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Room and high temperature flexural failure of spark plasma sintered boron carbide

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Abstract

Dense (95–98.6%) bulk boron carbide prepared by Spark Plasma Sintering (SPS) in Ar or N_2 atmospheres were subject to three-point flexural tests at room and at 1600 °C. Eight different consolidation conditions were used via SPS of commercially available B_4C powder. Resulting specimens had similar grain size not exceeding 4 μm and room-temperature bending strength ($\sigma_{25\ ^\circ C}$) of 300–600 MPa, suggesting that difference in $\sigma_{25\ ^\circ C}$ is due to development of secondary phases in monolithic boron carbide ceramics during SPS processing. To explain such difference the composition of boron carbide and secondary phases observed by XRD and Raman spectroscopy. The variation in intensity of the Raman peak at 490 cm^{-1} of boron carbide suggests modification of the boron carbide composition and a higher intensity correlates with a higher room-temperature bending strength ($\sigma_{25\ ^\circ C}$) and Vickers hardness (HV). Secondary phases can modify the level of mechanical characteristics within some general trends that are not dependent on additives (with some exceptions) or technologies. Namely, HV increases, $\sigma_{25\ ^\circ C}$ decreases, and the ratio $\sigma_{1600\ ^\circ C}/\sigma_{25\ ^\circ C}$ ($\sigma_{1600\ ^\circ C}$ – bending strength at 1600 °C) is lower when fracture toughness (K_{IC}) is higher. The ratio $\sigma_{1600\ ^\circ C}/\sigma_{25\ ^\circ C}$ shows two regions of low and high K_{IC} delimited by $K_{IC}=4.1$ MPa $m^{0.5}$: in the low K_{IC} region, boron carbide specimens are produced in nitrogen.

Keywords: Boron carbide; Spark plasma sintering; Flexural mechanical properties

1. Introduction

Boron carbide (BC) is attracting significant attention [1,2] for different practical applications due to low specific weight, high elastic modulus, strength and hardness. However, BC is also considered a brittle material with relatively low fracture toughness. It is also a difficult-to-sinter material. Sintering and mechanical properties are the consequence of its strong covalent character. The density of samples obtained by pressureless sintering do not exceed 75–80% of the theoretical density even for heating temperatures as high as 2300 °C. Different additives [1–14] are employed to activate sintering and densities of 90% are achieved, but usually also for high temperatures above ~2100 °C. The amount of sintering aids ranges from a few percent to tens of weight percent. Their presence in BC influences mechanical properties. The optimum amounts of an additive as a sintering aid or as an effective addition improving mechanical properties can be very different. Pressure assisted sintering methods such as hot pressing or spark plasma sintering (SPS) can provide the necessary additional degree of freedom to obtain ceramics with density close to theoretical values and with controlled properties. In practice situation is complex and correlations additives-technology-microstructure-properties or properties–properties are not well understood. Literature presents many conflicting results and interpretations. It is also noteworthy that only a limited number of articles are investigating high temperature

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mechanical properties of BC such as flexural strength [4,5,10,15–22]. In articles [3,15–20], samples were polycrystalline, while in refs. [21,22] samples were B_4C–TiB_2 eutectic crystals. Results point on different mechanical behavior. For example, when compared with room temperature bending strength, the bending strength at high temperature can be approximately constant [15–17], can decrease [3,18,20] or it can be higher [19,21,22]. Various explanations were given.

In this work we present a study looking on room temperature and high temperature flexural properties of polycrystalline bulk boron carbide samples obtained by SPS in Ar or N_2 atmosphere. Heating and pressure conditions during SPS are also modified, while only one raw powder is used. The record high room temperature flexural strength of BC was reported for samples obtained by SPS [23]. SPS is shown to be more flexible than traditional hot pressing, e.g., in applying high heating rates. SPS also takes advantage of specific activation unconventional effects [24,25] that develop due to the pulsed current use. The consequences are a higher level of control and adaptability in conducting optimization processes with the possibility to pay a more careful attention to particular features of the raw materials. As already noted, mechanical properties of the bulk BC samples are influenced in a complex manner by impurities [26,27] and therein refs specially added or accidentally introduced during the raw powder synthesis/processing/sintering. Other factors are the boron to carbon ratio of the boron carbide (defined with the general chemical formula $B_{12+n}C_{n-3}$), microstructure and defects including porosity and chemical substitutions into the boron carbide crystal lattice. All these material details depend on processing. Therefore, the technology plays an important role. In particular, SPS is expected to generate new materials that cannot be obtained by traditional methods and, hence, they can exhibit improved or new properties. Despite this, considering also literature data, we show that some observed tendencies and correlations between mechanical characteristics are rather general regardless additives or technology. Within the general trends we discuss the role of the additives and of the other mentioned factors influencing mechanical properties. Results also indicate that high temperature flexural properties are depending on the room temperature ones and there are no major differences in the fracture mechanisms at room and high temperatures.

2. Experimental

A raw powder of boron carbide (BC) supplied by Sinopharm Chemical Reagent Co Ltd. (Singapore, lot 20070109) was used to prepare samples by SPS (SPS-1050, SPS-Syntex Inc., Japan). The purity indicated by Sinopharm is minimum 89–92% (B 75–77 at%, C 18–21 at%, Fe_2O_3 0.5–1 at%, and Si 0.2–1.2 at%). Apart from impurity elements O, Fe, and Si, our EDS measurements indicate the presence of some Na, Ca and S. The BC raw powder has an average particle size of ~4 μm considering microscopy observations. Particles less than 1 μm and blocks up to 10 μm were also revealed. Particles of B_4C show angular shapes with sharp tips and edges typical for brittle materials. Impurity phases such as free carbon and H_3BO_3 (B_2O_3 with water) were detected by XRD. By Rietveld analysis their wt% was less than 0.5 and 2.9 wt%, respectively. Compounds based on Fe were not observed by XRD suggesting that their amount and particle size are small and below the detection limit of XRD. Situation is similar for Si although apparently few peaks with a very low intensity that are observed with difficulty may indicate on traces of SiO_2 and SiC.

The raw powder wrapped by C-paper was loaded into a graphite mold (with the inner diameter of 2 cm) between two punches. The loaded mold system was introduced into a SPS furnace (SPS-1050, SPS-Syntex Inc., Japan) and a uniaxial pressure of 5 KN was applied on the punches. After vacuuming down to a pressure of 10 Pa, Ar or N_2 gas was introduced (0.8 atm). Heating was performed up to a maximum temperature of 1850 °C and the dwell time was 10 min. During heating from 700 to 1850 °C with different times of 25, 40 or 60 min, the uniaxial pressure was increased up to 60 or 80 MPa. Cooling from the maximum processing temperature down to 900 °C was with a rate of 90 °C/min and afterwards down to room temperature with a rate of 170 °C/min. Samples and SPS processing regimes are presented in Table 1.

The density of the samples was measured by Archimedes method (Table 1).

Bulk samples were extracted from the mold after SPS processing, cleaned, polished with diamond paper and paste and cut into rectangular bars of $3 \times 2.5 \times 20\ mm^3$ using a spark erosive cutter. Bars were used as specimens in the three-points bending experiment. The remaining parts of the bulk samples were grounded for X-ray diffraction (XRD) measurements.

XRD patterns on the raw powder and on spark plasma sintered samples were taken with a Bruker ($Cu_{K\alpha}$ radiation) diffractometer. Phase identification was made using EVA software and JCDD powder diffraction database.

Samples were observed by electronic microscopy. We used scanning electron microscopes (SEM) SU 8000 cold-emission FE-SEM Hitachi and JEOL 6500F equipped with energy dispersive spectroscopy (EDS) detectors. Observations were made on fractured surfaces after SPS and after bending tests.

Raman spectra were measured with a confocal microscope WiTec CRM200 (488 nm). Each Raman spectra is integrated

Table 1
Samples, SPS processing regime, relative density (theoretical density of B_4C samples was taken constant at 2.52 g/cm^2 [2,14]).

Sample	SPS heating time (min)	SPS pressure (MPa)	SPS atmosphere	Relative density (%)	Symbol
40	25	60	N_2	95	○
41	40	60	N_2	95.2	□
43	60	60	N_2	97.85	▽
40A	25	80	N_2	96.2	●
41A	40	80	N_2	97.9	■
43A	60	80	N_2	98.5	△
42	25	60	Ar	98.3	×
42A	25	80	Ar	98.6	┼