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Thermal conductivity of AlN ceramics sintered with CaF_2 and YF_3

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Abstract

Dense AlN ceramics with a thermal conductivity of 180W/m·K were obtained at the sintering temperature of 1750 °C using CaF_2 and YF_3 as additives. At temperatures below 1650 °C, the shrinkage of AlN ceramics is promoted by liquid $(Ca,Y)F_2$ and $Ca_{12}Al_{14}O_{32}F_2$. Liquid $CaYAlO_4$ mainly improves the densification of the sample when the sintering temperature increases to 1750 °C. The formation of liquid $(Ca,Y)F_2$ at a relatively low temperature results in homogeneous YF_3 distribution around the AlN particles, which benefits the removal of oxygen impurity in the AlN lattice, and thus a higher thermal conductivity.

Keywords: A. Sintering; B. Microstructure-final; C. Thermal conductivity; Aluminum nitride

1. Introduction

Aluminum nitride is a promising substrate and package material for high power integrated circuits because of its high thermal conductivity, low dielectric constant and thermal expansion coefficient close to that of silicon and high electrical resistivity [1,2]. However, AlN is difficult to sinter due to its high covalent bonding. For full densification, rare-earth and/or alkaline earth oxides are often added as sintering aids in the fabrication of AlN ceramics [3,4]. These sintering aids play a double role during the sintering. One is to form a liquid phase that promotes densification by liquid-phase sintering. The other is to improve the thermal conductivity by reducing the oxygen impurities in the AlN lattice. Hundere et al. [5] studied the chemical reactions when sintering AlN ceramics with YF_3 additions. Liu et al. [6] achieved AlN ceramics with a thermal conductivity above 170 W/m·K using CaF_2 and YF_3 as additives. However, the effect of YF_3 on the thermal conductivity was not clear from their study. In this paper, CaF_2, YF_3 and Y_2O_3 were used as sintering aids to explore the effect of YF_3 on the thermal conductivity of AlN ceramics.

2. Experimental procedure

The commercial AlN powder (H type, Tokuyama, Japan) used in this study has an oxygen impurity content of 0.9 wt.% and a specific surface area of 2.7 m^2g^{-1}. AlN powder was mixed with CaF_2, YF_3 and Y_2O_3 (analytical reagents) and ball-milled by planetary milling for 2 h using ethanol as a mixing medium. The dried powder was mixed with polyvinyl butyral (PVB) binder before uniaxially pressing the powder into pellets 10 mm in diameter and 5 mm thick. The pellets were de-waxed at 550 °C and then placed into a BN crucible and sintered at 1350, 1500, 1650 and 1750 °C for different times in a graphite furnace with a flowing nitrogen atmosphere. The compositions of the specimens are shown in Table 1.

Shrinkage of the sintered pellets was measured with a vernier caliper. Densities of samples CYFA and CYOA sintered at 1750 °C for 4 h were measured by Archimedes displacement method with distilled water as the immersion medium. Using XRD with CuK_α radiation, the secondary phases in AlN specimens after sintering were identified. Microstructure of fracture surfaces was observed by scanning electron microscopy (SEM, OPTON, CSM950). The thermal conductivity at room temperature was measured by a laser flash technique. To determine the lattice parameters, the samples sintered at 1750 °C for 4 h were scanned from 90° to 140 at the rate of 0.1 °/min using XRD with CuK_α radiation.

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Table 1
Compostions of different samples in the experiments

Sample	(wt.%)			
	CaF_2	YF_3	Y_2O_3	AlN
YFA	0	3	0	97
CYFA	4	3	0	93
CYOA	4	0	2	94

3. Results

Table 2 shows that the secondary phases in samples YFA and CYFA after sintering at different temperatures for 0.5 h. The chemical composition of the secondary phases in YFA samples changes in the order YOF → $Y_3Al_5O_{12}$ (YAG) → $Y_4Al_2O_9$ (YAM) → YN when the firing temperature increases from 1350 to 1650 °C. This is similar to the results achieved by Hundere et al. [5] However, it seems impossible that Y_2O_3 can be formed as an intermediate product from the reaction between YF_3 and Al_2O_3 as Hundere et al. [5] presumed since no Y_2O_3 is found with the formation of yttrium aluminates before 1500 °C in Sample YFA. YF_3 is supposed to react with Al_2O_3 and form YOF (Tetragonal) and AlF_3 as follows:

$$3YF_3(l) + Al_2O_3(s) = 3YOF(s) + 2AlF_3(g) \quad (1)$$

In sample CYFA, $(Ca,Y)F_2$ and $Ca_{12}Al_{14}O_{32}F_2$ form at 1350 °C. Considering the greater shrinkages of Sample CYFA fired below 1650 °C compared with that of sample YFA, the formation of liquid $(Ca,Y)F_2$ and calcium aluminates promotes densification of sample CYFA at temperatures lower than 1650 °C. With increasing temperature, YF_3 is presumably released from $(Ca,Y)F_2$ and reacts with Al_2O_3 to form YAP and YAM, which are detected at 1500 °C as shown in Table 2. After heating at 1650 °C, the yttrium aluminates change into Y_2O_3 under the nitrogen ambient in a graphite furnace.

Samples CYFA and CYOA sintered at 1750 °C for 4 h reach full densification with similar densities of 3.28 g/cm^3. However, the thermal conductivity of sample CYFA is 180 W/mK, which is much higher than the 152 W/m·K of sample CYOA. The X-ray patterns in samples CYFA and CYOA sintered at 1750 °C for 4 h are shown in Fig. 1. It can be seen from this figure the similar phase compositions containing YAM, $CaYAlO_4$ and Y_2O_3 in the two samples. Considering their similar densities, liquid $CaYAlO_4$ promotes densification of sample CYFA at 1750 °C [7,8].

Table 2
Secondary phases in samples YFA and CYFA after sintering at different temperatures for 0.5 h

Sintering temperature (°C)	Sample	
	YFA	CYFA
1350	YOF	$(Ca,Y)F_2$, $Ca_{1\ 2}Al_{14}O_{32}F_2$
1500	$Y_3Al_5O_{12}$	CaF_2, YOF, $Ca_{12}Al_{14}O_{32}F_2$, $YAlO_3$, $Y_4Al_2O_9$
1650	$Y_4Al_2O_9$,YN	Y_2O_3

Fig. 2 shows the morphology of fracture surfaces of sample CYFA and CYOA sintered at 1750 °C for 4 h. As shown in this figure, the grains in the two samples have a close contact between them, which agrees with the high densification of the sintered bodies. However, the polyhedral grains in sample CYFA grow homogeneous, which is different than the irregular grain shape in sample CYOA. The addition of YF_3 obviously improves the grain growth in the sintering regardless of the slight effect on the densification compared with adding Y_2O_3.

4. Discussion

In general, densification, grain boundary phases and oxygen content in the AlN lattice play an important role on the thermal conductivity of AlN ceramics. Since both sample CYFA and sample CYOA reach the density at 1750 °C, densification is not the main reason for the different thermal conductivities of the two samples.

Kurokawa et al. [9] published the relationship between thermal conductivity and oxygen concentration for a series of AlN ceramic samples, which were prepared with a sintering additive containing Ca. The measured oxygen content of the sintered body strongly reflects the oxygen content in the AlN lattice since all the second phases produced from this sintering aid vaporized during sintering. The thermal conductivity is

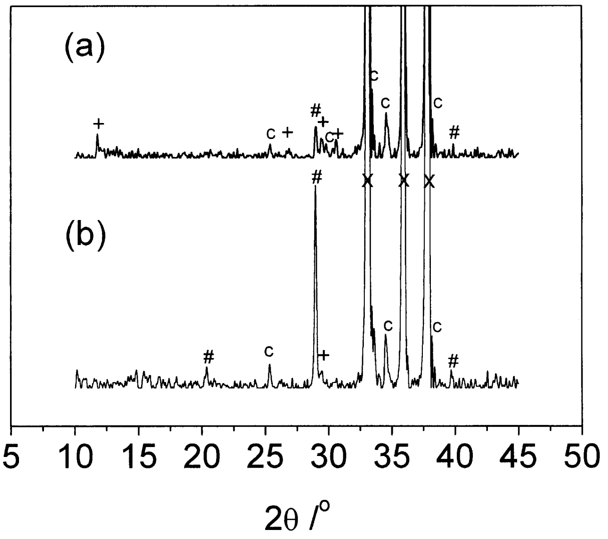

Fig. 1. X-ray patterns of samples CYFA (a) and CYOA (b); (+YAM,×AlN, # Y_2O_3, c $CaYAlO_4$).

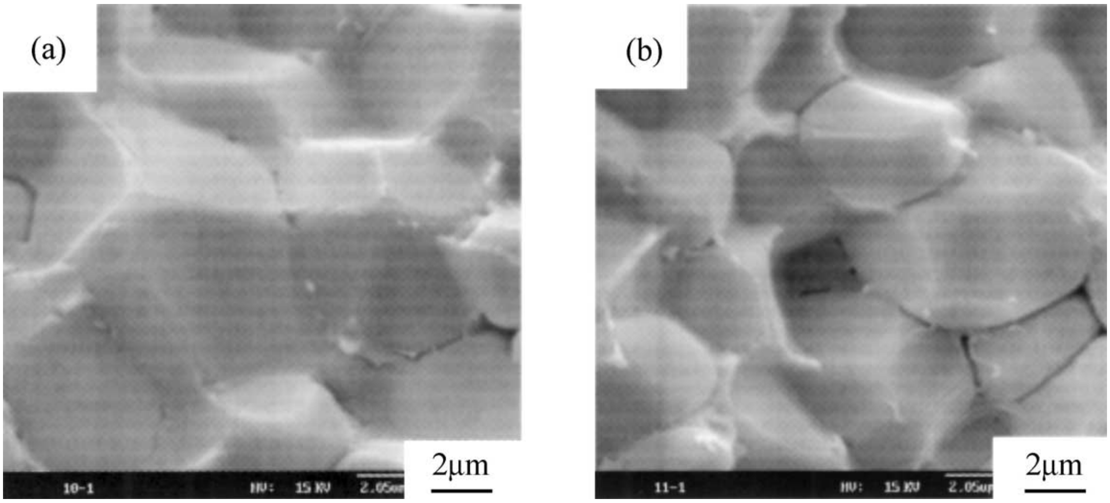

Fig. 2. Morphology on the fracture surface of different samples sintered at 1750 °C for 4 h; (a) CYFA and (b) CYOA.

mainly controlled by the oxygen content in the AlN lattice when there are no grain boundary phases. Thus, the effect of grain boundary phases on the thermal conductivity can be indirectly shown by measuring AlN cell volume and oxygen content in the AlN lattice of sintered bodies. The measurement of the unit cell volume of samples CYFA and CYOA sintered at 1750 °C for 4 h shows that the cell volume of sample CYFA is 41.760 Å^3, greater than that of sample CYOA, which is 41.753 Å^3. According to the relations between the thermal conductivity and AlN cell volume, as shown in Fig. 3, it can be seen that the thermal conductivities of samples CYFA and CYOA have a good agreement with the polynomial fit curve. This implies that the grain boundary phases have no prominent effect on the thermal conductivity.

Oxygen, covering the surface of AlN powder, diffuses into the AlN lattice to form oxygen-related defects at temperatures between 1400 and 1800 °C during the sintering of AlN ceramics [10]. At low oxygen level, the AlN cell volume decreases with increasing oxygen concentration due to the formation of Al vacancies. However, a higher oxygen concentration also produces a larger cell volume at the high oxygen content side of the transition, as Harris et al. summarized [11]. From the normalized change in AlN unit cell volume as a function of oxygen concentration [11], the oxygen concentrations of samples CYFA and CYOA are calculated to be 0.78 and 0.9 at.%, respectively. Thus, it is obvious that the higher thermal conductivity of sample CYFA is attributed to the lower oxygen concentration compared with sample CYOA.

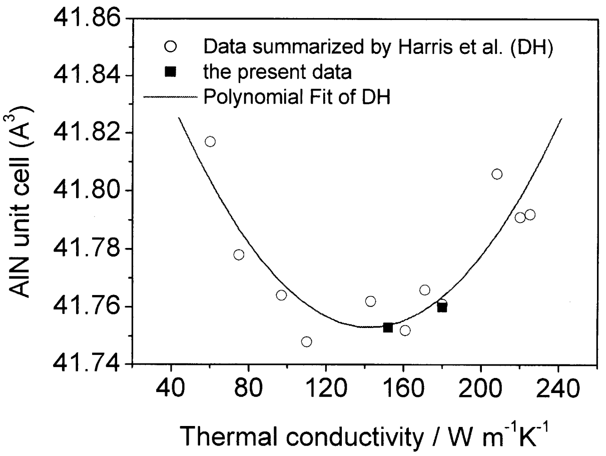

Fig. 3. AlN unit cell volume, as determined by X-ray diffraction measurements, as a function of thermal conductivity. The curve is polynomial fit of data published by Kurokawa et al. [9].

Here a possible mechanism is proposed to explore the reason why sample CYFA has a lower oxygen concentration from the phase change in the firing. During sintering of AlN ceramics with Y_2O_3 addition, the complete reaction between Y_2O_3 and the oxygen on the AlN particles is necessary to decrease the final oxygen concentration in AlN lattice [12]. Using concurrent addition of CaF_2 and Y_2O_3, oxygen is difficult to completely react with Y_2O_3 to form the stable yttrium aluminates before 1650 °C due to the solid phase reaction between Y_2O_3 and Al_2O_3 and the inhomogeneous liquid distribution, which makes oxygen have chances to enter AlN lattice to form oxygen-related defects and decrease the thermal conductivity of AlN ceramics [8]. However, in CaF_2–YF_3 system, phase $(Ca,Y)F_2$ occurs at a relatively low temperature of 1350 °C and becomes liquid above 1400 °C according to the phase diagram [13]. The flow and redistribution of liquid $(Ca,Y)F_2$ make YF_3 have sufficient chances to contact oxygen on AlN surface and react with it, which can limit the diffusion of oxygen from the surface of AlN particles to AlN lattice at temperatures above 1400 °C. As shown in Fig. 1, the remaining Y_2O_3 in Sample CYFA sintered at 1750 °C for 4 h also implies a complete oxygen elimination of AlN particles since all the oxygen in the second phases comes from the surface of the original AlN particles. Furthermore, YAM phase, in which oxygen has low activity

[12], forms easily during sintering of CYFA samples due to no additional oxygen in CaF_2 and YF_3. This benefits the removal of oxygen from the AlN lattice at 1750 °C. Thus, the oxygen concentration in the AlN lattice is lower in sample CYFA compared with that in sample CYOA.

5. Conclusions

Using CaF_2 and YF_3, dense AlN ceramics was achieved with a thermal conductivity of 180 W/m·K. The occurrence of liquid $(Ca,Y)F_2$ and $Ca_{12}Al_{14}O_{32}F_2$ is the main reason for the densification of AlN ceramics before 1650 °C. While, the densification is promoted by the action of liquid $CaYAlO_4$ at 1750 °C. Compared with the sample added with CaF_2 and Y_2O_3, grain boundary phases have no prominent effect on the thermal conductivity of AlN ceramics with CaF_2 and YF_3 addition. Oxygen concentration in the AlN lattice is the main controlling factor for the difference in the thermal conductivities of dense AlN ceramics. The concurrent addition of CaF_2 and YF_3 decreases the oxygen concentration in the AlN lattice of the sintered samples due to the formation of liquid $(Ca,Y)F_2$ at a relatively low temperature, and thus benefits achieving a high thermal conductivity.

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