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

Yong-Li Li *, Jian Zhang, Jiu-Xing Zhang

Key Laboratory of Advanced Functional Materials, Ministry of Education of China, School of Materials Science & Engineering, Beijing University of Technology, Chaoyang District, Beijing 100124, China

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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,

* Corresponding author. Tel.: +86 10 67396129; fax: +86 10 67392840.
E-mail address: waterle@hotmail.com (Y.-L. Li).

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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

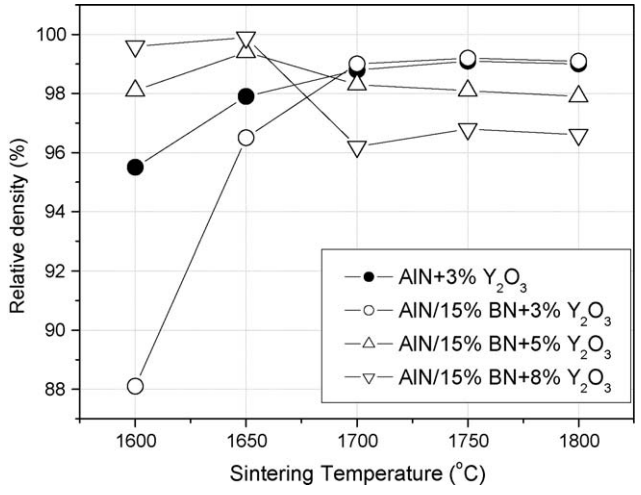

Fig. 1. The effect of SPS temperature on relative density of AlN and AlN/BN ceramics with doped various Y_2O_3.

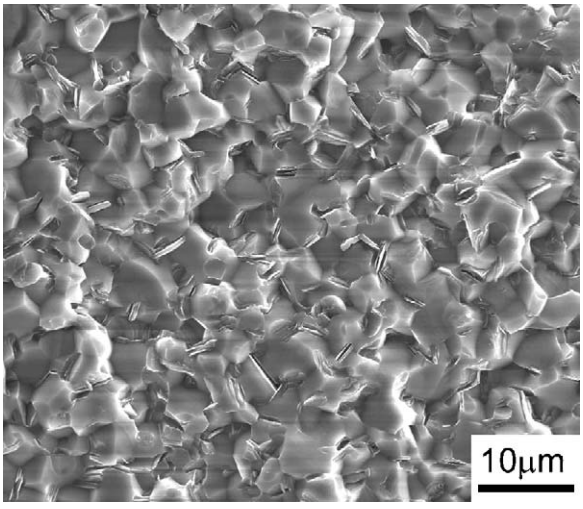

Fig. 2. SEM morphology of the fracture surface of AlN/BN ceramic.

Table 1
Yttrium-contained phases in AlN/15 vol.% BN samples sintered at 1800 °C with doped different content of Y_2O_3.

Y_2O_3 content	Yttrium-contained phases
3 wt.%	Y_2O_3, $Y_3Al_5O_{12}$, $Y_4Al_2O_9$*
5 wt.%	$Y_3Al_5O_{12}$, $Y_4Al_2O_9$
8 wt.%	$Y_4Al_2O_9$[a]

[a] Here peaks from $Y_4Al_2O_9$ were very weak.

be the explanation for above results. The detailed discussions will be presented later in this article. A good machinability will be promised if 15 vol.% BN or more is incorporated into AlN matrix [9]. Therefore, taking the ease of machining into account, the subsequent results and discussions will mainly focus on the sample with incorporation of 15 vol.% BN.

3.2. Phase composition and microstructure development

It is well known that the densification of AlN and AlN-based ceramic with additives is attributed to a liquid-phase-sintering process and is significantly influenced by the liquidus temperature, which forms, for Y_2O_3-doped AlN ceramics, one of several Yttrium aluminates grain boundary phase due to the reaction between Y_2O_3 and Al_2O_3 on the particle surface. The improvement of presence of the liquid phase was also found in present AlN-BN-Y_2O_3 system. The special sintering mechanism of SPS leads to local high temperature, which is over the Al_2O_3-Y_2O_3 eutectic point, so that the liquid can form at a sintering temperature even lower than the eutectic point. Table 1 showed dependence of Yttrium-contained phases on the amount of doped Y_2O_3 in samples sintered at 1800 °C. It was found, increase of doped Y_2O_3 content helped to increase the Y/Al ratio of the grain boundary phases in the order $Y_3Al_5O_{12}$ (YAG) → $Y_4Al_2O_9$ (YAM). When doped 3 wt.% Y_2O_3 into AlN/BN, YAG was identified to be main grain boundary phase. Y_2O_3 and YAM could also be identified. When 8 wt.% Y_2O_3 was doped, only YAM was remained. Based on the results of Yttrium-contained phases in the sample after SPS, the chemical composition of yttrium aluminates transformed according to the following equation:

$$7Y_2O_3 + 2Y_3Al_5O_{12} \rightarrow 5Y_4Al_2O_9 \quad (1)$$

One notable feature is, XRD patterns showed that peaks arising from YAM became very weak when the amount of doped Y_2O_3 increased up to 8 wt.%, suggesting the residual grain boundary phase was probably too minute. The corresponding microstructures of sintered samples are shown as in Fig. 3. The distribution of phases can be easily distinguished in the backscattered electron contrast. When 3 wt.% Y_2O_3 was used, Yttrium-contained grain boundary phase, as seen the bright contrast, was spot distribution dominantly at the triple junctions. With increasing of Y_2O_3, the isolated liquid attempted to transfer to the edge of the grains and link together. For 5 wt.% Y_2O_3-doped sample, the residual

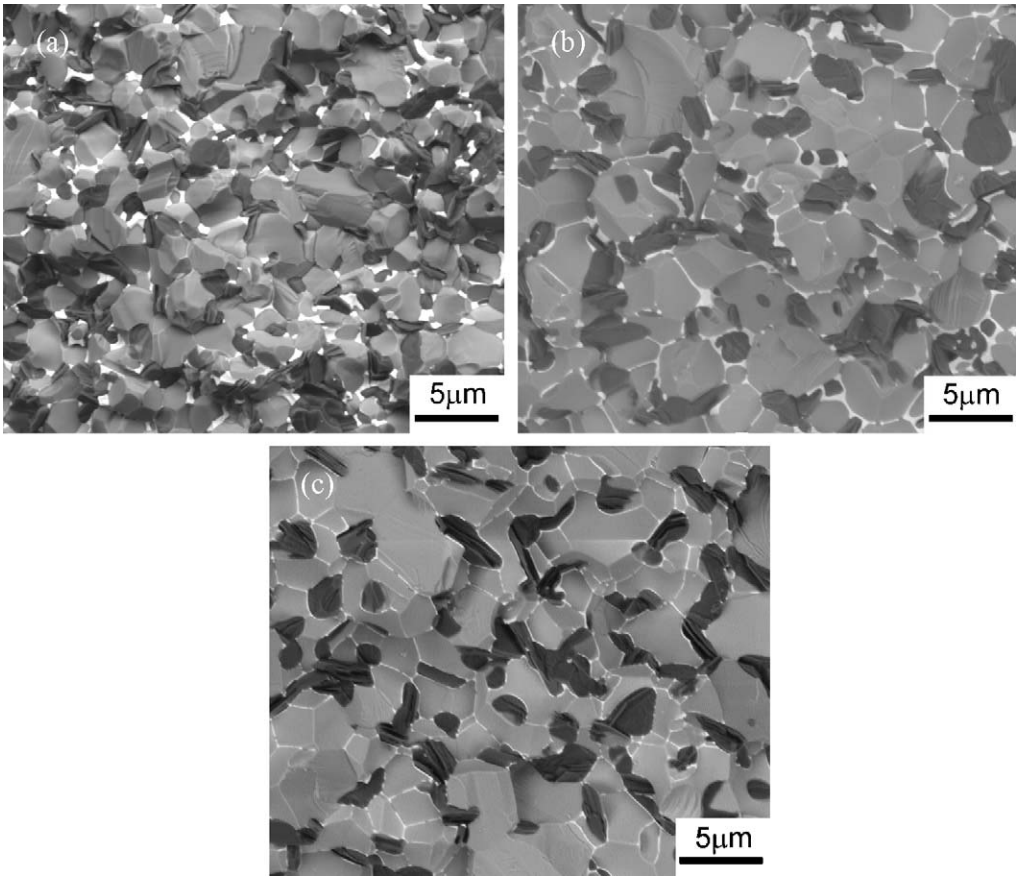

Fig. 3. Back-scattered SEM images of AlN/BN ceramics sintered at 1800 °C with doped Y_2O_3 of (a) 3 wt.%, (b) 5 wt.% and (c) 8 wt.%.

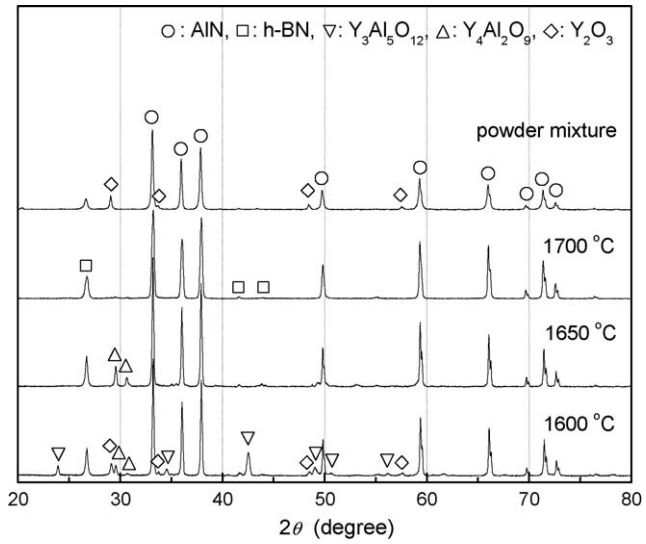

Fig. 4. . XRD patterns of AlN/BN ceramics sintered at different temperature.

liquid seemed not more that that of 3 wt.% doped one, and comparatively, when 8 wt.% Y_2O_3 was used, it was found that contiguous liquid had formed along the AlN grain boundaries after SPS although a little liquid was maintained.

Fig. 4 shows the effect of sintering temperature on phase compositions. When sintered at 1600 °C, grain boundary phases mainly consisted of Y_2O_3 and YAG, indicating Y_2O_3 was not consumed at this temperature. Peaks of YAM with weak intensity could also be seen in the pattern. Higher temperature at 1650 °C led to disappearance of the peaks arising from Y_2O_3. The grain boundary phase was identified to be merely YAM and no observable peaks of YAG were identified. This suggests an increase in Y/Al ratio of yttrium aluminates with increasing sintering temperature. It is worth noting that the amount of the residual Yttrium-contained phase was drastically reduced when the sintered temperature rose up to 1700 °C and higher because peaks of YAM were very weak in XRD pattern. Coupled with the significant drop of relative density, we believe that most of the boundary phases were eliminated at high temperature after SPS process.

Fig. 5 shows the effect of sintering temperature on microstructure of the sintered AlN/BN ceramics related to Fig. 4. When the sample was sintered at low temperature of 1600 °C, the grain boundary phase was located on both AlN-AlN and AlN-BN boundaries. As a result of doped Y_2O_3 as high as 8 wt.%, the grain boundary phase occupied the most intervals of grain boundaries. SEM morphology also implied that the liquid had appeared at 1600 °C. With temperature increased up to 1650 °C, the compositions of grain boundary phase were much different from the former, but their microstructures were similar. However, when higher temperature of 1700 °C was employed, the microstructure showed a great change. In particular, the amount of residual grain boundary phase remarkably decreased and the distribution of them was much

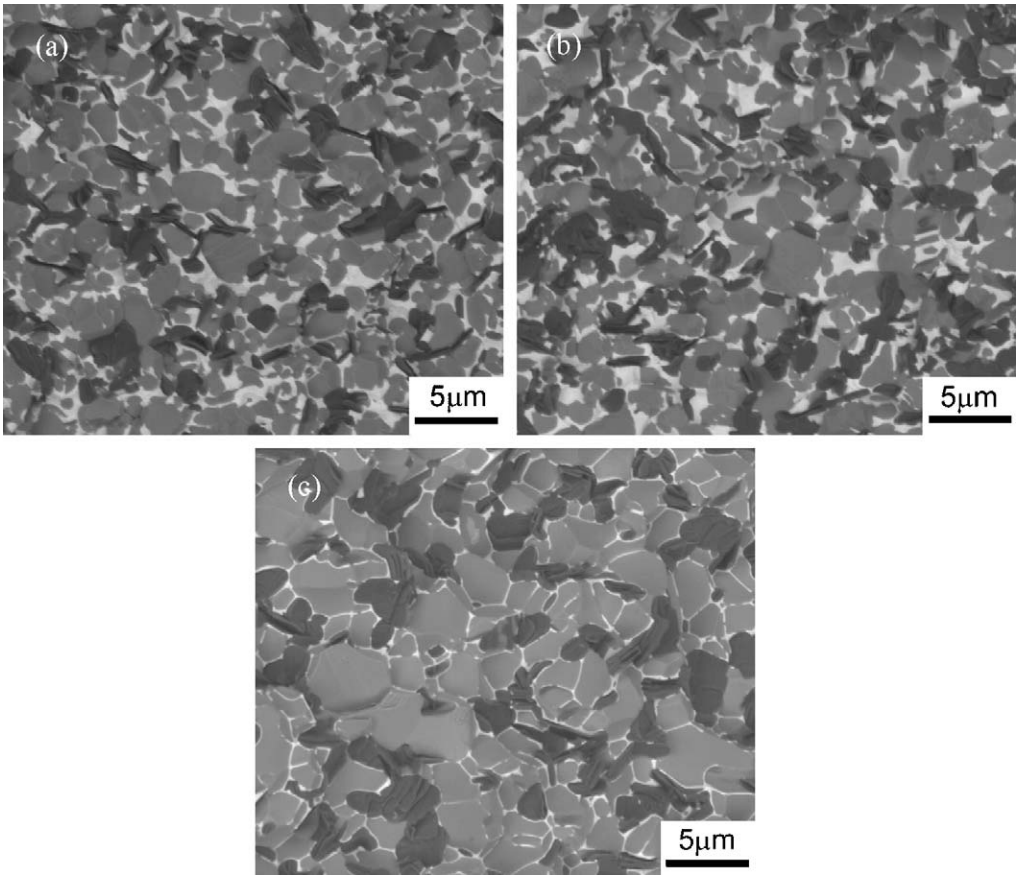

Fig. 5. Back-scattered SEM images of 8 wt.% Y_2O_3-doped AlN/BN ceramics sintered at (a) 1600 °C, (b) 1650 °C and (b) 1700 °C.

more homogeneous than that sintered at lower temperature. These observations agreed with the XRD analysis result that the massive elimination of grain boundary phase happened in SPS process.

It is well known that a discharge occurs in non-conductive powders during SPS process due to the electrical breakdown with the application of alternating DC current, and a plasma is generated between the particles, although it has not been identified directly. For Y_2O_3-doped AlN/BN, the results of our present research may be attributed to a mechanism as follow: during SPS process, the existence of high temperature plasma that generated by alternating DC current may induce a very high local temperature at particle intervals, which is much higher than the liquidus temperature of the Al_2O_3-Y_2O_3 system. Massive liquid forms on the AlN and BN particles, exerting large capillary forces to pull the particles together. By doped high amount of Y_2O_3 aid, hereby fully dense AlN/BN ceramics can be obtained at a relatively low sintering temperature (around 1600 °C). When increased sintering temperature up to 1700 °C, viscosity of liquid phase is depressed, which make it easier to flow and to distribute homogeneously at the grain boundaries. The liquids that have been originally separated each other link together and then form contiguous phase along the grain boundaries. Since SPS is carried out under reduction vacuum atmosphere, the chamber pressure is lower than 6 Pa, by which the liquid phase migrates to the sample surface through their contiguously liquid micro-channels, and then is removed through evaporation. According to this mechanism, a relatively high amount of doped Y_2O_3 aid and an appropriate SPS temperature should be required. It was generally considered, excessively doped aids are unfavorable for the thermal conductivity, because grain boundary phases attempt to baffle the heat flow if they are highly kept in the sintered ceramics. Thus, the amount of aids for AlN was always meticulously manipulated. In most cases, sintering aids were not more than 5 wt.% in order to control the block against the connection of AlN grains. On the other hand, enhanced thermal conductivity can be achieved if grain boundary phases are eliminated after sintering. However, a rigorous condition had to be employed by traditional sintering method, typically at an ultra high temperature of 1900 °C for 100 h [18]. In our present research, a novel conclusion is achieved. That is, within the experimental amount variation, the more aid is used, the easier the grain boundary phase is removed under the SPS conditions. Since significant amount of grain boundary phase could be eliminated only at 1700 °C within 10 min, thermal conductivity of the materials will be improved. Further increasing of doped Y_2O_3 did not work better in elimination of grain boundary phase and the thermal conductivity kept unchanged.

3.3. Thermal conductivity

The thermal conductivity of AlN/BN ceramics is plotted in Fig. 6, in which curve A illustrates the conductivity value of sintered samples that was added an appropriate Y_2O_3 according to curve C prescribed, and curve B shows the results of reference frame with adding 3 wt.% Y_2O_3 for all samples. The

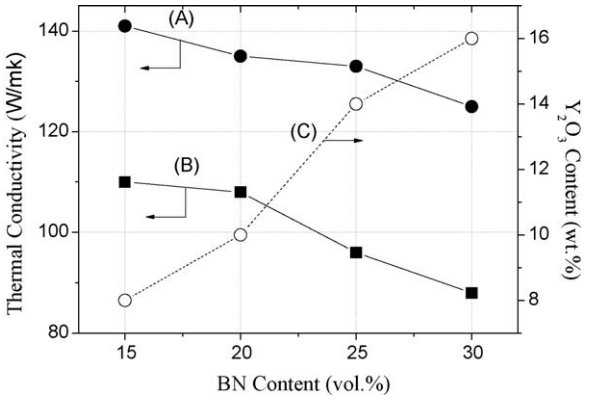

Fig. 6. Effect of BN and Y_2O_3 on the thermal conductivity of AlN/BN ceramics sintered at 1800 °C.

thermal conductivity of sintered samples maintained a relatively high value although decreased due to the incorporation of low conductive h-BN phase. With comparison to the counterparts with a given amount of Y_2O_3, optimized amount of doped-Y_2O_3 led to a significant enhancement in their thermal conductivity, especially for the samples containing 15 vol.% BN and more. When incorporated second phase BN, the optimal amount of doped-Y_2O_3 aid also increased along with the BN content, e.g., 8 wt.% Y_2O_3 matched the incorporated 15 vol.% BN sample, and the resulting thermal conductivity was 141 W/m K, which is only slightly lower than that of Y_2O_3-doped AlN ceramics (148 W/m K). The AlN/30 vol.% BN sample required doping an amazing Y_2O_3 content as high as 16 wt.%, by which thermal conductivity value still reached 125 W/m K.

4. Conclusion

Taking advantages of SPS technique, fully dense AlN/BN ceramics were fabricated at a low sintering temperature in short cycle time. The following results were obtained:

Densification of the samples was observably promoted by appropriately increasing amount of doped Y_2O_3, and the relative density showed a sudden drop when SPS temperature rose up to 1700 °C in high amount of Y_2O_3-doped samples, while the densification level were not degraded.

At a certain range of sintering temperature (1700–1800 °C), the residual grain boundary phase decreased as the amount of doped Y_2O_3 increase, and the phase compositions and the microstructures had a dramatic change.

As a result of increasing Y_2O_3 (dependent on the content of incorporated BN), AlN/BN ceramics showed a significant enhancement in thermal conductivity when sintered at 1700–1800 °C compared with their counterparts with a given Y_2O_3 content of 3 wt.%, which made thermal conductivity is insensitive to increasing content of low conductive BN.

Elimination of Yttrium-contained boundary phase by evaporation during SPS was considered to account for the

sintering behavior and high thermal conductivity achieved in these samples.

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