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Hard and tough boron suboxide based composites

T.C. Shabalala [a], D.S. McLachlan [a], I. Sigalas [b,*], M. Herrmann [c]

[a] School of Physics, University of Witwatersrand, P/Bag 3, Wits, 2050 Johannesburg, South Africa
[b] DST/NRF Centre of Excellence in Strong Materials, and School of Chemical and Metallurgical Engineering, University of Witwatersrand, P/Bag 3, Wits, 2050 Johannesburg, South Africa
[c] Fraunhofer Institute for Ceramic Technologies and Systems, Winterbergstrasse 28, D-01277 Dresden, Germany

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Abstract

Boron suboxide (B_6O) powder was synthesized at temperatures of about 1400 °C from the reaction of amorphous boron powder with boric acid. The synthesized B_6O powders were hot pressed at temperatures up to 1900 °C and at pressures of 50 MPa. Additionally to pure B_6O materials, composites with aluminium were prepared. The microstructure and properties of the sintered compacts were investigated. The addition of aluminium in the composites results in the formation of an additional aluminium borate phase. The composites showed a similar hardness (~30 GPa) as the pure B_6O samples but increased fracture toughness (~3.5 MPa m$^{1/2}$).

Keywords: Hot pressing (A); Toughness and toughening (C); Cutting tools (E); Boron suboxide

1. Introduction

The first laboratory synthesis of diamond triggered extensive efforts to develop materials with a combination of properties approaching or even improving on those of diamond. The best known of these materials is cubic boron nitride (cBN). It is also known that boron rich compounds provide good candidates for this type of materials. They give rise to a large family of refractory materials with unique crystal structures and a range of interesting physical and chemical properties related to their short interatomic bond lengths and their strong covalent bonds [1]. Boron rich phases with a structure based on that of α-rhombohedral boron include boron carbide and boron suboxide (nominally B_6O), which combine high hardness with low density and chemical inertness, making them potentially useful as abrasives and for other high-wear applications [2].

The synthesis of boron suboxide (B_6O) and a description of its properties have been extensively reported in the literature, even though pure material with a high degree of crystallinity is difficult to synthesize. Boron suboxide materials formed at or near ambient pressure are generally oxygen deficient materials. They also have poor crystallinity and very small grain size. High pressure applied during the synthesis of B_6O can significantly increase the crystallinity, oxygen stoichiometry and crystal size of the products [2]. Although boron suboxide is reported as the nominal composition B_6O, it is widely accepted to be non-stoichiometric. For brevity, we use nominal formula B_6O in this investigation.

Recently, a microhardness of 45 GPa (100 g load) was measured for boron suboxide single crystals, which is closely rivaling that of cubic boron nitride [3]. In addition to this hardness, the fracture toughness of this material (B_6O single crystal) was found to be 4.5 MPa m$^{1/2}$. These properties proved that this material (B_6O) is a good candidate for cutting tool and other applications where abrasive wear resistance is a desirable property. Moreover, unlike both diamond and cBN, boron suboxide bulk powders may be produced without the need for high pressures. The above mentioned applications for B_6O have not been realised yet, even though there has been a great deal of research on this material, because the pure B_6O compacts [4] and B_6O composites [5–7] produced so far have low fracture toughness (0.5–1.8 MPa m$^{1/2}$). This paper aims to present

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* Corresponding author at: DST/NRF Centre of Excellence in Strong Materials, School of Chemical and Metallurgical Engineering, University of Witwatersrand, P/Bag 3, Wits, 2050 Johannesburg, South Africa.

E-mail addresses: shabalalat@science.pg.wits.ac.za (T.C. Shabalala), davidsm@sun.ac.za (D.S. McLachlan), iakovos.sigalas@wits.ac.za (I. Sigalas), mathias.herrmann@ikts.fraunhofer.de (M. Herrmann).

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Table 1
Results of the ICP measurement to determine the amount of Al in the coated B_6O powders

Sample	Al (wt%)
Coated B_6O powder 1	2.2
Coated B_6O powder 2	3.7
Coated B_6O powder 3	5.6

the work done on B_6O composites with respectable hardness, and with improved fracture toughness values.

2. Experimental procedure

Two types of B_6O powders were used for the experiments. The one was pure B_6O produced from boric acid and amorphous boron powder, following methods reported in the literature [4–7]. The starting powder B (2 μm) and H_3BO_3 were mixed in the 8:1.03 mole ratio, which is slightly higher than the stoichiometric ratio (8:1). The powder mixture was heated in a tube furnace under flowing Ar at 1380 °C for 6 h. The second type of powder was produced using synthesized B_6O powder. This powder was coated with alumina (in different amounts) using the technique described in patent [8].

To quantify the amount of aluminium on the B_6O grains (second type of powder) chemical analysis was carried out using inductively coupled plasma (ICP) technique. A mixture of hydrofluoric acid (HF) and nitric acid (HNO_3) was used to digest all the coated B_6O powders (0.1 g for each sample). This was done in a microwave oven (power of 1200 W) for 65 min (45 min of heating and 20 min of cooling). The results are given in Table 1 below. The XRD analysis of the samples showed that the phases present on the coated powder were Al_2O_3 and $Al_4B_2O_9$ (traces). The grain sizes of both types of powders were measured using the Mastersizer 2000. The mean particle size of the uncoated and coated powder was 3.5 μm.

The synthesized B_6O and coated B_6O powders were sintered, using a hot pressing furnace (HP20 Thermal Technology) under argon atmosphere, at temperatures of 1700–1900 °C for 20 min, while the applied pressure was kept at 50 MPa. hBN crucibles and graphite dies were used during sintering. The sample diameter was 18 mm.

The synthesized B_6O powder and all other sintered B_6O compacts were analyzed in terms of phase composition using X-ray diffraction, with Cu Kα radiation. Diffractograms were collected over a 2θ range of 10–80°, with a step size of 0.02°. All the microstructure observations were done using scanning electron microscopy (Phillips, XL30 SERIES). The sintered samples were metallographically polished (on the cross-sections) using diamond slurry. Further microstructural analyses were done using optical microscopy as well as transmission electron microscopy (TEM, Phillips CM 20 operating at 200 kV with point-to-point resolution of 0.27 nm and Phillips EM 420 operating at 120 kV). The Vickers hardness (Hv) and the fracture toughness (K_{IC}) were measured using indentation techniques under loads of 1 kg (for pure B_6O sintered samples) and 5 kg (for B_6O composites). The average of five measured hardness or fracture toughness values was used to determine the properties of the B_6O samples. The K_{IC} was measured by using DCM method, using Anstis et al.'s equation [9], with 0.016 as the calibration constant (ξ).

The elastic constants of hot pressed pure B_6O and of the composite B_6O materials with Al content of 2.2 and 5.6 wt% were measured using ultrasonic pulse-echo technique. For the material with Al content of 3.7 wt% Al a linear approximation between the elastic constants was used for the calculation of the fracture toughness.

The procedure in naming the hot pressed (sintered) B_6O materials is as follows, HP17B_6O, HP18B_6O and HP19B_6-O:B_6O samples hot pressed at 1700, 1800 and 1900 °C, respectively. Furthermore, HPB_6O2.2wt% Al, HPB_6O3.7wt% Al and HPB_6O5.7wt% Al:B_6O composites hot pressed (at 1900 °C) containing 2.2, 3.7 and 5.7 wt% Al in secondary phases, respectively. All the samples were hot pressed under an applied load of 50 MPa for 20 min.

3. Results and discussions

3.1. Sintering of pure B_6O powder

Pure B_6O powder was hot pressed at different temperatures between 1700 and 1900 °C. Only hot pressing at 1900 °C produced a nearly dense material which contained no new phases. The properties of the samples are given in Table 2. The fracture toughness of the material could not be determined because the material was very brittle. This was expected as similar results for sintered B_6O compacts had been obtained in the past by other researchers using ultra high pressures [4]. Fig. 1 shows SEM image of a pure sintered B_6O sample (HP19B_6O); the grain size cannot be seen due to the unavailability of a good etchant for this material but some pores (dark spots) are evident. TEM experiments have shown that the grain size of B_6O is in the range of 2–10 μm (see Fig. 2). Fig. 2 also shows that the B_6O samples have defects in their structures.

Table 2
Mechanical properties of hot pressed B_6O materials

Sample name	Density (g/cm^3)	Hv$_5$ (GPa)	K_{IC} (MPa m$^{1/2}$)	Phases (after sintering)
HP17B_6O	1.84	–	–	B_6O
HP18B_6O	2.12	–	–	B_6O
HP19B_6O	2.50	30.1 ± 1.2 (1 kg load)	Brittle	B_6O
HPB_6O2.2 wt% Al	2.52	29.3 ± 0.47	3.11 ± 0.12	B_6O, $Al_4B_2O_9$
HPB_6O3.7 wt% Al	2.45	28.2 ± 1.55	3.23 ± 0.15	B_6O, $Al_4B_2O_9$
HPB_6O5.6 wt% Al	2.51	27.8 ± 1.11	3.37 ± 0.13	B_6O, $Al_4B_2O_9$

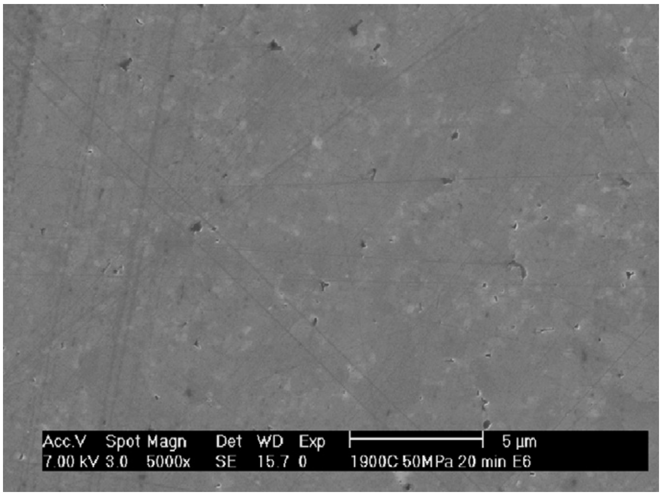

Fig. 1. SEM micrograph for B_6O sintered (HP19B_6O) sample at 1900 °C, for 20 min, with an applied pressure of 50 MPa.

3.2. Sintering of the coated B_6O powders

The coated B_6O powders were only hot pressed at 1900 °C for 20 min at a pressure of 50 MPa. The densities and the mechanical properties of the materials are given in Table 2. Fig. 3 shows the XRD results for the coated B_6O-powder, with an Al content of 5.6 wt%, before and after hot pressing. The main second phase, α-Al_2O_3, in the composite powder changes into $Al_4B_2O_9$ in the hot pressed material. The XRD results for other coated-B_6O samples (i.e. with different aluminium contents) showed similar phases after coating as well as after hot pressing.

The peak at about $2\theta = 16.8^\circ$ in the diffractogram of the sintered powder is strong and quite broad. It must be mentioned that this peak belongs to $Al_4B_2O_9$, as well as other Al_2O_3–B_2O_3 compounds especially $Al_{18}B_4O_{33}$. The composition of the grain boundary phases may as well depend on the amount of alumina in the sample and on the cooling and heat treatment conditions. It is assumed that at the temperatures prevailing in this process, aluminium oxide dissolves in the liquid boron oxide (B_2O_3), present on the surface of the B_6O powder. According to the phase diagram of B_2O_3–Al_2O_3, both $Al_4B_2O_9$ and $Al_{18}B_4O_{33}$ phases appear to crystallize during the cooling of the material from sintering temperature.

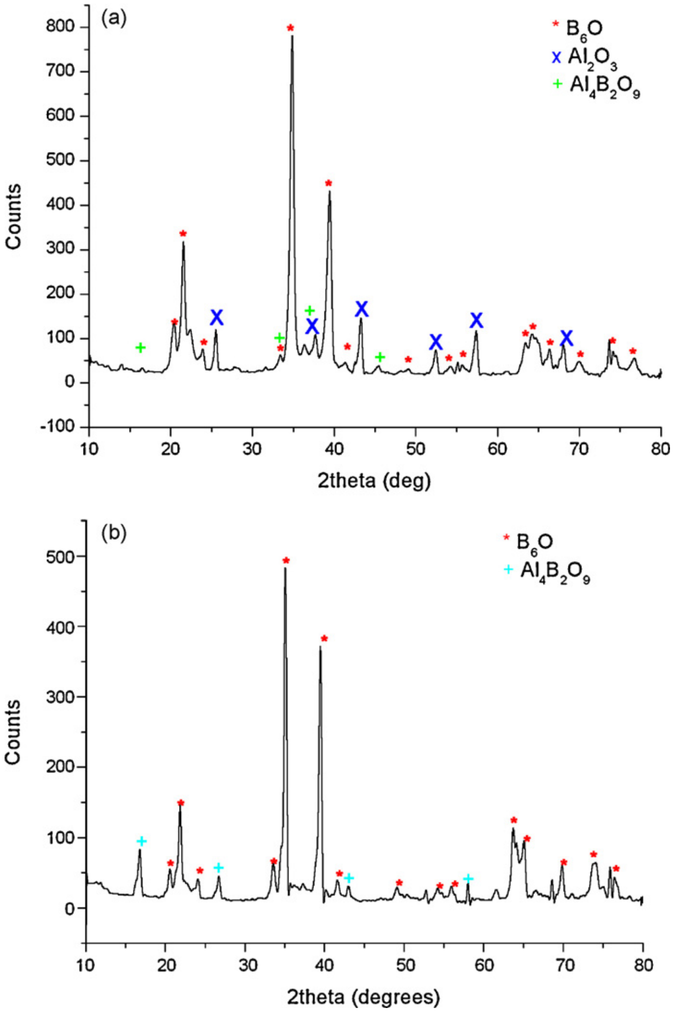

Fig. 3. XRD patterns of B_6O powder with 5.6 wt% Al (a) after coating and (b) after hot pressing at 1900 °C (i.e. HPB_6O5.6wt% Al).

Fig. 4 shows the SEM images for hot pressed B_6O materials (HPB_6O2.2 wt% Al and HPB_6O5.6 wt% Al). The white phase on the micrographs is the aluminium borate phase while the black phase is the boron suboxide phase. The SEM micrographs reveal that the aluminium borate phases are homogeneously distributed and that the samples are nearly dense. TEM investigations (Fig. 5) reveal that there is not much grain growth occurring in these materials. However, some large grains were

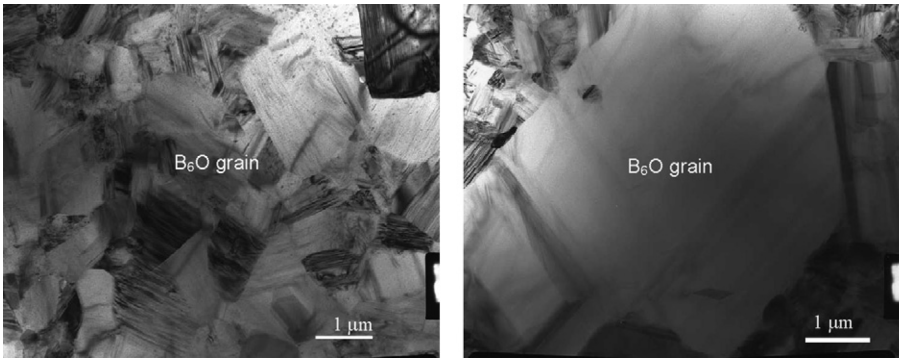

Fig. 2. TEM micrographs for B_6O sintered (HP19B_6O) sample at 1900 °C, for 20 min, with an applied pressure of 50 MPa.

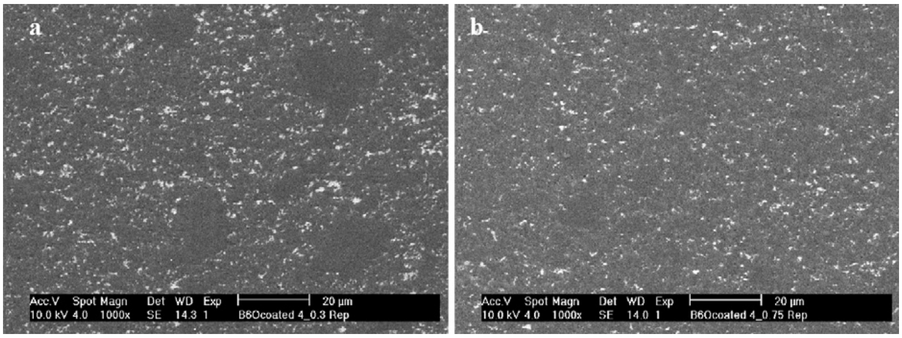

Fig. 4. SEM images of hot pressed B_6O composite materials. (a) $HPB_6O2.2$wt% Al and (b) $HPB_6O5.6$wt% samples.

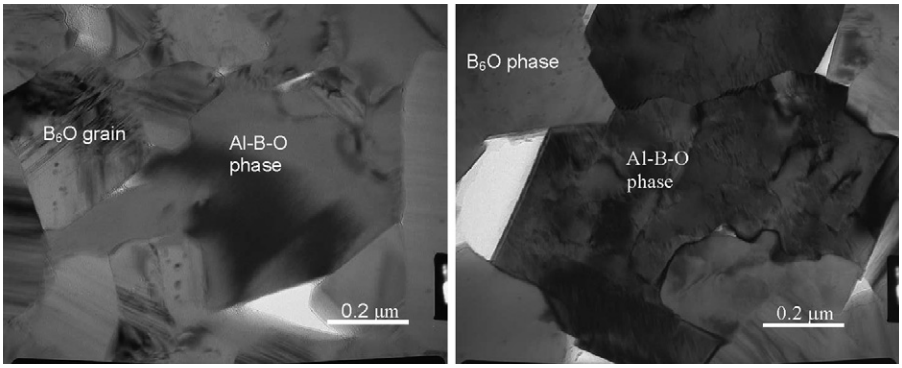

Fig. 5. TEM images of hot pressed B_6O composite material ($HPB_6O5.6$wt% Al) after sintering.

observed, at large Al-free regions in the SEM micrographs. The SEM micrographs indicate that the enhanced grain growth is larger for the material with a lower Al-content.

The elastic constants of the hot pressed B_6O and the composite materials are given in Table 3. These data are a little bit higher than the data found in the literature [10,11]; this may be due to differences in the oxygen content of the synthesized B_6O powder as well as the amount of boron oxide (B_2O_3) present in the samples. The elastic constant values decrease with the addition of Al. This is probably due to the lower elastic modulus of the aluminium borate phases.

The hardness and the fracture toughness of the materials are given in Table 2. With increase in Al content the hardness (Hv) decreases from 29.3 to 27.8 GPa but the fracture toughness increases from 3.1 to 3.4 MPa $m^{1/2}$. This means that the aluminium borate phases that were formed after sintering improve the fracture toughness of the material without degrading the hardness of the materials significantly, as compared to that of pure B_6O materials ($Hv_{0.2}$ = 31–33 GPa [4], $Hv_{0.1}$ = 30–31 GPa [10,11]). A possible mechanism of toughening could be that at the grain boundaries alumina borates are formed instead of pure B_2O_3. Detailed TEM investigations are necessary to determine the nature of the grain boundary phases of the different composites.

Table 3
Elastic properties of hot pressed B_6O and B_6O composites

Material	Elastic modulus *E* (GPa)	Shear modulus (GPa)	Bulk modulus (GPa)
$HP19B_6O$	540	227	300
$HPB_6O2.2$ wt% Al	514	221	255
$HPB_6O3.7$ wt% Al	467	199	240
$HPB_6O5.6$ wt% Al	419	179	214
B_6O [10]	470	206	230
B_6O [11]	483	–	–

4. Summary

A laboratory synthesized B_6O powder was densified using hot pressing techniques at 1900 °C for 20 min, with an applied pressure of 50 MPa, which resulted in a B_6O material with Vickers hardness (1 kg load) of 30 GPa. Higher loads could not be applied due to the brittleness of the material. The Al_2O_3 coated B_6O powders were densified using the same conditions as for the pure B_6O material. This resulted in B_6O materials (composites) with improved fracture toughness with only a slight decrease in hardness. The composite material with the lowest Al_2O_3 content (2.2 wt% Al) had the highest hardness of 29.3 GPa and still a potentially useful fracture toughness of 3 MPa $m^{1/2}$. This fracture toughness of the B_6O composites is better than that of pure B_6O compacts. Further investigations are necessary to clarify the reasons for the improved toughness of the composite materials.

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