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Spark Plasma Sintering of Boron Carbide Ceramics Using Different Sample Geometries and Dimensions

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B_4C ceramics were fabricated by spark plasma sintering technique at 1700 °C–1800 °C for 5 min under applied pressure of 50 MPa under vacuum atmosphere. Two different grades of B_4C powder from H.C. Starck Company namely HP grade and HS grade were used in all related experiments. Effect of sample geometry and dimensions as well as sample thickness on sintering parameters were analyzed. Samples having 5 mm thickness and 50 mm diameter, 8 mm thickness in circular geometries and 50×50 square cross-section, 8 mm thickness were fabricated. Using the powder, which provided the densest sample, yttrium oxide (Y_2O_3) was added, mixed and sintered. Optimization of SPS method production parameters for pure B_4C samples and B_4C samples with 5 wt% yttrium oxide additive were accomplished. The effect of geometry on density, Vickers hardness, fracture toughness, and microstructure were examined. The hardness and fracture toughness values of the samples were evaluated by the Vickers indentation technique.

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1. Introduction

Ceramic materials are attractive materials for ballistic protection applications due to their high hardness, high flexural strength, and low density when compared to metals. Among those materials, boron carbide (B_4C) is evaluated as an ideal material for ballistic protection applications, especially for light armor, since it is the third hardest material after diamond and cubic boron nitride and it exhibits higher hardness and lower density when compared to other ceramics [1, 2].

In recent years, spark plasma sintering (SPS) technique has been used widely for manufacturing boron carbide and related boron carbide ceramics because of the positive effects on microstructure since it prevents grain coarsening [2]. With applying external electric field, SPS enhances densification and the sintering process is completed at lower temperatures in short times without grain growth compared to the traditional methods (pressureless sintering, hot pressing, and hot isostatic pressing). These unique properties make SPS a preferable candidate for producing boron carbide ceramics [3, 4].

In this study B_4C ceramics are produced by using SPS method and physical and mechanical characterization of those ceramics are performed. Optimization of SPS method production parameters for B_4C ceramics having geometries (50 mm diameter, 5 mm thickness, 50 mm diameter, 8 mm thickness circular; $50 \times 50 \times 8$ mm^3 square cross-section) and 5 wt% Y_2O_3 added B_4C will be performed. Sintering additives are expected to affect the sintering behavior, sintering conditions and enable production of secondary phases leading to mechanical changes in the sintered compacts [5].

2. Experimental

Commercial HS and HP grade B_4C powders from German H.C. Starck Company, with an average particle size of 1.78 μm and 2.95 μm, respectively and from the same company yttrium oxide (C quality, average particle size 0.9 μm) were used in the present study. In most of the experiments pure B_4C was used. In the experiment that yttrium oxide was used as additive, suspensions were prepared by mixing B_4C and Y_2O_3 powder with alumina balls in Merck quality ethanol medium by ball milling for 24 h. The slurry was then dried and screened from 150 μm openings. After screening, the dry powder was loaded in a graphite die for conducting in SPS.

The samples were sintered by using the SPS apparatus (SPS-7.40MK-VII, SPS Syntex Inc.). After applying a pressure of 50 MPa, two different heating regimes were used for sintering: one is 100 °C/min and the other is 75 °C/min from room temperature to sintering temperature. The temperature of the die was measured by an optical pyrometer. All of the samples were subjected to 5 min soaking time. Whole process was carried out in vacuum atmosphere and shrinkage, displacement, heating current, and voltage for every 5 s was recorded. At the end of the process, sintered compacts were obtained.

After the sintering process, the Archimedes method was used to determine the final relative densities of the compacts. Specimens, polished with a diamond paste having particle size of 1 μm were subjected to the hardness and fracture toughness tests at room temperature and were evaluated by the Vickers indentation technique at a load of 1 kg. The micrographs of all sample surfaces were observed by scanning electron microscopy (SEM; model JSM 7000F, JEOL, Tokyo, Japan).

3. Results and discussion

Starting powders, sample dimensions, and SPS conditions along with the relative density values of the sintered ceramics are given in Table I. The first two samples have 50 mm diameter and 5 mm thickness. 50 MPa pressure is applied under vacuum atmosphere and the powders are heated with 100 °C/min heating rate and sintered for 5 min. The sintering temperatures are defined by checking the completion of the shrinkage amounts. Maximum relative density values are achieved at the temperatures where the shrinkage is completed and the samples are kept constant at that temperature for 5 min. Shrinkage of the HP and HS graded cylindrical samples having 50 mm diameter and 5 mm thickness are completed at 1800 °C and 1770 °C, respectively. This sintering temperature difference resulted from the average grain size difference where HS is 1.78 μm and HP is 2.97 μm. HS grade B_4C have 99.4% relative density whereas HP grade B_4C has 97.9% relative density.

TABLE I

Density values of differently processed HP and HS grade sintered boron carbide ceramics.

	Starting powder	Dimensions	SPS process [°C, MPa, min]	Relative density [%]
1.	B_4Cpowder (HP grade)	(Ø50 mm, 5 mm thickness)	1800, 50, 5	97.9
2.	B_4C powder (HS grade)	(Ø50 mm, 5 mm thickness)	1770, 50, 5	99.4
3.	B_4C powder (HP grade)	(Ø50 mm, 8 mm thickness)	1700, 40, 5	98.6
4.	B_4C powder (HS grade)	(Ø50 mm, 8 mm thickness)	1670, 40, 5	99.1
5.	B_4C powder (HP grade)	(50 mm × 50 mm square cross-section, 8 mm thickness)	1550, 40, 5	98.7
6.	B_4C powder (HS grade)	(50 mm × 50 mm square cross-section, 8 mm thickness)	1530, 40, 5	98.9
7.	B_4C powder (HS grade) +5% Y_2O_3	(Ø50 mm, 5 mm thickness)	1740, 40, 5	99.5

TABLE II

Hardness and fracture toughness values of HP and HS grade sintered boron carbide ceramics.

	Starting powder	SPS process [°C, MPa, min]	Hardness [GPa]	Fracture toughness [MPa m$^{1/2}$]
1.	B_4C powder (HP grade)	1800, 50, 5	32.6 ± 0.5	4.30 ± 0.70
2.	B_4C powder (HS grade)	1770, 50, 5	32.2 ± 0.5	4.30 ± 0.70
3.	B_4C powder (HP grade)	1700, 40, 5	31.04 ± 0.5	4.21 ± 0.70
4.	B_4C powder (HS grade)	1670, 40, 5	30.67 ± 0.5	4.20 ± 0.70
5.	B_4C powder (HP grade)	1550, 40, 5	32.9 ± 0.5	2.69 ± 0.30
6.	B_4C powder (HS grade)	1530, 40, 5	33.5 ± 0.5	2.55 ± 0.30
7.	B_4C powder (HS grade) +5% Y_2O_3	1740, 40, 5	36.7 ± 0.5	3.70 ± 0.30

The third and fourth samples stated in Table I have 50 mm diameter and 8 mm thickness. Shrinkage of the HP and HS graded cylindrical samples having 50 mm diameter and 8 mm thickness are completed at 1700 °C and 1670 °C, respectively. 40 MPa pressure is applied under vacuum atmosphere and the powders are heated with 75 °C/min heating rate with 5 min soaking time. The third sample (HP grade) has 98.6% relative density whereas the fourth sample (HS grade) has 99.1% relative density.

The fifth and sixth samples stated in Table I have 50×50 mm^2 square cross-sectional area. Shrinkage of the HP and HS graded square samples are completed at 1550 °C and 1530 °C, respectively. 40 MPa pressure is applied under vacuum atmosphere and the powders are heated with 75 °C/min heating rate and sintered for 5 min. The fifth sample (HP grade) has 98.7% relative density whereas the sixth sample (HS grade) has 98.9% relative density. The seventh sample which has 5% Y_2O_3 has 99.5% relative density. The thicker the sample gets, the lower the sintering temperature gets due to the heat created from the excess powder in thicker samples.

The hardness and fracture toughness values of the sintered ceramics are given in Table II. Hardness values of the HP grade B_4C ceramics sintered at 1800 °C are obtained as 32.6 ± 0.5 GPa; HS grade B_4C ceramics sintered at 1770 °C are obtained as 32.2 ± 0.5 GPa. Addition of 5% mass Y_2O_3 to HS grade B_4C resulted in an increase in hardness values from 32.2 ± 0.5 to 36.7 ± 0.5. The highest fracture toughness values are obtained as 4.3 ± 0.7 MPa m$^{1/2}$ from the samples with smaller dimensions (Ø50 mm, 5 mm thickness) heated with 100 °C/min heating rate and spark plasma sintered at 1800 °C for 5 min.

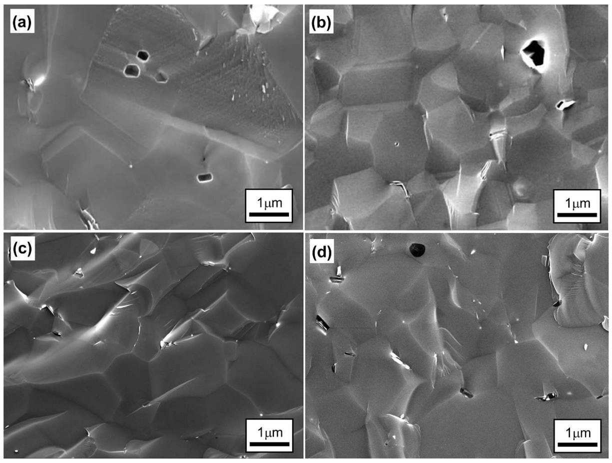

Fig. 1. SEM micrographs of (a) HP grade sintered B_4C at 1800 °C and (b) HS grade sintered B_4C at 1770 °C with 100 °C/min heating rate and 5 min soaking time, applied pressure of 50 MPa, (c) HS grade B_4C (Ø50 mm, 8 mm thickness) sintered at 1670 °C under 40 MPa pressure for 5 min, (d) HS grade B_4C (50 mm × 50 mm square cross-section, 8 mm thickness) sintered at 1530 °C under 40 MPa pressure for 5 min.

Fracture surface SEM images are given in Fig. 1, which provided the best result of relative density values. HS grade B_4C is observed to have 1–2 μm average grain size

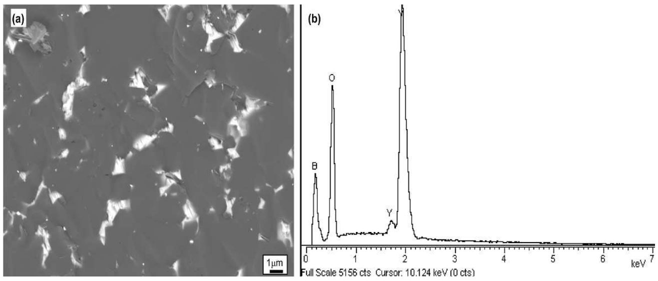

Fig. 2. (a) SEM micrographs of HS grade sintered B_4C with 5% Y_2O_3 additive sintered at 1740 °C with 100 °C/s heating rate and 5 min soaking time, applied pressure of 50 MPa and under vacuum atmosphere, (b) EDS analysis of the white sections in HS grade B_4C sample with 5% Y_2O_3 additive.

whereas HP grade B_4C is observed to have 2–3 μm average grain size. Difference of the grain sizes of sintered HS and HP grade ceramics are due to the starting powder grain size difference. The sintered ceramics are observed to have pores which are not equal in size and distribution from each other.

SEM micrographs of Y_2O_3 added B_4C samples which exhibits equal or higher relative density values are given in Fig. 2. Pore level is detected to be less than 1% and the white sections are assumed to be YB_{12} and Y_4C_7 phases. As provided in Fig. 2 in the EDS analysis white parts contain Y, O, and B elements. XRD analysis shows that YB_{12} is present in the structure. EDS analysis shows the presence of oxygen which leads to the assumptions of B_2O_3 presence.

4. Conclusions

In this study, highly densified boron carbide ceramics processed under argon atmosphere with density values higher than 97% was attained by SPS technique at various temperatures: 1770 °C, 1670 °C, 1530 °C and 1740 °C for HS graded B_4C powders. HP graded powders with 100 °C/min heating rate under 50 MPa applied pressure and 5 min soaking times. The Vickers hardness of the samples ranged between 30.67 ± 0.5 and 36.7 ± 0.5 GPa and fracture toughness values were measured between 2.55 ± 0.3 and 4.3 ± 0.3 MPa $m^{1/2}$. Hayun et al. measured the fracture toughness values from the Palmqvist crack system equations to be between 3.9 and 4.9 MPa $m^{1/2}$ [6]. In addition, the pure HS and HP graded ceramics which had the highest fracture toughness values were achieved from the process where higher heating regime and higher pressure was applied. Moreover, the sample with smallest dimensions and volume led to the highest sintering temperature and fracture toughness.

When cylindrical geometry is used in SPS, it is possible to relate the measured temperature to the temperature measured by the value from the optical pyrometer using a simple model. If the sample is assumed to be small, thin and centrally positioned, the temperature distribution will be according to the graphite die. The temperature difference between the edge of the die and the centre of the sample is therefore strongly dependent on the die surface temperature, the properties and geometry of the die and the sample. Very minor changes in the die geometries, dimensions and die wall thickness affect the SPS process parameters drastically [7].

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