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Fabrication and thermal conductivity of AlN/BN ceramics by spark plasma sintering

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Abstract

Aluminum nitride/boron nitride (AlN/BN) ceramics with 15–30 vol.% BN as secondary phase were fabricated by spark plasma sintering (SPS), using Yttrium oxide (Y_2O_3) as sintering aid. Effects of Y_2O_3 content and the SPS temperature on the density, phase composition, microstructure and thermal conductivity of the ceramics were investigated. The results revealed that with increasing the amount of starting Y_2O_3 in AlN/BN, Yttrium-contained compounds were significantly removed after SPS process, which caused decreasing of the residual grain boundary phase in the sintered samples. As a result, thermal conductivity of AlN/BN ceramics was remarkably improved. By addition of Y_2O_3 content from 3 wt.% to 8 wt.% into AlN/15 vol.% BN ceramics, the thermal conductivity increased from 110 W/m K to 141 W/m K.

Keywords: C. Thermal conductivity; Aluminum nitride; Boron nitride; SPS; Grain boundary phase

1. Introduction

AlN ceramics have been extensively investigated and applied to electronic devices as substrate and package materials because of its high thermal conductivity (320 W/m K for the pure single crystal, 110–270 W/m K for sintered polycrystalline), excellent electric resistivity and a thermal expansion coefficient close to that of silicon, etc. [1–3]. Based on the weak-boundary phase concept, h-BN was introduced into AlN matrix to improve the machinability [4–6]. h-BN has an anisotropic crystal structure that is similar to graphite. When thin leaf-shaped particles were randomly oriented during sintering, BN ceramics did not exhibit a high thermal conductivity, usually not up to 80 W/m K [7]. As a result, the AlN ceramics with dispersed BN second phase showed an inevitable loss in thermal conductivity. A drastic degradation of conductivity occurred when BN content increased to a high level and in some cases, the conductivity of machinable AlN/BN ceramics was unbearably low. Nowadays, it has been a challengeable subject to keep the inherent high thermal conductivity of AlN ceramics from sudden decrease and to improve its machinability as well. At present, many works have been carried out to deal with coordination between machinability and thermal conductivity [8–11].

Recently, spark plasma sintering (SPS) technique was applied to sinter AlN ceramics [12,13]. By virtue of special heat effects such as Joule heat, electromagnetic field and electrical discharge, highly densified AlN ceramics were obtained at a low temperature with short cycle SPS time as compared with the traditional sintering method. The resulting materials showed a finely homogeneous microstructure, and high thermal conductivity was achieved when added a small amount of aids [14–16]. Comparatively, the research on SPS sintering AlN-BN system is at the very beginning. Few articles can be cited so far [17]. In this paper, attentions were focused on SPS sintering behavior of AlN-BN system where different quantities Y_2O_3 were used as the sintering aid. The effects of sintering temperature and sintering aid on the phase composition, microstructure and thermal conductivity were discussed.

2. Experimental procedure

The starting powders were commercially available AlN powder (1.3 μm mean size, JC Grade, Toyo Aluminium K.K.), h-BN powder (10 μm agglomerated particle size, 99% purity,

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Matech-inno Co. Ltd.) and Y_2O_3 (99.99% purity, Sinopharm Chemical Reagent Co. Ltd.). As second phase, the BN contents were adjusted to be 15–30 vol.% (volume percent). The quantity of sintering aid Y_2O_3 was changed from 3 wt.% to 16 wt.% (mass percent), according to variation of BN content. AlN, BN and Y_2O_3 were ball milled in a plastic bottle for 12 h with absolute ethanol as dispersant using zirconia balls to ensure the homogeneity of mixed powders. As-mixed slurry was distilled off using a rotary evaporator and then dried at 80 °C for 2 h. Following this, the powder mixtures were loaded in a graphite die and then sintered in a SPS 3.20-MK-V apparatus. Before sintering, the chamber was pumped to low vacuum (<6 Pa), and a pressure of 30 MPa was applied between upper and lower punches. The sample was heated by passing alternating DC current through the die and punches from room temperature to 1600–1800 °C and held for 10 min at desired sintering temperatures. During SPS process, both heating and cooling rate were controlled to be 100–200 °C/min for all samples. The temperature of the samples during sintering was measured by means of an optical pyrometer, which was focused on to the sintered sample through a small hole in the die. For comparison, BN-free sample was also fabricated under the same SPS conditions. Bulk density was measured by the Archimedes immersion technique with deionized water, and relative density was calculated through the theoretic density of raw materials. The crystalline phases were identified by X-ray diffraction (XRD), and the microstructure was observed by scanning electron microscope (SEM). The thermal conductivity was measured by a laser-flash technique (TC-7000 Laser Flash Thermal Constant Analyzer, Japan) for the test piece, a Ø10 mm × 1.5 mm pellet.

3. Results and discussion

3.1. Densification

Fig. 1 gives the relative density as a function of sintering temperature. It was seen that with a given Y_2O_3 content of 3 wt.%, incorporation of BN rendered the densification of AlN/BN ceramics more difficult, but the density did not show obviously difference when sintering temperature got up to 1700 °C and above, which indicates that the influence on densification, caused by the poor sintering behavior of BN and the flake structure of BN component, can be neglected under the SPS conditions. On the other hand, increasing of dopant Y_2O_3 was found to be favorable for the sample densification, that is to say, given a content of BN, the sintering temperature decreased with increasing of Y_2O_3, e.g., when doped 3 wt.% Y_2O_3, the sintering temperature with density of more than 98% of theoretical density for the sample with 15 vol.% BN was 1700 °C. It allowed 1650 °C when doped 5 wt.% Y_2O_3 and 1600 °C when doped 8 wt.%, as shown in Fig. 1. It is noted that, for the samples with increasing aid, higher temperature led to a decrease of relative density. Particularly for the 8 wt.% Y_2O_3-doped sample, the relative density had a sudden drop from 99.9% to 96.2% when temperature increased from 1650 °C to 1700 °C. Providing doped relatively high amount of Y_2O_3 aid, all the sintered AlN/BN samples in present work showed a similar sintering behavior, even BN content increased to a high level of 30 vol.%. However, the loss of relative density does not mean degradation of densification level of the samples sintered at a temperature over 1700 °C. Actually, the samples were fully sintered. Fig. 2 shows a representative fracture surface of 8 wt.% Y_2O_3 doped AlN/15 vol.% BN sample sintered at 1800 °C. It was observed that the sample manifests a fine and homogeneous microstructure. No pores and abnormal grains were found in all fields of view of SEM observations although its relative density was only 96.6 %. AlN grains showed a distinct faceted features and the plate like BN grains were randomly located along the grain boundaries. It seems to be inconsistent between the results of relative density and SEM observations, and the 'inconsistency' was found in AlN/BN ceramics as a whole if doped high amount of Y_2O_3 aid.

We considered that there were significant changes of phase compositions before and after SPS, so that the values of relative density could not show the real densification level, which would

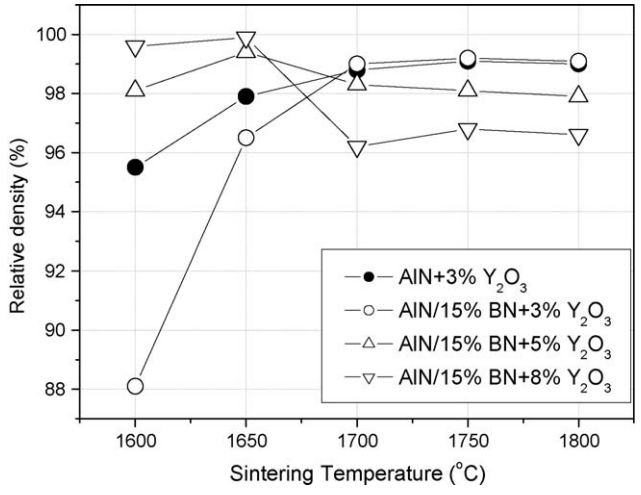

Fig. 1. The effect of SPS temperature on relative density of AlN and AlN/BN ceramics with doped various Y_2O_3.

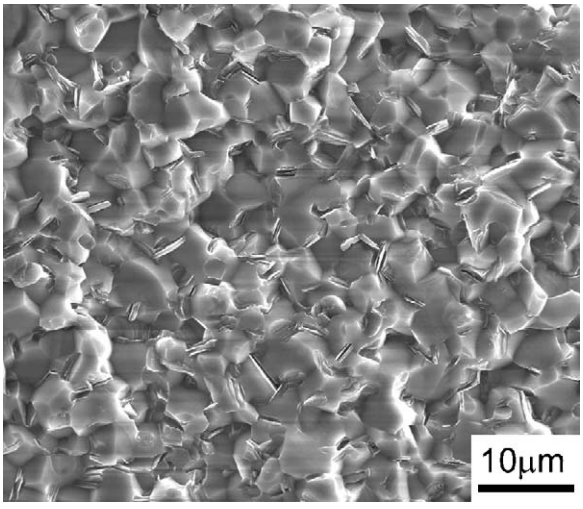

Fig. 2. SEM morphology of the fracture surface of AlN/BN ceramic.