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Hardness and toughness control of brittle boron suboxide ceramics by consolidation of star-shaped particles by spark plasma sintering

Ievgen Solodkyi[a], Dmytro Demirskyi[b], Yoshio Sakka[a], Oleg Vasylkiv[a,b,*]

[a]National Institute for Materials Science, 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan
[b]Nanyang Technological University, 50 Nanyang Avenue, 639798 Singapore, Singapore

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Abstract

The hardness and fracture toughness of boron suboxide ceramics synthesized under ambient pressure and consolidated by spark plasma sintering (SPS) are reported. The structure and characterization of ceramics with a hardness of up to 43 GPa under a 9.8 N load and almost 28 GPa under a load of 198 N are reported. It was shown that an increase in the stoichiometry of boron suboxide by promoting the occupancy of the *6c* position in the rhombohedral cell is the effective for achieving both hard and tough pure B_6O ceramics. SPS consolidation preserved the unique fivefold symmetry of the boron suboxide grains and thus promoted additional toughening due to numerous crack deflections on fine 100 nm subgrains.

Keywords: C. Hardness; Indentation fracture toughness; Boron suboxide; Spark plasma sintering

1. Introduction

Boron suboxide (B_6O) is a lightweight ceramic material with high chemical stability and excellent mechanical properties: an average microhardness of 45 GPa and fracture toughness of 4.5 MPa m^{-2} were reported for monocrystalline samples synthesized by high-pressure synthesis at 5.5 GPa [1]. B_6O powders synthesized at ambient or high-pressures usually possess slightly interior mechanical properties owing to introduction of defects in the covalent B_6O structure, namely the "oxygen deficiency" level (i.e. $x < 1$ in B_6O_x) [2]. Despite its excellent mechanical properties the mass production of B_6O ceramic has not been achieved the poor sinterability of the mass-synthesized powder being the main limiting factor.

For the commercialization of B_6O, a cost-efficient synthesis method should be developed. Furthermore, boron suboxide is difficult to consolidate and requires extreme processing conditions or sintering activation [2–4]. The materials fabricated at high pressure (1–5 GPa) have good hardness but very low fracture toughness (1–2 MPa m^{-2}) [4]. The biggest challenge is to improve the fracture toughness while preserving the high hardness of B_6O-based ceramic; similar to other lightweight boron containing covalent compounds (i.e., B_4C, BN, SiB_6), B_6O is a brittle ceramic.

Solodkyi and coworkers [5–7] proposed a synthesis method for high-quality B_6O powder at ambient pressure using spark plasma sintering (SPS) to consolidate ex situ and in situ synthesized powder. The B_6O ceramics subjected to SPS had a density exceeding 98% of its theoretical value and possessed a Vickers hardness of 37 GPa and fracture toughness of 4.2 MPa m^{-2} [5–7]. Moreover, a recent study of the morphology of boron suboxide powder synthesized at ambient pressure [8] showed that it consists of a large number of distinctive five-pointed star-shaped particles with various single- and multilayer structures. Furthermore, since this boron suboxide powder had a low oxygen deficiency level in its B_6O_x cells (i.e., high x), hardness comparable to that of ceramic tiles synthesized at high pressure is expected for dense specimens. This paper thus focused on the effect of the star-shaped particles on the mechanical properties of

*Corresponding author at: National Institute for Materials Science, 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan. Tel.: +81 80 4144 4747.
E-mail address: oleg.vasylkiv@nims.go.jp (O. Vasylkiv).

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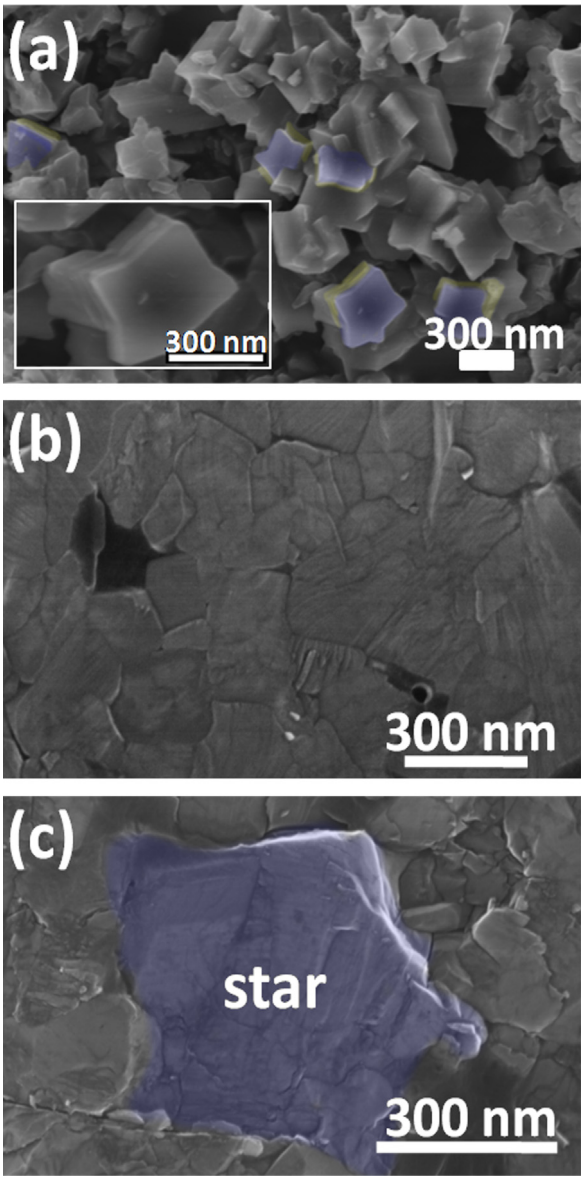

Fig. 1. SEM microstructures of boron suboxide ceramic after SPS consolidation at 1800 °C. (a) Structure of as synthesized B_6O–6:1 powder, (b, c) B_6O–6:1 ceramic after SPS consolidation: (b) polished surface after etching and (c) fracture surface.

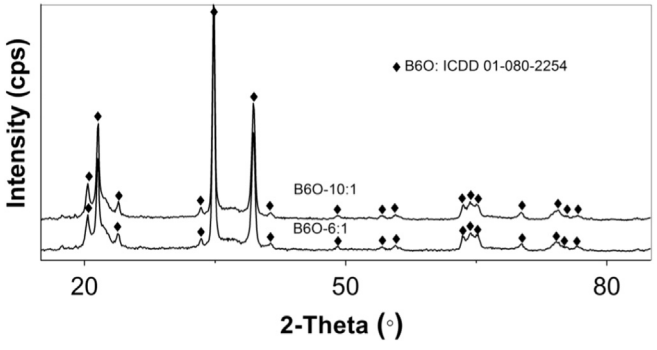

Fig. 2. XRD patterns of boron suboxide ceramics consolidated by SPS. Phases were identified on the basis of ICDD powder diffraction file 01-080-2254.

boron suboxide ceramics consolidated by SPS. The effect of the sharp-edged grains that originate from the star-shaped particles on the indentation fracture toughness and hardness is also a focus of the present study.

2. Materials and methods

Two commercially available powders, amorphous boron (aB, 97%, Wako Pure Chemical Industries, Ltd., Japan) and B_2O_3 powder (99.0%, Kanto Chemical, Japan), were used as the starting materials. The mixing procedure for the B_2O_3 and aB raw powders was the same as that in our previous works [8]. The raw powders were mixed in two mole ratios: aB: B_2O_3 = 10:1 and 6:1. 15 wt% of presynthesized B_6O powder seeds were added to the mixture. According to [8], B_6O powders with different particle morphologies can be synthesized. The B_6O powder synthesized with the aB:B_2O_3 = 10:1 mol ratio (hereafter referred to as B_6O–10:1) had sharp angular edges which, however, did not result in the development of star-shaped multilayer particles [8]. An increase in the boron oxide concentration (aB:B_2O_3 = 6:1, hereafter referred to as B_6O–6:1) in the initial powder mixture led to the growth of B_6O particles on the initial seeds, and the growth of multilayer boron suboxide was initiated.

The synthesized B_6O powder was loaded into a graphite die with inner diameter of 20 mm and subjected to SPS. The outer surface of the die was wrapped in 5-mm-thick graphite felt to homogenize the temperature distribution and reduce heat loss by radiation. To prevent the diffusion of carbon into the powder mixture, tantalum foil (Sigma-Aldrich Chemie, 0.025 mm thick, 99.9 + % metal basis) was inserted between the powder and the graphite foil. The mold system containing the powder mixture was placed in an SPS furnace ('Dr. Sinter' SPS Syntex 1050, Japan). Initially, a pressure of 20 MPa was applied to ensure sufficient electrical contact between the powder tablet and the graphite die, which was then increased to 80 MPa and the temperature was increased to 1700 °C. A dwell time of 1 min at 800 °C was used to focus a side pyrometer on the outer die wall surface. Then we increased the temperature at a rate of 110 °C min^{-1} up to a sintering temperature of 1800 °C with a dwell time of 1 min. Each specimen was gradually cooled to 600 °C at a rate of 100 °C min^{-1} and then naturally to room temperature in the furnace. The sintering process was performed in an argon gas medium with a flow rate of 2 L min^{-1}.

The sintered specimens were ground with diamond disks with a particle sizes of up to 0.5 μm. Microstructural observations and analyses were carried out on mirror-polished sections by scanning electron microscopy (SEM, SU 8000, Hitachi, Japan).

X-ray diffraction (XRD) patterns were taken with a Rigaku Ultima IV (Japan) diffractometer ($Cu_{K\alpha}$ radiation). The intensity data were collected over a 2θ range of 15–85°, in steps of 0.02° with a sampling time of 5 s for each step. Before measurement, the diffractometer was calibrated using Si as an internal standard. The program used for Rietveld refinement was PDXL. The value of x in B_6O_x cell was evaluated by