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Thermal conductivity of hot-pressed hexagonal boron nitride

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ABSTRACT

The thermal conductivity parallel and perpendicular to the hot-pressing direction of hot-pressed *h*-BN was measured to investigate the effects of oxide additive species and compositions on the thermal conductivity. CaO, MgO, Y_2O_3, Yb_2O_3, and their mixtures were selected as oxide additives owing to their previously demonstrated ability to enhance the thermal conductivities of non-oxide materials such as AlN and Si_3N_4. The investigated additive concentrations were calculated to be 5, 10, and 15 vol%. A thermal conductivity of approximately 210 W/m·K was attained by hot-pressing mixed powders of *h*-BN and a Yb_2O_3–MgO or Yb_2O_3–CaO additive at a concentration of 15 vol%.

Hexagonal boron nitride (*h*-BN) ceramics have been widely applied in the field of high-temperature structural materials because of their excellent corrosion resistance to molten metal, high refractoriness, good thermal shock resistance, and good machinability [1–3]. Recently, *h*-BN has attracted the attention of researchers in polymer science as a high-thermal-conductivity filler in electrical insulation because of its intrinsically high thermal conductivity, which is a consequence of its strong covalent bonds between light elements B and N [4–6]. However, unlike highly thermally conductive non-oxide ceramics such as AlN and Si_3N_4 bulk materials, whose thermal conductivity can be measured using a laser flash method, a sintered *h*-BN ceramic material with a thermal conductivity greater than 100 W/m·K has not been reported [1,7,8]. Thermal conductivity measurements of high-purity single crystals and theoretical calculations have revealed that the intrinsic thermal conductivity of AlN at room temperature is 320 W/m·K [9]. Watari et al. have achieved a high thermal conductivity of 272 W/m·K by sintering at 1900 °C for 100 h under a reduced N_2 atmosphere with carbon to decrease crystal defects and grain boundaries [10]. Haggerty and Lightfoot have predicted that the intrinsic thermal conductivity of Si_3N_4 might be 200 to 320 W/m·K at room temperature [11]. Zhou et al. fabricated Si_3N_4 having a high thermal conductivity of 177 W/m·K by sintering high-purity Si powder with Y_2O_3 and MgO under an N_2 atmosphere [12].

The crystal structure of *h*-BN is analogous to that of graphite, comprising layers of six-membered rings of alternating, covalently bonded B and N atoms in the *c*-plane direction, where the layers are stacked and weakly bound in the *c*-axis direction by van der Waals forces (Fig. 1(c)). The anisotropic crystal structure of *h*-BN leads to faster crystal growth in the *c*-plane direction and to the formation of platelet particles that exhibit anisotropic properties. The thermal conductivity in the planar direction (*a*-axis) of *h*-BN platelets is potentially higher (400 W/m·K) [13,14] than that in the thickness direction; the thermal conductivity in the thickness direction is only approximately 2 W/m·K [15]. Considering the higher in-plane thermal conductivity of 400 W/m·K, one would expect *h*-BN bulk ceramics with a thermal conductivity greater than 200 W/m·K to be prepared by sintering and orienting platelet *h*-BN powders. However, the thermal conductivity of such *h*-BN sintered bodies has been reported to be only 100 W/m·K [1,7].

In this study, platelet *h*-BN powder having a relatively large particle diameter was readily oriented via a hot-pressing method. Additionally, rare-earth oxides and alkaline-earth oxides such as Y_2O_3, Yb_2O_3, CaO, and MgO were used as sintering additives to increase the thermal conductivity by purifying the nitride grains through a solution reprecipitation reaction during liquid-phase sintering [16–18]. We investigated various species and compositions of sintering additives to improve the thermal conductivity of *h*-BN bulk ceramics.

Mixtures of Y_2O_3 or Yb_2O_3 and CaO or MgO were selected as composite additives because rare-earth oxide–alkaline-earth oxide composite additives are better promoters of non-oxide ceramic densification than single-component additives. The additive fraction was adjusted to 5, 10, or 15 vol%, with the molar ratio between rare-earth oxides and alkaline-earth oxides set to 100/0, 50/50, or 0/100. CaO as a sintering additive was added as $CaCO_3$ (reagent grade, Wako Pure Chemical Industries, Tokyo, Japan), which decomposed to produce CaO during sintering. Commercially available BN powder with an average grain size of 18 μm (SGP-Grade, DENKA Corp., Tokyo, Japan), Y_2O_3 powder (YT3CP, Nippon Yttrium Co., Ltd., Tokyo, Japan), Yb_2O_3 powder (YB3CP, Nippon Yttrium Co., Ltd., Tokyo, Japan), MgO powder (2000A,

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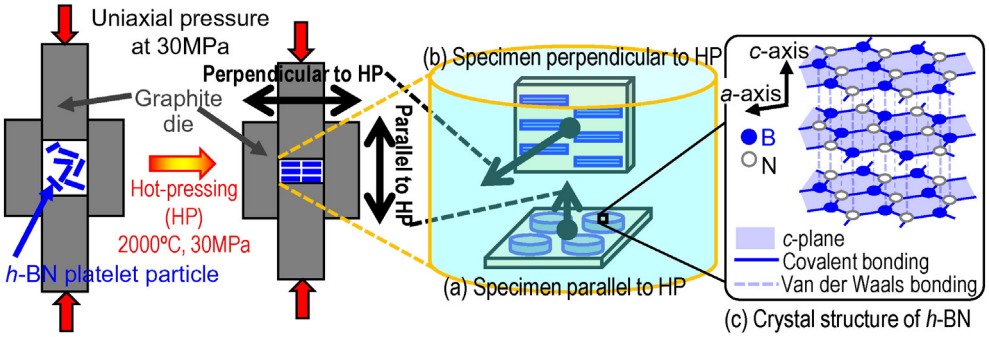

Fig. 1. Schematic of the anisotropy of preferred orientation and crystallographic anisotropy of the hot-pressed *h*-BN ceramics.

Ube Industries, Ltd., Yamaguchi, Japan), and $CaCO_3$ were mixed using the conventional wet ball-milling method with Si_3N_4 balls and ethanol for 20 h in a polyethylene bottle to obtain homogeneously mixed powders. After drying, the mixed powders were placed in a graphite die coated with BN slurry to avoid a reaction between the powder and die. *h*-BN bulk ceramics disks having a diameter of 30 mm and thickness of 11 mm were hot-pressed at 2000 °C for 1 h under an N_2 atmosphere and 30 MPa of applied pressure.

Two types of specimens—one perpendicular and one parallel to the hot-pressing direction—were prepared for each hot-pressed sample to investigate the anisotropy of their microstructure and thermal conductivity, as shown in Fig. 1(a) and (b). The crystalline phases of the sintered samples were determined by X-ray diffraction (XRD) using Cu Kα radiation (XRD-6100, Shimadzu Co., Ltd., Kyoto, Japan). To evaluate the orientation of the (00*l*) plane of the specimen parallel to the hot-pressing direction (Fig. 1(a)) in the hot-pressed *h*-BN, the orientation factor, which provides a quantitative estimate of the degree of orientation for the *c*-axis on the basis of the XRD pattern diffraction intensity, was calculated using the Lotgering method [19,20]. The microstructure was observed using scanning electron microscopy (SEM, model S-5000, Hitachi, Tokyo, Japan). Microchemical analysis of the grain-boundary phase was performed via SEM in conjunction with energy-dispersive X-ray analysis. Thermal diffusivity was measured using a laser-flash thermal constant analyzer (LFA447 NanoFlash, Netzsch, Selb, Germany) at room temperature. The samples used for the measurements were 10 mm × 10 mm × 2 mm machined plates. The specific heat was measured using differential scanning calorimetry (DSC200F3, NETZSCH, Selb, Germany). The thermal conductivity value was calculated from thermal diffusivity, specific heat, and density.

Fig. 2 shows XRD patterns of the hot-pressed BN samples with the Yb_2O_3–MgO composite additive of 15 vol%. *h*-BN and Yb_2O_3 were the main identified crystalline phases. The microchemical analysis of grain-boundary phases indicated the presence of Yb, O, and Mg (see Fig. S1 in the supplementary material), which, given the XRD results, indicates that some MgO formed conveys a solid solution with the Yb_2O_3 crystalline phase. The XRD pattern of the specimen perpendicular to the hot-pressing direction showed an intense (00*l*) refraction of *h*-BN, whereas that of the section parallel to the hot-pressing direction showed intense (100) and (110) refractions rather than a (00*l*) refraction. These XRD profiles strongly suggest that planar *h*-BN grains were preferentially oriented perpendicular to the hot-press direction during hot-pressing.

Fig. 3(a), (b), (d), and (e) exhibits SEM micrographs of the fractured surface parallel and perpendicular to the hot-pressing direction. BN platelet particles were oriented perpendicular to the hot-pressing direction, and the Yb_2O_3–MgO additive enhanced the grain growth of *h*-BN compared to the single-component MgO additive. The orientation factor as the degree of preferred orientation for the *c*-axis in the specimen perpendicular to the hot-pressing direction was estimated as functions of the additive species and content by the Lotgering method. The orientation factors of the hot-pressed *h*-BN with 5, 10, and 15 vol% of the single-component Y_2O_3 additive were 98%, 97%, and 97%, respectively. Furthermore, all hot-pressed samples with additives other than single-component Y_2O_3 exhibited high orientation factors of approximately 100%. These estimated orientation factors imply that most *h*-BN plate particles lie perpendicular to the hot-pressing direction. The 18-μm grain size of *h*-BN used as a starting material in this study is much larger than that used in a previous study [7]. Larger platelet particles are expected to more easily orient than smaller ones during hot-pressing [21]. Additionally, the flexible, graphite-like sheets of six-membered rings of B and N are speculated to deform under a simple applied pressure during hot-pressing. The highly preferred orientation of *h*-BN induced by hot-pressing is attributed to a larger grain size of starting platelet particles and to flexibility in the *c*-plane direction of *h*-BN.

Fig. 4 shows the relations between thermal conductivity, additive species, and additive contents. The thermal conductivity of *h*-BN parallel to the hot-pressing direction ranged from only 10 to 14 W/m·K, irrespective of additive species and contents; this thermal conductivity is low compared to those of Si_3N_4 and AlN [10,12]. Generally, the planar surfaces of platelet particles easily orient perpendicular to the hot-pressing direction. These low thermal conductivity values result from

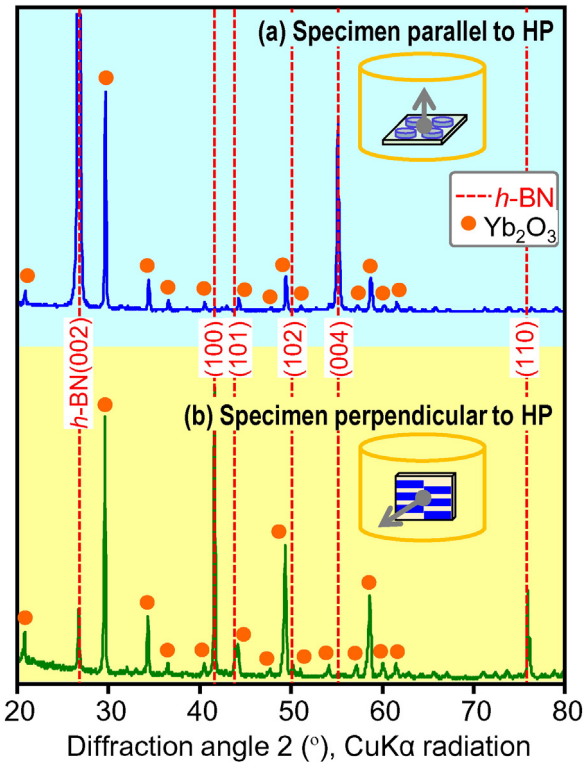

Fig. 2. XRD patterns of specimens (a) parallel and (b) perpendicular to the hot-pressing direction in hot-pressed BN samples with Yb_2O_3–MgO composite additive.