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Boron suboxide materials with Co sintering additives

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Abstract

Difficulties in the densification as well as the low fracture toughness of the resulting polycrystalline materials have delayed the application of boron suboxide as a superhard material in industry. In this work, efforts have been made to improve the fracture toughness and densification of these materials by incorporating suitable secondary phases. Possible candidates are transition metals, which form under sintering conditions a liquid phase. Therefore different Co containing additives (metal, oxide and boride) were used to densify boron suboxide powder by hot pressing. The resulting materials have a significantly improved fracture toughness (3.9 MPa $m^{1/2}$) and still high hardness (H_{V5} = 28.6 GPa.).

Keywords: A. Hot pressing; Superhard material; Boron suboxide; Fracture toughness

1. Introduction

Currently, only diamond and cubic boron nitride (cBN) based materials are used in industry as superhard materials [1]. However, the application of diamond and cBN is limited due to the onset of the transformation to graphite and hBN respectively as well as oxidation at high temperatures and their interaction at high temperatures with many metals [1]. Furthermore, the dominant methods for the industrial synthesis of diamond and cBN materials require high pressures and temperatures, which renders their manufacturing expensive and limit the sizes and geometric forms possible [1].

Recent investigations of boron suboxide (B_6O) indicate that it qualifies as a superhard material, having an average Vickers hardness of 45 GPa (100 g load) comparable to that of diamond (H_V = 70–100 GPa) and cubic boron nitride (H_V = 60 GPa) [2,3]. In addition to this hardness, the fracture toughness of B_6O single crystals was found to be 4.5 MPa $m^{1/2}$, which approaches that of single crystal diamond at 5 MPa $m^{1/2}$ [4] and is significantly better than that of single crystal cubic boron nitride at 2.8 MPa $m^{1/2}$ [5]. These properties proved that materials based on B_6O could be good candidates for cutting tool and other applications where abrasive wear resistance is important. Moreover, unlike both diamond and cBN, boron suboxide (B_6O) bulk powders may be produced without the need for high pressures.

Boron suboxide exhibits a similar structure as B_4C having eight B_{12} icosahedral units situated at the vertexes of a rhombohedral unit cell connected via oxygen. It can be synthesized by reducing B_2O_3 with B or by the oxidation of boron with zinc oxide or other oxidants [6–10]. The B_6O powders formed at or near ambient pressure are generally oxygen deficient. However, it was reported that application of high pressure during the synthesis of B_6O can significantly increase oxygen stoichiometry [6–8].

Previous hot pressing studies concerning the densification of boron suboxide powders, made from mixing amorphous boron with boron oxide or with zinc oxide, have produced B_6O materials with densities in the range of 85–97% of theoretical density. These materials were hot pressed either under vacuum or argon at temperatures in the range of 1600–2200 °C. Although, an average Knoop hardness (100 g load) between 30 and 38 GPa was measured, the fracture toughness values were low ($\leq$2 MPa $m^{1/2}$) or not reported [11–15]. Attempts made to improve the fracture toughness by making polycrystalline B_6O through high-pressure high-temperature processes yielded

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hardness ranging from 31 to 38 GPa and fracture toughness less than 1.5 MPa $m^{1/2}$ [3]. Furthermore, composites made via high-pressure techniques with other ultrahard materials such as diamond, boron carbide (B_4C), and cBN yielded fracture toughness values not exceeding 1.8 MPa $m^{1/2}$ [7–9].

Recently it was shown that B_6O materials with the addition of Al_2O_3 and rare earth oxides can be hot pressed or densified by the hot pressing or SPS/FAST technique at 1800–1900 °C. The resulting sintered materials had improved fracture toughness (3–5 MPa $m^{1/2}$) and only a slight reduction in Vickers microhardness (31 GPa under 500 g load) in comparison to pure B_6O materials (34 GPa) [16–18,23,26]. The investigation of the microstructure reveals that the material was densified predominantly by liquid phase sintering. Herrmann et al. [23] have shown that different transition metals can also be suitable sintering additives. Independently if the additives are oxides or metals they will be converted during sintering into borides according to reactions:

$$Co + 0.1875B_6O \rightarrow 0.0625B_2O_{3(l,g)} + CoB \quad (1)$$

$$CoO + 0.3125B_6O \rightarrow 0.4375B_2O_{3(l,g)} + CoB \quad (2)$$

The B_2O_3 formed during the above reactions can remain as B_2O_3 in triple junctions as found in pure B_6O materials [17], or evaporate or can be partially incorporated into the B_6O lattice increasing the stiochiometry. The Co–B phase diagram [19] reveals that cobalt boride would be liquid at temperatures higher than 1460 °C. Therefore it would be expected that Co, and other transition metals like Fe and Ni can be used as sintering additives for liquid phase sintering of B_6O.

This paper aims to investigate the possibility to densify B_6O materials with transition metal additions and to explore the properties of the resulting materials.

2. Experimental procedure

The starting B_6O powder was prepared by the reaction of B with B_2O_3 as described elsewhere [10,16,20]. The powder produced was jet milled up to a grain size of 2.5 μm and then attrition milled for 30 h with 2.5 mm steel balls at a speed of 200 rpm. The mean particle size of the powder was 0.5 μm measured using a Mastersizer 2000 (Malvern Instruments, Germany).

The milled B_6O powder was repeatedly washed in 1 M HCl for 5 days followed by washing in ethanol to remove remaining $H_3B_3O_3$. 0.09 wt% Fe and 0.01 wt% Cr were found as impurities after washing (ICP-OES SPECTRO CIRUS CCD, Spectro analytical Instrument (Pty) Ltd, South Africa).

The B_6O powder was mixed with Co powder (36 μm, Alfa Aesar), CoO (4.3 μm, Alfa Aesar) or Co_2B (620 μm, Alfa Aesar) in methanol for 2 h using the planetary ball mill (Fritsch Pulverisette 6). The mixing speed was kept at 200 rpm, while using 2.5 mm steel balls. After the mixing, the slurry was dried using a rotavap. The iron content in the material under these conditions was less than 0.1 wt%. The mixing procedure was not effective enough, due to the fact that additive agglomerates were found in the final sintered materials. An increase in the intensity of mixing resulted in higher wear of the iron balls. Therefore, additionally, B_6O was mixed with Co using a precipitation method, which involves the precipitation of $Co(OH)_2$ on the surface of B_6O using the reaction of $Co(NO_3)_2{\cdot}6H_2O$ and alkaline solutions. The CoO was then reduced in an H_2/Ar atmosphere at 800 °C.

Pure B_6O materials were hot pressed (HP20 Thermal Technology) in hBN-lined-graphite dies in argon at 1900 °C and a pressure of 50 MPa for 20 min, while the powders with additives were sintered at 1850 °C at the same pressure and isothermal sintering time. Hot pressed samples were 18 mm in diameter and 3–4 mm in thickness. The pure B_6O powder densified at 1850 °C had shown only a density of less than 90% theoretical density.

After sintering the materials were ground to clean their surface from reaction products with the hBN lining. The density of the samples was determined using Archimedes principle. Cross-sections of the materials were polished using diamond slurry and were characterized using X-ray diffraction (PW1830; Philips; Cu Kα radiation, 2θ range: 10–80°, step size 0.02°).

Microstructure observations were carried out using scanning electron microscopy (Philips, XL30 SERIES) with attached EDX system. TEM characterization was performed on the material containing precipitated Co. TEM foil preparation followed standard ceramographic techniques, including cutting, grinding, polishing and dimpling down to 10 μm. The dimpled discs were ion beam thinned with a Gatan Duo Mill 600 in two steps to electron transparency. During the first step, the acceleration voltage was set to 5 kV and the angle of incidence to 15°. This condition was maintained until the first transparent area was observed under an optical microscope. Then, the acceleration voltage was lowered to 2.5 kV and the angle of incidence to 12°.

The thinned samples were lightly coated with carbon (Edwards Auto 306) to minimize charging under the incident electron beam. TEM characterization was performed with a FEI CM20 microscope (FEI, Eindhoven, Netherlands) operating at 200 kV.

The Vickers hardness (H_V) and fracture toughness (K_{IC}) were measured using indentation techniques under loads of 1 kg (for pure B_6O sintered sample) and 5 kg (for B_6O materials). The average of five measurements was used to determine the properties of the samples. The K_{IC} was determined via the direct crack measurement method using Anstis's equation [21], with the calibration constant $\xi = 0.016$ and elastic constant $E = 470$ GPa [22].

3. Results

The densities and properties of the materials are given in Table 1. The B_6O material hot pressed without additives at temperature of 1900 °C resulted in a material having 96.5% of the theoretical density. Phase analysis of the sintered pure B_6O sample reveals only B_6O. The Vickers hardness of this sample was 30.2 GPa measured using 1 kg load. Higher load caused fracturing. Hence, the fracture toughness of this material could

Table 1
Compositions, density and mechanical properties of hot pressed B_6O materials.

Sintered material	Additive content (wt %)	Volume content of boride (vol.%)	Density (g/cm^3)	Open porosity (%)	H_{V5} (GPa)	K_{IC} (MPa m$^{1/2}$)
B_6O	–		2.46	3.7	30.2 ± 1.0[a]	–
B_6O + Co[b]	1.33	0.54	2.53	1.2	24.8 ± 0.9	3.2 ± 0.5
B_6O + Co[c]	3.41	1.44	2.56	0.7	28.6 ± 1.1	3.9 ± 0.4
B_6O + CoO	2.70	0.88	2.55	1.6	23.6 ± 0.8	3.4 ± 0.6
B_6O + Co_2B	2.10	0.80	2.51	1.5	25.6 ± 0.4	3.9 ± 0.1

[a] H_{V1}.
[b] Admixed powder.
[c] Coated powder.

not be determined. This agrees with the result presented by other researchers using ultra-high pressures [7–9].

The density of all materials containing additives was more than 96% theoretical density. The theoretical densities of hot pressed materials were calculated on the basis of the rule of mixtures of the phases formed. The value 2.55 g/cm^3 was used as the theoretical density of B_6O. It was assumed that all additives in the powder completely transformed to their respective secondary phase after sintering. The microstructures (Fig. 1) reveal an even lower porosity. This could be caused by the uncertainty of the determination of the theoretical density. This density depends on the stiochiometry of B_6O and the amount of remaining B_2O_3. Both factors cannot be easily determined with a high enough accuracy.

The densities obtained were higher than those of pure B_6O hot pressed at 1900 °C, despite the lower hot pressing temperature of these materials. XRD pattern of the densified materials showed the formation of CoB as a secondary phase by the additives [23]. In the materials, borides are formed independently if cobalt metal, oxide or boride was added [23]. This means that the boride is in equilibrium with B_6O, and is liquid under the sintering conditions thus being able to accelerate the sintering process. The formation of CoB was also confirmed by electron beam diffraction by TEM (Fig. 2). SEM images of these materials are shown in Fig. 1. The dark area represents B_6O and the white area represents the cobalt boride secondary phase.

The distribution of the boride phase is similar for both the near surface and the centre of the samples. Homogeneity of the CoB within the B_6O matrix varies with the type of Co additive that was used. The best distribution of the CoB phase was found in the sample with oxide addition and with the chemical precipitation of Co while the least was in the material to the initial Co boride additive. As indicated before this inhomogeneity is mostly connected with the imperfect mixing of the additives due to the large grain sizes of the starting Co_2B (d_{50}:

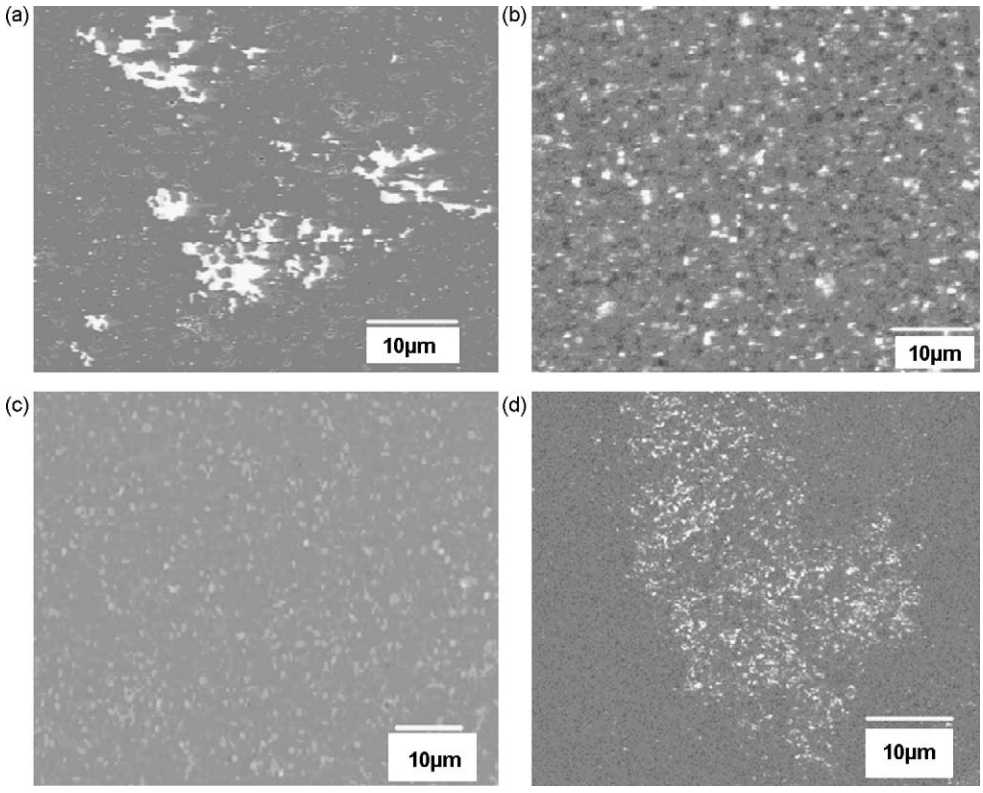

Fig. 1. SEM micrographs of the polished surfaces of B_6O materials: (a) B_6O + Co (admixed); (b) B_6O + Co; (coated) (c) B_6O + CoO; (d) B_6O + Co_2B.

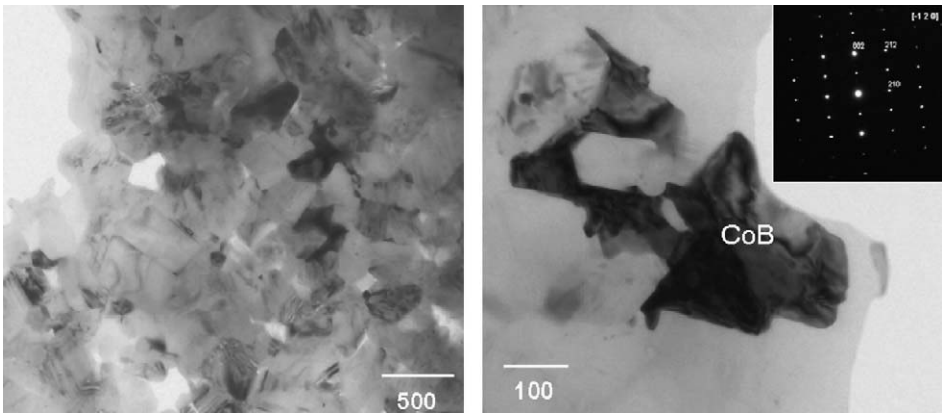

Fig. 2. TEM micrographs of B_6O material with Co additive (B_6O + Co (b)) the b shows the diffraction pattern observed from the CoB phase revealing the formation of CoB.

620 μm) and Co-powders (d_{50}: 36 μm). The homogeneous distribution of the Co boride phase in the material precipitated and the material with CoO reveal that the reason for segregations of the Co phase can not be caused by the wettability of B_6O by the second phase present during sintering.

The data in Table 1 reveal that the addition of cobalt containing additives caused an improvement in the fracture toughness of the material up to values of 3.9 MPa $m^{1/2}$ and only a moderate reduction of the hardness values.

4. Discussion

The density of B_6O materials as a function of the additives used is shown in Fig. 3. Due to the uncertainties in the determination of the theoretical density these values are the lower limit. The SEM micrographs show even lower porosity revealing densities of about 98–99%.

The B_6O materials with sintering additives showed higher density in comparison with the pure B_6O material despite the fact that the sintering temperature of these materials was 50 °C lower.

The lowest density of the materials with Co additives was measured for the material with the initial CoB addition. This material exhibits also the most inhomogeneous distribution of the additives.

The data therefore reveals that the use of Co, CoO and CoB as sintering additives resulted in improved sintering behavior. The reason for the improved sintering is the formation of a stable B–Co containing liquid phase at temperatures above 1460 °C, in which B_6O partially dissolves allowing the liquid phase sintering process to take place. The existence of solution precipitation processes are also supported by the formation of well facetted B_6O grains surrounded by the CoB phase (Fig. 2). During cooling the boride liquid crystallizes as CoB phase in triple junctions as shown by XRD and by diffraction of the electron beam in the TEM (Fig. 2).

The Vickers hardness of the hot pressed B_6O material without additives yielded a value of 30.2 ± 1.0 GPa using a load of 1 kg. This value is comparable with the data in the literature (31–33 GPa, 200 g load) [3] at high-pressure materials, 34.8 GPa by Shabalala [22], 38 GPa (100 g load) by Holcombe and Ottis [24] considering the higher load used in this investigation.

The hardness of the composites is slightly lower to that of the pure B_6O materials. This is mostly caused by the lower hardness of the CoB phase.

In this study, the addition of cobalt containing additives produced materials with improved fracture toughness comparable to that of the materials with mixed oxide additions [18,22]. Fig. 4 shows SEM image of the crack path in the hot pressed B_6O material with Co addition. The image reveals some crack

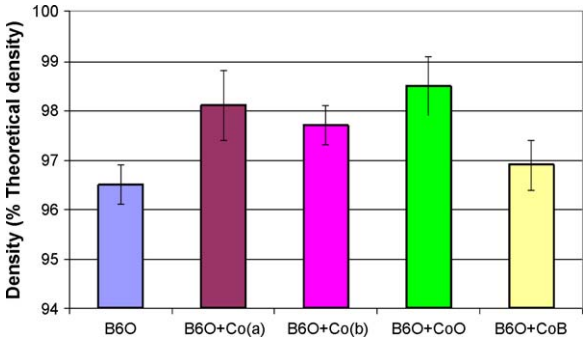

Fig. 3. Density of B_6O materials as a function of the theoretical density.

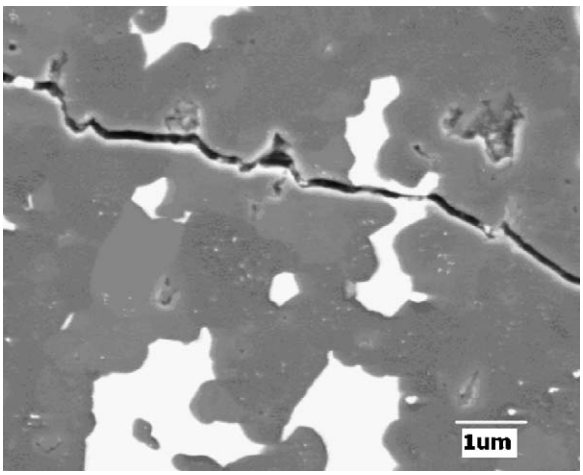

Fig. 4. SEM micrograph of some polished surfaces (with crack induced by the Vickers indentation) of B_6O sintered materials B_6O + Co (admixed).

deflection. However no direct influence due to the boride phase can be seen. Although the mechanism of fracture toughness improvement is not completely clear, it could be connected with the formation of internal stresses due to different coefficients of thermal expansion, CTE ($\alpha_{B_6O} = 5.5 \times 10^{-6}/^{\circ}C^{-1}$ [12] and $\alpha_{CoB} = 7.24 \times 10^{-6}/^{\circ}C^{-1}$ [25]) resulting in changed fracture modes; however a pronounced crack deflection was not observed.

5. Conclusion

B_6O materials with cobalt containing additives were hot pressed at 1850 °C to more than 96% theoretical density. In all compositions CoB as a secondary phase was observed independent on the starting additive (metal, oxide or boride). This is in agreement with the thermodynamic calculations [23]. The analysis of the phases and the microstructure reveal that in these materials liquid phase sintering takes place. The results are the first evidence that B_6O can be sintered by liquid phase sintering in a boride as sintering additive. Similar behavior can be expected using other transition metals like Ni Fe [20,27]. Fracture toughness as high as 3.9 MPa $m^{1/2}$ and a corresponding hardness (H_{V5}) of 28.6 GPa were obtained for the B_6O + Co material. The mechanisms of the significant improvement in the fracture toughness in comparison to the pure B_6O material are not completely clear and need further investigation.

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