Mechanical Properties of Hot-pressed Boron Suboxide with Chromium Boride Additive

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Abstract— **This study investigated and compared the mechanical properties of boron suboxide (B_6O) with and without chromium bromide (CrB_2) additive, hot pressed at 1900^oC and 1850^oC and for 20 minutes, with applied pressures of 50 and 80 MPa respectively. The theoretical density attained for these materials was More than 96%. The phase relationship, microstructures and mechanical properties of these materials were examined and good combination of mechanical properties was obtained with the B_6O-CrB_2 material (HV 32.1 GPa, K_{IC} 4.5 $MPa.m^{0.5}$) compared to pure B_6O material. Mixing with a small amount (1.7 wt.%, equivalent of 0.4 vol.%) of CrB_2 additive resulted in a pronounced improvement in both the hardness and fracture toughness values. The improvement in the fracture toughness was attributed to the introduction of the second phase and the toughening mechanism is presumed to be by crack bridging and deflection due to bimetallic stress.**

Keywords — Boron suboxide, chromium boride, fracture toughness, hardness, hot isostatic pressing.

I. INTRODUCTION

CONSIDERABLE fundamental and technological interests have been a great challenge in recent times to the synthesis of new materials with hardness comparable to or even harder than that of diamond [1].

Diamond and cubic boron nitride (cBN) combine excellent mechanical, chemical, and physical properties. Diamond cannot be however used as a cutting tool for steel, due to its chemical interaction with that metal at high temperatures. cBN attributes of great hardness and abrasion resistance, coupled with a higher chemical stability than diamond when in contact with ferrous alloys, can be used to machine both steel and cast iron. However, increase in temperature weakens cBN due to diffusion wear and transformation to its hexagonal structure (hBN) [1].

In addition, both materials also require high pressures and temperatures for their synthesis, which make their production expensive and limit the sizes and geometric forms possible. For this reason and because of the need to replace expensive diamond in many applications, new hard materials with comparable or even superior properties are required.

Boron suboxide (nominally B_6O) is the third hardest material with the hardness values between 31 to 38 GPa, after diamond (HV: 70–100 GPa) and cBN (HV: 60 GPa) [2–9]. Its single crystal can have a hardness of 45 GPa and with abrading properties compared to those of diamond. In addition to this hardness, its fracture toughness has been reported to be 4.5 $MPa.m^{0.5}$ [10, 12], approaching that of single crystal of diamond at 5 $MPa.m^{0.5}$ and significantly better than that of a single crystal of cBN at 2.8 $MPa.m^{0.5}$ [11]. B_6O has a better thermal stability compared to that of diamond [10, 12] and can be produced at lower pressure [13–16]. All these properties suggest that B_6O may be a good candidate for cutting tool and other wear part applications where abrasive wear resistance is important.

The development of thermodynamic data for B_6O at elevated temperatures has allowed the prediction of the stability and crystalline phases in B_6O composites [17]. This suggests that a careful selection of additives with controlled sintering conditions can result in a production of B_6O materials with unique combination of mechanical properties for industrial applications. In order to achieve a complete densification, high pressures between 1–5 GPa are usually required, but the resulting fracture toughness does not exceed 2 $MPam^{0.5}$ [18–19]. Several attempts have been made to improve on the fracture toughness of B_6O through the addition of different materials.

B_6O-composite made via high-pressure technique with the addition of materials such as diamond, boron carbide and cBN yielded a fracture toughness of 1.8 $MPa.m^{0.5}$ [3–4, 7]. The addition of Al_2O_3 has been reported to increase the fracture toughness to a value of 3.1 $MPa.m^{0.5}$ but with a slight reduction in hardness in comparison to pure B_6O material [13–14, 17]. The addition of different cobalt containing additives resulted in a fracture toughness of between 3.2 – 3.9 $MPa.m^{0.5}$ [15], and recently, B_6O materials with different amount of rare-earth oxide additives reported a fracture toughness between 3.9 – 5.6 $MPa.m^{0.5}$ [16].

Although B_6O can be cost effectively synthesized at ambient pressure with enhanced properties [13–17], its commercial use is actually prevented by its poor sinterability (due to low diffusion coefficients and a high vapour pressure) and low fracture toughness of polycrystalline materials. A good understanding of the role of sintering additives on the sintering behaviour and the

resulting microstructures is essential for specific tailoring and optimization of the physical properties of B_6O materials. Therefore, in this study, B_6O materials containing chromium boride additive was prepared by hot isostatic pressing (HIP) and the densification, the phase and microstructural transformation correlated with the resulting mechanical properties and compared with that of pure B_6O material.

II. METHODOLOGY

The B_6O powder used in this study was produced from the reaction of boric acid and amorphous boron powder described elsewhere [6, 20–21]. An excess amount (3 mol. %) of boric acid was added to compensate for the evaporation of B_2O_3 that occurred during synthesis. The mixture was heated in a furnace under argon at 1380^oC for 5 hours. The powder, (3 μm particle size) produced and supplied by IKTS – Dresden, Germany produced was crushed and then milled for 20 hours in an attrition mill at 400 rpm using steel balls (2.5 mm diameter), with propan-2-ol as a grinding media to reduce ball wear. The charge to ball ratio was kept at 3:1. The weight of the balls was measured before and after milling to determine weight loss during milling.

The mean particle size of the milled powder was 0.5 μm measured using a Mastersizer 2000 (Malvern Instruments, Germany). Washing of the milled B_6O powders was done in 1 M HCl for 3 days followed by washing in ethanol and warm methanol to remove any B_2O_3 remaining resulting from milling operation. Chemical analysis by an inductively coupled plasma optical emission spectrometry (ICP-OES SPECTRO CIRUS CCD), revealed that minor impurities of Fe (0.06 wt.%) and Cr (0.04 wt.%) were introduced through the milling operation. The washed B_6O powder was thereafter mixed with 1.7 wt.% chromium boride (CrB_2) in methanol for 2 hours using the planetary ball mill (Fritsch Pulversette 6). The mixing speed was kept at 200 rpm, while using 2.5 mm steel ball as the media. After the mixing, the slurry was dried using a rotavap, and then characterized using X-Ray diffraction (XRD), to identify the phases present and SEM to examine the homogeneity of the admixed powder.

Sintering and densification of the materials was done by hot-isostatic pressing (HIP) using a uniaxial hot press HP20 Thermal Technology, (Thermal Technology Industries, USA) in a hexagonal boron nitride (hBN) crucible. For pure B_6O, the furnace was heated to 1700^oC at 15^oC/min and held at this temperature for 20 minutes, the applied pressure was increased gradually to 30 MPa at this temperature, after which the temperature was increased at a rate of 10^oC/min to 1900^oC. The holding time at 1900^oC was 20 minutes during which time the applied pressure was kept constant at 50 MPa. The furnace was then cooled to room temperature at 20^oC/min.

For the B_6O-CrB_2 material, the furnace was heated to 1400^oC at 20^oC/min and held at this temperature for 5 minutes, to apply a load of 80 MPa (this load was maintained throughout the hot pressing). The furnace was further heated to 1850^oC (sintering temperature) at 20^oC/min and held at this temperature for 20 minutes. The furnace was then cooled to room temperature at 20^oC/min. The sintered samples were 18 mm in diameter and between 3 – 4 mm thick.

After sintering, the samples produced were surface grounded to remove hBN and also any decomposed layer. The density of the densified samples was determined by the Archimedes method and compared with theoretical densities, which were estimated on the basis of the rule of mixture using 2.55 g/cm^3 for B_6O and 4.24 g/cm^3 for CrB_2. The cross-sections of all materials were prepared by polishing with diamond suspensions and characterized for phase analysis using X-ray diffraction (XRD) a Philips PW 1713 fitted with a monochromatic Cu Kα radiation set at 40 kV and 20 mA in the 2Θ range of $10 – 90^o$, and the phase identification was performed with X'Pert HighScore, while the microstructural changes were investigated using an environmental scanning electron microscope (Philips ESEM XL30) equipped with energy dispersive X-ray spectrometer (EDX) for various elemental compositions present in the materials.

For all the materials prepared, the hardness (HV) was measured by the indentation technique using a LECO V-100-A2 Vickers Hardness Tester machine, with a load of 1 kg for pure B_6O, and 5 kg for B_6O-CrB_2 sintered sample. The fracture toughness (K_{1C}) of the hot pressed samples was determined using the direct crack measurement using the Antis' equation [22], with the calibration constant ξ =0.016 and elastic constant E = 470 GPa [23]. The average hardness, fracture toughness and the standard deviation were calculated on the basis of measuring five indentations.

III. RESULTS

The B_6O powder hot pressed at temperature of 1900^oC and pressure of 50 MPa for 20 minutes resulted to a nearly dense sample having 96.5% of the theoretical density, while the B_6O-CrB_2 sample hot pressed at 1850^oC and pressure of 80 MPa showed 98.4% density of the calculated theoretical values. Some quantifiable amounts of the remaining porosity present in both sintered samples is between 1 and 1.4 %, respectively. In comparison to the sintering behavior of pure B_6O sample, the small amounts of CrB_2 sintering additive significantly promoted the densification. Whereas the densification of pure B_6O started at about 1700^oC, the onset of pronounced sintering was reduced to about 1400^oC for the B_6O-CrB_2 sample. Hence, the addition of CrB_2 additive improved the densification rate and lowered the sintering temperature required for good densification from 1900^oC for pure B_6O to about 1400^oC.

Figure 1(a & b) shows the XRD pattern of the hot pressed B_6O samples with and without CrB_2. XRD pattern for the hot pressed pure B_6O sample showed a reduction in the width of the peaks and increased crystallinity during hot pressing (Figure 1a). For the B_6O-CrB_2 sample, the XRD patterns revealed that CrB_2 crystalline grain boundary phase was retained beside B_6O in the material (Figure 1b). There is no evidence in the variation of lattice constants for both B_6O and CrB_2 in the hot pressed sample, which suggests neither formation of solid solution nor new compound under the sintering conditions employed.

Figure 2 shows the SEM images of the hot pressed materials with their respective EDX analyses. No evidence of any other material was present in the pure B_6O material as evidenced in Figure 2(a & b). There are evidences of inhomogeneous distribution of the secondary phase in the B_6O-CrB_2 sample (Figure 2c). EDX analyses revealed that

the sintered sample has two phases (B_6O and CrB_2) (Figure 2d). These analyses agrees with the results obtained from the XRD patterns. There are no differences in the distribution of the additives between the center and the near surface area of the sintered materials. Although the microstructural investigations of cross-sections by electron microscope showed a good densification for both samples (Figure 2(a & c)), however, some amount of porosity were observed at higher magnifications. The pores retained in the samples can be attributed to the decomposition at the sintering temperature and/or pull-out of the softer secondary phase during grinding of the material.
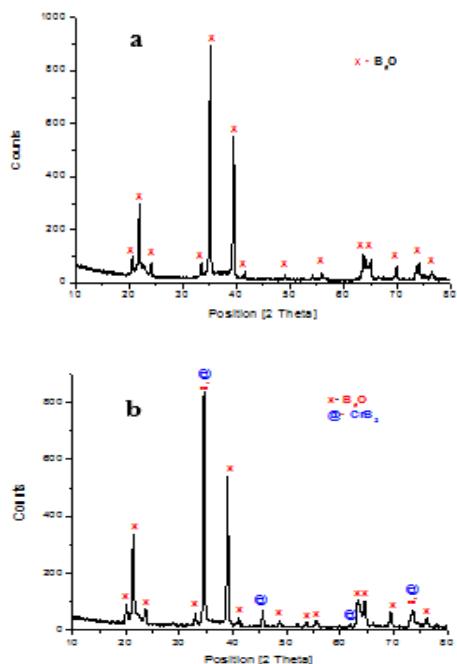

Figure 1 XRD pattern of hot pressed (a) B_6O, and (b) B_6O-CrB_2 material.

The Vickers hardness value obtained for the pure B_6O sample in this study (Table 1), shows good agreement with those of other researchers using ultra-high pressure [2–4, 7]. At a load of 1 kg, the pure B_6O sample fractured. Hence, the fracture toughness could not be determined and so the material was considered brittle. The Vickers hardness value of the B_6O-CrB_2 (32.1 GPa) material shows a slight increase compared to that of the pure B_6O (30.5 GPa), which could have been as a result of the change in the load applied. The CrB_2 clusters were seen to form around the B_6O grains, therefore the hardness values obtained in this area was low while the fracture toughness was high. At higher magnification no grain growth was observed in the hot pressed material. The addition of CrB_2 to B_6O powder resulted in a significant improvement in the fracture toughness considering the brittleness of the pure B_6O material.

IV. DISCUSSION

B_6O powders hot pressed either under vacuum or argon conditions at temperatures in the range of 1600–1900°C, have produced B_6O samples with densities in the range of 85-97% of the theoretical density [5, 23–25]. Table 1 shows

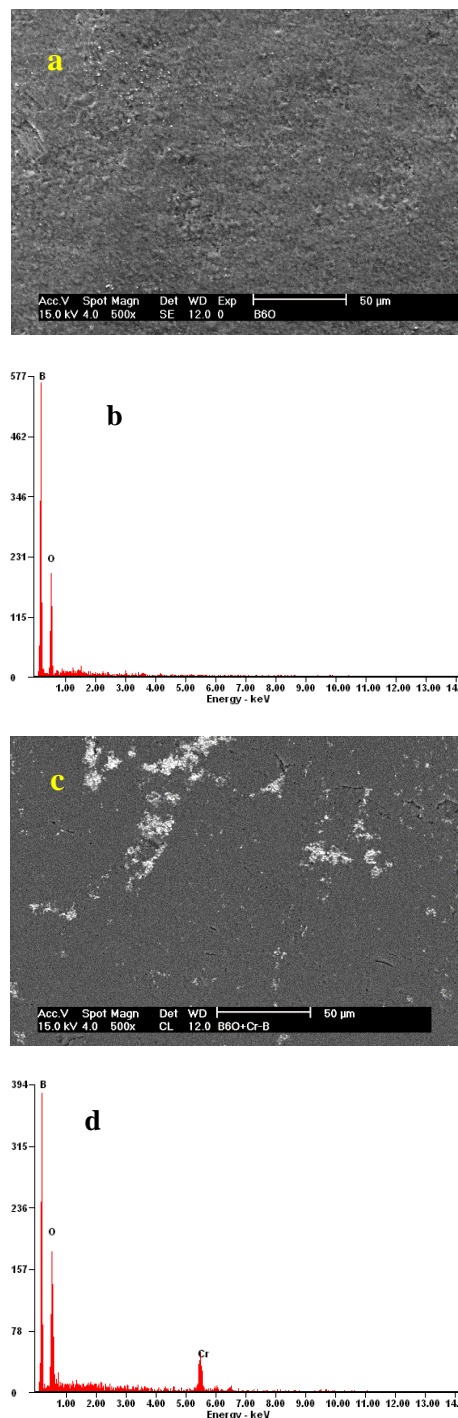the summary of the resulting properties of the sintered materials.

Figure 2 SEM images of hot pressed (a) B_6O, (b) EDX of (a), (c) SEM image of B_6O-CrB_2 and (d) EDX of (c).

This study produced a density of 2.45 g/cm^3 for pure B_6O sample, which was 96.1% of the theoretical density. The amount of porosity measured in the hot pressed B_6O samples in this work is very low compared to the others. The SEM image of the hot pressed B_6O sample Figure 2(a) at higher magnifications, reveals some small holes representing pores. This could have resulted from the small amount of B_2O_3, which may have volatilized at high temperatures (partly acting as the source of small pores) and/or could have been caused by the removal of the remaining B_2O_3 during polishing or due to bad polishing.

The theoretical density of B_2O_3 is 2.46 g/cm^3, which is less than that of B_6O (2.55 g/cm^3); therefore a small amount of B_2O_3 in the material will lower the overall theoretical density of a hot pressed B_6O and hence, the density could not attain a 100% theoretical.

Table 1 Properties of hot pressed samples

Sintered material	Additive weight (%)	Density (g/cm^3)	Open porosity (%)	HV (GPa)	K_{IC} (MPa.m$^{0.5}$)
Pure B_6O	-	2.45	0.9	30.5 ± 2.1[a]	Brittle
B_6O-CrB_2	1.7	2.51	1.4	32.1 ± 1.6[b]	4.5 ± 0.4

[a] – hardness measured at 1 kg; [b] – hardness measured at 5 kg.

The addition of 1.7 wt% of CrB_2 additive improved the densification of the B_6O powders in comparison to the pure B_6O powder. Figure 3 shows a typical phase diagram of the Cr-B system [26]. The type of CrB_2 formed was identified with the XRD pattern shown in Figure 1(b), which gives an indication of the composition under consideration (arrow in Figure 3). From the phase diagram, at 1850°C there will not be any liquid present in the material at sintering temperature. Nevertheless, there is some level of solubility of B_6O in the system resulting in the formation of transient liquid or it could be that the composition is not pure CrB_2 and therefore a liquid is formed which lowers the melting point in this system, creating enough liquid for densification to occur via liquid phase sintering.

A good combination of hardness (32.1 GPa) and fracture toughness (4.5 MPam$^{0.5}$) was obtained when 1.7 wt.% CrB_2 was hot pressed with B_6O. CrB_2 clusters was formed at the grain boundaries and it is believed that the grain boundary composition increased the toughness of this material. The difference between the thermal expansion coefficients of the B_6O matrix and the CrB_2 secondary phase induces a tangential compressive stress near the particle/matrix interface and diverts the crack around the particle, thus making the material tough. Figure 4 shows the examples of the crack paths in B_6O-CrB_2 hot pressed material.
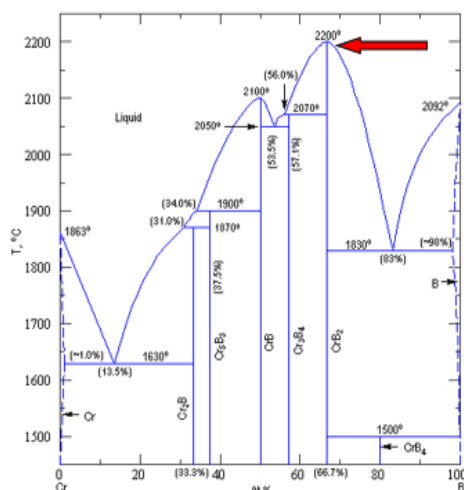

Figure 3 Phase diagram of Cr-B system (ACerS-NIST phase equilibrium diagram, figure 08865a). The arrow represents the composite under consideration [26].

The effect of residual stresses on fracture toughness that resulted from the mismatch between the thermal expansion coefficients of the two components in ceramic materials has been reported in the literatures [27–28, 30–32]. The residual stress between B_6O and CrB_2 is estimated, using equations 1 from [28, 30], to be between 571–751 MPa, assuming the change in temperature is about 1000°C.

$$\sigma = \left(\frac{(\Delta\alpha.\Delta T)}{[(1+v_m)/2E_m + (1-2v_s)/E_s]} \right) \quad (1)$$

Where:

$\Delta\alpha$ = Difference in thermal expansion coefficient between B_6O (α_{B6O} = 5.5×10^{-6} / ^{o}C^{-1} [5, 24] and the secondary phase, CrB_2 (α_{B6O} = 7.8×10^{-6} / ^{o}C^{-1} [29]).

ΔT = Change in temperature at which sufficient softening occurs to alleviate the stresses (~1000°C)

$v_{m,s}$ = Poison ratios [B_6O = 0.197; $CrB_{2=}$ 0.2–0.3]

$E_{m,s}$ = Elastic moduli [B_6O = 540 GPa; CrB_2 = 211.04 GPa].

This differences also induces stresses in the final material thus preventing crack propagation. The fracture toughness enhancement via this mechanism is very common in ceramic materials. The reason for the increase in fracture toughness could also be due to many reasons such as crack bridging and crack deflection due to bimetallic stresses, or due to crack arrest in the secondary phase, or due to the solidification of the grain boundaries between B_6O particles being present as films or by many other mechanisms. Both of these crack-path modification mechanisms would give rise to an increase in fracture toughness. The CrB_2 additives used had the potential of removing the B_2O_3 present at the surfaces of B_6O particles by forming other phases that cause bimetallic strain toughening at the grain boundaries.
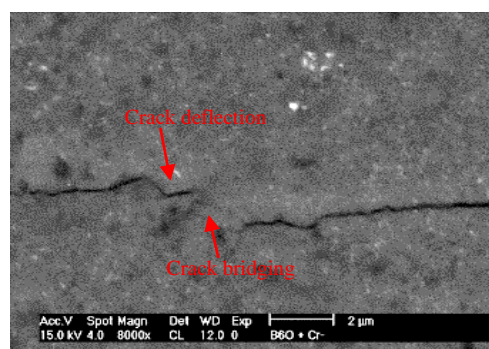

Figure 4 Indentation crack paths on the hot pressed B_6O-CrB_2 material.

V. CONCLUSIONS

In conclusion, the materials developed in this study are promising candidates for a new class of liquid phase sintered materials produced without ultrahigh pressure. B_6O with and without CrB_2 additive was successfully hot pressed at 1900°C and 1850°C for 20 minutes, with an applied pressure

of 50 and 80 MPa respectively. More than 96% of the theoretical density was attained for these materials. The phase relationship, microstructures and mechanical properties were examined and good combination of mechanical properties was obtained. Mixing with even a small amount of CrB_2 additive resulted in a pronounced improvement in both the hardness and fracture toughness values. The improvement in the fracture toughness was attributed to the introduction of the second phase and the toughening mechanism is presumed to be by crack bridging and deflection due to bimetallic stress.

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