Effects of adding $Y(NO_3)_3 \cdot 6H_2O$ on the phase change behavior and thermal conductivity of Aluminum Nitride ceramics

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The phase change behavior and thermal conductivity of Aluminum nitride (AlN) ceramics with $Y(NO_3)_3 \cdot 6H_2O$ and Y_2O_3 as an additive were studied. Sintering was performed in the temperature of 1,900 °C for up to 3 h under a N_2 atmosphere to optimize the sintering conditions for each composition. The microstructure and assemblage of the secondary phase have a significant effect on the final thermal conductivity of the sintered AlN. The mechanical property and thermal conductivity of the AlN composition of using the Y_2O_3 additive were improved by adding $Y(NO_3)_3 \cdot 6H_2O$, which decreased the porosity. At 13.56 wt% $Y(NO_3)_3 \cdot 6H_2O$, the AlN ceramic exhibited the highest strength of 375 MPa, the highest hardness of 10.60 GPa, and the highest thermal conductivity of 200.2 W/m·K.

Keywords: AlN, $Y(NO_3)_3 \cdot 6H_2O$, Phase change behavior, Thermal conductivity, Mechanical property.

Introduction

Aluminum nitride (AlN) may be highly suitable as substrates and packages for IC/LSI because of its high thermal conductivity (theoretical value of 320 W/m·K), low dielectric constant (8.0 at 1 MHz), and thermal expansion coefficient (4.8×10^{-6} K^{-1} at 20-500 °C) that is close to that of silicon [1-3]. However, because of its high covalent bonding, it is difficult to sintering. Several sintering additives, such as CaO, CaC_2, C, $CaO-Al_2O_3$, and Y_2O_3, were reported to be useful for the fabrication of high densification and thermal conductivity AlN ceramics [4-6]. Y_2O_3 is widely used as a sintering additive because it forms binary eutectics at temperatures around of ~1,800 °C with native Al_2O_3, which is present on the surface of AlN particles, resulting in a material with high density and high thermal conductivity [7, 8]. A typical feature in ceramic processing is the addition of a limited fraction of sintering additives, typically oxides, to promote densification. However, an associated disadvantage is that non-negligible alterations may occur of the bulk property for which the ceramic phase has been originally selected. The thermal conductivity of poly phase ceramics is strongly affected by internal phase geometry and other microstructural details [9-11]. High thermal conductivity constitutes an attractive property of AlN ceramics for high-power semiconductor devices [12, 13]. However, the usual preparation of dense polycrystalline AlN bodies involves the additive

Y_2O_3 which, by virtue of its good wet-ability of the AlN grain surface, enables ready densification by pressureless sintering [4, 14, 15]. As substrates and packages, the thermal conductivity of AlN ceramics is very important. Most studies look at the influence of different sintering additives on the thermal conductivity of AlN ceramics.

In this work, we studied to compare the sintering behavior and crystalline phases change related with the densification of AlN with Y_2O_3 and $Y(NO_3)_3 \cdot 6H_2O$ additives.

Experimental

Commercially available AlN powders (Grade H, Tokuyama Soda, Japan) was used as a starting material. First, the $Y(NO_3)_3 \cdot 6H_2O$ (99.99%, High Purity Chemicals, Japan) or Y_2O_3 (99.9%, High Purity Chemicals, Japan) was dissolved in ethanol, and the AlN powders were dispersed in the solution using ultrasonic technology. The $Y(NO_3)_3 \cdot 6H_2O$ and Y_2O_3 were added into a AlN suspension and then sonicated for 24 h to obtain a metal ion doped AlN suspension via surface adsorption. After dried and calcinated (500 °C), the mixed powders were densified by hot pressing at 1,900 °C for 3 h under a pressure of 20 MPa in flowing N_2. The sintering additive of $Y(NO_3)_3 \cdot 6H_2O$ was added in the following amounts: 10.1198, 11.8684, 13.5638, and 15.2594 wt% (equivalent to 6, 7, 8 and 9 wt% Y_2O_3 respectively), referred to here after as A-6YP, A-7YP, A-8YP and A-9YP for the sintered samples. For comparison, monolithic AlN was also prepared in the same process. The composition of powder mixture was indicated in Table 1.

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Table 1. Specimen notation of AlN with addition of Y_2O_3 and $Y(NO_3)_3 \cdot 6H_2O$.

Notation	Composition
AlN	Monolithic AlN
A-2Y	AlN + 2 wt% Y_2O_3
A-3Y	AlN + 3 wt% Y_2O_3
A-4Y	AlN + 4 wt% Y_2O_3
A-6YP	AlN + 10.1198 wt% $Y(NO_3)_3 \cdot 6H_2O$
A-7YP	AlN + 11.8684 wt% $Y(NO_3)_3 \cdot 6H_2O$
A-8YP	AlN + 13.5638 wt% $Y(NO_3)_3 \cdot 6H_2O$
A-9YP	AlN + 15.2594 wt% $Y(NO_3)_3 \cdot 6H_2O$

Table 2. Densities and Mechanical properties of sintered samples.

Composition	Density (g/cm^3)	Vickers' hardness (GPa)	Flexural strength (MPa)
AlN	2.97	10.6461±1.37	218.42±9.87
A-2Y	3.02	10.6294±1.19	258.36±10.75
A-3Y	3.19	10.1652±0.56	332.68±12.11
A-4Y	3.24	10.2774±0.36	334.12±35.19
A-6YP	3.17	10.0302±1.42	320.63±16.38
A-7YP	3.23	10.6324±1.56	368.56±30.52
A-8YP	3.31	10.6049±1.72	375.90±35.16
A-9YP	3.36	10.4234±0.87	378.27±28.77

Crystalline and 2nd phases were identified with X-ray diffraction pattern (D/MAX-2500V, RIGAKU) with Cu Kα radiation (λ = 1.5406 Å). All the samples for mechanical test were prepared by diamond saw and then grinded by diamond disc. Mechanical properties of specimen were evaluated by four-point flexural strength (5882, Instron, USA) with a cross head speed of 0.5 mm/min and micro vickers hardness tester (HM124, Akashi, Japan) at a load 9.8 N for 5 sec. The dimension of mechanical test specimen was $3 \times 4 \times 40$ mm (width × length × height) and the inner span and outer span were 10 and 30 mm, respectively. Fracture surfaces of the pellets were observed by Field emission scanning electron microscopy (FE-SEM, S-4700, HITACHI, Japan). Thermal diffusivity measurement (LFA 457, NETZSCH, Germany) at room temperature is measured by the laser flash method. Thermal conductivity (K) is calculated using a heat capacity (C_p) of AlN at room temperature where λ and d are the thermal diffusivity and the density, respectively [16].

$$K = C_p \lambda d \qquad (1)$$

Results and Discussion

Density and mechanical properties

The densities and mechanical properties of the sintered AlN ceramics are summarized in Table 2. The density increases with the additive content. Compared with AlN when the additive is Y_2O_3, better mechanical properties, such as Vickers' hardness, flexural strength, are obtained for sintered samples when the additive is ≤8 wt% $Y(NO_3)_3 \cdot 6H_2O$, A-8YP exhibits the highest strength of 375 MPa, hardness of 10.60 GPa. This high density is due to the formation of an aluminum oxy nitride (Al–O–N) liquid by reaction between surface alumina and AlN. The addition of Y_2O_3 promotes more extensive liquid formation due to reaction to form a quaternary liquid (Y–Al–O–N) at lower temperature.

Phase change behavior and microstructure

Fig. 1 gives the X-ray powder diffraction patterns for the all samples after sintering at 1,900 °C for three

Fig. 1. X-ray powder diffraction patterns of AlN addition of Y_2O_3 and $Y(NO_3)_3 \cdot 6H_2O$.

hours. Each composition shows strong peaks associated with AlN in addition to minor peaks associated with the secondary grain boundary phase.

Fig. 1(a) showed peaks for AlN, $YAlO_3$ (YAP) on the 2 wt% of Y_2O_3. The YAP phases disappeared with increasing Y_2O_3 content and then $Y_3Al_5O_{12}$ (YAG) phases (3 wt% of Y_2O_3) $Y_4Al_2O_9$ (YAM) phases (4 wt% of Y_2O_3) appeared. But Fig. 1(b) showed peaks for AlN, YAP and YAG phases with increasing $Y(NO_3)_3 \cdot 6H_2O$ content. Because compared with AlN when the additive is Y_2O_3, the improved dispersion properties are attributed to the increase in reactivity
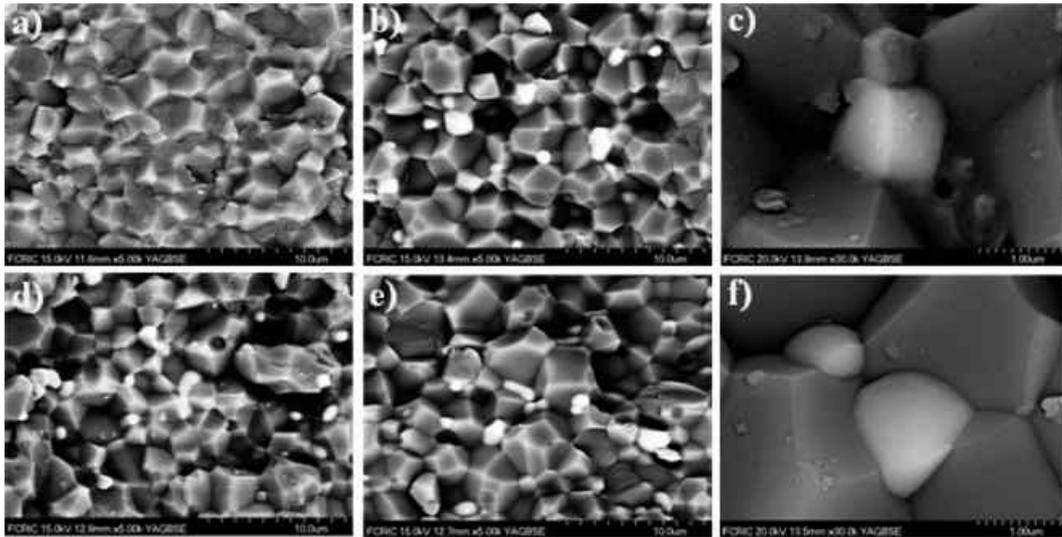
Fig. 2. Back-scattered electron SEM fractured surface images of AlN specimens sintered at 1,900 $^{\circ}$C : (a) AlN, (b) A-3Y, (c) high magnification of (b), (d) A-6YP, (e) A-8YP, (f) high magnification of (e).

between Al_2O_3 and $Y(NO_3)_3 \cdot 6H_2O$.

Al_2O_3 peaks were not detected because the amount of residual Al_2O_3 is very small and below the detection limit of the equipment. Moreover, Al_2O_3 occurs as a thin surface layer on AlN grains. Because of this surface layer and residual spinel, thermal conductivity is very low for this sample, as can be seen in Fig. 3. This means that the amount of added Y_2O_3 was insufficient to fully react with residual Al_2O_3 and to purify the AlN and to complete the oxygen removal from both the lattice and the surface.

From previous reports [17, 18], the Y_2O_3 decomposed from $Y(NO_3)_3 \cdot 6H_2O$ reacts with Al_2O_3, which is also present on the surface of AlN particles, to form yttrium aluminates:

$$Al_2O_3 + Y_2O_3 = 2YAlO_3 \text{ (YAP)} \qquad (2)$$
$$Al_2O_3 + 2\,Y_2O_3 = Y_4Al_2O_9 \text{ (YAM)} \qquad (3)$$
$$5\,Al_2O_3 + 3\,Y_2O_3 = 2Y_3Al_5O_{12} \text{ (YAG)} \qquad (4)$$
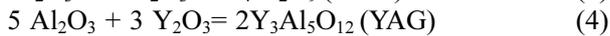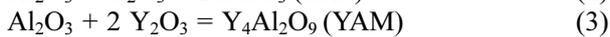
The formation of liquid phase ($Y_4Al_2O_9$ and/or $Y_3Al_5O_{12}$) during sintering process will play an important role in the densification of the AlN ceramics.

The FE-SEM microstructure of composition containing Y_2O_3 and $Y(NO_3)_3 \cdot 6H_2O$ is shown in Fig. 2. The secondary phase (white) shows up at the grain junctions only and not along grain edges. Compared with AlN when the additive is Y_2O_3, the addition of $Y(NO_3)_3 \cdot 6H_2O$ appears to have a further effect of changing the wetting behavior of the liquid phase with respect to the AlN grains. Indeed, the dihedral angle of the secondary phase at the grain junction is high. This has a significant effect on the thermal conductivity (k).

Jackson *et al*. [19] suggest that thermal conductivity rises to a maximum and then decreases due to the increase in volume fraction of aluminates with further
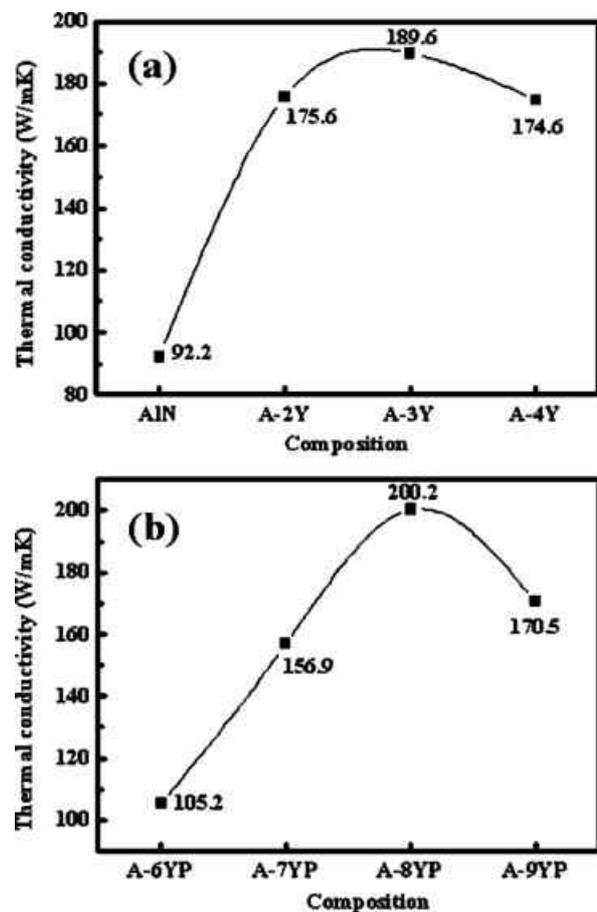
Fig. 3. Variation in thermal conductivity of AlN addition of Y_2O_3 and $Y(NO_3)_3 \cdot 6H_2O$.

Y_2O_3 addition.

Thermal conductivity

Fig. 3 shows the trend in thermal conductivity of the

compositions. The thermal conductivity of the aluminate phase is low (<10 W/m·K), hence as the volume fraction increases, a decrease in the overall thermal conductivity is expected. The thermal conductivity of AlN sintered without sintering additives has a significantly low value of 92.2 W/m·K. Therefore, the effect of the additive has a major impact on the conductivity in two ways: (a) it removes oxygen from particle surface and (b) a micro structural change occurs as the aluminates de-wets the grain boundaries and segregates to the grain junctions leading to AlN–AlN grain boundary contact. Also, this figure shows, that compositions of using the $Y(NO_3)_3 \cdot 6H_2O$ additive have higher thermal conductivity than composition of using the Y_2O_3 additive. Because of the oxide layer was consumed to produce YAP, YAG as secondary phases. Furthermore, it was shown by the experimental work of Medraj *et al.* [20] that YAP wets the surface of AlN more than YAG or YAM if all the experimental conditions are considered. Also, the presence of YAP phase will prevent AlN–AlN surface contact. But higher YAP content is associated with lower thermal conductivity.

Conclusions

Aluminum nitride (AlN) ceramics were prepared by hot-pressing with $Y(NO_3)_3 \cdot 6H_2O$ and Y_2O_3 as sintering additive. When increasing Y_2O_3 content, the $YAlO_3$ (YAP) phase disappeared and then $Y_3Al_5O_{12}$ (YAG) phase (3 wt% of Y_2O_3) $Y_4Al_2O_9$(YAM) phase (4 wt% of Y_2O_3) appeared. But increasing $Y(NO_3)_3 \cdot 6H_2O$ content showed peaks for AlN, YAP and YAG phase. Because compared with AlN when the additive is Y_2O_3, the improved dispersion properties are attributed to the increase in reactivity between Al_2O_3 and $Y(NO_3)_3 \cdot 6H_2O$. The mechanical properties and thermal conductivity are obtained for sintered samples when the additive is ≤13.5638 wt% $Y(NO_3)_3 \cdot 6H_2O$, A-8YP specimen exhibits the strength of 375 MPa, hardness of 10.60 GPa and the highest thermal conductivity of 200.2 W/m·K. The addition of $Y(NO_3)_3 \cdot 6H_2O$ appears to have a further effect of changing the wetting behavior of the liquid phase with respect to the AlN grains. It was confirmed that AlN using $Y(NO_3)_3 \cdot 6H_2O$ showed relatively higher thermal conductivity and mechanical properties than the Y_2O_3.

Acknowledgements

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