

Boron Suboxide Materials with Rare-earth Metal Oxide Additives

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Abstract — The basis of this study is that the mechanical properties of Boron suboxide (B_6O) materials, especially fracture toughness are greatly influenced by the composition of the grain boundary phase and the grain size of the phases in the sintered material. Therefore, in this work, effort has been directed towards improving the fracture toughness and densification of this material by incorporating potential rare-earth oxide phases and tailoring the microstructure to the desired properties. Boron suboxide (B_6O) powder was synthesized from the reaction of amorphous boron and boric acid powders. The powder was hot pressed at 1900 °C and 50 MPa. Additionally to pure sintered B_6O , materials with rare-earth oxides were prepared at 1850 °C. The microstructure, phase composition and properties were investigated. More than 95% of the theoretical density was attained and fracture toughness up to $5.6 \pm 0.2 \text{ MPa}\cdot\text{m}^{1/2}$ was obtained for the materials. Although the pure B_6O sample was brittle, fracture toughness was strongly improved in the materials.

Index Terms— Boron suboxide, Rare-earth oxide, Mechanical properties, Fracture toughness.

I. INTRODUCTION

SUPERHARD materials are always required in modern technology because of their high hardness and mechanical/ chemical stability particularly when used as cutting tools, dies, molds or protective coatings. The higher the mechanical properties of the work piece materials become, the harder the tools for cutting them should be [1]. This relationship accelerates the demand to develop new superhard materials, which can be used under severe working conditions at high cutting speeds, high temperatures and highly corrosive environments. An ideal cutting material combines high hardness with good toughness and chemical stability. In particular hardness and toughness represent opposing properties and there is no single cutting material, which achieves all three conditions simultaneously [2], [3].

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Recent investigation of B_6O indicates that it qualifies as a superhard phase, having an average Vickers hardness of 45 GPa (100g load) comparable to that of diamond ($V= 70\text{-}100$ GPa) and cubic boron nitride ($V= 60$ GPa) [4], [5]. In addition to this hardness, the fracture toughness of this material (B_6O single crystal) was found to be $4.5 \text{ MPa}\cdot\text{m}^{1/2}$, which approaches that of single crystal diamond at $5 \text{ MPa}\cdot\text{m}^{1/2}$ [6] and is significantly better than that of single crystal cubic boron nitride at $2.8 \text{ MPa}\cdot\text{m}^{1/2}$ [7]. These properties proved that materials on the basis of B_6O could be good candidate for cutting tools 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. The combination of high hardness and the possibility of cheaper cost of production are the reason why B_6O could be an interesting material for wear application.

However, it is very difficult to sinter B_6O powders to full density, and an adequate sintering agent has not been found. Hot pressed B_6O materials have not produced a combination of good mechanical properties, with hardness values between 30 and 38 GPa [8]-[10] but the fracture toughness measurements were not reported. Efforts have been made to increase the fracture toughness by forming B_6O composites via high-pressure techniques with other ultrahard materials such as diamond, boron carbide (B_4C), and cBN [11]-[13]. High hardness values were recorded for the composites produced ($H_v \sim 46$ GPa under 200g load) but fracture toughness values did not exceed $1.8 \text{ MPa}\cdot\text{m}^{1/2}$. It was found that neither solid solutions nor new compound was formed under the sintering conditions and that the sintered composite consists of the mixed phases of B_6O and B_4C , cBN, and diamond respectively. Strong interparticle bonding between B_6O and sintering additives increased the hardness and toughness of the sintered composites.

The basis of this study is that the mechanical properties of B_6O materials, especially fracture toughness are greatly influenced by the composition of the grain boundary phase (which activates toughening mechanisms such as crack bridging and crack deflection) and the grain size of the phases in the sintered material. The search for additives that could wet B_6O and therefore help in liquid phase sintering of B_6O is of great importance. This could have an added advantage of reducing the sintering temperature and also the use of low pressures to densify these composites. Low pressure sintering will also allow the production of B_6O composites in different shapes. This work is therefore focussed on enhancing the mechanical properties, especially

fracture toughness of B₆O-based materials by incorporating rare-earth oxides as second, minority phases

II. PROCEDURE

The boron suboxide (B₆O) powder used was produced from the reaction of boric acid and amorphous boron powder, according to methods in the literature [9], [14]-[15]. An excess amount (3 mol %) of boric acid was added to compensate for the evaporation of B₂O₃ that occur during synthesis. The mixture was heated in a furnace under argon at 1380 °C for 5h. The powder produced was crushed and then milled for 30 h in an attrition mill to induce particle reduction, with the mean particle size of 0.5µm measured using a Mastersizer 2000 (Malvern Instruments, Germany). In order to recover pure B₆O powder for further processing, contaminants (mainly Fe and Cr) introduced during milling were minimized by continuous washing of the milled B₆O powders in 1 M HCl followed by washing in ethanol to remove any B₂O₃ remaining in the powder. After the washing, an inductively coupled plasma optical emission spectrometer, ICP-OES (SPECTRO CIRUS CCD), was used to determine the level of the concentrations of Fe and Cr in the washed powders, which was found to be less than 0.15 wt% in the washed powder.

Sub- micron B₆O powder was mixed with rare-earth oxides (Sc₂O₃, La₂O₃ and Yb₂O₃) in methanol for 2 hours using the planetary ball mill (Fritsch Pulversette 6). The mixing speed was kept at 200 rpm, while using 2.5mm steel ball as the media. The amount of the additive content was kept at 1.0vol% of the mixture. After the mixing, the slurry was dried using a rotavap, and then characterize using the XRD, to identify the phases present and SEM to show the homogeneity of the admix powder.

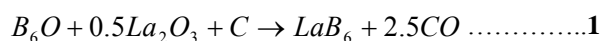
The B₆O powder was hot pressed (HP20 Thermal Technology) in hBN-lined-graphite dies at 1900 °C and pressure of 80 MPa for 20 minutes in an argon atmosphere, while the powders with additives were sintered at 1850 °C and pressure of 50 MPa for 20 minute. Hot-pressed samples were 18 mm in diameter and 3-4 mm in thickness.

After sintering the materials were ground on the surface to remove any h-BN and also to remove any decomposed layer. The density of the samples was determined using Archimedes principle. Cross- sections of the materials were polished using diamond slurry and were characterized 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 (Philips, XL30 SERIES) with attached EDX system. The Vickers hardness (H_v) and fracture toughness (K_{IC}) were measured using indentation techniques under loads of 1kg (for pure B₆O sintered sample) and 5kg (for B₆O 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' equation [16], with the calibration constant ξ=0.016 and elastic constant E=470 GPa [17].

III. RESULTS

B₆O powder hot pressed at temperature of 1900 °C and pressure of 50 MPa for 20 minutes resulted into a nearly dense material having 96.5% of the theoretical density. Phase analysis of the sintered pure B₆O sample shows only peaks of B₆O on the XRD pattern. The Vickers hardness of this sample was 30.2 GPa measured using 1kg load, but higher load cause the fracturing of the sample. Hence, the fracture toughness of the material could not be determined because it was very brittle. This agrees with the result presented by other researchers using ultra-high pressures ^{11, 12, 13}.

Fig. 1 shows the XRD patterns of the B₆O-rare earth oxide sintered materials. For B₆O+Sc₂O₃ material, only peaks for B₆O were found, which implies that the grain boundary phase was amorphous and could not be detected by XRD technique. On the other hand, in the B₆O+La₂O₃ and B₆O+Yb₂O₃ materials, boride secondary phase (LaB₆ & YbB₆) were formed; suggesting that oxidation of B₆O occurred at the sintering temperature, which could bring about an improvement in the oxygen stoichiometry of the boron suboxide phase. The other explanation is that a strong reduction occurred during the sintering process as shown in equation 1.



The backscatter images of the hot pressed materials are shown in Fig 2. It could be seen from the micrographs for the B₆O+Sc₂O₃ material, that there was segregation of liquid phase in the microstructure which might be due to the presence of liquid B₂O₃ or bad wetting behaviour of Sc₂O₃. Energy dispersive X-ray (EDX) analysis shows that the grey phase represents B₆O, while the pockets of white phase constitute an amorphous Sc-B-Mg-Al-O compound. The Mg detected originates from the boron powder used to produce B₆O, while Al might come from the mixing of the powder in an alumina vessel. It was also noted that there was segregation of the secondary phase in the B₆O+ La₂O₃ composite, with evidence of porosity in the micrograph at higher magnification. The segregation also gives an indication of the bad wetting behaviour of La₂O₃ on B₆O. The B₆O+ Yb₂O₃ composite has much finer B₆O grains (no grain growth observed) with an even distribution of the secondary phase although agglomerates of this binder phase were also present. The microstructure also shows that this hot pressed material was nearly dense without any evidence of porosity.

Table 1 gives a summary of the properties obtained for each sample. It could be seen that the open porosities obtained for the materials were lower than that of the hot pressed B₆O sample. This implies that the additives improved the densification of the boron suboxide materials. The fracture toughness of the pure B₆O could not be measured, due to the chipping of the B₆O crystals during indentation. The Vickers hardness measured under a load of 5kg for all the hot pressed materials were similar. Also, the fracture toughness values were also similar except for the B₆O+Yb₂O₃ material where lower fracture toughness was obtained. This might be connected to the low amount of open porosity which could have assisted in arresting crack propagation.

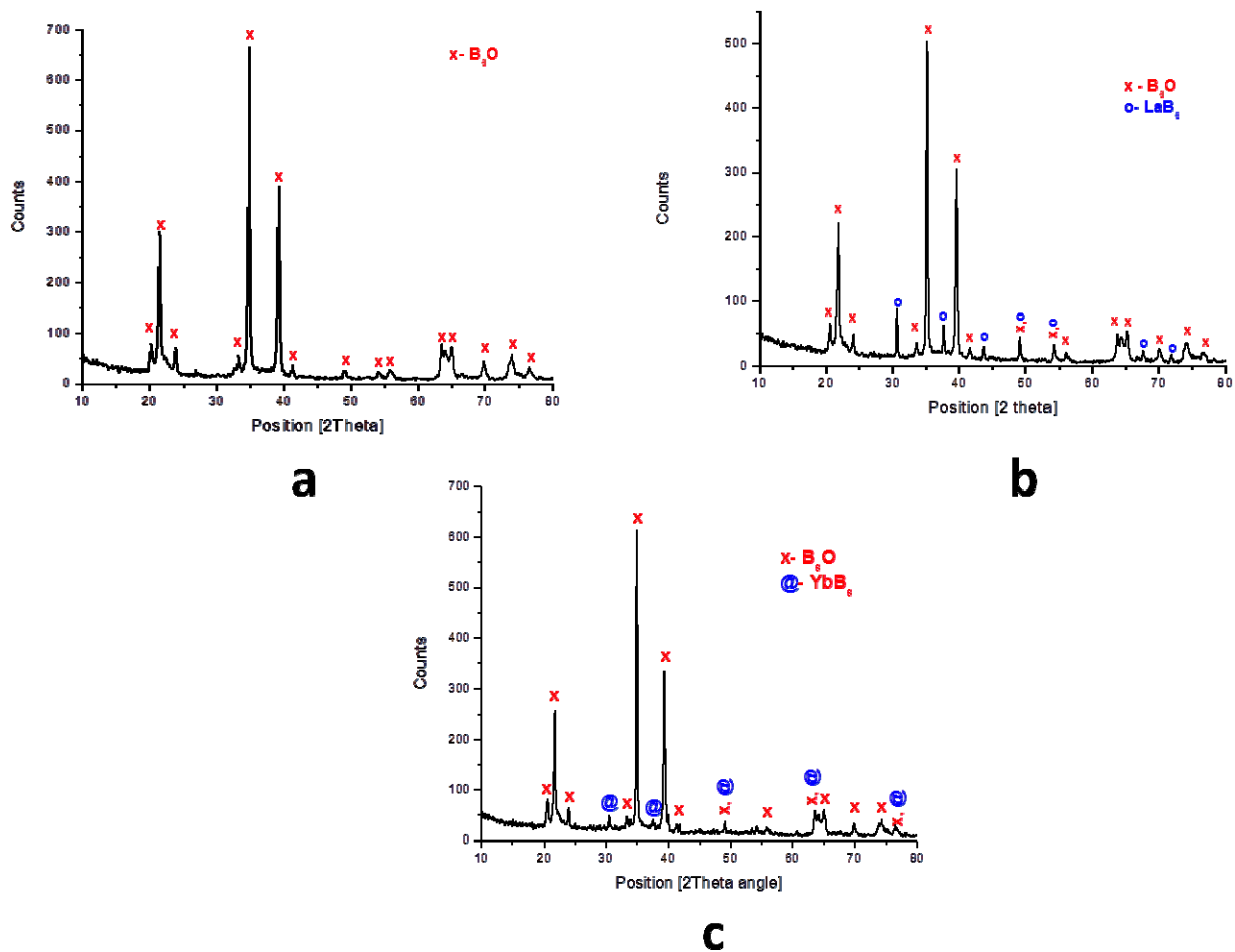


Fig. 1: XRD pattern of sintered B_6O material with (a) 1.5wt% Sc_2O_3 (b) 2.5wt% La_2O_3 (c) 1.5wt% Yb_2O_3

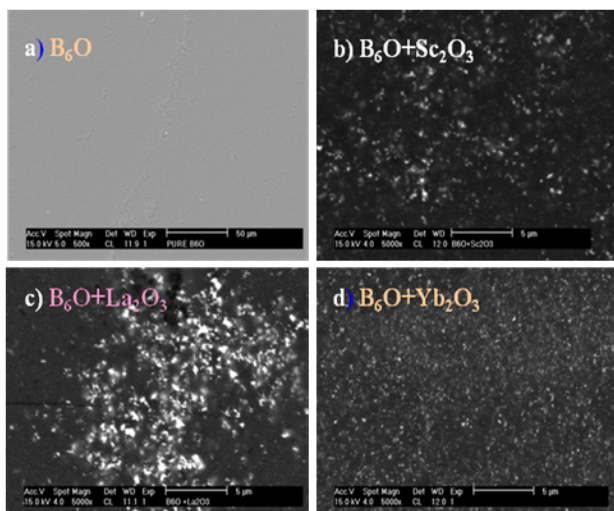


Fig. 2: SEM images of B_6O and rare- earth metal oxide containing materials

Table 1: Mechanical properties of hot pressed B_6O materials

Sintered Material	Additive Ratio (wt %)	Hv (GPa)	K_{IC} MPa.m ^{0.5}	Density (g/cm ³)	Open porosity (%)
Pure B_6O	-	30.2 ± 1.0	-	2.46	3.7
$B_6O+ Sc_2O_3$	1.50	31.6±0.9	5.6±0.2	2.48	1.6
$B_6O+ La_2O_3$	2.50	31.0±1.8	5.6 ±0.8	2.47	2.1
$B_6O+Yb_2O_3$	1.50	30.5±1.7	3.9±0.8	2.51	0.9

IV. DISCUSSION

Previous hot pressing studies [17], [18] concerning the densification of boron suboxide (B_6O) 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% theoretical density. In this study, the density of pure B_6O obtained was 2.46 g/cm^3 , which was 96.5% of the theoretical density and agrees with other authors [17]-[19]. An open porosity of 3.7% was measured on this sample. It is possible that the small amount of B_2O_3 , which may have volatilized at high temperatures, partly acts as the source of these pores.

Fig 3 shows a plot of percentage densification against B_6O of the rare-earth metal oxide containing materials. The trend of the densities obtained and the observed microstructures are an indication that these materials are to some extent densified via liquid phase sintering. A sharp increase in densification was observed from $B_6O+La_2O_3$ material to $B_6O+Yb_2O_3$ material. This trend is in agreement with the SEM images of these materials shown in fig 4. It could be observed from the microstructure that the higher the homogeneity of the distribution of the binder phase of the hot pressed material the higher the degree of densification.

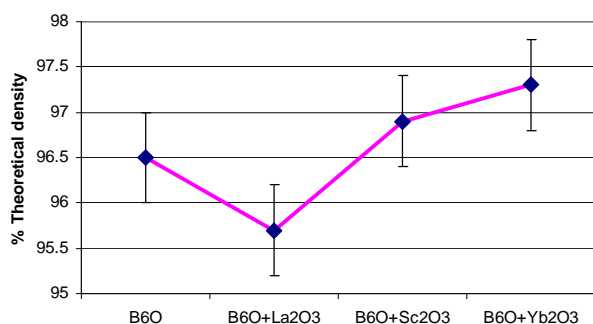


Fig 3: % Theoretical density of B_6O and rare-earth metal oxide containing materials.

In $B_6O+La_2O_3$ material, there was complete segregation (pockets) of liquid phase in the microstructure which might be due to bad wetting behaviour of La_2O_3 on B_6O . This liquid tends to decompose at sintering temperature leaving pores within the material, which has a negative influence on the densification at such temperature. Also the $B_6O+Sc_2O_3$ material had segregation of the secondary phase within the matrix, but less liquid compared to the $B_6O+La_2O_3$ composite. On the other hand the $B_6O+Yb_2O_3$ composite had much finer B_6O grains (no grain growth observed) with an even distribution of the secondary phase. The microstructure also shows that this hot pressed material was nearly dense without any evidence of porosity.

The hardness values obtained for the B_6O composite containing rare-earth metal oxide (Sc_2O_3 , La_2O_3 and Yb_2O_3) were similar. Nevertheless, the macro-hardness value of $B_6O+Sc_2O_3$ composite was slightly higher than those of $B_6O+La_2O_3$ and $B_6O+Yb_2O_3$ composites. The variation in the hardness values obtained gives an indication

of the intrinsic hardness values of the secondary phases formed after hot pressing.

A similar fracture toughness value of $5.6 \text{ MPa.m}^{1/2}$ was obtained for $B_6O+Sc_2O_3$ and $B_6O+La_2O_3$ materials, while the toughness decreased to $3.9 \text{ MPa.m}^{1/2}$ for the $B_6O+Yb_2O_3$ material. SEM images of the crack paths of polished Sc_2O_3 -doped, La_2O_3 -doped and Yb_2O_3 -doped B_6O materials are shown in Fig 4. There was some form of toughening mechanism produced by the second phase in these materials. A large-scale bridging of the crack was observed in the Sc_2O_3 -containing material; while deflection of propagating crack was observed in the La_2O_3 -containing material. Both of these crack-path modification mechanisms would give rise to an increase in fracture toughness. A straight-line crack which cut across the $B_6O+Yb_2O_3$ material only requires minimum amount of energy to progress, which agrees with the lower fracture toughness measured for this material.

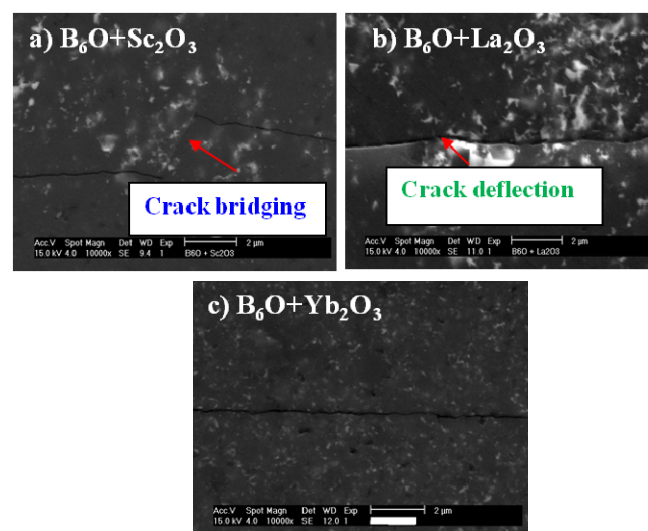


Fig 4: SEM micrographs of the polished surfaces (with propagating cracks) of B_6O sintered composites ((a) Sc_2O_3 , (b) La_2O_3 (c) Yb_2O_3 additives).

V. CONCLUSION

B_6O with rare-earth oxides were sintered using hot pressing techniques at 1850°C for 20 minutes, with an applied pressure of 80 MPa. More than 95% of the theoretical density was attained for the materials. The phase relationship, microstructures and mechanical properties were examined. Good combinations of fracture toughness and hardness were obtained for B_6O materials doped with rare-earth oxides, mainly with the $B_6O+Sc_2O_3$ material. The fracture toughness enhancement was attributed to the introduction of a second, minority phase. Further investigations are necessary to understand the relation between the achieved mechanical properties and the observed microstructures in these samples and also to vary the volume content of this secondary phase in the sintered material.

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