

## Methanol washing effects on spark plasma sintering behavior and mechanical properties of B<sub>4</sub>C ceramics

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B<sub>4</sub>C ceramics were fabricated by a spark plasma sintering process and their sintering behavior, microstructure and mechanical properties were evaluated. The relative densities of B<sub>4</sub>C ceramics obtained by spark plasma sintering method reached were as high as a 99% at lower temperature than used in the conventional sintering method, in addition, without any sintering additives. The mechanical properties of B<sub>4</sub>C ceramics were improved by a methanol washing process which can remove B<sub>2</sub>O<sub>3</sub> coatings from the B<sub>4</sub>C powder surface. This improvement results from the formation of a fine and homogeneous microstructure because the grain coarsening was suppressed by the elimination of the B<sub>2</sub>O<sub>3</sub> coating. In particular, the fracture toughness of the sintered specimen using a methanol washed powder improved by more than 30% compared with the specimen using an as-received commercial powder.

**Key words:** B<sub>4</sub>C, spark plasma sintering, microstructure, mechanical property.

### Introduction

Boron carbides (B<sub>4</sub>C) are very useful ceramics in engineering applications because of their excellent mechanical properties. B<sub>4</sub>C is a premier material for personal ballistic armor because it is the third hardest material behind diamond and cubic boron nitride (c-BN), in addition to its low theoretical density (2.52 g/cm<sup>3</sup>) [1]. B<sub>4</sub>C is also used in abrasive applications such as for abrasive powder and nozzles due to its excellent abrasion and wear resistance [1]. Its ability to absorb neutrons without forming long-lived radio nuclides make the material attractive as an absorbent for the radiation arising in nuclear power plants [1, 2].

It has been reported that the mechanical properties of B<sub>4</sub>C ceramics depend on the B/C ratio because boron carbide exists as a solid solution in the range of 8.8 to 20 at% carbon (B<sub>10.5</sub>C-B<sub>4</sub>C) [3-5]. Niihara et al. reported that the hardness and fracture toughness values were maximum at essentially the stoichiometric composition B/C=4 and decreased for B/C<4 (composition region of B<sub>4</sub>C + C) and for B/C>4 (non-stoichiometric region of B<sub>4</sub>C) [5].

Effective ballistic armor should have a very high hardness combined with a high fracture toughness [6, 7]. In general, these mechanical properties are closely related to chemical composition and microstructure.

Densification of pure B<sub>4</sub>C is quite difficult because of its strong covalent bonding characteristics. Although, high density pure B<sub>4</sub>C ceramics which have up to 95% relative density may be obtained using a hot-press sintering method at least at 2200°C, deterioration of mechanical property was inevitable because of microstructural coarsening at a high sintering temperature [8-10].

Additives such as SiC, TiB<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and some transition metals have been used as sintering aids to fabricate B<sub>4</sub>C ceramics [11-14]. The best known sintering additive for B<sub>4</sub>C is carbon, commonly added in the form of phenol resin, which can remove the boron oxide phase from the powder surface and induce a non-stoichiometric composition during the sintering process, consequently accelerating densification via enhanced grain boundary diffusivity [6, 10, 15, 16]. However, the non-stoichiometric boron carbide composition and the secondary phases induced by the additives often have deleterious effects on the mechanical properties [1, 5].

Recently, the spark plasma sintering (SPS) process has gained significant interest for fabrication of poorly sinterable materials such as borides, carbides and nitrides. The SPS process is a type of pressure sintering method which uses a high-temperature spark plasma generated by discharging the gaps between powder particles with on-off electrical current [17]. The generation of the spark plasma in the initial stage of the SPS process accelerates the neck formation and thermal diffusion, and has a surface-activating and cleaning effect on the particles being sintered. Also, the electrical field formed by the DC current accelerates diffusion. Therefore, the SPS process has been applied for densification of

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poorly sinterable materials at lower temperatures and in shorter times than is impossible with conventional sintering process [17-19].

The present study is an attempt to use SPS to obtain fully densified B<sub>4</sub>C ceramics without additives in order to improve in the mechanical properties. In particular, we have studied the effect of methanol washing of B<sub>4</sub>C powder which can remove boron oxide (B<sub>2</sub>O<sub>3</sub>) coatings from the particle surfaces [20]. The presence of B<sub>2</sub>O<sub>3</sub> coatings on B<sub>4</sub>C particles inhibits densification until they are volatilized away, and this facilitates B<sub>4</sub>C particle coarsening resulting in microstructural coarsening [10, 21].

### Experimental Procedure

Commercially available B<sub>4</sub>C powder (HS grade, H.C. Starck, Germany) was used as a starting material. Table 1 shows the characteristics of the powder based on the manufacture's data. The commercial B<sub>4</sub>C powder was suspended in methanol (99.9%, J.T. Baker, USA) and ultrasonicated (B3200, Branson, USA) for 1 hour. The suspension was then placed in a dry oven at 80°C for 12 hours to volatilize the methanol. This process was repeated three times for the purpose of removing B<sub>2</sub>O<sub>3</sub> coatings from the surfaces [20].

The powders were loaded into a graphite mold inside the SPS system (Dr. Sinter 515S, Sumitomo Coal and Mining Co., Japan). After applying an initial pressure of 40 MPa, the loaded powers were heated in the sintering temperature range from 1800°C to 2000°C for 5 minutes at a heating rate of 100 K/minute in a vacuum (<10 Pa). After finishing the sintering process, the pressure was relaxed and the specimens were cooled in the chamber. The sintered bodies were typically 15 mm in diameter and 4 mm in thickness.

The density was measured by the Archimedes method and an X-ray diffractometer (M03XHF22, MAC Science Co., Japan) was used for analyzing the phases in the powders and sintered bodies. The hardness and fracture toughness were measured using a Vickers indenter (HM-

124, Akashi, Japan) with a 9.8 N load for 15 seconds. The microstructural characterization was carried out with scanning electron microscope (SEM, 5900LV, JEOL, Japan) after electrolytic etching in 1% KOH solution for 30 seconds with 3.5 V and 0.1 A/cm<sup>2</sup>. The average grain size was calculated using the linear intercept method (ASTM E 112-96) based on 1000 measurements on SEM micrographs.

### Results and Discussion

Figure 1 shows XRD patterns of the B<sub>4</sub>C powders and sintered bodies at 2000°C. B<sub>2</sub>O<sub>3</sub> peaks were detected in the commercial powder, but they were removed from the methanol washed powder. This result indicates that the methanol washing process is very effective in removing B<sub>2</sub>O<sub>3</sub> coatings from the B<sub>4</sub>C powder surfaces. Also, B<sub>2</sub>O<sub>3</sub> peaks were removed from the sintered body using a commercial powder because the B<sub>2</sub>O<sub>3</sub> phase has a tendency to vaporize above 1200°C [6, 10].

Figure 2 shows the relative density of specimens as a function of sintering temperature. The final density of each powder was not affected by the conditions of their

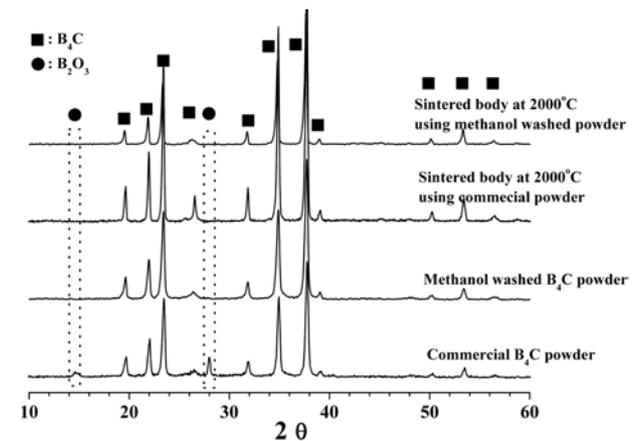


Fig. 1. XRD patterns of commercial B<sub>4</sub>C powder, methanol washed powder and sintered bodies at 2000°C.

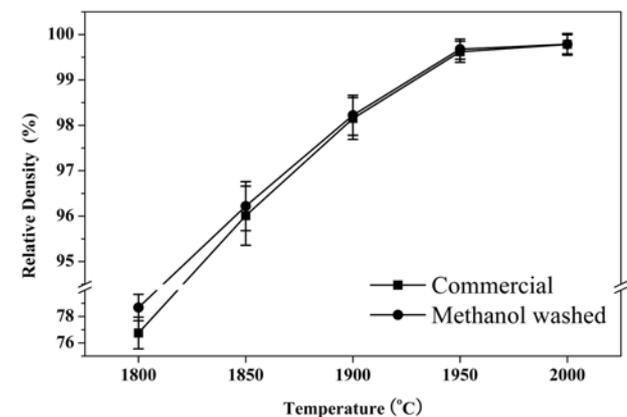


Fig. 2. Variation of relative density of commercial and methanol washed specimens as a function of sintering temperature.

Table 1. Characteristics of B<sub>4</sub>C powder

Specific surface area	≤18 m <sup>2</sup> /g
Particle size	D 90% of particles 3.0 μm D 50% of particles 0.8 μm D 10% of particles 0.2 μm
Impurity levels	Max. 1.7 wt% of O Max. 0.7 wt% of N Max. 0.05 wt% of Fe Max. 0.15 wt% of Si Max. 0.05 wt% of Al Max. 0.5 wt% of other
Total boron	75.65 wt%
Total carbon	21.2 wt%
B/C molar ratio	3.7

surfaces but depended on the sintering temperature. The relative density dramatically increased at 1850 °C up to 95%, and it reached over 99% at 1900 °C. It is very difficult to obtain full density pure B<sub>4</sub>C ceramics at such a low temperature, 1900 °C, using conventional sintering methods. This result demonstrated the excellent sinterability of the SPS process.

Figure 3 shows the displacement of the total height of the graphite mold assembly during the SPS process at 1950 °C. This displacement directly represents the shrinkage profile during densification of the powders in real time. It is seen that the commercial B<sub>4</sub>C powder

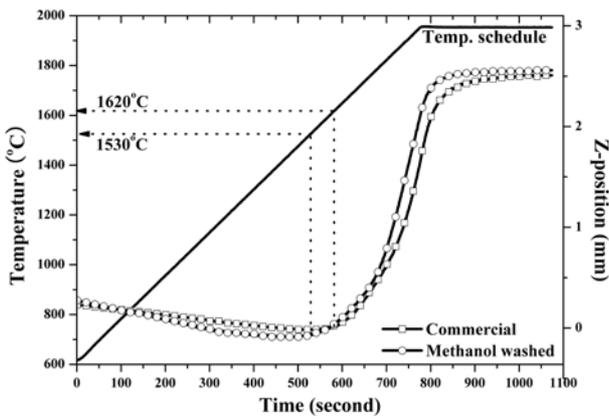


Fig. 3. Densification behavior of B<sub>4</sub>C powders during the spark plasma sintering process.

starts to densify at about 1620 °C, but the methanol washed powder begins at about 1530 °C. The result clearly shows that the presence of B<sub>2</sub>O<sub>3</sub> coatings on the surfaces of B<sub>4</sub>C particles delayed the onset of sintering. The removal of B<sub>2</sub>O<sub>3</sub> coatings permitted direct B<sub>4</sub>C-B<sub>4</sub>C contact resulted in low temperature densification by the acceleration of lattice and/or grain boundary diffusion [6, 8, 15].

Figure 4 shows the change in average grain size with the sintering temperature. The average grain size of the commercial powder specimens was larger than that of

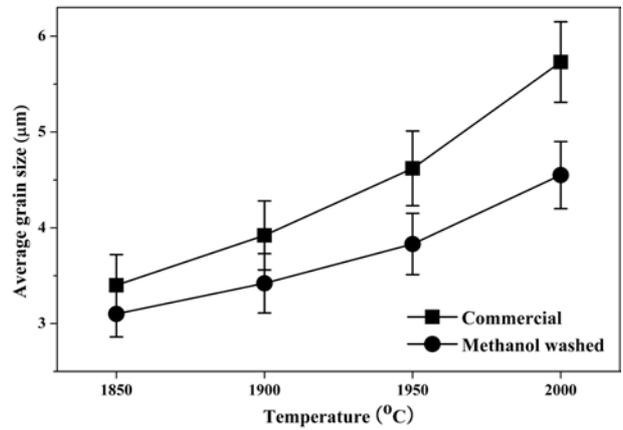


Fig. 4. The change of average grain sizes of commercial and methanol washed specimens as a function of sintering temperature.

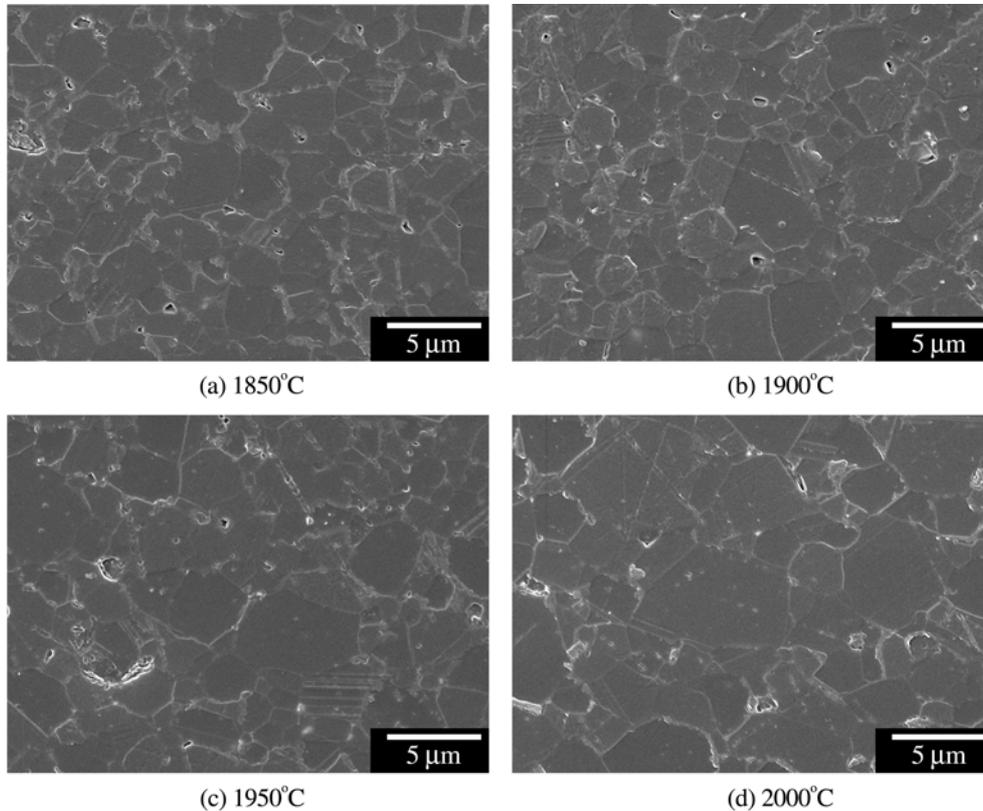


Fig. 5. SEM micrographs of etched surface B<sub>4</sub>C specimens sintered at (a) 1850 °C, (b) 1900 °C, (c) 1950 °C and (d) 2000 °C using commercial powder.

methanol washed powder specimens. In general, the grain coarsening of covalently bonded materials originates from surface diffusion and an evaporation-condensation mechanism. It has been suggested that the existence of  $B_2O_3$  coatings may provide a rapid diffusion path on particle surfaces because the firing temperatures are well above its melting point,  $450^\circ C$  [10]. Also, the volatility of  $B_2O_3$  causes the microstructural coarsening above  $1500^\circ C$  because the vapor pressure of  $B_2O_3$  is sufficiently high for mass transport [10]. Thus the retardation of densification (as indicated in Fig. 3) and the microstructural coarsening are due to the existence of  $B_2O_3$  phases on the particle surfaces.

Figure 5 and Fig. 6 show the etched surface morphology of sintered bodies at different sintering temperatures using the commercial  $B_4C$  powder and the methanol washed  $B_4C$  powder, respectively. A near fully dense microstructures are shown in both specimens above  $1950^\circ C$ . The grain coarsening during SPS sintering is clearly seen in the commercial powder specimen (as shown in Fig. 5) with increase sintering temperature. However, the microstructure of methanol washed specimens (as shown in Fig. 6) is finer and more homogeneous than that of commercial powder specimens. Referring to the result of average grain size shown in Fig. 4, these results show that the removal of  $B_2O_3$  coatings is very effective in restricting the grain coarsening and consequently in obtaining a fine and

homogeneous microstructure.

Figure 7 and Fig. 8 show Vickers hardness and fracture toughness, respectively, of sintered bodies as a function of sintering temperature using the commercial  $B_4C$  powder and the methanol washed  $B_4C$  powder. The increase of Vickers hardness values (as shown in Fig. 7) of both samples with increase sintering temperature up to  $1950^\circ C$  may have originated from the increase of density and the values are saturated above  $1950^\circ C$ . The Vickers hardness value of methanol washed specimens is higher than that of commercial specimens because the methanol washed specimens have a smaller

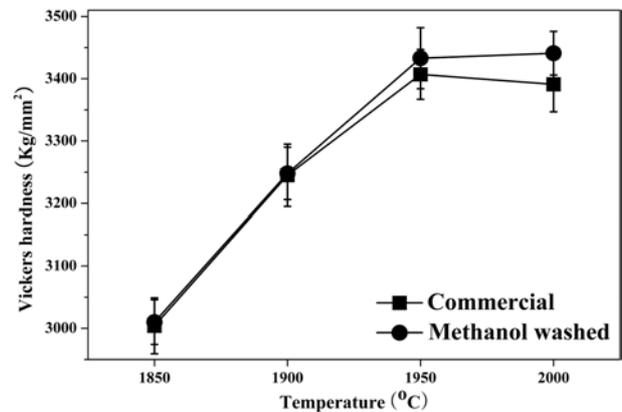


Fig. 7. Variation of Vickers hardness of commercial and methanol washed specimens as a function of sintering temperature.

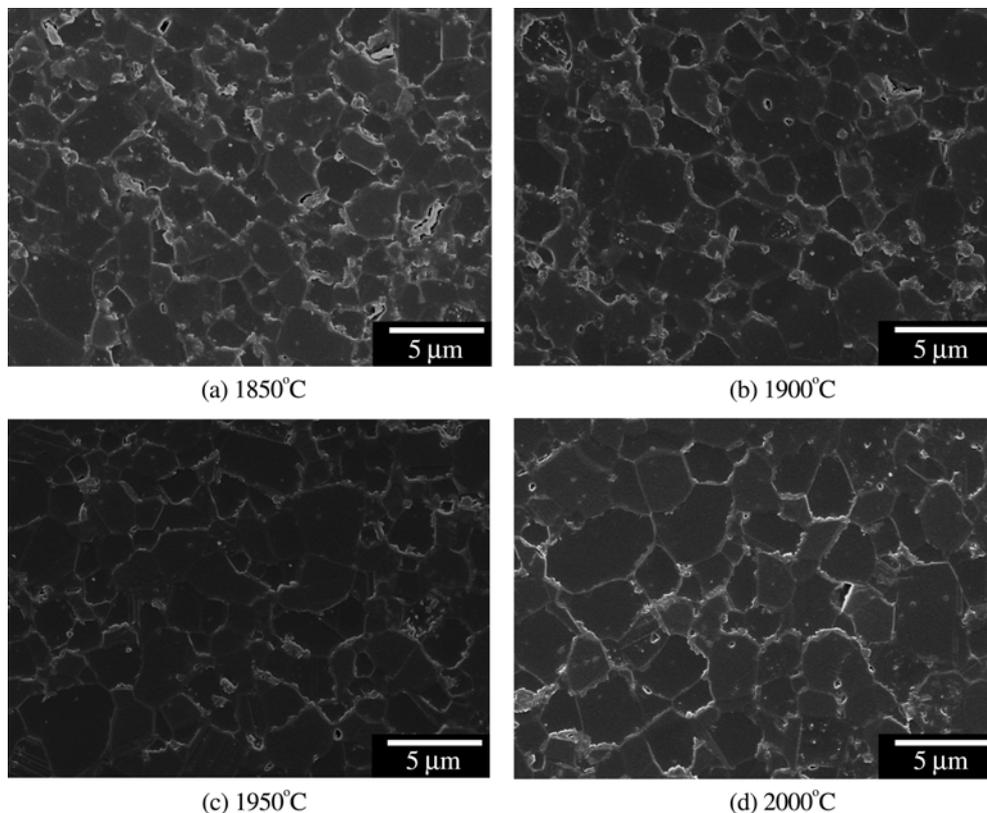


Fig. 6. SEM micrographs of etched surface  $B_4C$  specimens sintered at (a)  $1850^\circ C$ , (b)  $1900^\circ C$ , (c)  $1950^\circ C$  and (d)  $2000^\circ C$  using methanol washed powder.

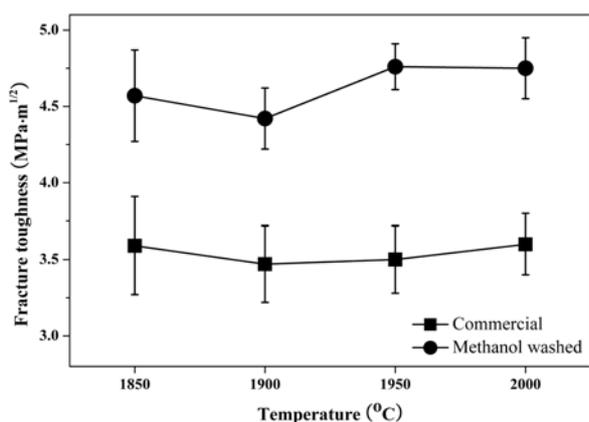


Fig. 8. Variation of fracture toughness of commercial and methanol washed specimens as a function of sintering temperature.

grain size. In particular, the improvement in the fracture toughness (as shown in Fig. 8) is significant for the methanol washed  $B_4C$  powder. The fracture toughness of methanol washed specimens increased by more than 30% over the commercial specimens. The fine and homogeneous micro-structure make a great contribution to the improvement of the mechanical properties.

### Conclusions

Poorly sinterable  $B_4C$  ceramics were successfully fully densified even without additives at a lower temperature than by using a conventional sintering method. The microstructural coarsening was effectively inhibited by the removal of boron oxide coatings on  $B_4C$  particle surfaces by the methanol washing process. The removal of  $B_2O_3$  coatings could permit a direct  $B_4C$ - $B_4C$  contact which resulted in low temperature densification and suppression of coarsening by the acceleration of lattice and/or grain boundary diffusion. As a result, the mechanical properties were significantly improved by

the formation of a fine and homogeneous microstructure.

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