vacancies in AlN lattice by the solid solution of oxygen when the contamination level was low. At high oxygen levels, the formation of AlN polytypoid is expected in accordance with the AlN-Al_2O_3 phase relation [7]. The polytypoids have long layer sequences based on the AlN (2H) structure. The chemical composition is also shifted a little from AlN by incorporating the layers made of AlO_6 octahedra [8,9]. Thus, the composition and the unit cell dimensions are closely related to those of AlN. The 27R polytypoid is the closest to AlN in chemical composition. An oxide layer is inserted every nine layers which is the reason for low thermal conductivity of 6.3 W/m·K [10,11]. The decrease in thermal conductivity in AlN ceramics due to oxygen contamination is thus attributed to the phonon scattering by Al vacancies in AlN grains or the oxide layer in AlN polytypoids.

There are many works on improving the thermal conductivity of AlN ceramics by densification with oxide additives. High conductivity (exceeding 120 W/m·K) makes them attractive as electronic substrates. The lattice oxygen should react with added oxide to decrease the total free energy of the system [3,4]. However, the kinetics of oxygen diffusion out of AlN grains is not well understood. It is generally accepted that a surface alumina as an oxidized layer on AlN particles and dissolved oxygen in AlN grains are absorbed in the grain boundary phase during liquid phase sintering [12–15]. The determination of the oxygen content in AlN particles has been investigated by determining unit cell dimensions by X-ray diffraction [16], hot gas extraction [17], mass spectroscopy [18], or analytical transmission electron microscopy (TEM) [19,20]. It is not easy to determine the kinetics of oxygen diffusion out of AlN grains because of the lower accuracy of the methods and higher sensitivity of thermal conductivity of AlN ceramics on oxygen content.

Although the crystal structure of 27R polytypoid is a little different from that of AlN, the present work will investigate the reaction with oxide additive at high temperature to know the behavior of the oxide component in AlN structures. The stoichiometric addition of Y_2O_3 may produce AlN and $Y_3Al_5O_{12}$ (YAG) according to the reaction,

$$5Al_9O_3N_7 + 3Y_2O_3 = 35AlN + 2Y_3Al_5O_{12} \quad (1)$$

* Corresponding author. Fax: +81-298-52-7449.

E-mail address: mitomo@nirim.go.jp (M. Mitomo).

[1] Present address: Korea Electrotechnology Research Institute, Changwon, PO Box 20, Kyungnam 641-600, South Korea.

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The reaction can easily be traced by X-ray diffraction. The thermal conductivity of sintered materials will be discussed in relation to the reaction and resultant microstructures.

2. Experimental procedure

The starting powders used in the present study are high-purity AlN (Tokuyama Co., Tokyo, Japan; F grade), Al_2O_3 (Taimei Chemical Co., Nagano, Japan; TH-D grade) and Y_2O_3 (Shin-etsu Chemical Co. Tokyo, Japan; 99.9% pure.). In order to form 27R polytypoid, a powder with a molar ratio of $AlN/Al_2O_3 = 7/1$ was mixed in a planetary mill for 2 h using hexane as the mixing liquid. After drying, the mixed powder was heated at 1950°C for 2 h in N_2.

The reacted compact was broken into small pieces, then ground in a SiC mortar to pass through a 105 μm sieve. A sintering additive of 0.6 mol% Y_2O_3 was added to the 27R powder to complete the reaction shown by Eq. (1). The final composition of the powder mixture corresponds to $AlN:Al_2O_3:Y_2O_3 = 35:5:3$ to form AlN and YAG ($Y_3Al_5O_{12}$) as the reaction products.

A different oxynitride powder was also examined to investigate the effect of the reaction route on the thermal conductivity. A cubic phase with the composition of $Al_{23}O_{27}N_4$(AlON, $5AlN{\cdot}9Al_2O_3$) [21] was used as an oxynitride. It is suggested that oxygen is distributed uniformly in the structure. The oxynitride powder was prepared from AlN and Al_2O_3 in the same way as 27R powder. The oxynitride powder was mixed with AlN and Y_2O_3, and the reaction was

$$290AlN + 5Al_{23}O_{27}N_4 + 27Y_2O_3 = 315AlN + 18Y_3Al_5O_{12} \quad (2)$$

About 1.6 g of powder composition was put into a BN-coated carbon die and hot-pressed in a high-frequency induction furnace in static nitrogen by applying 20 MPa. The sample was heated at a rate of 25°C/min and cooled by simply turning off the electricity.

The phase change was investigated by X-ray powder diffraction (XRD). It was quite difficult to evaluate the crystalline compositions quantitatively because of the overlapping main peaks of 27R, AlN and YAG. A qualitative evaluation was made based on the relative intensities of selected peaks. The microstructures were observed on polished surfaces by scanning electron microscopy (SEM). The metallic composition in grains was determined by an energy disperse X-ray analyzer (EDX) equipped on the SEM. In order to estimate the volume fraction of YAG phase, the micrographs were quantitatively evaluated by an image analyzer (Luzex III model, Nireco Co., Tokyo, Japan).

Thermal diffusivity was measured by the laser flash method using a ruby laser (LTC model, Rigaku, Tokyo, Japan). Disc specimens were machined to approximately 2 mm thick, then mirror-polished to a surface roughness (Ra) below 0.4 μm. The polished samples were coated with Pt layer and subsequently sprayed with carbon to prevent direct transmission of the laser. The thermal conductivity, s, was calculated according to the relation,

$$\sigma = D \cdot \rho \cdot C_p \quad (3)$$

where D is the measured thermal diffusivity, ρ is the density of the material and C_p is the specific heat. Density was measured by Archimedes method using deionized water as the liquid. The specific heat was measured by differential scanning caloriemetry (DSC, Perkin-Elmer DSC7, Connecticut, USA).

3. Result

3.1. Phase change during heating

The average particle size of 27R polytypoid was about 3 μm as shown in Fig. 1. Fig. 2 represents the relative amount of crystalline phases in hot-pressed specimens at 1350–1800°C for 1 min. The figure reveals that the amount of 27R decreases drastically between 1350 and 1600°C, which means 27R polytypoid easily reacts with Y_2O_3 at low temperatures. An intermediate phase of $Y_4Al_2O_9$ (YAM) was detected at 1350°C. It should be noted that the Al_2O_3 constituent in the polytypoid has already excluded from the grains, even though the presence of liquid phase is not expected. The formation of the reaction products, i.e. AlN and YAG, was detected

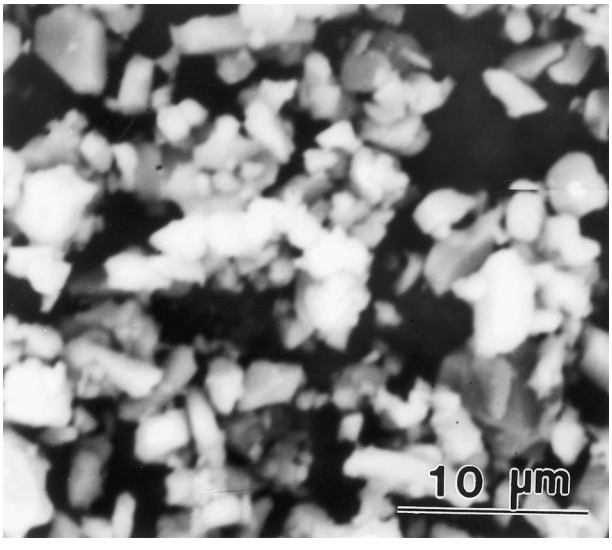

Fig. 1. SEM micrograph of 27R powder.

at low temperatures. However, they appeared as main components above 1450°C. The final reaction took place above 1600°C. Polytypoid and YAM phases finally disappeared at 1650°C.

3.2. Densification during hot-pressing

The density of the fully densified specimen was estimated to be 3.74 g/cm^3 which is the theoretical value for material sintered from 62.2 vol% AlN and 37.8 vol% YAG based on Eq. (1). The densification curve after hot-pressing for 1 min is shown in Fig. 3 together with the change of thermal conductivity of specimens. The first stage of densification began at about 1320°C, then 70% density was achieved at about 1570°C. The maximum densification rate was observed between 1630 and 1680°C. In this temperature range, the reaction of polytypoid with oxide was completed as shown in Fig. 2.

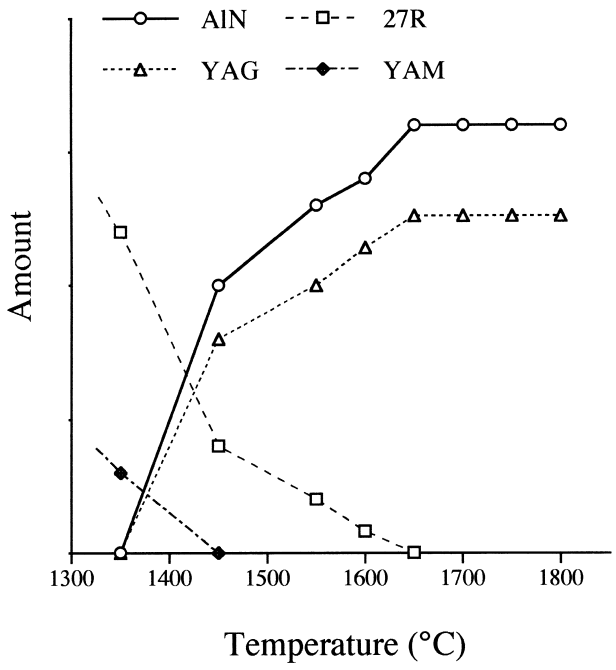

Fig. 2. Change in relative amount of phases present as a function of temperature for the specimens hot-pressed for 1 min.

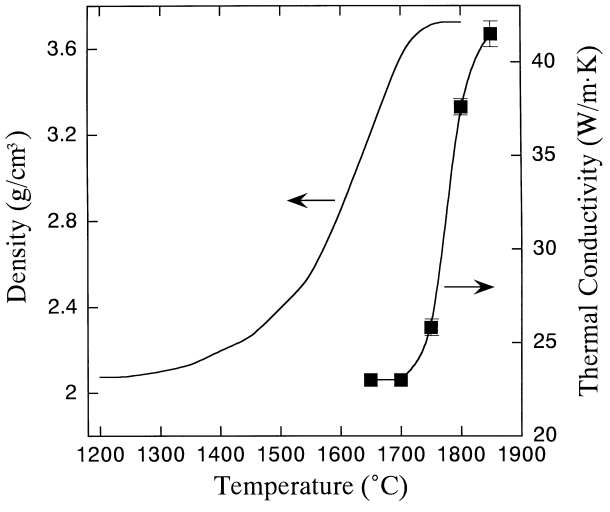

Fig. 3. Change in density and thermal conductivity as a function of temperature after hot-pressing for 1 min.

The weight loss during isothermal heating at 1800°C was measured to be 1.1% in the specimen hot-pressed for 1 min and climbed to 9.1% after 5 h. The weight loss increased sharply during heating above 1800°C. For example, a 6.2% weight loss occurred while holding for just 1 min at 1850°C.

3.3. Microstructures

The SEM microstructures in specimens hot-pressed at 1800°C are shown in Fig. 4. The distribution of YAG phase (bright) is revealed as the minor phase in the figure. The AlN grains (dark) are equiaxed and constitute the matrix. It is noted that shape of YAG phase changes during isothemal holding at 1800°C from party continuous grains with a low dihedral angle after 1 min (as shown later) into isolated grains with a high dihedral angle after 5 h. The fraction of YAG phase for the specimen hot-pressed at 1800°C decreased gradually with holding time, 33 vol% after 1 h, 28 vol% after 2 h, and 24 vol% after 5 h, as determined by an image analysis. Fig. 5 shows a SEM micrograph after heating for 1 min at various temperatures. The isolation of YAG grains was also accelerated at high temperature.

EDX analysis showed that the gray grains in Fig. 5(a) prepared at 1350°C are 27R polytypoid as shown in Fig. 6(a). Fig. 6(b) also shows that white grains in Fig. 5(a) are aluminum yttrium oxide (YAM), the yttrium content of which is lower than that in YAG. It is quite interesting that the materials sintered at 1750°C [Fig. 5(c)] consist of major AlN grains and minor YAG phase. The AlN grains at this temperature should be highly saturated with oxygen impurities despite the complete change of 27 R into AlN as detected by XRD (Fig. 2).

3.4. Thermal conductivity

Thermal conductivity was measured in the sample hot-pressed for 1 min at 1650, 1700, 1750, 1800 or 1850°C. The values are shown in Fig. 3 to compare with densification behavior. As shown in the figure, thermal conductivity increases sigmoidally with the increase of temperature from 23 W/m·K at 1650°C to 42 W/m·K at 1850°C. It should be noted that the disappearance of 27R occurred primarily at 1400–1500°C and was completed at 1650°C. However, the increase in thermal conductivity was observed only above 1750°C.

The effect of isothermal heating on thermal conductivity was investigated in the samples hot-pressed at 1800°C in which only reaction products, AlN and YAG,

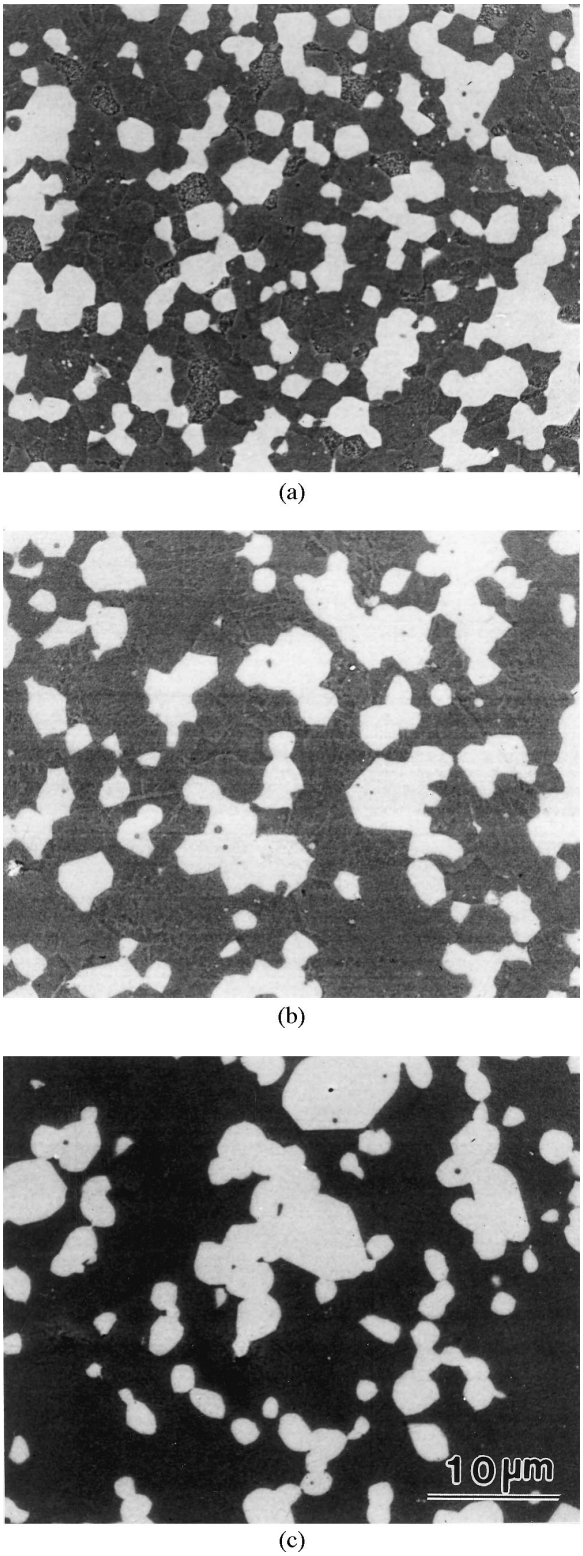

Fig. 4. SEM micrograph for the specimen hot pressed at 1800°C (a) for 1 min, (b) for 1 h and (c) for 5 h.

are detected in the materials. Fig. 7 shows the change of thermal conductivity as a function of hot-pressing time. Thermal conductivity increased from 38 to 54 W/m·K as holding time increased from 1 min to 5 h.

The microstructure of material from AlN, AlON and Y_2O_3 sintered at 1750°C for 1 h is shown in Fig. 8. It is similar to that from 27 R and Y_2O_3 at 1800°C [Fig. 4(b)]. Table 1 shows the difference in thermal conductivity from different starting powders in the early stage of heating (1 min). It clearly reveals that the thermal conductivity of materials from cubic oxynitride is higher than that from 27 R.

4. Discussion

The composition used in this study falls on the line between AlN and YAG in the ternary AlN–Al_2O_3–Y_2O_3 system [4]. Based on the subsolidus phase relation [14], the lowest temperature in the system for liquid formation was reported as 1690°C, which is lower than that of any composition in an Al_2O_3–Y_2O_3 system. It should be emphasized that oxygen diffused out of 27R grains below 1600°C in the absence of liquid phase. The phenomena is clearly shown in the change of crystalline compositions in Fig. 2. The reaction products with 27 R polytypoid and Y_2O_3 at low temperatures were yttrium aluminate, $Y_4Al_2O_9$ (YAM), which is Al_2O_3-deficient compared to YAG. However, the formation of the aluminate as an intermediate phase suggests that the diffusion of oxygen out of 27R grains was very fast even at low temperatures. It is distinctly different from the purification of AlN grains. The purification and resultant high thermal conductivity of AlN ceramics are interpreted in many papers [3–6] to mean that impurity oxygen diffused out of AlN grains only through the process of dissolution of impure AlN grains into grain boundary liquid and the reprecipitation as high-purity AlN grains.

An oxide layer composed from AlO_6 octahedra was inserted in between every eight AlN layers in the 27R structure. The dissolution of oxygen in AlN grains is supposed to be substitution in N sites, which accompany the vacancy formation in Al sites. The ease with which Al_2O_3 composition in the 27R grains reacts with grain boundary Y_2O_3 as compared with AlN might be attributed to this difference in the defect structure. It is quite difficult to exactly follow the diffusion behavior of oxygen from AlN grains. The change in oxygen content during sintering has been investigated by determining lattice parameters [16,22]. However, it has been shown that thermal conductivity is more sensitive to the oxygen content in the grains [4,16].

The absence of a liquid phase was also confirmed by the densification curve in Fig. 3 in which the densification was only accelerated above 1650°C. High density was attained at 1700°C or higher. It is expected that the final densification occurred in the presence of liquid phase. It can be seen in Fig. 2 that the reaction of 27R with Y_2O_3 was completed above 1700°C.

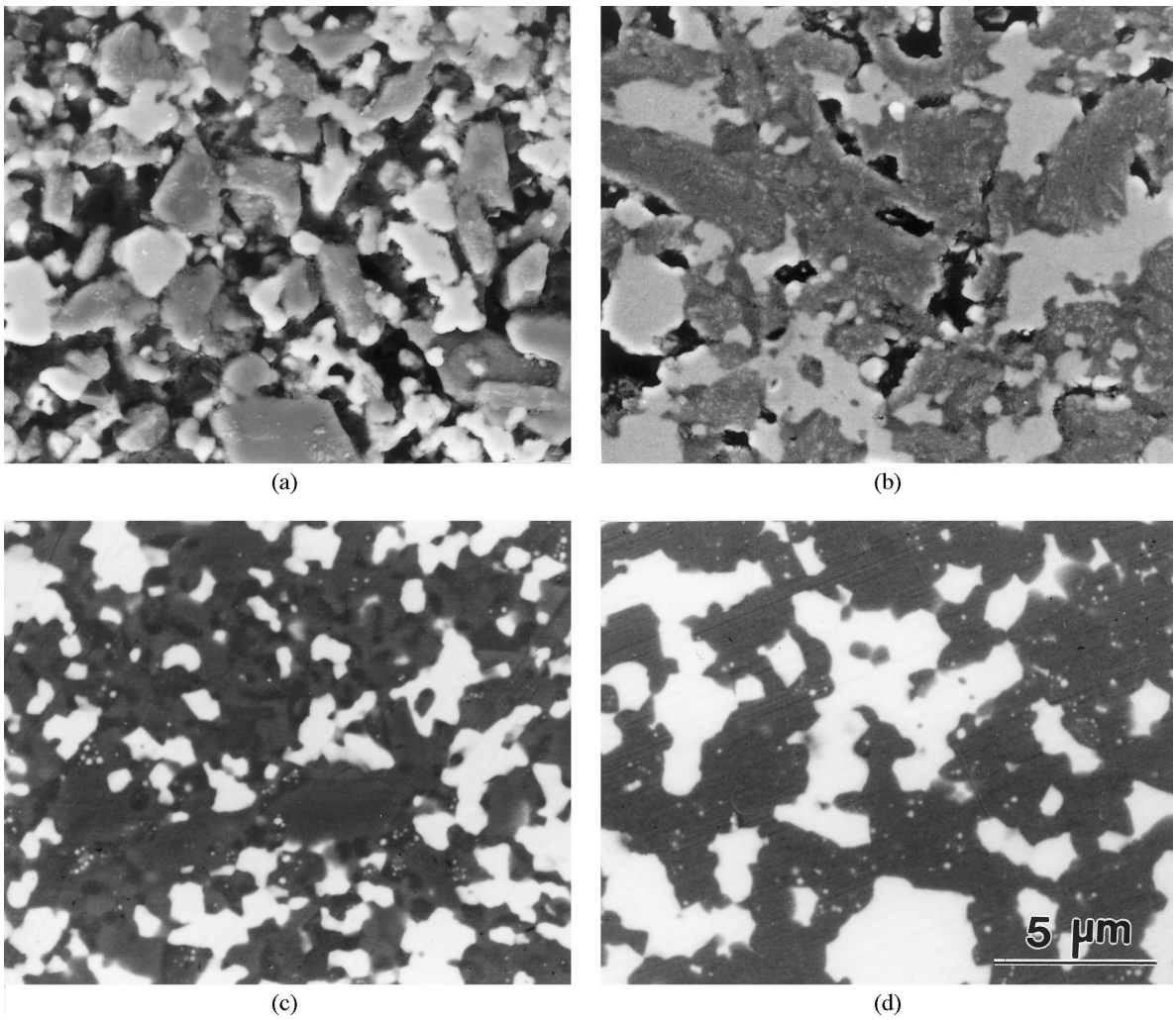

Fig. 5. SEM micrograph after heating for 1 min at (a) 1350°C, (b) 1600°C, (c) 1750°C and (d) 1800°C.

It has been reported that the sintering additives accelerated the liquid phase sintering. The liquid forms by the reaction of additives with AlN and Al_2O_3. During sintering, AlN is purified through the dissolution of impure AlN grains and the reprecipitation as purer AlN grains [22]. Therefore, the thermal conductivity of sintered materials largely depends on the solid solubility of oxygen in AlN grains [6,18]. Sigmoidal increase of thermal conductivity with sintering temperature is shown in Fig. 3. The low thermal conductivity of materials at 1650°C might be due to high porosity. It is interesting to note that the materials at 1700 and 1750°C have low thermal conductivity despite their high density and nearly complete reaction to AlN. It is not clear in the present work whether the residual oxygen is distributed uniformly in AlN grains or is sedimented in residual 27R grains. However, it might be reasonable to assume that AlN grains are highly saturated with impurity oxygen. The partition function of oxygen in AlN grains and grain boundary, c_g/c_b, is a function of free energy of formation of grain boundary aluminate [3], where c_g and c_b is the oxygen concentration in grains and at grain boundaries, respectively.

Microstructure observation revealed that YAG grains tend to be isolated at high sintering temperatures (Fig. 5) and after long heating times (Fig. 6). The same tendency was revealed in the materials from cubic aluminum oxynitride in Fig. 8. The thermal conductivity of $27R + Y_2O_3$ and AlN + YAG materals is calculated for comparison with the observed values. The isolated model was used for the calculation, i.e. the matrix from 27R and AlN is continuous, and Y_2O_3 and YAG grains are isolated [5,23]. Thermal conductivity at room temperature of 27R [10], Y_2O_3 and YAG [24] was reported as 6.3, 27 and 13 W/m·K, respectively. In the isolated model, that thermal conductivity of composites (k_c) is roughly given by [25]

$$k_c \sim k_m[(1 - v_d)/(1 + v_d)] \quad (4)$$

if $k_m > k_d$ as in AlN + YAG system, in which k_m, k_d and v_d are the thermal conductivities of the matrix and isolated

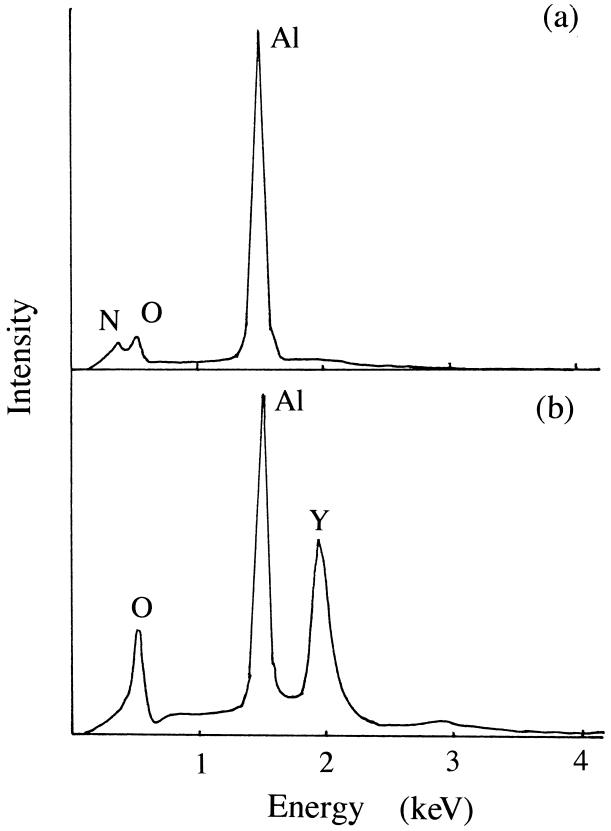

Fig. 6. EDX spectra from (a) gray grains (27R) and (b) white grains (YAM) in Fig. 5(a).

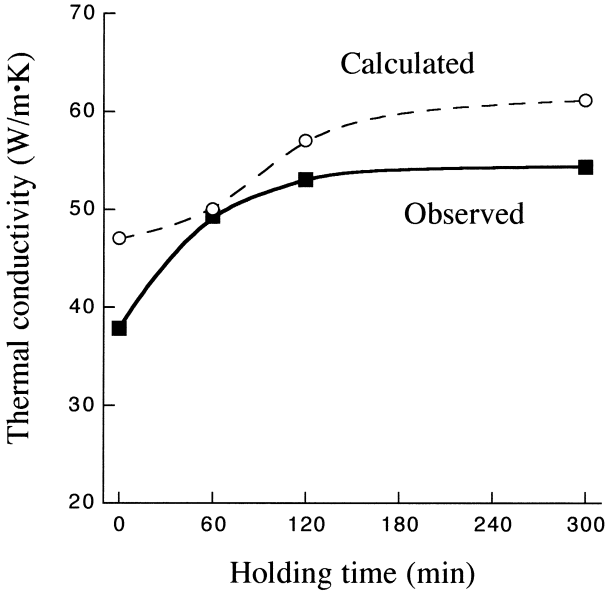

Fig. 7. Increase in observed thermal conductivity during heating at 1800°C compared with calculated values.

grains, and the volume fraction of isolated grains, respectively. The thermal conductivity of AlN ceramics depends largely on the chemical composition of the grain boundary aluminate, i.e. thermal conductivity is

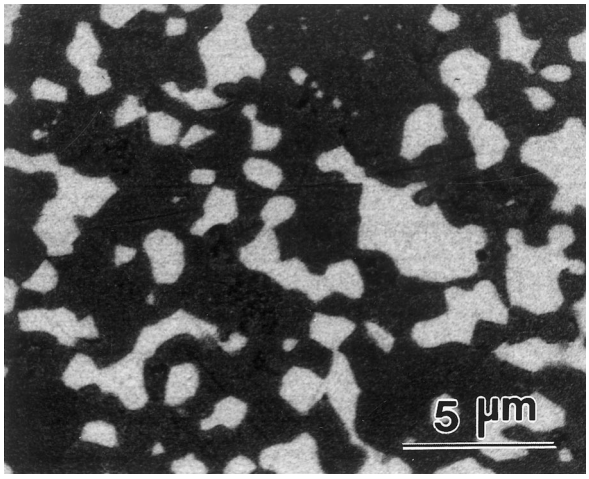

Fig. 8. SEM micrograph after sintering AlN + AlON + Y_2O_3 powder at 1750°C for 1 h.

Table 1
Difference in thermal conductivity (W/m·K) due to the starting powder. The material was sintered for 1 min at each temperature

	Sintering temperature (°C)		
Starting powder	1700	1750	1800
27R	23	26	37
AlN + AlON	31	39	43

higher with higher Y_2O_3 content. The thermal conductivity of AlN with 10 wt% YAG was 86 W·mK [5]. Therefore, the calculated value for AlN in equilibrium YAG is 100 W/m·K. The calculated value for the material with 62.2 vol% AlN and 37.8 vol% YAG in present work is 45 W/m·K. The higher observed value after heating at 1800°C for a long time is attributed to the decrease of YAG phase by evaporation. Image analysis of the microstructure indicated that YAG phase decreased from 35.9 vol% after sintering for 1 min to 31.0 vol% after sintering for 1 h at 1750°C. Calculated values considering this microstructural change during heating agree well with observed behavior as shown in Fig. 7.

$$\text{For } k_m < k_d \text{ as in the } 27\text{R} + Y_2O_3 \text{ system,} \quad K_c \sim K_m[(1 + 2v_d)/(1 - v_d)] \tag{5}$$

The thermal conductivity of the material from 81.4 vol% 27R and 18.6 vol% Y_2O_3 as the starting system in the present work was calculated as 10 W/m·K.

The increase of thermal conductivity with sintering temperature (Fig. 3) and heating time (Fig. 4) agreed well with the calculated value. It revealed that the structural oxygen in 27R diffused in the grains and reacted with Y_2O_3 at the grain boundary even at low temperature of 1350–1500°C at which no liquid was

present. The increase of thermal conductivity by the elimination of oxygen from AlN grains occurred above 1750°C in the presence of a liquid phase. The result in the present work shows that the small amount of oxygen in AlN grains largely influenced the thermal conductivity of ceramics.

5. Summary

The phase change from 27R to AlN during heating to 1850°C in the presence of 25 wt% Y_2O_3 has been investigated by X-ray diffraction analysis. The 27R phase begins to change into AlN below the liquidus temperature in the ternary system of AlN–Al_2O_3–Y_2O_3. This result implies that oxygen release from a AlN polytypoid occurs kinetically without the aid of liquid phase. It was also shown that the elimination of a small amount of dissolved oxygen only occurred in the presence of a liquid phase at above 1750°C and resulted in a sharp increase in thermal conductivity.

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