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High pressure consolidation of B_6O-diamond mixtures

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Sintered composites in the B_6O-$x$diamond ($x = 0$–80 vol%) system were prepared under high pressure and high temperature conditions (3–5 GPa, 1400–1800°C) from the mixture of in-laboratory synthesized B_6O powder and commercially available diamond powder with various grain sizes (<0.25, 0.5–3, and 5–10 μm). Relationship among the formed phases, microstructures, and mechanical properties of the sintered composites was investigated as a function of sintering conditions, added diamond content, and grain size of diamond. Sintered composites were obtained as the B_6O-diamond mixed phases when using diamond with grain sizes greater than 0.5 μm, while the partial formation of the diamond-like carbon was observed when using diamond grain sizes less than 0.25 μm. Microhardness of the sintered composite was found to increase with treatment temperature and pressure, and the fracture toughness slightly decreased. A maximum microhardness of $H_v \sim 57$ GPa was measured in the B_6O-60 vol% diamond (grain size $<$ 0.25 μm) sintered composite under the sintering conditions of 5 GPa, 1700°C and 20 min.

1. Introduction

Hexaboron monoxide (B_6O) is well known as one of the boron suboxides [1, 2], which possess high hardness comparable with boron carbide (B_4C) and ranked next to cubic boron nitride (cBN). B_6O has a structure related to α-rhombohedral boron [3–8], where strong covalent bonding within and between icosahedral clusters at the corners of unit cell contributes to such high hardness. Recent studies by Hubert *et al.* [9, 10] stimulated interest in relation to the fine structure and morphology of B_6O crystallites synthesized under high pressure. However, B_6O is a typical unsinterable material under normal pressure condition. No appropriate sintering agent has been found because B_6O is easily oxidized to form B_2O_3 with the mechanical strength of the resultant sintered compact degraded. Fully densified compact of B_6O is rather difficult even by high pressure sintering techniques such as hot-pressing or hot isostatic pressing [11]. A wide range of microhardness $H_v = 34$–38 GPa is reported [3, 12–14] and even less information is available on chemical or mechanical properties of B_6O sintered compact. We reported that a single phase of B_6O sintered compact was prepared by high pressure (3–5 GPa) sintering of B_6O powder, which was synthesized by a high temperature (1300–1500°C) reaction of amorphous boron with B_2O_3 in an inert atmosphere [15–17]. This consolidation process of B_6O has the advantage that dense and homogeneous sintered compact can be formed by using fine-grained sinterable B_6O powder. Vickers microhardness of the single phase B_6O sintered compact was 32–34 GPa and a sluggish oxidation behavior was observed in air up to 1000°C.

The present authors have reported previously on the sintering behavior and mechanical properties in the quasi-binary B_6O-B_4C [18] and B_6O-cBN [19] systems to obtain new super-hard materials. These systems gave well-dispersed sintered composites of almost full density under high pressure and temperature conditions. The sintered composites prepared showed the maximum microhardness of $H_v \sim 50$ GPa for both quasi-binary systems. Moreover, a comparably high fracture toughness was attained in terms of the contribution of B_6O-B_4C/cBN grain boundary to densification and microstructural control. In the present paper, the mixtures of B_6O and diamond powder, as a new quasi-binary system, were treated under high pressure and temperature conditions, and the microstructure and mechanical properties of sintered composites were examined as a function of treatment parameters.

2. Experimental procedures

2.1. Preparation of B_6O powder

B_6O powder was synthesized by a solid-liquid reaction [11, 15–17] between amorphous boron and amorphous boron sesquioxide (B_2O_3). Commercially available powders of amorphous boron (Rare Metallic Co., grain

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size: 0.5–3 μm, purity > 96.9 wt%) and amorphous B_2O_3 (Kojundo Chemical Lab. Co., purity > 99.9 wt%) were mixed for 30 min in an agate mortar with a mole ratio of B : $B_2O_3 = 16 : 1.03$ using ethanol as solvent. The slightly excess amount of B_2O_3 for stoichiometric mixing mole ratio of 16 : 1 was added to compensate the evaporated B_2O_3 during the heat treatment process. The mixed powder was charged in an alumina boat and heat-treated in an argon stream (100 mL/min) at 1350°C for 4 h to form B_6O powder.

2.2. High-pressure treatment of B_6O-diamond powder

The synthesized powder was mixed in ultrasonically agitated acetone at room temperature with commercially available diamond powder (0–80 vol%) with different particle sizes of <0.25, 0.5–3.0, or 5–10 μm. Then the mixed powder was treated in vacuum 1×10^{-5} Pa at 600°C for 60 min to eliminate the adsorbed moisture and oxygen gas. Subsequently, the degassed powder was charged quickly into hBN capsule of the specimen cell, and high pressure and high temperature treatment was carried out using the girdle-type high-pressure apparatus [20, 21]. The cell assembly for high pressure sintering is shown in Fig. 1. The specimen was treated under the conditions of 3–5 GPa and 1400–1800°C for 20 min. The calibration method for pressure and temperature is the same as that described in the previous literature [22].

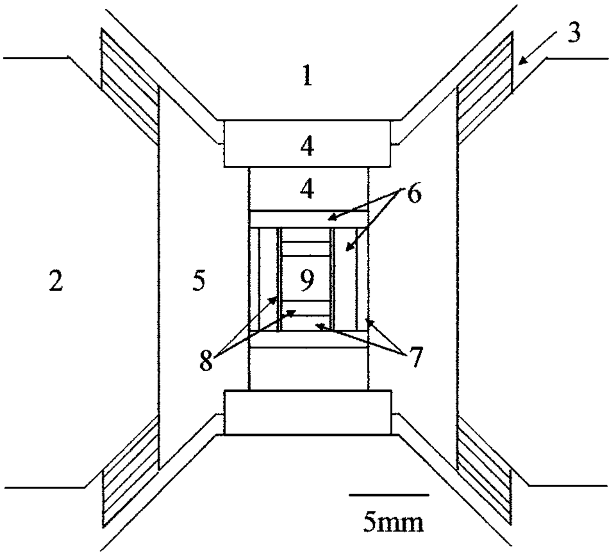


Figure 1 Cell assembly for high pressure sintering of B_6O-Diamond composites. 1: anvil, 2: cylinder, 3: composite gasket, 4: WC-Co disk, 5: pyrophyllite, 6: graphite heater, 7: fired pyrohyllite, 8: hBN sleeve, and 9: sample space.

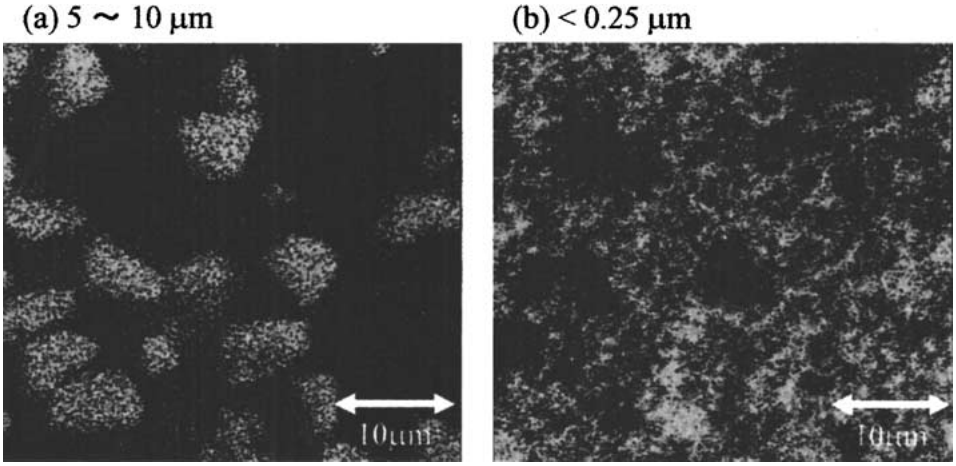
2.3. Characterization of sintered composites and evaluation of mechanical properties

The specimens before and after the high-pressure treatments were identified and characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy-dispersed X-ray spectroscopy (EDS), and Raman spectroscopy. The Vickers microhardness (H_v) and the fracture toughness (K_{Ic}) were measured using indentation techniques under the load of 1.96 N (200 gf). Niihara's equation was applied to measure the fracture toughness. The average of five measured hardness or toughness values was plotted in each figure, excluding the maximum and minimum data in seven trials.

3. Results and discussion

3.1. Sintering behavior of B_6O-diamond composites

Fig. 2 shows the carbon image of B_6O-40vol% diamond sintered composites given by EDS measurement. Gray parts in figures, which correspond to the existence of carbon, were almost well dispersed in the sintered composites regardless of the grain size of diamond. In the case of using large grain size of diamond (Fig. 2a), diamond particles can be seen to scatter over the B_6O matrix, because the grain sizes of diamond particles are much larger than those of B_6O particles. In contrast, diamond particles would behave as matrix material for dispersing B_6O particles, when the diamond grain size is small (Fig. 2b). This is because the grain sizes of diamond particles are smaller than those of B_6O particles and B_6O agglutinates among diamond particles.


(a) 5 ~ 10 μm

(b) < 0.25 μm

Figure 2 EDS image for carbon of B_6O-40 vol% diamond composites sintered at 5 GPa, 1700°C, and 20 min. Grain size of added diamond particles is (a) 5–10 μm and (b) below 0.25 μm.

Fig. 3 shows the XRD patterns of (a) diamond powder, (f) B_6O powder, and (b)–(e) the prepared sintered composites. Intensity of typical diffraction peak of diamond increased with an increase in diamond content. Then, the feature of diffraction patterns was independent on the grain size of starting powder of diamond. Moreover, the diffraction patterns originated from B_6O species did not change basically by the addition of diamond particles. These results indicated that the present composites are mixtures of B_6O and diamond, containing no B-O-C compounds, which were supposed to be synthesized by chemical reaction under high pressure and temperature conditions. However, some weak unknown diffraction peaks were observed around $2\theta = 26°$ (cf. Fig 3b), when the grain size of source diamond was less than 0.25 μm and the diamond content was more than 40 vol% (cf. inset of Fig. 3). It would be difficult to identify the chemical species of these diffraction peaks from XRD pattern because of its weak intensity.

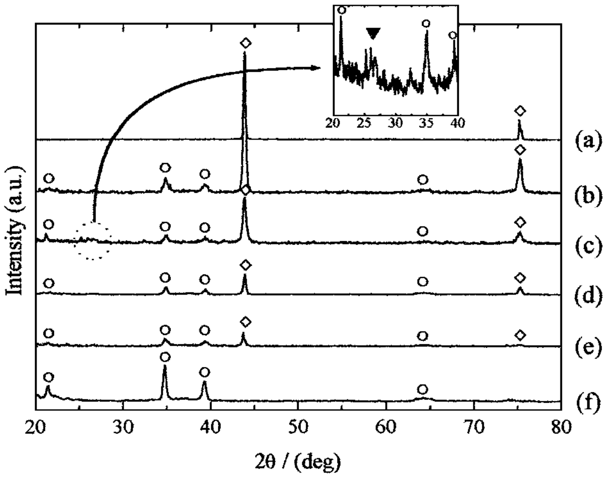


Figure 3 XRD patterns of the B_6O-$x$diamond specimens for $x = 100$ vol% (a), 60 vol% (b: 5–10 μm and c: <0.25 μm), 20 vol% (d: 5–10 μm and e: <0.25 μm), and 0 vol%(f). Sintering conditions: 5 GPa, 1700°C, and 20 min. ○: B_6O, ◇: diamond and ▼: unknown. Inset shows the data (c) magnified from 20° to 40°.

Raman spectra were measured for clarifying the origin of some weak diffraction peaks observed in the XRD pattern. Raman spectra of B_6O-40vol% diamond composite, in which the grain sizes of diamond are both (a) 5–10 and (b) <0.25 μm, are shown in Fig. 4. In the case of the grain size as large as 5–10 μm, a sharp raman peak was observed at ca. 1330 cm^{-1} (cf. Fig. 4a). This peak, which is observed in all cases for using large grain sizes more than 0.5 μm, is well known as a typical diamond peak. These results indicate that diamond structure would be maintained even under high pressure and temperature conditions in the B_6O-diamond composites that were obtained from the coarse diamond grains. On the other hand, Raman spectrum of the B_6O-40vol% diamond composite obtained by using small grain size diamond showed two broad peaks (cf. Fig. 4b), which could be identified as G- and D-bands of so-called diamond-like carbon. This result obtained by using fine-grade diamond grains, indicates that a part of diamond structure in the composite is transformed into a new phase during high pressure and temperature treatment. Since smaller grain size diamond has higher activity and surface energy, the structure of diamond located at grain boundary between diamond and B_6O particles could transform into the diamond-like carbon species. Therefore, the weak unknown peak observed in the XRD pattern could be ascribed to the product of the diamond-like carbon in sintered composite.

3.2. Mechanical properties of B_6O-diamond sintered composites

Fig. 5 shows the temperature dependence of Vickers microhardness H_v, which was measured at 200 gf for 20 s with regard to the B_6O-diamond composites prepared at 3 (▲) and 5 (●) GPa. In all the cases of grain sizes and diamond contents, the value of H_v increased with an increase in sintering temperature and pressure. In our previous work, there was little effect of the sintering pressure on the microhardness of single-phase sintered B_6O. In the present study, however, the large increment

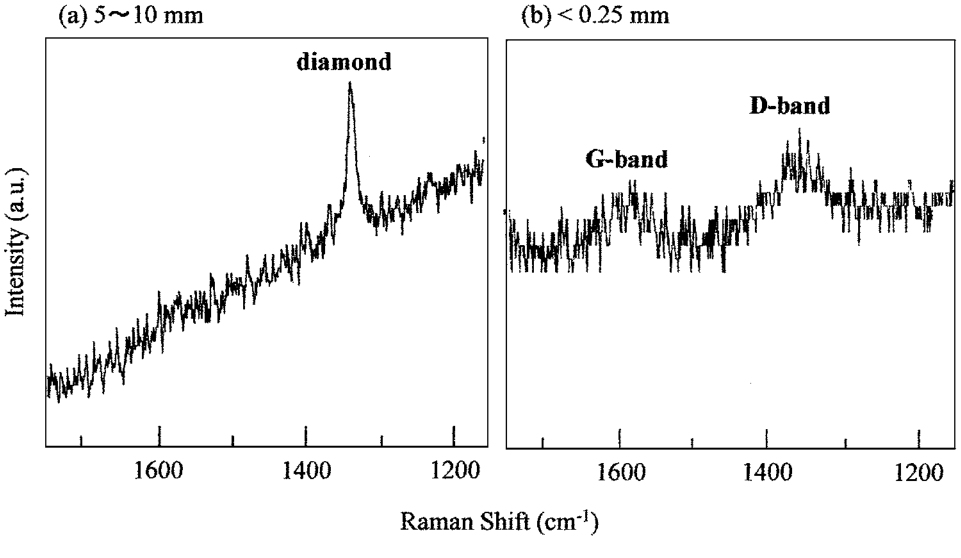


Figure 4 Raman spectra of the B_6O-40 vol% diamond composites sintered at 5 GPa, 1700°C, and 20 min. Grain size of added diamond particles is (a) 5–10 μm and (b) below 0.25 μm.

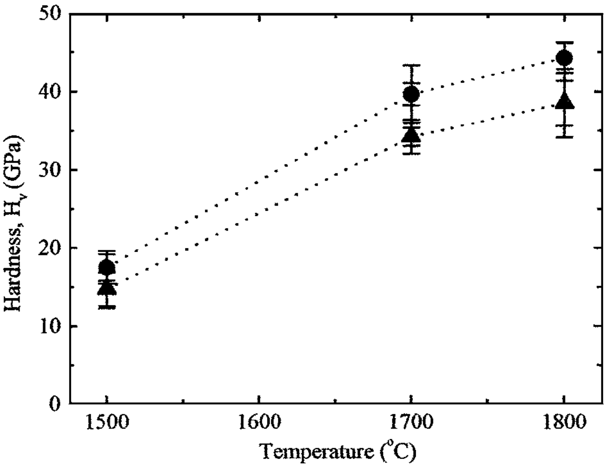


Figure 5 Vickers microhardness of the B_6O-30 vol% diamond sintered composites as a function of sintering temperature. Pressure: 3 (▲) and 5 (●) GPa, holding time: 20 min.

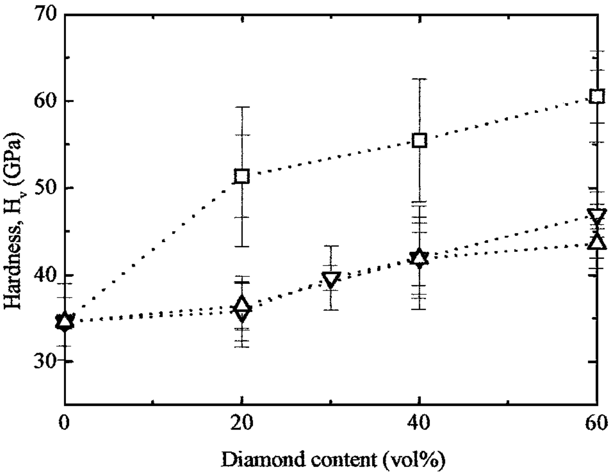


Figure 6 Vickers microhardness of the B_6O-diamond sintered composites as a function of diamond content. Grain size of added diamond particles is 5–10 (▽), 0.5–3 (△), and <0.25 (□) μm. Sintering conditions: 5 GPa, 1700°C, and 20 min.

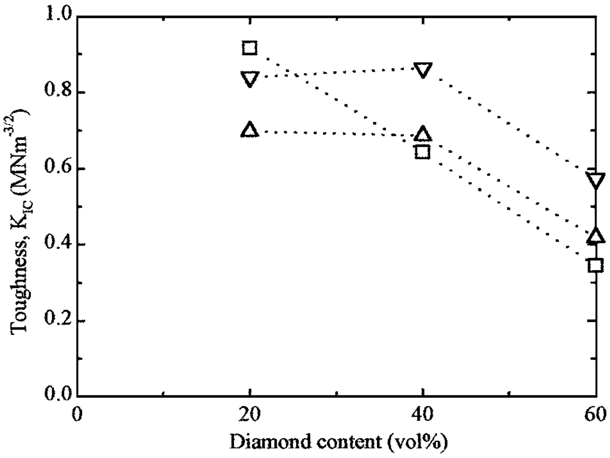


Figure 7 Fracture toughness of the B_6O-diamond sintered composites as a function of diamond content. Grain size of added diamond particles is 5–10 (▽), 0.5–3 (△), and <0.25 (□) μm. Sintering conditions: 5 GPa, 1700°C, and 20 min.

of H_v as ca. 20% was observed from 3 to 5 GPa. The present increment of H_v could be caused by attaining the strong bonding between different phases, i.e., B_6O and diamond under higher pressure and temperature conditions.

The values of H_v are plotted in Fig. 6 against the diamond content in the prepared sintered composite. When the grain size of the added diamond particles was more than 0.5 μm (shown by △ and ▽ in the figure), H_v values increased with an increase in diamond content, and almost saturated at the hardness of ca. 45 GPa over ca. 40 vol% content. This tendency would arise from the underestimation of the mean H_v of the composite due to the measurement of the microhardness of B_6O matrix part in most cases, especially at higher diamond contents, because the grain sizes of diamond particles used are larger than those of B_6O particles. In the case of using the small grain sized diamond shown by □ in the figure, the H_v value monotonically almost increased with increasing diamond content, and the value of H_v reached ca. 60 GPa at 60 vol% diamond content. This monotonic increment of H_v verifies the high sinterability of the composite in using diamond with the grain size below 0.25 μm, which would be caused by large relative surface area and interfacial energy due to the small grain size of diamond particles. However, these H_v values cannot be directly compared with those H_v in the case of using the grain size above 0.5 μm, because the microhardness in using coarse diamond grains could be inadequatly measured, especially at higher diamond contents.

Fig. 7 shows the effect of diamond content on fracture toughness under the constant conditions of pressure 5 GPa, temperature 1700°C and holding time 20 min. Toughness of the composites mixed with large grain size diamond decreased rapidly above 40 vol%. This nonlinear degradation behavior could be related with a decrease in the Young's modulus and fracture energy by increasing the porosity in sintered composite, since the content of B_6O particles agglutinating large diamond particles decreased. Toughness in the case of using small grain size diamond decreased linearly with an increase in diamond content. This linear decrease suggests that the diamond particles added as a second phase would inefficiently contribute to the crack deflection, because the grain size of added diamond particles is too small. The effect of the diamond-like carbon formed at the grain boundary should be considered in this case, but it was difficult to estimate its effect, quantitatively.

4. Conclusions

B_6O-$x$diamond ($x = 0$–60 vol%) sintered composites were prepared under high pressure and temperature conditions using the mixture of in-laboratory synthesized B_6O powder and commercially available diamond powder as starting powder. The phases formed, microstructures, and mechanical properties of the sintered composites were investigated on varying the added diamond content and sintering condition. The following conclusions were obtained.

1) Neither solid solution nor new chemical compounds formed under the conditions of the pressures

of 3–5 GPa and temperature of 1400–1800°C. Sintered composites of full density consisting of the mixed phase of B_6O and diamond were prepared.

2) When using diamond with a grain size below 0.25 μm, the transformation to the diamond-like carbon was confirmed by Raman spectroscopy. This diamond-like carbon was formed at the grain boundary under the high pressure.

3) The grain size of the added diamond particles greatly affects the microhardness and fracture toughness of B_6O-diamond sintered composites.

4) The treatment temperature has a great influence on the formation of strong interparticle bonding between B_6O and diamond, which increases the hardness of the sintered composites. The value of Vickers microhardness reached 60 GPa, when the sintered composite was prepared by using diamond with grain size below 0.25 μm under the sintering conditions of 5 GPa, 1700°C and 20 min.

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