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Thermal conductivity and dielectric property of hot-pressing sintered AlN–BN ceramic composites

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Abstract

A study was conducted of the effects of sintering temperature and CaF_2 additives on densification, microstructure, dielectric property and thermal conductivity of AlN–BN composites. Increasing sintering temperature and CaF_2 contents help to improve the densification, thermal conductivity, and purification of the grain boundaries. Thermal conductivity value reached 110 W m^{-1} K^{-1} for AlN–BN composites with 3 wt.% CaF_2 and sintered at 1850 °C. Increasing sintering temperature decreases relative dielectric constant and tan δ. The increase in CaF_2 content increases relative dielectric constant and decreases tan δ. Relative dielectric constants values were between 7.29 and 7.64 and dielectric loss tangent values ranged from 6.36 to 7.83 $\times$ 10^{-4} at 1 MHz.

Keywords: C. Dielectric property; C. Thermal property; AlN–BN composites; Densification; Hot-pressing sintering

1. Introduction

Aluminum nitride is considered to be a promising material for microwave-transparent because of its high thermal conductivity, low dielectric constant and dielectric loss tangent (tan δ), high bending strength, and good chemical stability [1–3]. Hexagonal boron nitride (h-BN) exhibits excellent dielectric behavior, high thermal conductivity, and is easily machinable [4]. So it is possible to develop AlN–BN ceramic composites with excellent thermal conductivity, dielectric property, and machinability [5,6].

It is difficult to sinter and fabricate dense AlN–BN ceramic composites for the reason that AlN and BN are predominantly covalently bonded. Another reason is that BN agglomerates resulting in large BN particles/platelets within sintered composites [7]. This study focused on the effect of a CaF_2 sintering aids and pressure-sintering on densification, density, dielectric behavior and thermal conductivity of AlN–BN composites.

2. Experimental

Commercially available AlN powder (grade F, Tokuyama Co., Tokyo, Japan), h-BN powder (Matech-inno Co. China, average particle size 0.34 μm, purity >98.5%) and CaF_2 powder (Shanghai Chemistry, China, purity >98.5%) were used as the starting materials. Powders containing 85:15 (wt.%) of AlN:BN and 0–4 wt.% CaF_2 were mixed in ethanol, and dried in vacuum. The mixtures then placed into a graphite mold, and pressure sintered in a furnace (916 G-G Press, Thermal Technology Inc., USA) heated to 1750–1900 °C at a heating rate of 10 °C/min and held at temperature for 3 h at a pressure of 30 MPa in a nitrogen atmosphere.

The densities of the sintered pellets were measured by the Archimedes displacement method. XRD (D/Max-RB, Rigaku) with Cu Kα radiation was employed to identify the produced phases. The fracture surfaces were inspected by SEM (JSM-5640LV, JEOL). TEM (JEM-2010FEF, JEOL) with EDX was also utilized to analyze the microstructure and the elements in the selected areas. To measure relative dielectric constant (ε_r) and dielectric loss tangent (tan δ), samples were machined and polished to 50 mm in diameter and 2.5 mm in thickness, and painted Ag thin film on the double round faces. ε_r and tan δ were measured within the range of 40 Hz to 1 MHz at room

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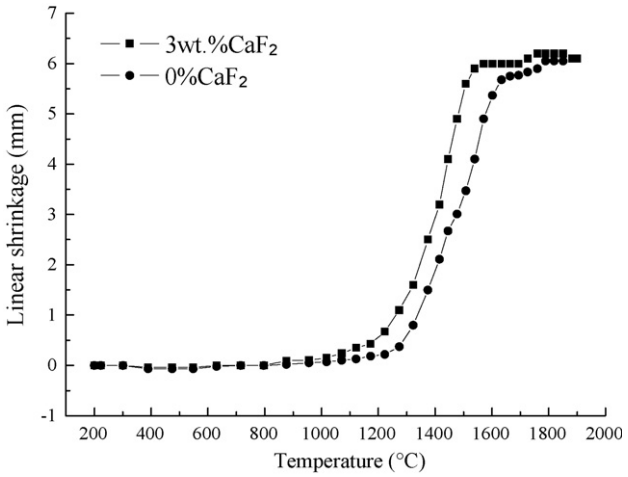

Fig. 1. Linear shrinkages of AlN–BN composites with 0 and 3 wt.% CaF_2 at sintering temperature from 200 to 1900 °C.

temperature, using an HP 4294A precision impedance analyzer (HP/Agilent). The thermal conductivity at room temperature was measured by TC-7000 Laser Flash Thermal Constant Analyzer (ULVAC SINKU-RIKO, Inc.).

3. Results and discussion

3.1. Sinterability

Fig. 1 shows the shrinkage of the samples with 0 and 3 wt.% CaF_2 during hot-pressing sintering. It can be found that the shrinkage of the sample with 3 wt.% CaF_2 starts at about 1000 °C and that of the sample without CaF_2 starts at about 1200 °C, which indicates that adding CaF_2 as sintering aids is effective in lowering the sintering temperature. The slight shrinkage from 300 to 600 °C is caused by the rearrangement of the particles under the uniaxial pressure. The shrinkage of the samples with 3 wt.% CaF_2 increases more quickly than that of the sample without CaF_2 from about 1200 °C to about 1500 °C, which is attributed to the liquid phase sintering induced by CaF_2 [8]. The sample with 3 wt.% CaF_2 reached the largest shrinkage from 1750 to 1850 °C. The shrinkage decreases slightly when the temperature higher than 1850 °C, which is likely attributed to the growth of AlN grains and BN particles/platelets.

Relative density of AlN–BN composites is shown in Table 1. The relative density of samples with 3 wt.% CaF_2 increases from 1750 to 1850 °C, and reaches a maximum value of 98.53% at 1850 °C. The presence of the CaF_2 had a great influence on the relative density of AlN–BN composites, which is improved continuously with increasing CaF_2 content.

Table 1
Compositions and properties of different samples

Sample	CaF_2 (wt.%)	Sintering temperature (°C)	Relative density (%)	$\tan\delta \times 10^{-4}$ (at 1 MHz)
1	0	1850	98.29	8.15
2	1	1850	98.39	6.89
3	2	1850	98.45	6.49
4	3	1850	98.53	6.36
5	4	1850	98.54	6.28
6	3	1750	98.02	7.83
7	3	1800	98.47	6.36
8	3	1900	98.52	6.42

3.2. Microstructure

The morphology of fracture surfaces of samples with 3 wt.% CaF_2 sintered at 1750–1850 °C is shown in Fig. 2. When the sintering temperature increases from 1750 to 1850 °C, grains grow larger and contact with one another more closely. Fig. 3 shows the microstructure of AlN–BN composites sintered at 1850 °C. It reveals that the development of the grains is remarkably improved and the distribution of BN phases is more homogeneous with the increase in CaF_2 content. These results can be concluded that the addition of CaF_2 and increasing sintering temperature enhanced the grain growth and contacts. In AlN–BN composites, using CaF_2 as sintering aid leads to the reactions between the alumina layer at the surface of AlN grains with the additives, which formed a liquid phase in the sintering process, and promoted the development of AlN and BN grains.

TEM micrograph of a sample with 3 wt.% CaF_2 sintered at 1850 °C is shown in Fig. 4(a and b). It can be seen that the sintered body is densely compacted. The grain boundaries and triple grain junctions are clean. Therefore, it can be concluded that the addition of CaF_2 helped to form a liquid phase that enhanced densification and purified the grain boundaries.

Fig. 5 shows XRD pattern of the samples with 3 wt.% CaF_2 sintered at 1750–1900 °C. It is observed that all peaks are attributed to AlN and BN grains when the sample sintered at 1850 °C and above. The peak of CaF_2 is rather weak in the sample sintered at 1750 °C, which indicates that increasing the sintering temperature promoted the evaporation of the residual CaF_2 from the sintered body. The sample with 3 wt.% CaF_2 sintered at 1850 °C was examined by TEM attached with EDX. The peaks of Ca and other impurity elements are rather weak in the EDX result shown in Fig. 4(c). The results of EDX and XRD implies that the addition of CaF_2 purified the grain boundaries through the evaporation of the Ca–Al–O compounds from the sintered bodies in a carbon-containing nitrogen atmosphere, as mentioned by Peter et al. [9] and Qiao et al. [10].

3.3. Thermal conductivity

Thermal conductivity of AlN–BN composites increases with the increase in sintering temperature shown in Fig. 6 and the increase in CaF_2 content shown in Fig. 7. In the fabricated AlN–BN composites, AlN phase is the main phase for its higher condition (85 wt.%). The primary heat transport mechanism of AlN is phonon propagation [1]. It is expected that impurities or other lattice and microstructural defects can cause phonon scattering and thus lower the thermal conductivity. Tajika et al. [11] previously pointed out that thermal conductivity of AlN ceramics was improved by the increasing in AlN grain contacts. The dihedral angles in the sample with 3 wt.% CaF_2 sintered at 1850 °C are about 120° between the polyhedral grains with

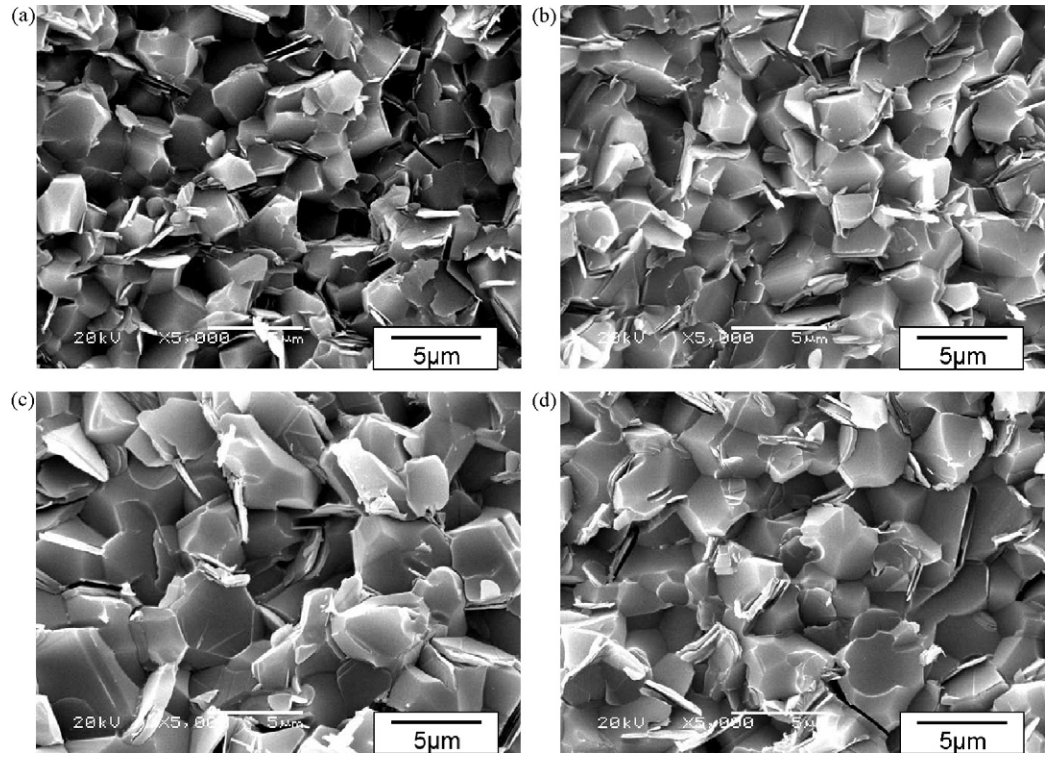

Fig. 2. Effect of sintering temperature on the microstructure of AlN–BN composites with 3 wt.% CaF_2 ((a) 1750 °C; (b) 1800 °C; (c) 1850 °C; (d) 1900 °C).

little grain-boundary phases at the three-grain junctions showed in Fig. 4. This implies that the increasing thermal conductivity of AlN–BN composite is probably attributed to the improvement of the density, more-contiguous grains and the purification of the grain-boundaries, which may improve the phonon conduction. The highest thermal conductivity value reached 110 $W\,m^{-1}\,K^{-1}$ when the AlN–BN composites were added 3 wt.% CaF_2 and sintered at 1850 °C.

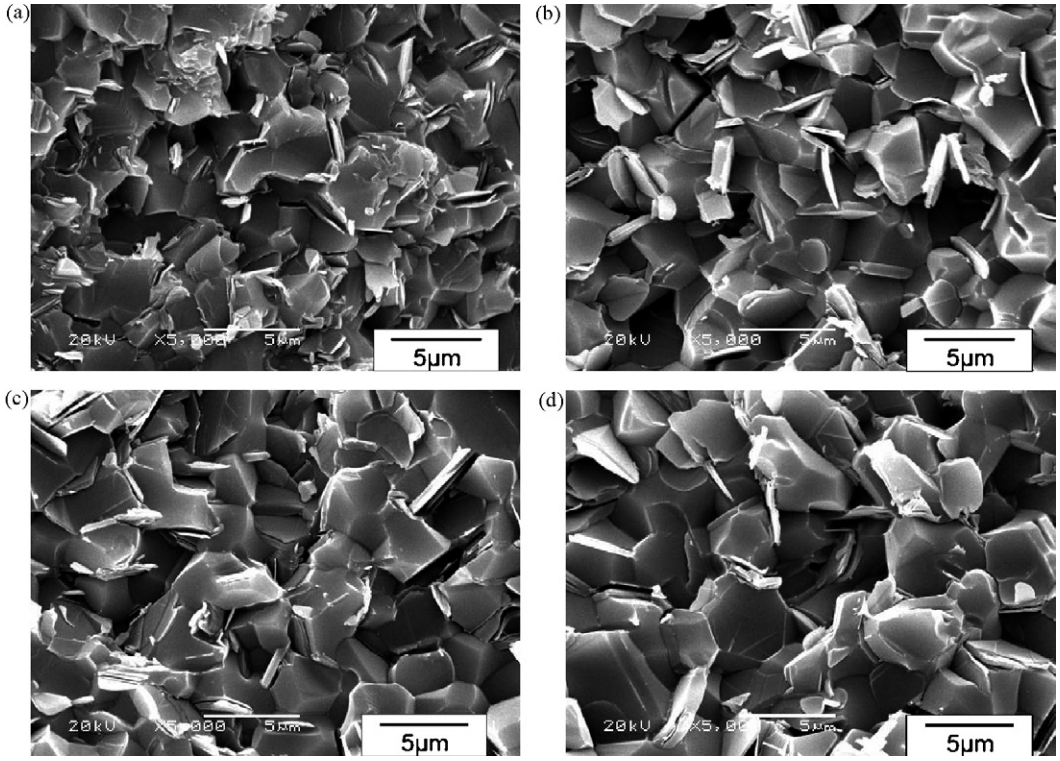

Fig. 3. Effect of CaF_2 content on the microstructure of AlN–BN composites sintered at 1850 °C ((a) 0 wt.% CaF_2; (b) 1 wt.% CaF_2; (c) 2 wt.% CaF_2; (d) 3 wt.% CaF_2).

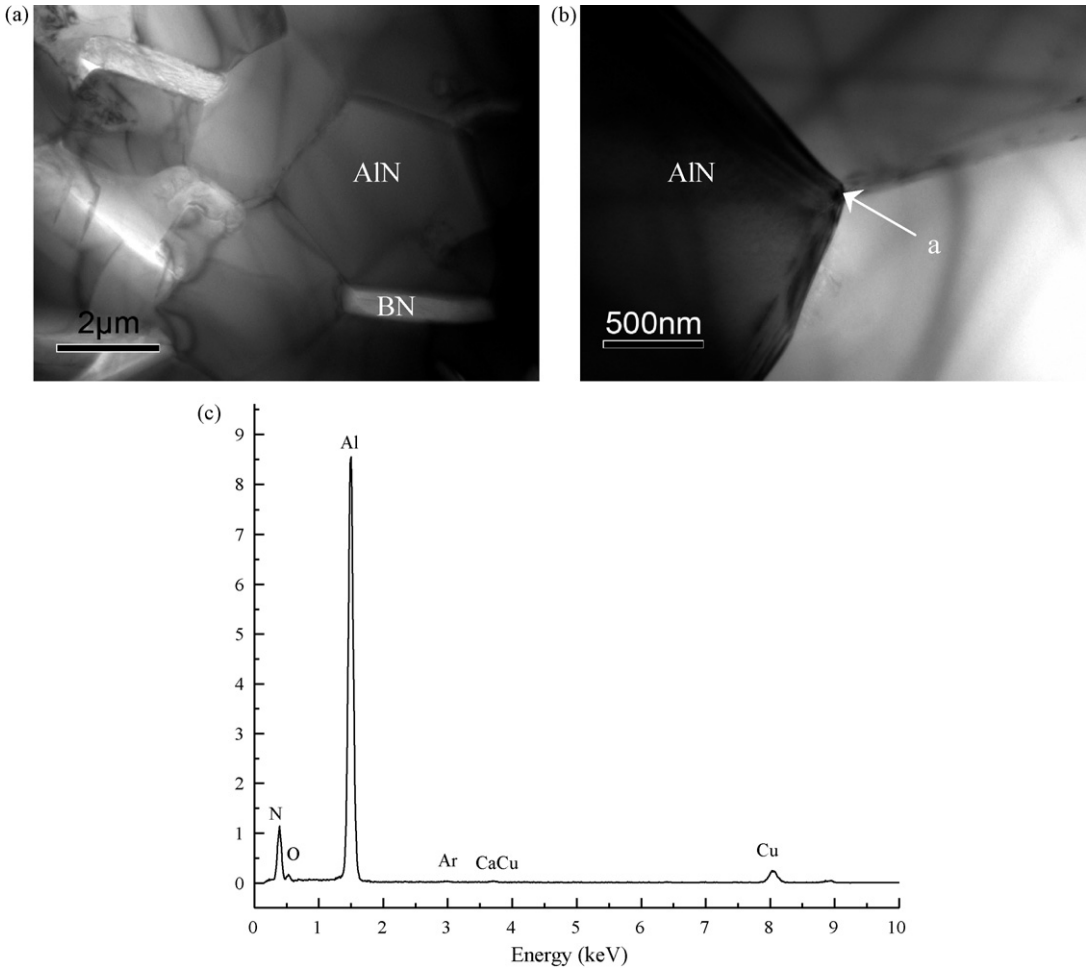

Fig. 4. (a and b) TEM micrograph of AlN–BN composites with 3 wt.% CaF_2 sintered at 1850 °C; (c) EDX spectrum at the triple grain junctions in (b).

3.4. Dielectric property

Effects of sintering temperature on relative dielectric constant of AlN–BN composites with 3 wt.% CaF_2 is shown in Fig. 6. It reveals that with increasing the sintering temperature from 1750 to 1850 °C, the relative dielectric constant of the samples with 3 wt.% CaF_2 decreases from 7.63 to 7.50. As is shown in Figs. 2 and 4, the grains of AlN–BN composites grow larger and contact closely. Therefore, the decrease in relative dielectric constant was due to the grain growth and decreased grain boundaries and microdefects, which resulted from increasing sintering temperature. In

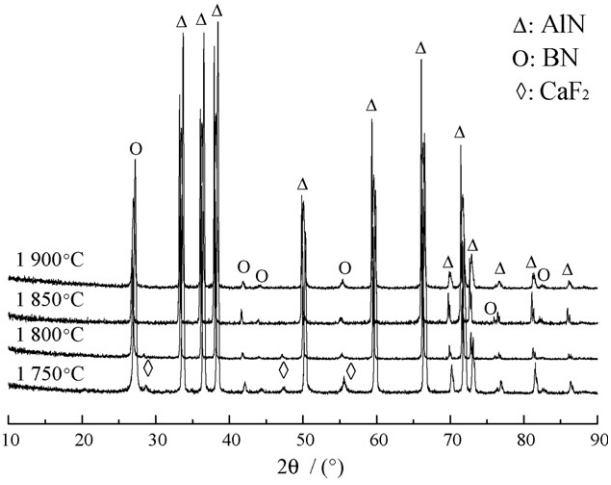

Fig. 5. XRD patterns of AlN–BN composites with 3 wt.% CaF_2 sintered at different temperatures.

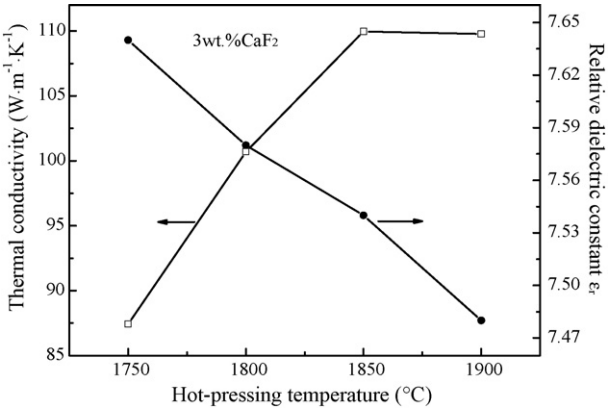

Fig. 6. Effects of CaF_2 content on thermal conductivity and relative dielectric constant of AlN–BN composites sintered at 1850 °C.

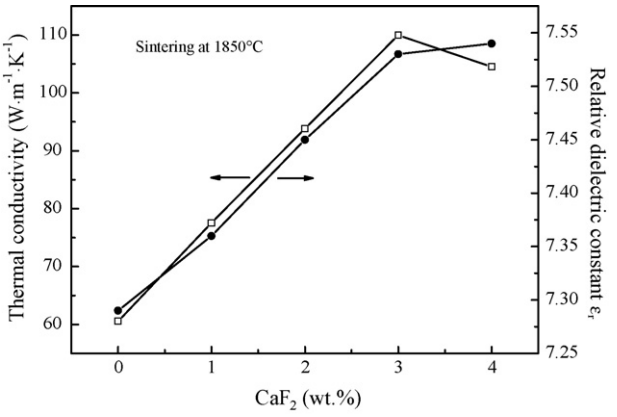

Fig. 7. Effects of sintering temperature on thermal conductivity and relative dielectric constant of AlN–BN composites with 3 wt.% CaF_2.

Table 1, the relative density of the samples sintered at 1850 °C increases from 98.29 to 98.54% with increasing the content of CaF_2. Therefore, the increase in relative dielectric constant in Fig. 7 can be related to the decreasing micropores in the sintered bodies. The dielectric loss in the present study is sufficiently lower than that of Takao et al. [5,6]. As is shown in Table 1, increasing the content of CaF_2 and sintering temperature help to decrease tan δ, which is related to increased density, the grain growth, decreased microdefects and purification of grain boundaries. When AlN–BN composites were added 3 wt.% CaF_2 and hot-pressed at 1850 °C, the relative dielectric constant and tan δ were 7.54 and 6.36×10^{-4} separately.

4. Conclusions

(1) Adding CaF_2 as a sintering aid effectively lowers the sintering temperature and promotes densification of AlN–BN composites. Samples with relative density of 98.53–98.54% were obtained, when the samples were added 3–4 wt.% CaF_2 and pressure sintered at 1850 °C.
(2) Increasing the content of CaF_2 and hot-pressing temperature help to increase thermal conductivity through improving the grain growth and the contact of the grains. The highest thermal conductivity value reached 110 W m^{-1} K^{-1} when the AlN–BN composites were added 3 wt.% CaF_2 and sintered at 1850 °C.
(3) Increasing sintering temperature helps to decrease relative dielectric constant and tan δ. The increase in CaF_2 content increases relative dielectric constant and decreases tan δ. When added 3 wt.% CaF_2 and hot-pressed at 1850 °C, the relative dielectric constant and tan δ of the AlN–BN composites were 7.54 and 6.36×10^{-4} separately.

Acknowledgements

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