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Microstructure and mechanical properties of B_6O-B_4C sintered composites prepared under high pressure

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Sintered composites in the B_6O-xB_4C ($x = 0$–40 vol%) system were prepared under high pressure and high temperature conditions (3–5 GPa, 1500–1800°C) from the mixture of in-laboratory synthesized B_6O powder and commercially available B_4C powder. Relationship among the formed phases, microstructures and mechanical properties of the sintered composites was investigated as a function of sintering conditions and added B_4C content. Microhardness of the sintered composite was found to increase with treatment temperature up to 1800°C, while fracture toughness decreased slightly. Maximum microhardness of $Hv \sim 46$ GPa was obtained from B_6O-30vol%B_4C sintered composite under the sintering conditions of 4 GPa, 1700°C and 20 min. *© 2000 Kluwer Academic Publishers*

1. Introduction

Hexaboron monoxide (B_6O) is known as one of the boron suboxides [1, 2] which possess high hardnesses comparable with B_4C or 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] stimulate the interests in relation to the fine microstructure and morphology of B_6O crystallites synthesized under high pressure. However, B_6O is a typical unsinterable material under normal pressure conditions. 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 to be prepared even by high pressure sintering techniques such as hot-pressing or hot isostatic pressing [11]. A wide range of microhardness $Hv = 34$–38 GPa is reported [3, 12–14] and less information is provided on chemical or mechanical properties of B_6O sintered compact. We reported [15–17] 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. This consolidation process of B_6O has an 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.

On the other hand, B_4C has a similar crystal structure (α-rhombohedral boron type), which is better represented as $B_{13}C_2$ with C—B—C chain on the trigonal axis [7, 18]. The sintered compact is known to have the microhardnesses as high as 34.5–40 GPa [4, 13, 18], which are scattered depending on the preparation method. Although its sinterability is supposed to be higher than that of B_6O, the sintered compact of single phase B_4C is still brittle and unstable in an oxidative atmosphere.

Both B_6O and B_4C have a tendency to form nonstoichiometric compositions under normal pressure [4–7, 18]. It is interesting to examine under high pressure and temperature conditions, whether solid solutions or new compounds are formed by a solid state reaction between these compounds [16, 17, 19, 20]. Investigations on sintering behavior and microstructure in the B_6O-B_4C systems are also important in order to improve the chemical or mechanical properties of these sintered composites. In the present paper, B_6O based sintered composites containing B_4C up to 40 vol% B_4C were prepared under high pressure and temperature conditions using our in-laboratory synthesized B_6O powder and commercially available B_4C powder as starting materials. Relationship among the formed phases, microstructure and mechanical properties of the sintered composites was examined and discussed.

2. Experimental procedure

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).

$$16B(s) + B_2O_3(l) \rightarrow 3B_6O(s) \cdots\cdots\cdots\cdots\cdots \quad (1)$$

Commercially available powders of amorphous boron (Rare Metallic Co., grain size: 0.5–3 μm, purity $>96.6\%$) and amorphous B_2O_3 (Kojundo Chemical Lab. Co., purity >99.9) 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 (70 ml/min) at 1400°C for 240–300 min to form B_6O powder.

2.2. High pressure treatment of B_6O-B_4C powder

The synthesized B_6O powder was mixed with commercially available B_4C power (Denki Kagaku Kogyo Co., average grain size: 0.7 μm) in ethanol for 30 min. The mixing volume fraction of B_4C was 0–40 vol%. Then the mixed powder was treated in vacuum 1.33×10^{-5} Pa at 600°C for 60 min to eliminate the adsorbed moisture or 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 [21, 22]. The cell assembly for high pressure sintering is shown in Fig. 1. The specimen was heated by a graphite heater in the temperature range of 1500–1800°C. The calibration method for pressure and temperature is the same as that described in the previous literature [23].

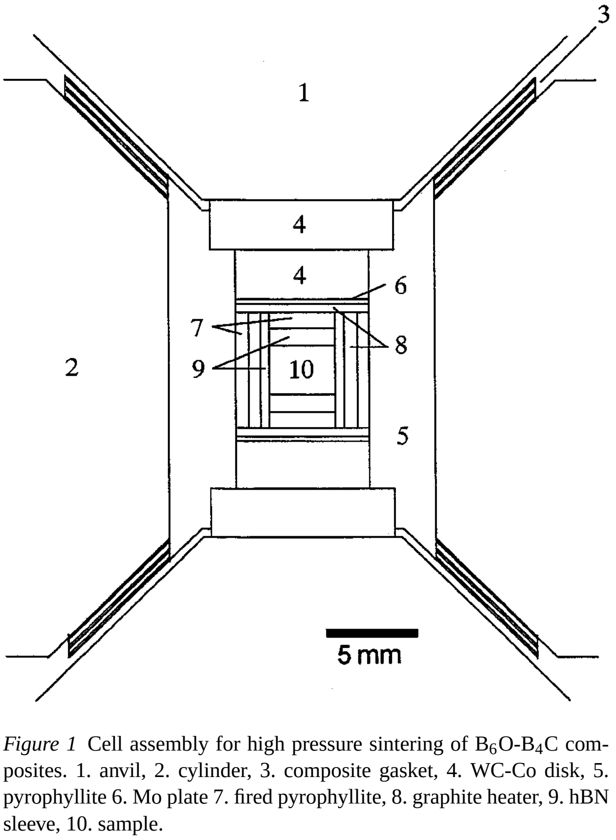

Figure 1 Cell assembly for high pressure sintering of B_6O-B_4C composites. 1. anvil, 2. cylinder, 3. composite gasket, 4. WC-Co disk, 5. pyrophyllite 6. Mo plate 7. fired pyrophyllite, 8. graphite heater, 9. hBN sleeve, 10. sample.

2.3. Characterization of sintered composites and evaluation of mechanical properties

The specimens before and after the high pressure treatments were identified by X-ray diffraction (XRD) and X-ray microanalysis (XMA). The fractured and polished surfaces of the sintered composites were observed by scanning electron microscopy (SEM). To observe the grain boundary microstructure of polished specimen, the surface was etched with concentrated nitric acid for 10 min or the Murakami reagent (10 g $K_3[Fe(CN)_6]$ + 10 g KCl in 100 ml water) for 5 min. The bulk density was measured by Archimedes' method. The Vickers microhardness (Hv) and fracture toughness (K_{Ic}) were measured by the indentation techniques under the loads of 1.96 N (200 gf) and 4.9 N (500 gf), respectively. An average for five measured values of hardness or toughness was plotted in each figure with excluding the maximum and minimum data in seven trials. This measurement technique is consistent in our data [16, 17, 21, 22, 23] of super-hard materials which can be compared each other.

3. Results and discussion

3.1. Phases formed after high pressure and temperature treatment

Fig. 2a shows the SEM photograph of the powder which was synthesized according to the reaction (1) at the heat treatment temperature of 1400°C for 300 min in an argon stream. This powder was identified as B_6O (JCPDS card no. 31-210) by XRD. The synthesized B_6O powder has a homogeneous particle size distribution with grain sizes from 0.8 to 1.2 μm, which is similar to the average grain size of starting amorphous boron powder [9]. B_6O fine particles would be formed by the reaction of boron with molten B_2O_3 impregnated along into the grain boundary at elevated temperature above 1300°C. B_6O powder formed is well-dispersed with less coagulation and grain growth. Nearly hexagonal platelet crystal of B_6O are found in some places in Fig. 2a. SEM photograph of as-purchased B_4C powder is also shown in Fig. 2b, where a uniform particle size distribution (0.4–1 μm) and an appropriate dispersibility are observed.

Fig. 3 shows the XRD patterns of the specimens after the high pressure treatment at 4 GPa, 1700°C and 20 min. Strong diffraction peaks for single phase B_6O can be observed without any addition of B_4C, as shown in Fig. 3a. In cases of 5 vol% or 40 vol% B_4C added, the diffraction lines for B_4C are confirmed with their intensities increased as the added content of B_4C increasing. No variation of lattice constants for both B_6O and B_4C suggests that neither formation of solid solution nor new compound occurs under high pressure and high temperature conditions employed. Existence of mixed phase, B_6O and B_4C only was confirmed at higher pressures up to 6 GPa and higher temperatures up to 1800°C. Hubert *et al.* [19] and Garvie *et al.* [20] synthesized solid solution of B_6O and B_4C by high pressure and temperature treatment (7.5 GPa, 1700°C, 30 min) of starting powder of B_2O_3, amorphous boron and

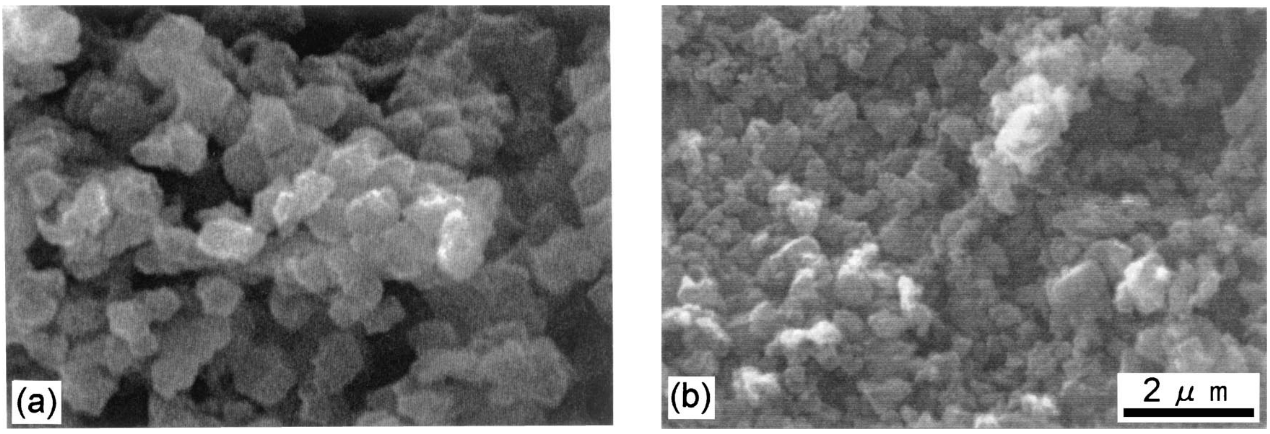

Figure 2 SEM photographs of (a) synthesized B_6O powder and (b) as-received B_4C powders.

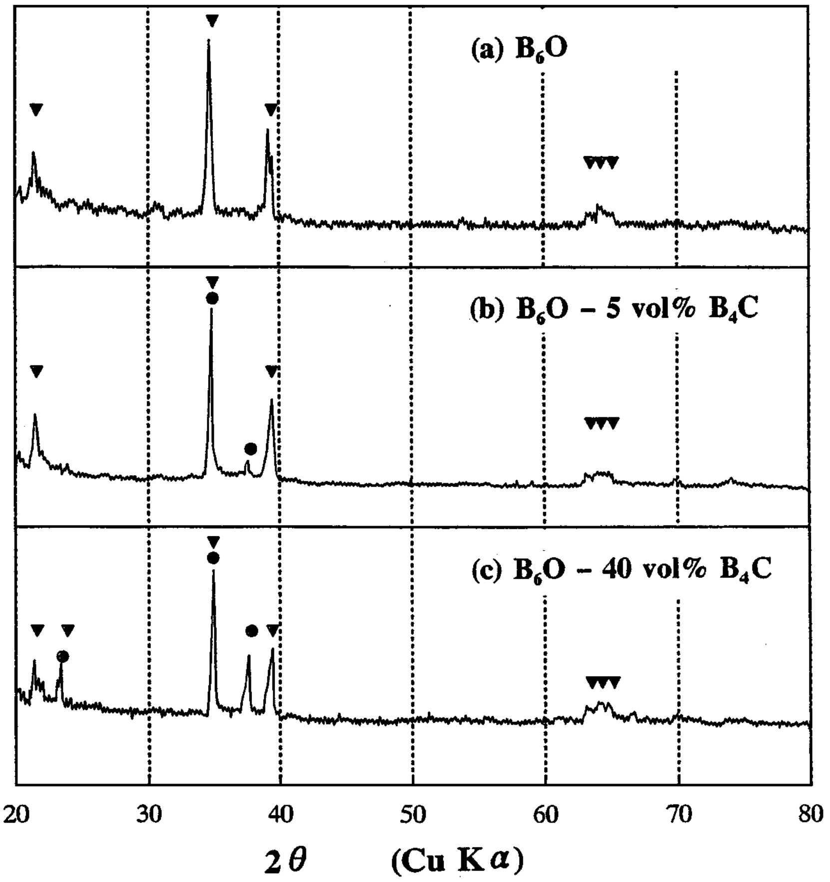

Figure 3 XRD patterns of the B_6O-xB_4C specimens for (a) $x = 0$ vol%, (b) $x = 5$ vol% and (c) $x = 40$ vol%. Sintering conditions: 4 GPa, 1700°C and 20 min. ▼ B_6O, ● B_4C.

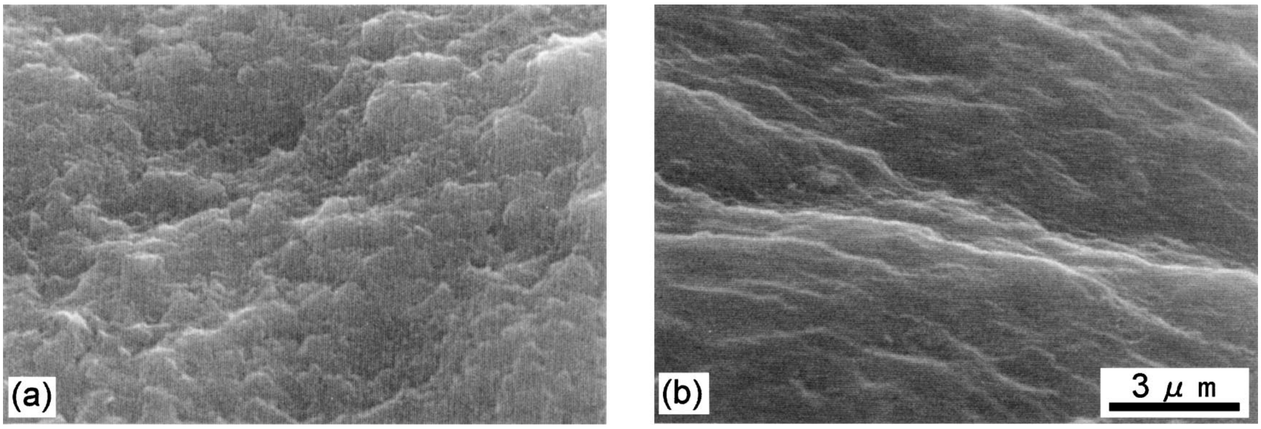

Figure 4 SEM photographs of the fractured surfaces of the B_6O-30vol%B_4C sintered composites. Sintering conditions: (a) 1500°C, (b) 1800°C; 4 GPa, 20 min.

graphite. No solid solution formed in our case from the starting mixed powder of B_6O and B_4C even by such high pressure and temperature treatments.

3.2. Microstructure of the B_6O-B_4C sintered composites

Fig. 4 shows the SEM photographs of the fractured surfaces of the specimens of the composition B_6O-30 vol%B_4C, which were prepared at the temperatures of (a) 1500°C and (b) 1800°C and under the identical conditions of 4 GPa and 20 min. At the sintering temperature of 1500°C in Fig. 4a, a rough surface with each grains distinguishable is seen, which represents that the fracture occurs in a grain boundary fracture mode. In contrast, a smooth but sharply edged fractured surface is observed in the specimen sintered at the elevated temperature of 1800°C, suggesting that an intragranular fracture prevails. These results show that strong intergranular bonding among B_6O grains and/or B_4C grains is formed at higher sintering temperatures.

Fig. 5 shows the SEM photographs of the polished sintered composites, which were prepared under the conditions of 4 GPa for 20 min. A smooth and dense polished surface of B_6O-30vol%B_4C composite sintered at 1700°C is observed along with a Vickers indentation for hardness measurement, as outlined by white dotted line in Fig. 5a. The relative bulk density of the sintered compact was >96%. The diagonal separation in the pyramidal indent is 12 μm, from which the microhardness of 40 GPa is measured. Fig. 5b shows the microstructure appeared after etching the polished surface with concentrated nitric acid for 30 min. No micropore is seen also with the B_4C content of 10 vol%. High chemical stability of this composite against strong acid can be verified by no appearance of grain boundary. The polished surface was further etched with Murakami reagent to observe the microstructure of the composite (B_6O-30vol%B_4C), which was sintered at higher temperature of 1800°C. Fig. 5c indicates that B_4C is preferentially etched with the result of grey colored portion appeared. It is found that no exaggerated grain growth of B_6O and B_4C can be seen and both grains are well-dispersed each other.

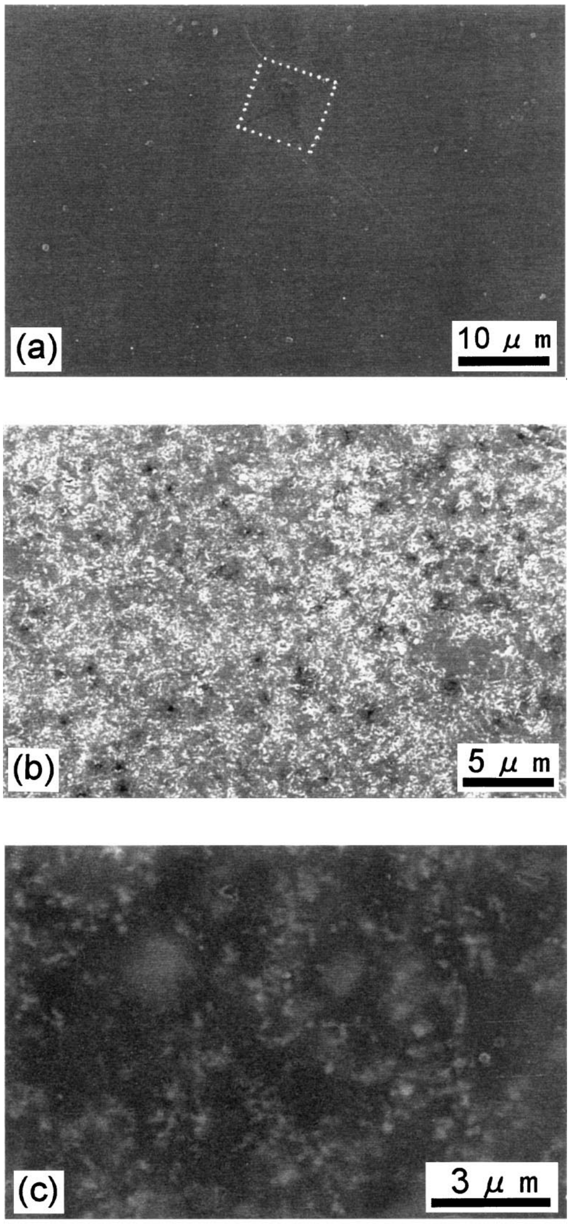

Figure 5 SEM photographs of the sintered composites prepared at 4 GPa for 20 min. (a) polished and indented surface of the B_6O-30vol%B_4C composite sintered at 1700°C, (b) polished and etched surface of the B_6O-10vol%B_4C composite sintered at 1700°C (etched with conc. nitric acid for 10 min), (c) polished and etched surface of the B_6O-30vol%B_4C composite sintered at 1800°C (etched with Murakami reagent for 5 min).

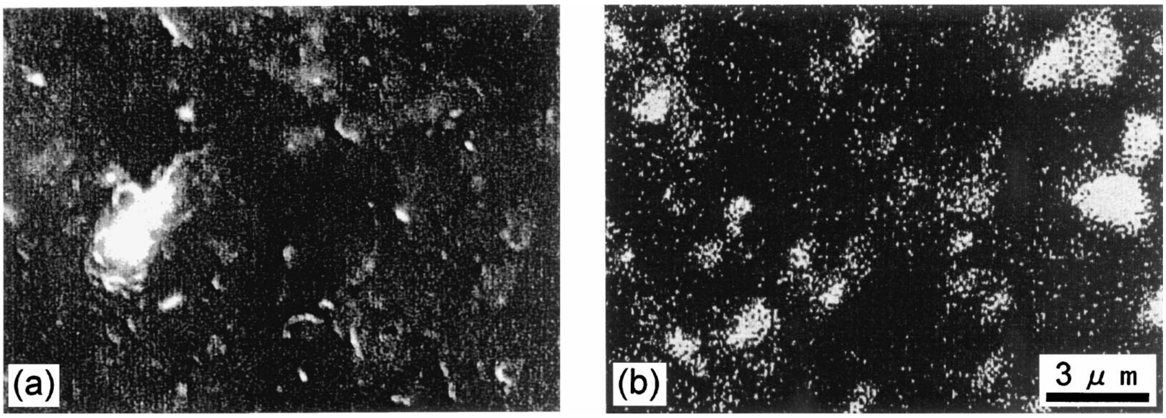

Figure 6 (a) SEM photograph and (b) XMA image for carbon after etching with Murakami reagent for B_6O-40 vol%B_4C composite sintered at 4 GPa, 1700°C and 20 min.

Fig. 6 shows SEM photograph and XMA image for carbon after etching with Mrakami reagent for the B_6O-40vol%B_4C sintered composite which was sintered at 4 GPa, 1700°C and 20 min. In such a higher content of 40 vol%, aggregated B_4C grains are observed in some places, as seen from the portions with higher carbon concentrations.

3.3. Mechanical properties of the B_6O-B_4C sintered composites

The effect of applied pressure on microhardness and toughness was found minor in the pressure range of 3–6 GPa, from which the pressure of 4 GPa was found sufficient to densify the composite. On the other hand, the influence of sintering temperature was found greater than that of pressure. Fig. 7 shows the Vickers microhardness and fracture toughness of the B_6O-30vol%B_4C sintered composites as a function of sintering temperature. The pressure and holding time were kept constant at 4 GPa and 20 min, respectively. The microhardness is found to increase linearly with increasing temperature from 27 GPa at 1500°C to 43 GPa at 1800°C. This conspicuously large dependence of microhardness on sintering temperature suggests that the intergranular bonding between B_6O and B_4C grains increases with temperature, as shown in Fig. 4. The fracture toughness is between 0.5 and 1 $MNm^{-3/2}$ decreasing slightly with temperature.

Fig. 8 shows the effect of B_4C content on the microhardness and fracture toughness under the constant conditions of pressure 4 GPa, temperature 1600°C and holding time 20 min. It is found that the effect of B_4C content is minor as far as microhardness is concerned. However, fracture toughness increases with increasing in B_4C content. Fig. 9 shows the SEM photographs indicating the crack propagation in the sintered composites of (a) B_6O-10vol% B_4C and (b) B_6O-30vol%B_4C, which were obtained under the sintering conditions of 4 GPa, 1700°C and 20 min. Crack deflection can be observed in the higher content of B_4C. This verifies that the toughness is greatly dependent on the microstructure of the sintered composite; i.e. the toughness increases with B_4C content and the fracture occurs along the grain boundary of B_6O and B_4C.

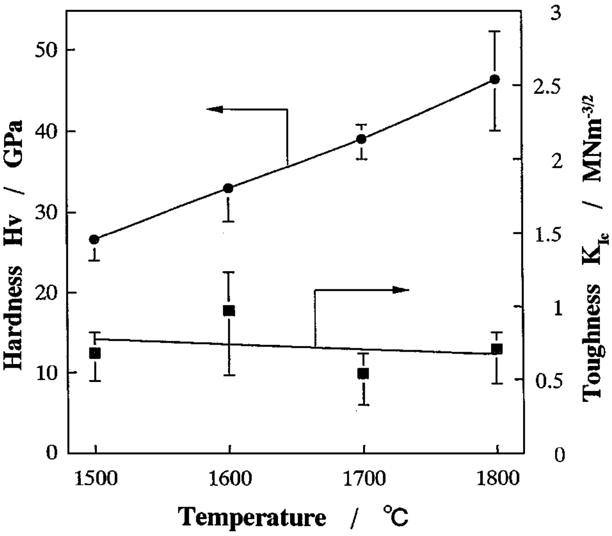

Figure 7 Vickers microhardness (●) and fracture toughness (■) of the B_6O-30vol%B_4C sintered composites as a function of sintering temperature. Pressure: 4 GPa, holding time: 20 min.

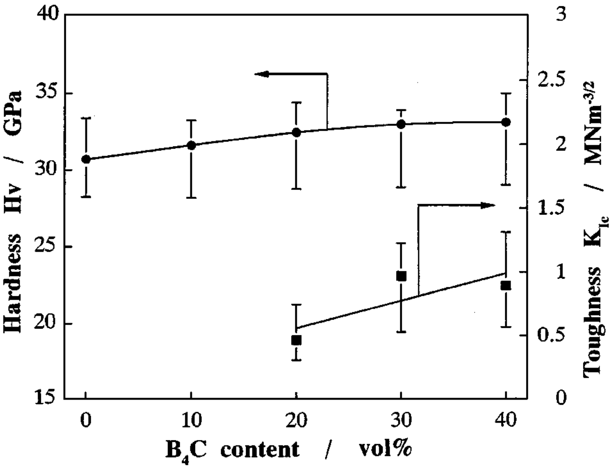

Figure 8 Vickers microhardness (●) and fracture toughness (■) of the sintered composites as function of B_4C content. Sintering conditions: 4 GPa, 1600°C, 20 min.

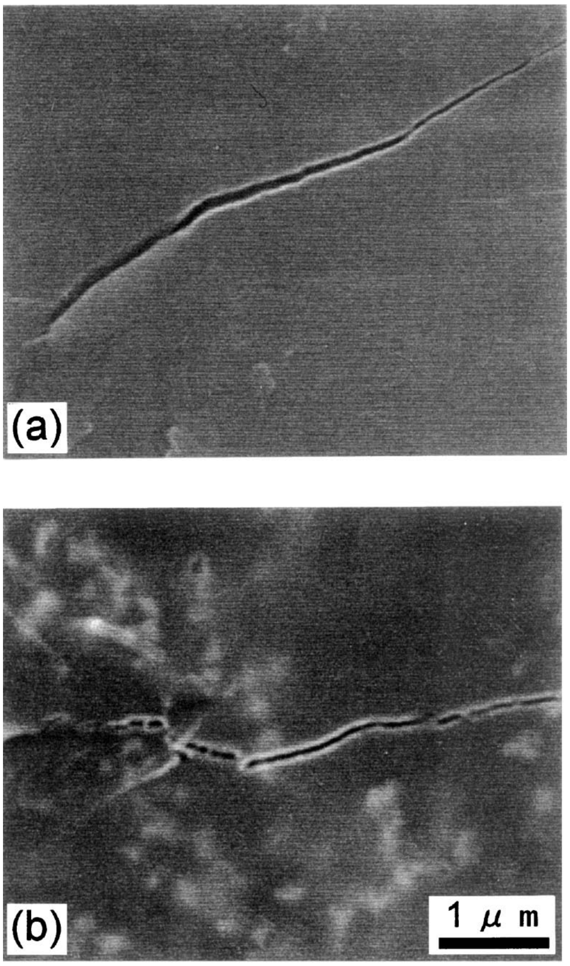

Figure 9 SEM photographs of crack propagations on the polished surface of the sintered composites: (a) B_6O-10vol%B_4C and (b) B_6O-30vol%B_4C. Sintering conditions: 4 GPa, 1700°C, 20 min.

Fig. 10 shows the summarized diagram between microhardness and sintering temperature for various

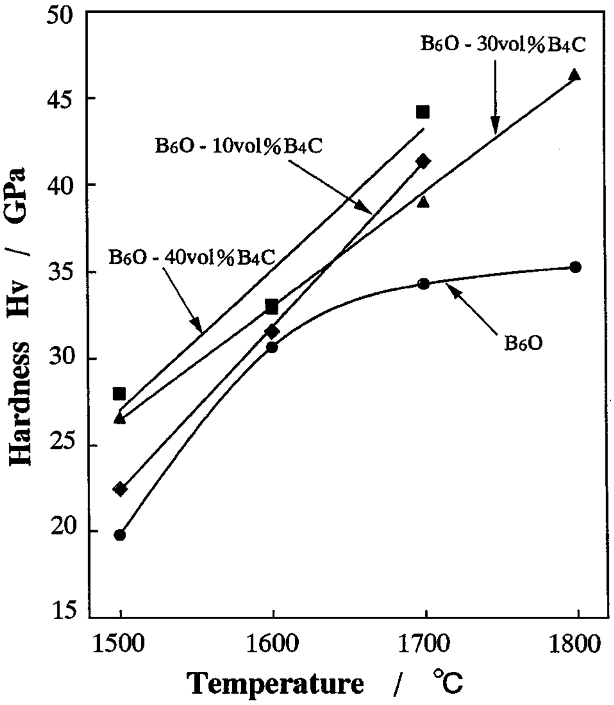

Figure 10 Vickers microhardness measured under various sintering temperatures and compositions of B_6O-xB_4C, ● B_6O, ◆ B_6O-10vol%B_4C, ▲ B_6O-30vol%B_4C, ■ B_6O-40 vol%B_4C. Pressure: 4 GPa, holding time: 20 min.

compositions of the sintered compacts prepared at the constant pressure of 4 GPa and at the constant holding time of 20 min. It is an outstanding feature that the microhardness increases with temperature in cases of higher content of B_4C. A maximum microhardness as high as 46 GPa is attained at 1800°C for the B_6O-30vol%B_4C composite. In contrast, the microhardness of monolithic B_6O sintered compact is 34 GPa even at 1800°C.

4. Conclusions

B_6O-xB_4C ($x = 0$–40 vol%) sintered composites were prepared under high pressure and high temperature conditions using the mixture of in-laboratory synthesized B_6O powder and commercially available B_4C powder as starting powder. Formed phases, microstructures and mechanical properties of the sintered composites were investigated varying the added B_4C content and sintering conditions. Following conclusions were obtained.

1) Neither solid solutions nor new compound formed under the conditions of the pressures of 3–6 GPa and the temperatures of 1500–1800 °C. Sintered composite in full density consisting of the mixed phase of B_6O and B_4C was prepared.

2) The treatment temperature has a great influence on the formation of strong interparticle bonding between B_6O and B_4C, which increases the hardness and toughness of the sintered composite. The pressure of 4 GPa is enough to densify the composite powder of B_6O and B_4C.

3) Microhardness was found to increase with treatment temperature up to 1800°C, while fracture toughness decreased slightly. A maximum microhardness of ~46 GPa was obtained from B_6O-30vol%B_4C powder under the sintering conditions of 4 GPa, 1700°C and 20 min.

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