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B_4C-CNT Produced by Spark Plasma Sintering

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H.C. Starck HS Grade boron carbide (B_4C) powders with multi-walled carbon nanotube (CNT) were sintered by Spark Plasma Sintering (SPS) method in a vacuum atmosphere to obtain highly dense and fine grained final ceramic products. Powder mixtures were densified by SPS at 1650 and 1725°C using 40 MPa pressure for 5 min. The effects of heating rate, spark plasma sintering temperature and CNT additive on density, hardness, fracture toughness and microstructures of B_4C-CNT samples are investigated. Density measurements were carried out using Archimedes method. Hardness and fracture toughness were examined by Vickers indentation technique. Scanning Electron Microscope (SEM) was used to observe microstructural investigation.

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1. Introduction

Boron carbide (B_4C) is one of the prominent materials for many high performance applications such as lightweight armor for individual protection, control rods in nuclear reactors and sandblasting nozzles etc. due to its outstanding properties like low density, high hardness, high elastic modulus, high melting point, high neutron absorption cross-section and chemical inertness. However, strong covalent bonds between boron and carbon obstruct the sinterability, so difficulty in obtaining high density B_4C compacts restricts the application of boron carbide.

Spark plasma sintering (SPS) which is a very effective means of consolidating boron carbide is attracting the attention of researchers in recent years [1–10]. Spark plasma sintering is a comparatively new sintering process that allows compaction of ceramics and powdered metals at low temperature with short holding time. The process is similar to conventional hot pressing in that they both use moderate uni-axial pressure. However instead of using an external heating source, an on-off direct pulsing current passes through the die and sample in SPS. This imlies that the powder is heated both from inside and outside.

Up to now, various kinds of sintering aids have been added to attain high density product. Carbon, which is one of the prevalent additives, enhances the densification by removing the negative species, boron oxide, on the B_4C surface at low temperature and forming the eutectic liquid phase at grain boundary at high temperature [11, 12].

The aim of this work was to determine the sintering conditions and behavior of boron carbide-carbon composites by SPS in order to achieve higher mechanical properties and further investigate the effects of two different forms of carbon (carbon black and carbon nanotube) addition on densification behavior and final properties.

2. Materials and method

Commercial HS grade B_4C powders (H.C. Starck, Germany) with an average particle size of 0.80 μm and CNT Carbon 71 NT&F21, MT-MW-010-02, (10–20 nm in diameter, 1–2 μm in length), C powders (Mitsubishi Chemical, Tokyo, Japan; 30 nm) were used in the present study. Carbon elements were introduced into boron carbide and mixed in ethanol medium first by using ultrasonic mixer. Then the batches were prepared by mixing B_4C and CNT or C-black by magnetic mixer at room temperature for 24 hours. The slurry was then dried and screened from 150 micron openings. After screening, the dry powder was directly loaded in a graphite die for SPS without any binder addition or preshaping application.

The samples were sintered by using the SPS apparatus (SPS-7.40MK-VII, SPS Syntex Inc.). After applying a pressure of 40 MPa, the powders were heated with approximately 150°C/min. The temperature of the SPS process was measured with an optical pyrometer that was focused on the surface of the die. All of the samples were subjected to 5 min soaking time. The current was controlled manually. The linear shrinkage of the specimens during the SPS process was continuously monitored by displacement of the punch rods. The effect of the thermal expansion of the graphite punch rods with increasing specimen temperature was negligible. The sintered products were in the form of discs that were 50 mm in diameter and 5 mm thick, which were sand blasted in order to remove the graphite sheet.

The crystalline phases were identified by X-ray diffractometry (XRD; MiniFlex, Rigaku Corp.) in the 2θ range of 10–90° with CuKα radiation. The samples were cut into smaller pieces with a diamond coated blade. The theoritical densities were calculated according to "composites mixing rule" based on weight percantage and Archimedes method was used to determine the final densities of the compacts. All of the samples were polished carefully with a diamond paste by standard dia-

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mond polishing techniques. The fractured surface micrographs of all samples were observed by scanning electron microscopy (SEM;Model JSM 7000F, JEOL, Tokyo, Japan). Then the hardness and fracture toughness values at room temperature were measured by the Vickers indentation technique (VHMOT, Leica Corp.) with the applied load of 1 kg. The fracture toughness values were calculated from the half-length of a crack formed around the indentations by using Eq. 1.

$$K_{IC} = 0.016(E/H)^{\frac{1}{2}}(P/c^{\frac{3}{2}}) \quad (1)$$

Equation 1 was derived from Anstis *et al.* for median cracks. In this equation, E is Young's modulus (GPa) of composites calculated assuming a mixture rule, H is Vickers micro-hardness (GPa), P is load (N), and c is half of the average crack length [13].

3. Results and discussion

Figure 1 shows the XRD patterns of monolithic boron carbide, 2% C-black and 2% CNT added composites which were heated with 150°C/min heating rate and spark plasma sintered at 1650°C for 5 min. under a pressure of 40 MPa. According to XRD patterns, only characteristic peaks of boron carbide (JCPDS: 35-0798) and carbon (JCPDS: 26-1076) were identified as expected. The densification of the specimens during SPS process

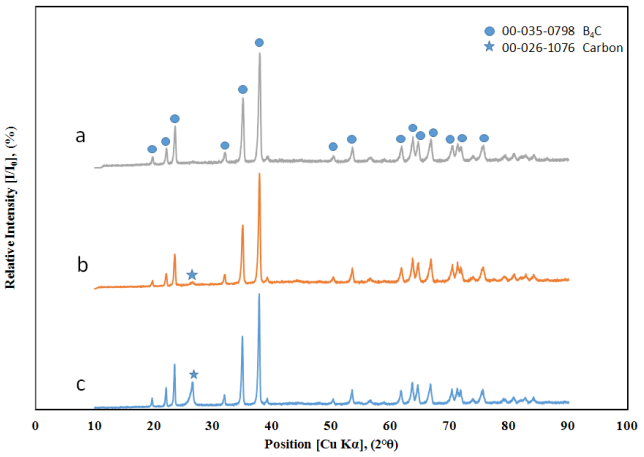

Fig. 1. XRD patterns of a) B_4C b) 2 % CNT containing B_4C c) 2% C-black containing B_4C samples spark plasma sintered at 1650°C for 5 min.

was evaluated by the displacement of punch rods due to the shrinkage of the composites. Figure 2 shows the displacement change of pure boron carbide powder, 2% C added B_4C and 2% CNT added B_4C powder mixtures that were spark plasma sintered at 1725°C for 5 min. The sample which only contains monolithic B_4C started to shrink at 1595°C, whereas the shrinking temperature was approximately same (1525°C) in C and CNT containing samples. The addition of carbon to boron carbide decreased and resulted in 70°C temperature difference between the starting temperatures of shrinkage. Densification curves also showed that the addition of both carbon and carbon nanotube was clearly effective in enhancing the sintering process.

A relative density of approximately 99% was obtained for 2% CNT added boron carbide composites which were spark plasma sintered at 1725°C. Addition of both carbon and carbon nanotube resulted in higher density values especially in the samples which were spark plasma sintered at lower temperature (1650°C). The relative densities (Table I) were in agreement with the shrinkage results presented in Fig. 2. The Vickers hardness of B_4C,

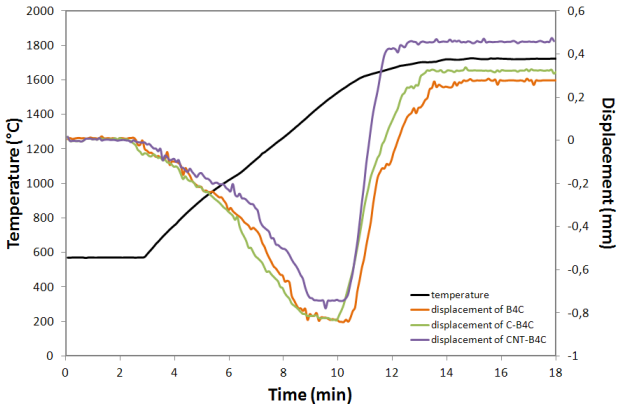

Fig. 2. Temperature and displacement curves versus time during SPS process.

B_4C with 2% C and B_4C+2% CNT composites at a load of 9.8 N is given in Table I. Both carbon black and CNT added composites showed higher hardness values than monolithic B_4C sintered body. Increased density resulted in higher density values. With the addition of carbon to boron carbide body, fracture toughness values were also tended to increase as can be seen from Table I.

TABLE I

Compositions, sintering temperatures and relative densities, hardness, and fracture toughness of spark plasma sintered samples

Composition	Sinter. Temper. [°C]	Relative density [%]	Hardness [GPa]	Fracture toughness [MPa m$^{1/2}$]
Pure B_4C		88.5	24.6 ± 0.21	3.8 ± 0.06
B_4C+2% C-black	1650	94.4	34.2 ± 0.17	4.0 ± 0.04
B_4C+2% CNT		97.9	34.6 ± 0.24	4.2 ± 0.06
Pure B_4C		96.9	34.0 ± 0.20	3.5 ± 0.02
B_4C+2% C-black	1725	98.4	35.8 ± 0.31	4.2 ± 0.05
B_4C+2% CNT		98.8	36.3 ± 0.19	4.5 ± 0.07

The highest fracture toughness, 4.5 MPa m$^{1/2}$, was achieved with the addition of 2% carbon nanotube to boron carbide. The increase in fracture toughness of composites with carbon addition is in agreement with study of Hirota *et al.* [14]. This could be related to homogeneous distribution of carbon nanotubes in the

structure, higher relative densities, crack inclination and bridging effects introduced by carbon nanotubes [14]. Figure 3 shows representative SEM images for the fracture surfaces of samples spark plasma sintered at 1650°C and 1725°C for 5 min soaking time applying pressure of 40 MPa under vacuum atmosphere. The micrographs clearly illustrate the trend of increasing density with the addition of carbon black, carbon nanotube and increasing spark plasma sintering temperature.

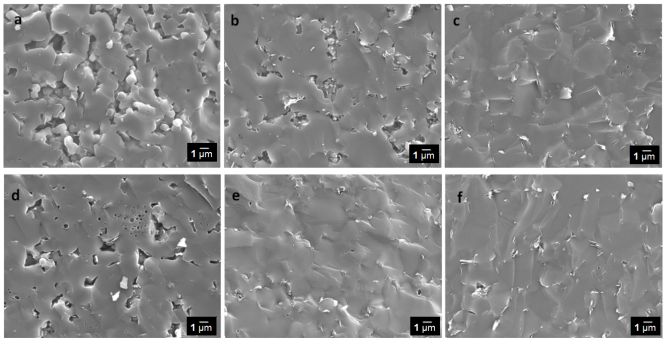

Fig. 3. SEM micrographs of a) monolithic B_4C b) 2% C added B_4C c) 2% CNT added B_4C spark plasma sintered at 1650°C for 5 min d) monolithic B_4C e) 2% C added B_4C f) 2% CNT added B_4C spark plasma sintered at 1725°C for 5 min C with 150°C/min heating rate, applied pressure of 40 MPa and under vacuum atmosphere.

4. Conclusion

The sintering and densification mechanism for monolithic boron carbide and 2% carbon black or 2% carbon nanotube added were studied using spark plasma sintering (SPS). Curves obtained from the displacement of punch rods due to the shrinkage of the composites were used to determine sintering mechanism. With the addition of carbon nanotube to boron carbide structure, densification is enhanced; hardness and fracture toughness values of composites are increased. The highest hardness value, as 36.3 GPa, is attained in the 2% CNT containing boron carbide which is spark plasma sintered at 1725°C for 5 min applied pressure of 40 MPa under vacuum atmosphere.

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