Fabrication of transparent AlN ceramics

YAN XIONG*, ZHENGYI FU, YUCHENG WANG, FENG QUAN
State Key Lab of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan 430070, People's Republic of China
E-mail: xyblaze@sina.com

Published online: 6 April 2006

Aluminum nitride (AlN) is mostly known for its high theoretical thermal conductivity (320 W mK^{-1}). In present work, special attention has been given to the fabrication of transparent AlN ceramics.

With a wide band gap (6.3 eV) [1], AlN can be made transparent, which when combined with its wear resistance make AlN attractive for some electrooptics applications [2]. AlN is also used as a phase contrast layer in optical disks and has potential as a phase shift material in lithographic photo mask [3]. These applications generate an interest in the optical properties of AlN.

But in many cases, AlN ceramics are translucent or opaque because of the difficulty of obtaining high density because of its highly covalent bonding structure. The fabrication of transparent AlN ceramics is by hot pressing traditionally [4–7]. However, the major problem is the long densification time at high temperatures.

Spark plasma sintering (SPS) is a newly developed densification technique by which ceramic powder can be very fast to full density at relatively lower temperature. Similar to hot pressing, SPS process is also carried out in a graphite die. But the heating is accomplished by spark discharges in voids between particles generated by the pulse current applied through electrodes at the top and bottom punches of the graphite die. Because of these discharges, the particle surface is activated and purified. The heat transfer and mass transfer can be completed in a very short time. In this paper, SPS was selected to reduce the need for long densification time and sinter transparent AlN ceramics rapidly.

Commercially available AlN powder (Tokuyama Soda Co. Ltd., Japan) was used as the starting material. The properties of the AlN powder, according to manufacture's date, were shown in Table I. Fig. 1 was the scanning electron microscope (SEM) microphotograph of the staring powder, which showed that AlN powder was uniformly spherical in shape with little agglomeration.

Three samples were prepared through the following processes:

1. Sample A: Pure AlN powder was sintered by SPS at 2123 K with a heating rate of 200 K/min in a nitrogen atmosphere. A pressure of approximately 30 MPa was applied from the beginning sintering. After 20 min, sample about 3–4 mm thickness was obtained.
2. Sample B: The mixture of AlN with 2–3% CaF_2 was planetary ball-milled for 8–12 hr, using ethanol as a mixing medium. After being dried at 343 K in vacuum, the mixture as pouring into the graphite die and sintering at 2073 K with the conditions as described in (a).
3. Sample C: Pure AlN ceramics without any addition was prepared by hot pressing, sintered at 2173 K for 1 hr under a pressure of 30 MPa in a flowing N_2 atmosphere.

TABLE I Properties of AlN powder

Item (unit)	Result
O (wt.%)	0.83
C (ppm)	340
Ca (ppm)	7
Si (ppm)	9
Fe (ppm)	<10
Specific surface area (m^2/g)	3.31

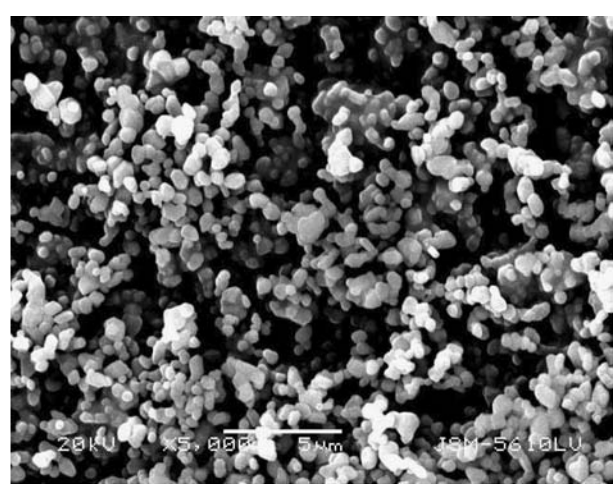


Figure 1 Scanning electron microscope (SEM) microphotograph of starting powder.

* Author to whom all correspondence should be addressed.

DOI: 10.1007/s10853-006-5314-8

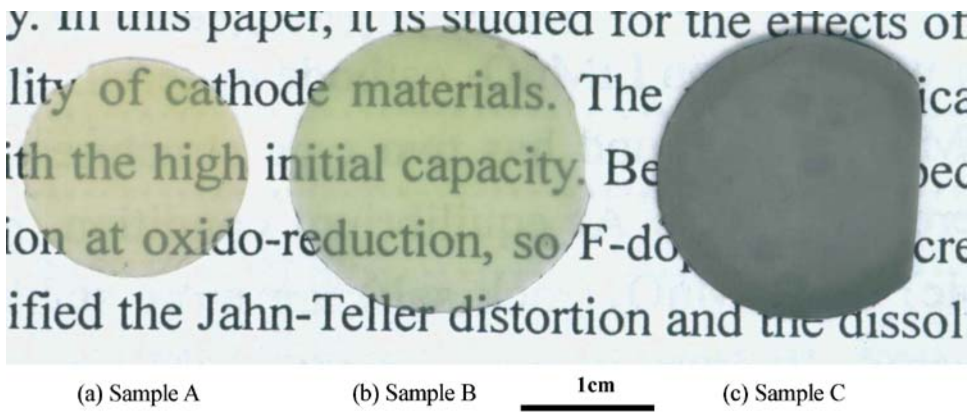


Figure 2 Appearance of sintered AlN ceramics.

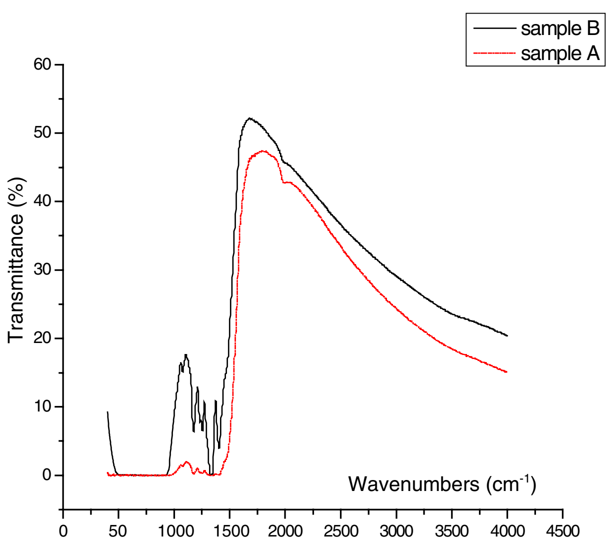


Figure 3 Transmittance against wavenumbers curve of transparent AlN ceramics.

High density is of primary importance for high transmittance of transparent ceramics. The measured densities of the sintered AlN bodies were (a) 3.227 gcm^{-3}, (b) 3.244 gcm^{-3}, (c) 2.973 gcm^{-3}, respectively. According to Borom [8], pure AlN powder was barely sintered at 2273 K by hot pressing. But sample A (pure AlN) sintered by SPS achieved over 99% of theoretical density in a very short time, which indicated the sintering process was greatly accelerated under the SPS conditions. Sample B achieved higher density at lower sintering temperature. This should be attributed to liquid phase sintering induced by the presence of CaF_2.

Then the sintered bodies were sliced up to about 0.5 mm thickness. After being burnished and polished, the appearance of the slices was shown in Fig. 2. Both sample A and sample B showed good transparency and the characters under the slices were legible through the specimens. But slice C was black and opaque. Fig. 3 was the transmittance against wavenumbers curves of the sintered transparent AlN ceramics. It was evident that sample B had higher transmittance than sample A in all wavenumbers region. The maximum transmittance of sample A was 47.3% at 1798 $\text{cm}^{-1}$and sample B was 52.0% at 1742 cm^{-1}. Both were observed in medium infrared wavenumber region. A small addition of additive improved the transmittance of sintered AlN ceramics.

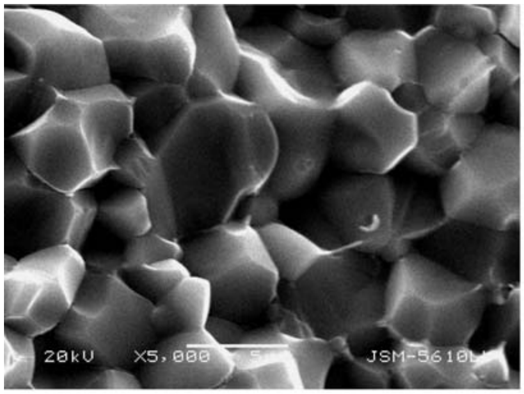
Fig. 4 showed the fracture surface microstructure of the sintered AlN ceramics. Even having been sintered at 2173 K for 1 hr, sample C was barely sintered by hot pressing. Microstructure of the grains had not formed and no clear grain boundary was observed. Many micropores were dispersed in the sintered body, which would cause light distraction and be badly detriment to the transmittance. Both A and B consisted of densely packed polyhedral AlN grains and clear grain boundaries. No secondary phase was observed (within the limits of resolution of the SEM). The average grain size was 4–5 μm, which indicated that there was no significant grain growth in the SPS process. Compared with sample A, grains in sample B were fairly hexagonal in shape and densely packed on each other.

Fig. 5 showed the X-ray diffraction of sample B. The peaks of AlN were intense. It would be suggested that the content of other phase was very low. In the sintering process, the following reaction might take place:

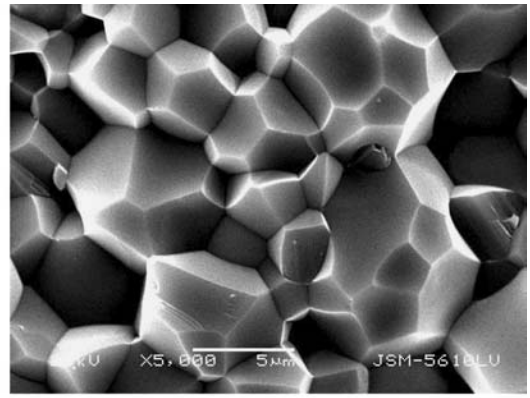
$$4Al_2O_3 + 3CaF_2 \rightarrow 3CaAl_2O_4 + 2AlF_3 \uparrow \qquad (1)$$

CaF_2 reacted with Al_2O_3 layers on the AlN particle surface to form liquid phases, which promoted the sintering process and purified the AlN lattice. During the soaking stage, those fluorides evaporated and further cleaned the sintered body. So content of secondary phase was very low and only peaks of AlN were detected in the XRD graph. A small addition of additive (CaF_2) not only lowered the sintering temperature but also improved the transparency of sintered AlN ceramics. CaF_2 was effective sintering additive for transparent AlN ceramics.

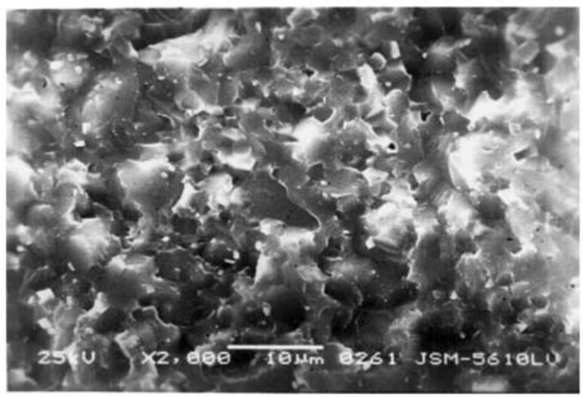
The rapid fabrication of transparent AlN ceramics confirmed the efficiency of SPS technique. And CaF_2 was an effective sintering additive for the fabrication of transparent AlN ceramics.



(a) Sample A



(b) Sample B



(c) Sample C

Figure 4 Fracture surface scanning electron microscope (SEM) graphs of the sintered AlN ceramics.

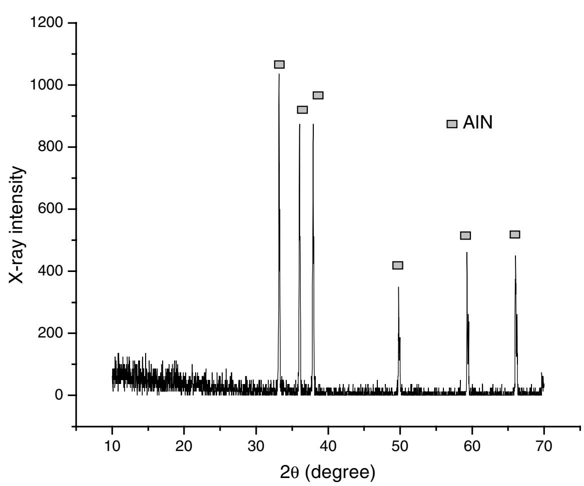


Figure 5 X-ray diffraction (XRD) micrograph of sample B.

Acknowledgment
The authors thank the National Natural Science Foundation for the financial support.

References
1. G. A. SLACK, *Phys. Chem. Solids* **34** (1973) 321.
2. L. M. SHEPPARD, *Ceram. Bull.* **69**(11) (1990).
3. D. J. JONES *et al.*, *J. Mater. Res.* **14**(1) (1999) 4337.
4. N. KURAMOTO *et al.*, *Ceram. Bull.* **68**(4) (1989) 883.
5. N. KURAMOTO and H. TANIGUCHI, *J. Mater. Sci. Lett.* (3) (1984) 471.
6. N. KURAMOTO *et al.*, *IEEE* **9**(4) (1987) 386.
7. Z. YANPING *et al.*,CN 1199036A, November 18, 1998.
8. M. P. BOROM, *Bull. Am. Ceram. Soc.* **51** (1972) 852.

Received 9 June 2004
and accepted 9 May 2005