JOURNALOF

Ceramic Processing Research

Sintering behavior and mechanical properties of B₄C ceramics fabricated by spark plasma sintering

Kyoung Hun Kim^{a,*}, Jae Hong Chae^a, Joo Seok Park^a, Jong Pil Ahn^a and Kwang Bo Shim^b

^aKorea Institute of Ceramic Engineering and Technology, Seoul 153-801, Korea ^bDivision of Advanced Materials Science and Engineering, Hanyang University, Seoul 133-791, Korea

The sintering behavior, microstructure and mechanical properties of boron carbide ceramics, which were fabricated by a spark plasma sintering process, were investigated. The relative density of B_4C ceramics using a spark plasma sintering method reached as high as 99% theoretical at a lower temperature than a conventional sintering method, and in addition, without any sintering additives. The mechanical properties of B_4C ceramics could be improved by soaking at 1,300 °C during the sintering process which removed the B_2O_3 phase from the B_4C powder surface. A remarkable improvement of mechanical properties could be achieved by the introduction of a soaking process during the spark plasma sintering process. In particular, the fracture toughness values of the specimens which experienced the B_2O_3 removal process improved by over 30% compared with the specimens without this process. These achievements resulted from the formation of a fine and homogeneous microstructure because the grain coarsening was suppressed by the elimination of the B_2O_3 phase.

Key words: B₄C, Microstructure, Mechanical properties, Spark plasma sintering.

Introduction

Boron carbide (B₄C) with its high hardness, wear resistance and rather low density is quite a promising material for industrial applications. It has been used for lightweight armor, as abrasive powder, in wear-resistant components such as blasting nozzles and grinding wheels. In particular, B₄C 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/cm³) [1-3]. Moreover, its nuclear properties such as high cross section for neutron absorption and resistance to irradiation have made it an attractive choice for neutronabsorbing parts in nuclear power plants [4, 5]. However, one of the major obstacles for wider applications of B₄C in industry is its relatively low strength and fracture toughness as well as difficulties related to it fabrication [1, 2].

Boron carbide exists in a wide range of compositions between B₄C to B_{10.5}C in the B-C system [6]. It has been reported that the hardness and fracture toughness values were a maximum at essentially the stoichiometric composition B/ C=4 and decreased for B/C < 4 (composition region of B₄C + C) and for B/C > 4 (non-stoichiometric region of B₄C) [7, 8].

The densification of pure B_4C is quite difficult because of its strong covalent bonding characteristics. Although, high density pure B_4C ceramics which have up to 95% theoretical density could be obtained using hot-press sintering at at least 2,200 °C, a deterioration of mechanical properties was inevitable because of the microstructural coarsening at a high sintering temperature [9, 10].

Additives such as SiC, TiB₂, Al₂O₃ and some transition metals have been used as sintering aids to fabricate B_4C ceramics [11-14]. The best known sintering additive for B_4C is carbon, commonly added in the form of phenol resin, which can remove the boron oxide phase from the powder surface and induce non-stoichiometric compositions during the sintering process, consequently accelerating densification via enhanced grain boundary diffusivity [3, 10, 15, 16]. However, non-stoichiometric boron carbide compositions and the secondary phases induced by the additives often have deleterious effects on the mechanical properties [1, 7, 8].

Recently, the spark plasma sintering (SPS) process has attracted significant interest for fabrication of poorlysinterable 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 an on-off electrical current [17]. The generation of the spark plasma in the initial stage of the SPS process accelerates 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 the densification of poorly-sinterable materials at lower temperatures and in shorter times than is impossible with a conventional sintering process [17-19].

The present research attempts to obtain fully-densified B_4C ceramics using the SPS method without sintering additives

^{*}Corresponding author:

Tel : +82-2-3282-7870 Fax: +82-2-3282-2490

Fax: +82-2-3282-2490

E-mail: khkim@kicet.re.kr

in order to improve the mechanical properties. In addition, we have studied the effect of having a soaking time during the sintering process which might remove boron oxide (B_2O_3) coatings from the particle surfaces [3, 20, 21]. The presence of B_2O_3 coatings on B_4C particles inhibits densification until they are volatilized away, and they facilitate B_4C particle coarsening resulting in microstructural coarsening [10, 21].

Experimental Procedure

The boron carbide specimens were produced with a commercially-available powder of the HS grade from H.C. Starck, Germany (See Table 1). 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 to 1,300 °C and soaked for 1 hour, and then they were heated to various sintering temperatures ranging from 1,800 °C to 2,000 °C at a heating rate of 100 K/minute in a vacuum (< 10 Pa). After 5 minutes sintering at the temperature, 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.

Bulk densities were 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 flexural strength was measured using a 4-point bend test method following the ASTM F394-78.

The microstructural characterization was carried out with a scanning electron microscope (SEM, 5900LV, JEOL, Japan) after electrolytic etching in a 1% KOH solution for 30 seconds at 3.5 V and 0.1 A/cm². The average grain size was calculated using the linear intercept method (ASTM E 112-96) based on 1,000 measurements on SEM micrographs.

Results and Discussion

Fig. 1 shows XRD patterns of the as-received B_4C powder and the powder soaked at 1,300 °C using the SPS equipment.

Table	1.	Characteristics	of B ₄ C	powder
-------	----	-----------------	---------------------	--------

Specific surface area	18 m ² /g		
Particle size	D 90% of particles $\leq 3.0 \ \mu m$ D 50% of particles $\leq 0.8 \ \mu m$ D 10% of particles $\leq 0.2 \ \mu m$		
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 Total carbon B/C molar ratio	75.65 wt% 21.2 wt% 3.7		



Fig. 1. XRD patterns of B_4C powders and specimens sintered at 2,000 °C.

B₂O₃ peaks were detected in the as-received powder, but they were removed from the soaked powder. This result indicates that the soaking process is very successful in removing B₂O₃ coatings from the B₄C powder surfaces. Lee *et al.* reported that soaking at 1,350 °C in H₂ gas could effectively remove the B₂O₃ phase through the reaction H₂(g) + B₂O₃(*l*) → H₂O(g) + B₂O₂(g), lowing the temperature for the onset of sintering [16]. However, in the present study, the B₂O₃ phase was extracted without the contribution of a H₂ gaseous atmosphere, presumably through the direct evaporation of the B₂O₃ phase due to the generation of the high-temperature spark plasma between particles, termed as the surface cleaning effect by spark plasma.

Fig. 2 shows the relative density of specimens as a function of the sintering temperature. The densification of the B_4C powder which experienced the soaking process was slightly faster than that of the powder without the soaking process. The relative density dramatically increased at 1850 °C to above 96% theoretical, and it reached above 99% theoretical at 1950 °C. It is very hard to obtain full density pure B_4C ceramics at such a low temperature, 1950 °C, using conventional sintering methods. This result suggests the



Fig. 2. Variation of relative density with the sintering process conditions.

excellent sinterability of the SPS process.

Fig. 3 shows the displacement in the total height of graphite mold assembly during the SPS process at 1950 °C. This displacement directly represents the sintering shrinkage profile during densification of the powders in real time. It is seen that the B₄C powder with the soaking process begins to densify at a lower temperature than that of the powder without the soaking process. The sintering shrinkage of the B₄C powder which experienced the soaking process finished at the sintering temperature, 1950 °C. However, in the case of the powder without the soaking process, it continued after reaching this sintering temperature. This result clearly shows that the presence of B₂O₃ coatings on the surface of B₄C particles delayed the onset of sintering. The removal of B₂O₃ coatings permitted direct B₄C-B₄C contact resulting in low temperature densification by the acceleration of lattice and/or grain boundary diffusion [3, 9, 15].

Fig. 4 shows the change in average grain size with the sintering temperature. The average grain size of the normal process specimens was larger than that of the specimens



Fig. 3. Densification behavior of B₄C powders during the spark plasma sintering process.



Fig. 4. Average grain size of sintered specimens as a function of the sintering process conditions.

given the soaking process. 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 sintering temperatures are well above its melting point, 450 °C [10]. Also, the volatility of B_2O_3 causes microstructural coarsening above 1500 °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 surfaces of particle.

Fig. 5 and fig. 6 show the etched surface morphology of the normal process and the specimens which experienced the soaking process as a function of the sintering temperature, respectively. Near fully dense microstructures are shown in both specimens sintered above 1950 °C. The grain coarsening during SPS sintering is clearly seen in the normal process specimens, as shown in Fig. 5, with an increase in the sintering temperature. However, the microstructure of specimens which experienced the soaking process, as shown in Fig. 6, are finer and more homogeneous than those of the normal process specimens. Referring to the results of the average grain sizes 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 fine and homogeneous microstructures.

Fig. 7, fig. 8 and fig. 9 show Vickers hardness, flexural strength and fracture toughness of sintered specimens, respectively. The increase of Vickers hardness and flexural strength values (as shown in fig. 7 and 8) of both set of samples with an increase of the sintering temperature may originate from the increase in density. The Vickers hardness and flexural strength values of specimens which experienced the soaking process are higher than those of the normal process specimens because specimens which experienced the soaking process have smaller grain sizes. In particular, the improvements in the fracture toughnesses (as shown in fig. 9) are significant for the specimens which experienced the soaking process. The fracture toughness of specimens which experienced the soaking process increased by more than 30% above the normal process specimens. These results show that a fine and homogeneous microstructure make a great contribution to the improvement of the mechanical properties.

Conclusion

Poorly-sinterable B_4C ceramics were successfully fully densified without additives at a lower temperature than by using conventional sintering method. The microstructural coarsening was effectively inhibited by the removal of boron oxide coatings on the surfaces of B_4C particles by the soaking process during spark plasma sintering. The removal of B_2O_3 coatings permitted a direct B_4C - B_4C contact resulting in low temperature densification and suppression of coarsening by the acceleration of lattice and/or grain



Fig. 5. SEM etched surface images of B_4C specimens fabricated by the normal spark plasma sintering process.



Fig. 6. SEM etched surface images of B₄C specimens which experienced the B₂O₃ removal during the spark plasma sintering process.



Fig. 7. Variation of Vickers hardness with the sintering process conditions.



Fig. 8. Variation of flexural strength with the sintering process conditions.



Fig. 9. Variation of fracture toughness with the sintering process conditions.

boundary diffusion. As a result, the mechanical properties were significantly improved by the formation of a fine and homogeneous microstructure.

References

- 1. F. Thevenot, J. Euro. Ceram. Soc. 6[4] (1990) 205-225.
- 2. F. Thevenot, Key Eng. Mater. 56-57 (1991) 59-88.
- 3. M. Grujicic, B. Pandurangan, K. L. Koudela and B. A. Cheeseman, App. Surf. Sci. 253[2] (2006) 730-745.
- K. Reinmuth, A. Lipp, H. Knoch and K.A. Schwetz, J. Nucl. Mater. 124 (1984) 175-184.
- 5. T.V. Hynes and M.N. Alexander, J. Chem. Phys. 54 (1971) 5296-5301.
- 6. R.D. Allen, J. Am. Chem. Soc. 75[14] (1953) 3582-3583.
- 7. K. Niihara, A. Nakahira and T. Hirai, J. Am. Ceram. Soc. 67[1] (1984) c13-c14.
- H. Lee and R. F. Speyer, J. Am. Ceram. Soc. 86[9] (2003) 1468-1473.
- 9. R. Angers and M. Beauvy, Ceram. Int. 10[2] (1984) 49-55.
- C. Greskovich and J. H. Rosolowski, J. Am. Ceram. Soc. 59[7/8] (1976) 336-343.
- T. Vasilos and S. K. Dutta, Am. Ceram. Soc. Bull. 53[5] (1974) 453-454.
- Y. Kanno, K. Kawase and K. Nakano, J. Ceram. Soc. Jpn. 95[11] (1987) 1137-1140.
- V. Skorokhod Jr., M. D. Vlajic and V. D. krstic, J. Mater. Sci. Lett. 15[15] (1996) 1137-1139.
- 14. C.H. Lee and C.H. Kim, J. Mater. Sci. 27[23] (1992) 6335-6340.
- S.L. Dole, S. Prochazka and R.H. Doremus, J. Am. Ceram. Soc. 72[6] (1989) 958-966.
- H. Lee, W.S. hackenberger and R.F. Speyer, J. Am. Ceram. Soc. 85[8] (2002) 2131-2133.
- 17. M. Tokita, J. Soc. Powder Tech. Jpn. 30[11] (1993) 790-804.
- 18. M. Omori, Mater. Sci. Eng. A 287 (2000) 183-188.
- 19. K.H. Kim and K.B. Shim, Mater. Character. 50 (2003) 31-37.
- N. Cho, Z. Bao and R. F. Speyer, J. Marer. Res. 20[8] (2005) 2110-2116.
- 21. H. Lee, W.S. hackenberger and R.F. Speyer, J. Am. Ceram. Soc. 85[8] (2002) 2131-2133.