FULL PAPER

Transparent AlN ceramics sintered from nanopowders produced by the wet chemical method

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Transparent aluminum nitride (AlN) ceramics were sintered by the hot-pressing (HP) method. Comparison has shown that AlN ceramics fabricated using as-prepared nanopowders exhibit relatively high transparency, while AlN ceramics prepared using commercial micro-powders seem almost opaque. The influences of different sintering additives on the phase composition, densification behavior, microstructure, transparency and thermal conductivity of AlN ceramics were investigated. X-ray diffraction and scanning electron microscope analyses revealed that AlN ceramics with fluoride additives exhibited the pure AlN phase, while secondary phases were observed when using oxide additives. The microstructure, especially the distribution of secondary phases and porosity, played an important role, moreover in the transparency and thermal conductivity. Thus, the transmittance and thermal conductivity of ceramics with a 3 wt % CaF₂ additive were higher than others.

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1. Introduction

Aluminum nitride (AlN) ceramics has attracted greater attentions recently due to their high intrinsic thermal conductivity, robust mechanical strength, good electrical insulation, and thermal expansion coefficient close to silicon.^{1)–3)} Besides serving as microelectronic substrates and packages, AlN ceramics with a wide band gap of 6.3 eV show great potential as transparent optical and window materials.^{4)–6)} The fabrication of transparent non-oxide ceramics has proved more difficult than oxide ceramics, however, due to their strong covalent band and low diffusion coefficients.⁷⁾ Up to now, there have been only a few reports on the preparation of transparent AlN with high sintering temperatures up to 2000°C.^{8)–15)} Then, the preparation of transparent AlN at low temperatures remains a challenge.

It is well-known that ceramic nanopowders can lower sintering temperatures and facilitate densification. Typically, commercial AlN powders have been synthesized mainly via the carbothermal reduction nitridation method.¹⁶⁾ High calcination temperatures and long dwelling times are required, however, for homogeneous sintering of raw materials leading to serious aggregation.¹⁷⁾ In our previous work, a novel wet-chemical method (the

hydrothermal-carbothermal route) was developed to synthesize AlN nanopowders with excellent sinterability.¹⁸⁾ To our best knowledge, the studies upon the preparation of transparent AlN ceramics using AlN nanopowders are still rare.

Additives have been widely used for sintering high-quality ceramics. Among these, yttrium oxide (Y₂O₃) is one of the most commonly used oxide additives, because it can react with the low-activity alumina layer on the surface of nitride particles and form liquid-phase yttrium aluminates to promote densification.^{19)–21)} The yttrium aluminates formed and distributed along the AlN grain-boundary do not evaporate easily, which seriously reduces their transparency. In addition, non-oxide additives including fluorides are also adopted, which promote the densification process by liquid-phase sintering along with clean grain boundaries by evaporation of the secondary phase.^{22),23)} AlN transparent ceramics were prepared successfully at 1850°C with CaF₂ as additive.¹⁵⁾ The effect of additives on transparency and thermal conductivity has not, however, been investigated comprehensively. Thus, it is still extremely important to carry out the related studies to attain a better understanding of the effects of additives.

Herein, we report the first preparation of transparent AlN ceramics sintered at relatively lower temperatures using different sintering additives, including CaF₂, MgF₂ and Y₂O₃. The effect of additives on phase composition,

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microstructure, transparency and thermal conductivity are investigated and are discussed in detail.

2. Experimental procedure

2.1 Synthesis of AlN nanopowders

Commercially available $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, urea and sucrose (Aladdin Reagent Co. Ltd., Shanghai, China, 99.95% purity) were used for the synthesis of the $\text{Al}_2\text{O}_3/\text{C}$ precursor via the hydrothermal route. The $\text{Al}_2\text{O}_3/\text{C}$ precursor was then calcined at 1500°C for 4 h to obtain AlN nanopowders through the carbothermal nitridation method. Finally, the resulting powders were calcined at 700°C for 1 h in air to remove residual carbon.¹⁸⁾

2.2 Preparation of transparent AlN ceramics

Commercial AlN micro-powders (Aladdin Reagent Co., Ltd., Shanghai, China, 99.9% purity) were also used as raw materials. Sintering additives in 3 wt % amount were chosen from CaF_2 , Y_2O_3 and MgF_2 , respectively (Aladdin Reagent Co., Ltd., Shanghai, China, 99.99% purity). The raw materials were mixed in an ethanol medium using a planetary mill with alumina balls for 12 h. After vacuum-drying, the resulting powders were ground slightly and sieved to 150 mesh. Finally, the powders were poured into a graphite die and sintered at 1800°C for 3 h under 30 MPa uniaxial pressure at a rate of $5^\circ\text{C}/\text{min}$ under a nitrogen atmosphere. The obtained ceramic fabricated using commercial AlN micro-powders with 3 wt % Y_2O_3 was denoted as M3YO, and the ceramics obtained using as-prepared nanopowders with different additives were denoted as N3CF, N3YO and N3MF respectively.

2.3 Characterization

Elemental analyses of raw materials and ceramics were conducted with an oxygen/nitrogen/hydrogen elemental analyzer (LECO ONH 836, LECO Corporation, USA).

The phase composition of the raw materials and ceramics were investigated by X-ray diffractometer (Rigaku Miniflex600, Japan) using $\text{Cu K}\alpha$ radiation operated at 40 kV. The morphology of the synthesized powders and ceramics were observed using a field emission scanning electron microscope (FESEM, Hitachi SU8010, Japan) equipped with an energy dispersive spectroscopy apparatus. The in-line transmittance was measured by a fourier transform infrared spectrometer (Vertex70, Bruker Optics, Germany). The thermal conductivity was determined by a laser thermal conductivity measuring instrument (NETZSCH, LAF457, Germany). Vickers hardness was measured on the polished surfaces of specimens with a HV-1000 Vickers hardness instrument with a load of 4.9 N and duration of 10 s. The densities of the sintered samples were determined by the Archimedes method.

3. Results and discussion

3.1 Properties of raw materials

Home-made AlN nanopowders produced using a hydrothermal-carbothermal method were used as the raw materials. As shown in **Fig. 1**, it is obvious that the as-prepared powders are phase pure and exhibit well-distributed sphere morphology with a mean partical size of 100 nm. The oxygen content of the raw material was determined to be 0.80 wt %, moreover suggesting that implying 1.70 wt % Al_2O_3 originated from the oxidation of Al layers on the surfaces of the AlN particles.

3.2 Transparency of AlN ceramics

Table 1 lists the selected properties of various AlN ceramics. All the AlN ceramics were well sintered and achieved nearly theoretical density. As shown in **Fig. 2**, the M3YO ceramic seems almost opaque, while the AlN ceramics prepared from nanopowders are relatively high transparency. The maximum in-line transmittance is 53.2%

Fig. 1. XRD patterns and SEM images of the as-prepared AlN nanopowders.

Table 1. Selected properties of prepared transparent AlN ceramics

	N3CF	N3YO	N3MF	M3YO
Sintering additive	3 wt % CaF_2	3 wt % Y_2O_3	3 wt % MgF_2	3 wt % Y_2O_3
Relative density (%)	99.8	99.6	98.1	99.3
Vickers hardness (HV)	1119.6	1179.8	1217.1	1131.3
Average grain size (μm)	5.2	4.6	1.7	10.4
Thermal conductivity ($\text{W}/\text{m}\cdot\text{k}$)	191.8	137.9	101.4	118.1

Fig. 2. Transmittance with respect to wavenumber curves of AlN ceramics.

Fig. 3. Appearances of sintered AlN ceramics (0.55 mm thick): (a) N3CF, (b) N3YO, and (c) N3MF.

Fig. 4. XRD patterns of sintered AlN ceramics: (a) N3CF, (b) N3YO, and (c) N3MF.

at 1910 cm^{-1} for the N3CF, 28.1% at 1817 cm^{-1} for the N3YO, and 12.7% at 1820 cm^{-1} for the N3MF, respectively. The appearance of the AlN ceramics prepared from nanopowders are presented in Fig. 3, demonstrating good transparency.

3.3 Phase composition and densification behavior

X-ray diffraction (XRD) analyses were conducted to clarify the effect of different additives on phase composition. As shown in Fig. 4, all the diffraction peaks in N3CF and N3MF were attributed to AlN. There are several

Fig. 5. Displacement curves versus temperatures of different AlN ceramics.

additional diffraction peaks in N3YO as well, which can be assigned to $\text{Al}_5\text{Y}_3\text{O}_{12}$ as impurities.

The shrinkage curves for different temperatures were investigated to study the densification mechanism of different additives during HP processes (Fig. 5). The curves of all the samples rise only slightly within the soaking temperature range, indicating that all the samples were already well-densified before reaching the soaking temperature. Compared with previous reports,^{7),8),15)} the green bodies of the nanopowders achieved full density at significantly low temperatures. For N3CF, the shrinkage temperature is about 1393°C with 0.59 mm shrinkage displacement, which can be interpreted by the reaction between the CaF_2 and Al_2O_3 layers to form liquid-phase calcium aluminates at this temperature. According to a previous study,^{15),23)} the evolution of grain-boundary phases can be mainly summarized as follow:

It is apparent from the above equations that the by-products including $\text{Ca}_3\text{N}_2(\text{g})$, $\text{CO}(\text{g})$, $\text{Ca}(\text{g})$ and $\text{AlF}_3(\text{g})$ can easily evaporate at high temperatures, which is beneficial for obtaining clean grain boundaries and high transmittance.

For N3YO, the shrinkage temperature is 1523°C , which is consistent with the $\text{Y}_2\text{O}_3\text{--Al}_2\text{O}_3$ phase diagram. Y_2O_3 reacts with alumina on the surface of AlN particles to generate liquid-phase $\text{Al}_5\text{Y}_3\text{O}_{12}$, which speeds up the densification processing. $\text{Al}_5\text{Y}_3\text{O}_{12}$ is stable and resistant to evaporation at 1850°C in this system, however.¹⁴⁾ Thus, distribution of $\text{Al}_5\text{Y}_3\text{O}_{12}$ along the AlN grain-boundary leads to lower transmittance than that of N3CF. When MgF_2 is used as a sintering additive, the shrinkage temperature and the shrinkage displacement are 1193°C and 0.12 mm , respectively. This may be attributed the fact that

Fig. 6. SEM images of fractured surfaces of sintered AlN ceramics: (a) N3CF, (b) N3YO, and (c) N3MF.

Fig. 7. SEM images of polished surfaces of sintered AlN ceramics: (a) N3CF, (b) N3YO, and (c) N3MF.

Fig. 8. Schematic demonstration of different defects in AlN ceramics: (a) grain boundary; (b) pore.

MgF_2 is stable at this temperature and does not react with Al_2O_3 or AlN. Considering that the melting point of MgF_2 is 1261°C , we can presumably assign the displacement at this temperature to the melting of MgF_2 , to promote the densification of AlN. N3MF and N3CF both exhibit a single AlN phase, but N3MF possesses much lower in-line transmittance of 12.7%, which can be attributed to lower density with porosity.

3.4 Microstructures of AlN ceramics

Figure 6 presents typical SEM images of the fractured surfaces of AlN ceramics. The average grain sizes and Vickers hardness together with the relative densities are summarized in Table 1. When CaF_2 or MgF_2 is used as a sintering additive, hexagonal AlN grains are closely packed together with clean grain boundaries. The grains have developed into comparatively regular hexagonal grains, but obvious secondary phases (red arrows) can be observed surrounding the AlN grains in N3YO, as shown in Fig. 6(b). In addition, the average grain sizes of N3CF and N3YO ceramic is 5.2 and $4.6\mu\text{m}$, respectively. Comparison show that N3MF possesses the smallest average grain size of $1.7\mu\text{m}$, leading to the highest Vickers hardness. The super fine grains in N3MF can presumably be assigned to the following causes: less of liquid phase is

produced and the densification temperature is lower than others (Fig. 5), resulting in a suppression of grain growth.

To investigate the effect of microstructure on transparency further, back-scattered SEM images of the polished surface of sintered AlN ceramics were measured (Fig. 7). The microstructures of N3CF and N3MF both exhibited pure AlN grains without any secondary phases, which were consistent with XRD results. As seen in Fig. 7(c), some cracks exist in N3MF, representing an adverse effect on the transparency of ceramics. Hence, the in-line transmittance of N3MF is 40.5% lower than that of N3CF. For the Y_2O_3 additive, the microstructure of N3YO is composed of grey AlN grains and white secondary phases, as shown in Fig. 7(b). It is well-known that both the secondary phase and pores consume part of the incident rays, exerting a negative influence on transparency (Fig. 8).

3.5 Thermal conductivity of AlN ceramics

Oxygen content is a critical parameter for the performance of AlN ceramics.²⁴⁾ Oxygen impurities can easily dissolve into AlN lattices to produce aluminum vacancies, thus decreasing the thermal conductivity by scattering phonons. The oxygen content and related thermal conductivity of various ceramics are shown in Fig. 9. The oxygen content of N3CF, N3YO, and N3MF is 0.37, 0.92,

Fig. 9. Oxygen contents and thermal conductivities of AlN ceramics.

and 0.62 wt% respectively, while the thermal conductivity is 191.8, 137.9, and 101.4 W/m·K, respectively. In comparison with the raw materials, the oxygen content of N3CF decreases from 0.80 to 0.37 wt%, in agreement with the fact that CaF_2 can react with Al_2O_3 layers to form evaporable secondary phase resulting in a decrease in oxygen content. Y_2O_3 reacts with Al_2O_3 layers to form a stable secondary phase in N3YO, however, with the oxygen content increasing to 0.92 wt%. The oxygen content of N3MF shows only a slight decline, which may be attributed to the ability of Al_2O_3 to react partially with carbon from graphite die at high temperatures.

It is apparent from a comparison between N3CF and N3YO that thermal conductivity increases with the decreases in oxygen content as expected. The abnormal thermal conductivity of N3MF accompanied by low oxygen content can be attributed to the cracks within the matrix. The cracks are filled with air, and the thermal conductivity is determined mainly by the air without much increase in the value of AlN.

4. Conclusion

Transparent AlN ceramics have been successfully sintered at relatively low temperature using AlN nanopowders. Additive effects on the microstructure and composition of AlN ceramics, such as the grain size, pores and secondary phases, have been studied. Compared with Y_2O_3 and MgF_2 additives, CaF_2 additives can reduce impurities and facilitate densification simultaneously. Thus, ceramics sintered with 3 wt% CaF_2 exhibit better transparency performance and thermal conductivity. These principles for the selection of additives will also be significant for the future development of highly transparent ceramics.

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