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Fabrication of high thermal conductive Al–cBN ceramic sinters by high temperature high pressure method

P.F. Wang [a,b], Zh. H. Li [b,*], Y.M. Zhu [b]

[a] State Key Laboratory of Transient Optics and Photonics, Xi'an Institute of Optics and Procession Mechanics, Chinese Academy of Sciences (CAS), Xi'an, Shanxi 710119, PR China
[b] Key Laboratory of Advanced Ceramics and Machining Technology of Ministry of Education, School of Material Science and Engineering, Tianjin University, 92, Weijin road, Nankai district, Tianjin 300072, PR China

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ABSTRACT

Al–cBN ceramic sinters were fabricated by sintering micro-powder mixture of Al and cBN under high temperature and high pressure condition. Differential scanning calorimetry (DSC), X-ray diffraction (XRD), scanning electronic microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) elemental mapping analyses and laser flashing thermal conductivity measurements were performed to investigate the sintering properties and thermal conductivity of the Al–cBN ceramic sinters. XRD analysis revealed these Al–cBN ceramic sinters were composed of a large portion of cBN and of a small portion of AlN, and very little amount of AlB_{12} and hBN. Formation of boundary phase resulted in the rapid densification of the sinters, as well as the increase of their relative density with increasing Al additions. The Al–cBN ceramic sinters have a maximum thermal conductivity of about 1.94 W/cm K at room temperature and a much higher value of about 2.04 W/cm K at 200 °C. Their high thermal conductivity over that of AlN–hBN composites promise Al–cBN ceramic sinters favorite candidates as high efficiency heat sink materials for wide band gap semiconductors.

1. Introduction

Among III-V nitride compounds, cubic boron nitride (cBN) and AlN have attracted both scientific and technological interests in recent years, due to their fascinating mechanical and functional properties [1,2]. They hold much promise as wide band gap semiconductors for the use in optoelectronic and microelectronic devices operating under extreme conditions. Especially, cBN has a number of extraordinary properties, e.g., chemical inertness, high melting temperature, and high thermal conductivity. Its electronic properties, dominated by a wide band gap (6.1–6.4 eV) [3] and a relatively small dielectric constant, may have potential applications in ultraviolet optics, high power/frequency microelectronics, and heat-conducting substrates. Because of these fascinating properties, cBN has received a great deal of attention from experimentalists and theoreticians [4].

Despite the wide variety of possible multifunctional applications, practical application of cBN is limited. The production of individual single crystals of cBN with large size is extremely costly, and film technologies have not given reassuring results of producing large-sized unique phase cBN films with requisite optical and electrophysical characteristics [5]. Meanwhile, a good alternative to cBN single crystals and thin films for functional applications can be sintered pure cBN ceramics or cBN compacts containing binders of metal or ceramics. Many works have provided useful information on sintering of cBN ceramics and compacts under high temperature and high pressure conditions [6–13].

Similar to cBN, AlN ceramics have been extensively investigated because of its relative high thermal conductivity (over traditional substrate materials, Al_2O_3 and BeO, etc.), excellent electric resistivity and a thermal expansion coefficient close to that of silicon, making AlN as heat sinks for Si substrate [14–16]. Usually, hBN is introduced into AlN matrix to improve the matrix's machinability [17–20], which, however, inevitably result in the degradation of AlN matrix's thermal conductivity. Even many works have been carried out to deal with coordination between the machinability and thermal conductivity of AlN–hBN composites [21–25]. However, with regard to the thermal conductivity of AlN–hBN composites, only a maximum of about 1.1 ~ 1.41 W/cm K [20, 22] was achieved.

Dislike hBN, cBN had isotropic crystal structure, and it maintains attractive functional properties superior to AlN, especially much larger band gap, higher thermal conductivity (theoretically 12 W/cm K for the pure cBN single crystal, about 4.5–6.5 W/cm K

* Corresponding author. Tel./fax: +86 22 27404260.
E-mail address: tjumarkli@yahoo.cn (Zh.H. Li).

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for hBN directly transitioned and long time sintered pure cBN polycrystals [26]) and lower dielectric constant. Meanwhile, little amount of binders always are introduced in order to reduce the sintering temperature of pure cBN polycrystals. Among which, high pressure sintering of cBN with Al binders are widely researched [7,9–13], and the researched AlN–cBN composites exhibit outstanding mechanical properties. However, to date, the functional properties of AlN–cBN composites, e.g. thermal conductivity and dielectric properties have rarely been reported.

In this paper, Al–cBN ceramic sinters with high density were fabricated by sintering the mixtures of cBN and Al micro-powders at high temperature and high pressure conditions, and the relations between microstructure, high relative density and thermal conductivity and Al additions were investigated. The high thermal conductivity property would give Al–cBN ceramic sinters large potential applications as high efficiency heat sink materials for wide band gap semiconductors.

2. Experimental

Al–cBN ceramic sinters were prepared directly from mixed micro-powders of cBN (cBN-M990, particle size 1.5–3 μm, >99.5% purity, Henan Funik Ultrahard Material Co. Ltd, China) and aluminum micro-powder (an average particle size 20 μm, >99.5% purity, Tianjin Keweier Metal Material Co., Ltd, China) under HTHP conditions. The micro-powders were manually mixed in ethyl alcohol, using an agate mortar and pestle for 4 h, at a proportion of 2, 4, 6, 8 and 10 wt% Al in Al–cBN system, respectively. The starting mixtures were degassed under vacuum of 4.0×10^{-3} Pa and temperature of 600 °C for 2 h prior to sintering process. The mixed micro-powders were set in synthesis capsule and sintered at 1400 °C under a pressure of about 5.0 GPa for 2 min, using a belt-type high pressure graphite apparatus. The pressure was estimated by the oil pressure reading calibrated with the method of silver melting point at high pressure [8], and the temperature calibration was performed using a Pt/Pt-13%Rh thermocouple.

DSC measurement of the Al–cBN mixtures was carried out using a Netzsch Model 449C instrument in the temperature range of room temperature to 1500 °C at a heating rate of 10 °C/min, in nitrogen atmosphere. Al–cBN ceramic sinters were disposed, polished to a flat surface, and finally cleaned ultrasonically in ethanol, acetone and distilled water, respectively, followed by a drying process in vacuum chamber (detail process referred to Ref. [8]). Archimedes method was used to measure the volume density of these specimens.

A Philips XL30E scanning electron microscope (SEM) was used to examine the cross-section microstructure fractured Al–cBN ceramic sinters, and XRD (Cu K_α radiation, $\lambda = 1.54056$ Å) was performed to analyze the phase compositions using an X-ray diffractometer (Rigaku D/Max 2500V/PC). Same samples shaped as cylinders with diameters of 12.7 ± 0.1 mm and heights of 1.9 ± 0.1 mm were coated with graphite for use in thermal diffusivity examination. Thermal diffusivity measurement of these samples was taken by the LFA 427 laser flashing thermal conductivity analyzer at room temperature in argon atmosphere with a flow speed of 100 ml/min. A single sample, with 10 wt% Al addition, was taken to research its temperature dependence of thermal conductivity within the range from room temperature to 500 °C.

3. Results and discussion

DSC curve of Al–cBN mixing micro-powders is shown in Fig. 1. Because the influence of air on the fast reaction of Al and cBN under high temperature and high pressure was very tiny, therefore, the DSC measurement of the Al–cBN mixtures was performed in nitrogen atmosphere to avoid the effect of air. In Fig. 1, the endothermic peak is observed at about 661 °C, which was attributed to Al melting's thermal effect. Furthermore, the obscure one in the range of 700 ~ 900 °C was attributed to the reaction of Al and cBN, and the peak at about 750 °C corresponded to the reaction of Al with N_2 to AlN. That of Al with cBN was mostly tense at about 1000 °C. Finally, the weak peaks at about 1283 °C and 1353 °C corresponded to the transformation of cBN to γBN, but around 1462 °C the obvious peak should be assigned to γBN→hBN structural change. It was regarded that the experimental high pressure condition resulted in the rapid distribution of molten Al simple substance between cBN grains and accelerated the diffusion of other atoms (B, N) through molten Al layer in relative low temperature range, which may lead to the rapid densification of Al–cBN ceramics sinters.

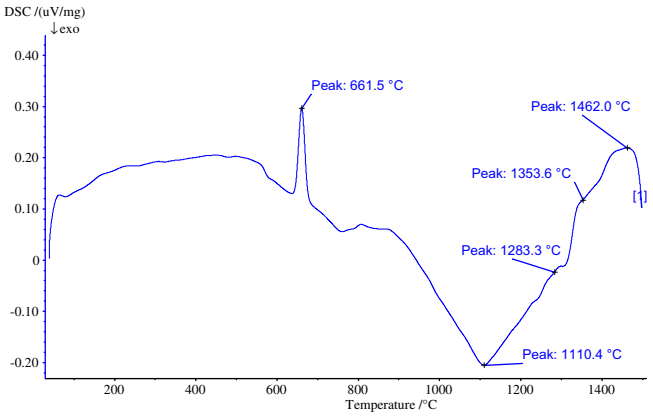

Fig. 1. DSC curve of Al–cBN mixing micro-powders in nitrogen atmosphere.

XRD patterns of the Al–cBN ceramic sinters are given in Fig. 2, which reveals the sintered samples are composed of a large portion of cBN and of a small portion of AlN, also very little amount of AlB_{12} and hBN. With increasing Al additions, the peaks of AlN were getting tenser and those of cBN weaker and peaks of hBN were observed to be gradually disappearing as well. Because, formation of high hardness boundary phase (AlN, AlB_{12}) under high pressure would to great extent impede cBN's transformation into hBN. In addition, no trace of Al simple substance in these sinters revealed high reactivity between Al and cBN at high temperature and high pressure condition.

Fig. 3 shows the SEM images of fractured Al–cBN ceramic sinters with various Al additions. As it can be seen, with increasing

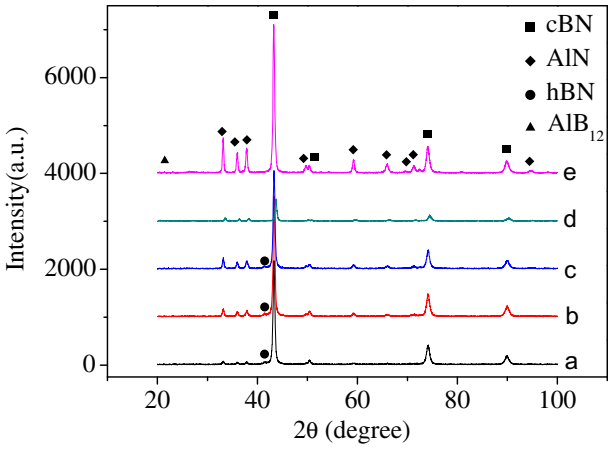

Fig. 2. XRD patterns of Al–cBN ceramic sinters with different Al addition: (a) 2 wt%, (b) 4 wt%, (c) 6 wt%, (d) 8 wt%, (e) 10 wt%.