

# Characterization of Sintered Boron Suboxide with Nickel Compounds

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**Abstract**— Although  $B_6O$  materials have shown excellent potentials for wear resistant and cutting tool applications, the problem of low fracture toughness and the difficulties to densify has delayed the application of  $B_6O$  materials in the industry. In this work, efforts have been directed towards improving the fracture toughness and densification of these materials by incorporating suitable secondary phases and tailoring the microstructure to the desired properties. Synthesized  $B_6O$  was hot pressed at  $1850^\circ C$  and 80 MPa in an argon environment, with nickel compounds (nickel (Ni) and nickel oxide (NiO)). The addition of 1.10 vol.% of additives improved the densification of the  $B_6O$  powders in comparison to the pure  $B_6O$  material. The fracture mode observed in the sintered materials is mainly transgranular.

**Keywords** — Boron suboxide, fracture toughness, hardness, superhard materials.

## I. INTRODUCTION

THE development of new processes and novel materials as well as the increase in efficiency of production has led to steadily increasing demands on wear-resistant ceramic materials, i.e. cutting tools, abrasives and protective hard coatings. This has increased the demands and new potential applications stimulate the development of new wear-resistant materials and composites.

Only diamond and cubic boron nitride (cBN) based materials are currently used in the industry as superhard materials. The application of these materials are however, limited at high temperatures due to their instability; as temperature increases, diamond and cBN weakens due to the onset transformation to graphite and hBN structures as well as oxidation [1].

Recent investigations on boron suboxide ( $B_6O$ ) reported a hardness comparable with that of cBN, as well as a toughness similar to that of diamond [2].  $B_6O$  has been found to be the third hardest material with hardness for single crystal, of about 45 GPa, closely rivalling that of cubic boron nitride [2]. In addition to this hardness, the fracture toughness ( $K_{IC}$ )

of this material ( $B_6O$  single crystal) was found to be  $4.5 \text{ MPa.m}^{0.5}$ , which approaches that of single crystal diamond at  $5 \text{ MPa.m}^{0.5}$  and is significantly better than that of single crystal cubic boron nitride (cBN) at  $2.8 \text{ MPa.m}^{0.5}$  [3]. Hence, materials on the basis of  $B_6O$  qualify as potential candidates for applications with a high demand in wear resistance.

Kleebe's et al 2008 [4], development of thermodynamic data for  $B_6O$  at high temperatures has allowed prediction of the stability and crystalline phases in  $B_6O$  materials, thus suggesting that careful selection of additives with controlled sintering conditions could result in the production of  $B_6O$  materials with unique combination of mechanical properties for industrial applications. On the basis of the development, several attempts have been made on the improvement of the fracture toughness ( $K_{IC}$ ) of  $B_6O$  through the addition of different materials.

The addition of materials such as diamond, boron carbide and cBN with  $B_6O$  produced via high-pressure technique yielded a  $K_{IC}$  of  $1.8 \text{ MPa.m}^{0.5}$  [5–6].  $B_6O\text{-Al}_2\text{O}_3$  reported an increased  $K_{IC}$  value of  $3.1 \text{ MPa.m}^{0.5}$  but with a slight reduction in hardness compared to pure  $B_6O$  material [7–8].  $B_6O\text{-(Al}_2\text{O}_3\text{/Y}_2\text{O}_3)$  materials reported a  $K_{IC}$  values between  $3.0\text{--}3.5 \text{ MPa.m}^{0.5}$  (for an addition of 2–3 vol% of the additive) [9].

The addition of different cobalt containing additives resulted in a fracture toughness of between  $3.2\text{--}3.9 \text{ MPa.m}^{0.5}$  [10].  $B_6O\text{-rare-earth metal oxide}$  additives reported a  $K_{IC}$  value between  $3.9\text{--}5.6 \text{ MPa.m}^{0.5}$  [11].  $B_6O\text{-CrB}_2$  material reported a  $K_{IC}$  value of  $4.5 \text{ MPa.m}^{0.5}$  [12], and recently  $B_6O\text{-alkaline earth metal oxide}$  reported between  $6.1\text{--}6.8 \text{ MPa.m}^{0.5}$  fracture toughness values [13]. This paper therefore aims to investigate the characterization of  $B_6O$  material sintered with nickel compounds via densification, microstructures and mechanical properties.

## II. METHODOLOGY

The  $B_6O$  powder was prepared by reaction of boron (B) with boron oxide ( $B_2O_3$ ) as described elsewhere [5–7,14–15]. The powder produced was crushed and milled for 20 hours in an attrition mill. The mean particle size of the powder was  $0.5 \mu\text{m}$  using a Mastersizer 2000 (Malvern Instruments, Germany).

In order to recover pure  $B_6O$  powder for further processing, contaminants (mainly Fe and Cr) introduced during milling were minimized by washing in 1 M HCl followed by washing in ethanol to remove  $B_2O_3$  remaining in the milled powder. After washing, ICP-OES SPECTRO CIRUS CCD, was used to determine the concentration levels of Fe and Cr in the washed powder. This was found to be 0.06 wt% Fe and 0.04 wt% Cr, respectively.

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Table 1 Summary of the properties of the sintered compacts

	Sintering conditions			Additive volume (%)	Density (g/cm <sup>3</sup> )	Open porosity (%)	HV (GPa)	K <sub>IC</sub> (MPa.m <sup>0.5</sup> )
	Atm.	Load (MPa)	Temp (°C)					
B <sub>6</sub> O	Argon	50	1900	0	2.46	3.7	30.2±1.0 <sup>a</sup>	Brittle
B <sub>6</sub> O-Ni	Argon	80	1850	1.10	2.53	1.95	30.7±1.5 <sup>b</sup>	6.4±0.6
B <sub>6</sub> O-NiO	Argon	80	1850	1.10	2.54	3.97	27.1±2.1 <sup>b</sup>	6.1±0.9

Atm – atmosphere <sup>a</sup> – represents a load of 1 kg; <sup>b</sup> – represents a load of 5 kg.

The B<sub>6</sub>O powder was then mixed with 1.10 vol. % of Ni and NiO additive in methanol for 2 hours using a planetary mill (Fristch Pulversette 6) at a speed of 200 rpm. After mixing, the powder slurry was then dried using a rotavap evaporator, and then characterized using XRD (for phase(s) identification, and SEM (to show homogeneity).

A uniaxial hot press (HP20 Thermal Technology) was used for all sintering experiment with hBN lined graphite dies in an argon atmosphere. Pure B<sub>6</sub>O powder at 1900°C and a holding pressure of 50 MPa for 20 min, while the B<sub>6</sub>O-nickel compounds additives were sintered at 1850°C at a pressure of 80 MPa and the same isothermal sintering time (pure B<sub>6</sub>O powder densified at 1850°C had shown only a density of less than 90% theoretical density). The sintered compacts were 18 mm in diameter and between 3–4 mm in thickness. After sintering the materials were ground to clean their surface from reaction products with the hBN lining. The density of the sintered B<sub>6</sub>O samples was determined using Archimedes method and compared with theoretical densities, which were estimated on the basis of the rule of mixture using 2.55 g/cm<sup>3</sup> for B<sub>6</sub>O. X-ray diffraction (XRD) for qualitative phase analysis were performed on cross-sections of the sintered materials with a Philips PW1830 using Cu K $\alpha$  radiation (2 $\theta$  range: 10 – 80°; step size 0.028; 40 kV 30mA), and PANalytical X'Pert HighScore with the ICDD database (release version 2010) for phase identification. Microstructural observations were carried out using scanning electron microscopy (Philips, XL30 SERIES) with attached EDX system.

The Vickers hardness (HV) and K<sub>IC</sub> were measured using indentation techniques under loads of 1 kg (for pure B<sub>6</sub>O sample) and 5 kg (for B<sub>6</sub>O-nickel compound materials). An average of five measurements was used to determine the properties of the samples, while the K<sub>IC</sub> was determined via the direct crack measurement method using Anstis's equation [16], (calibration constant,  $\xi = 0.016$ ; elastic constant,  $E = 470$  GPa [17]).

### III. RESULTS

The summary of the properties of the sintered materials is presented in Table 1. Pure B<sub>6</sub>O powder sintered at 1900°C resulted into a nearly dense material having 96.1% of the theoretical density. Phase analysis showed only peaks of B<sub>6</sub>O in the XRD pattern (Figure 1a). The Vickers hardness of this sample was 30.5 GPa measured using 1 kg load, as higher load caused fracturing in material. This made it difficult to determine the K<sub>IC</sub> of this material.

The density of the nickel compound additives resulted in 99% theoretical density of pure B<sub>6</sub>O. This was higher than that of pure B<sub>6</sub>O sintered at 1900°C, despite the lower sintering temperature of these materials. XRD patterns of the sintered materials (Figure 1b & c), shows the formation

of boride secondary phases at the grain boundaries of the B<sub>6</sub>O grains confirms the oxidation of B<sub>6</sub>O by the additives. The Vickers hardness values measured for the B<sub>6</sub>O-Ni material show a slight increase in hardness, while B<sub>6</sub>O-NiO material show a 10% reduction in hardness compared to pure B<sub>6</sub>O (but it should be noted that the load applied was different). However, the B<sub>6</sub>O-Ni and B<sub>6</sub>O-NiO sintered materials showed significant increases in the fracture toughness of the produced materials; 6.4 and 6.1 MPa.m<sup>0.5</sup> respectively.

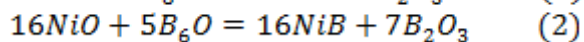
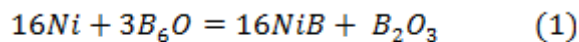
The SEM images with EDX of the sintered materials are shown in (Figure 2). The dark area represents pure B<sub>6</sub>O and the white area the boride secondary phases formed. Segregations of the secondary phases could be observed from the micrographs. In additions, some dark spots which represent pores pulled-out of the binder phase. No differences or evidence of grain growth was observed in the distribution of the additives between the centre and the near surface area of the sintered materials. The EDX analysis of all the materials confirmed that the grey phase represents B<sub>6</sub>O, while the white represents the boride phases, in agreement with the phase analyses obtained from the XRD analysis. The non-homogeneous distribution of the secondary phases on these materials could be a result of the poor wettability of the secondary phase with B<sub>6</sub>O.

### IV. DISCUSSION

B<sub>6</sub>O is known to be difficult to densify, especially through self-sintering, even if aided by hot pressing or ultrahigh pressure [14,17–18]. Previous studies [17–18] concerning densification of B<sub>6</sub>O powders made by mixing amorphous boron with boron oxide or with zinc oxide, have produced B<sub>6</sub>O materials with density in the range of 85–97 % theoretical density. In this study, the density of pure B<sub>6</sub>O obtained was 2.46 gcm<sup>3</sup>, which was 96.5% of the theoretical density and agrees with other authors [7,17–18]. An open porosity of 3.7% was measured on this material. It is possible that small amount of B<sub>2</sub>O<sub>3</sub> which may have volatilized at high temperatures, partly acts as the source of these pores. The presence of B<sub>2</sub>O<sub>3</sub> has also shown to lowers the theoretical density of B<sub>6</sub>O [17].

The comparison of the density of B<sub>6</sub>O materials as a function of the theoretical density is shown in (Figure 3). Observations from the densification of the sintered materials showed that the B<sub>6</sub>O-Ni and B<sub>6</sub>O-NiO materials sintered at 1850°C are better than the pure B<sub>6</sub>O sintered at 1900°C. This improvement on the densification is attributed to the formation of a liquid phase by the additives at the sintering temperature, in which B<sub>6</sub>O partially dissolves and assists with the densification of the materials at this temperature while recrystallizing during cooling to form boride secondary phase at the grain boundaries (Figure 1b

& c). The differences in the densification achieved between the B<sub>6</sub>O-Ni and B<sub>6</sub>O-NiO materials could also be connected to the amount of B<sub>2</sub>O<sub>3</sub> produced by the interaction of these additives with pure B<sub>6</sub>O. With the assumption of 1 wt% of B<sub>2</sub>O<sub>3</sub> in the starting powder, it can be deduced that more B<sub>2</sub>O<sub>3</sub> was produced in the B<sub>6</sub>O-NiO compared to that of the B<sub>6</sub>O-Ni material as shown in equations 1 and 2.



From the above reactions, it is expected that the same mol% of additive (Ni or NiO) will produce the same volume of second phase (NiB) after sintering, but for one (1) part by volume of B<sub>2</sub>O<sub>3</sub> produced for the B<sub>6</sub>O-Ni material, seven (7) parts by volume will be produced in the B<sub>6</sub>O-NiO material. With the addition of 3.7 wt% Ni to the B<sub>6</sub>O powder, 0.27 wt% B<sub>2</sub>O<sub>3</sub> was produced, while 2.8 wt% NiO added resulted in the formation of 1.14 wt% B<sub>2</sub>O<sub>3</sub> after sintering. This gives an indication of the higher amount of B<sub>2</sub>O<sub>3</sub> in the B<sub>6</sub>O-NiO material.

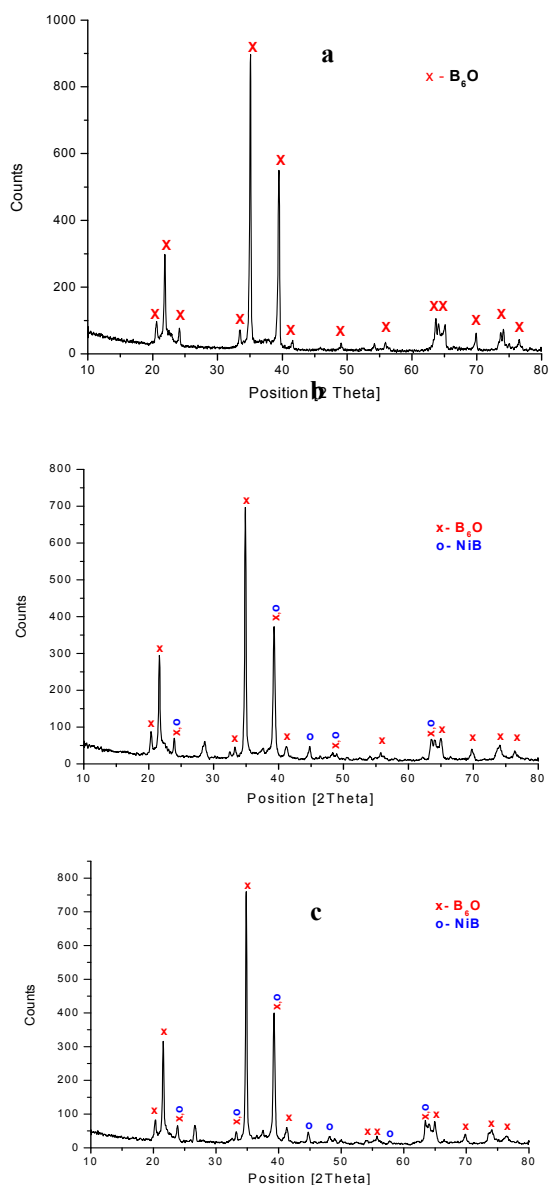


Figure 1 XRD phase analysis of sintered B<sub>6</sub>O materials (a) pure B<sub>6</sub>O, (b) B<sub>6</sub>O-Ni, and (c) B<sub>6</sub>O-NiO.

The hardness values obtained for the sintered B<sub>6</sub>O-Ni material were higher than that of the pure B<sub>6</sub>O compact, while that of the B<sub>6</sub>O-NiO showed a reduction compared to the pure B<sub>6</sub>O (Figure 5). The reduction in the hardness values obtained for the B<sub>6</sub>O-NiO materials could be connected to the formation of considerable B<sub>2</sub>O<sub>3</sub> which might have volatilized at high temperature and/or the possibility that indentations could have been made on the segregated boride phase in the matrix with lower intrinsic hardness compared with B<sub>6</sub>O. This is confirmed by the presence of pores at higher magnifications (see figure 2c). It could also be noted that the variation of the sintering conditions in terms of temperature, pressure, and time could affect the amount of porosity present which in turn has a negative effect on hardness. The increase hardness value in the B<sub>6</sub>O-Ni materials could be attributed to the formation of boride secondary phase in the material.

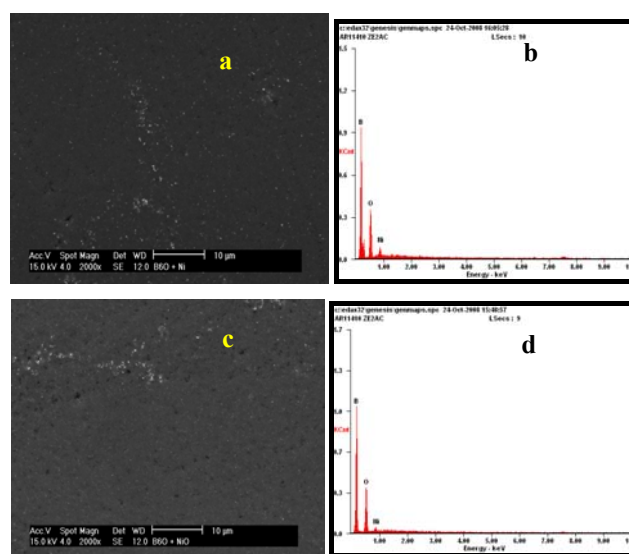


Figure 2 SEM images with EDX analysis of sintered (a & b) B<sub>6</sub>O-Ni, and (c & d) B<sub>6</sub>O-NiO materials.

Figure 4 showed the comparison of the hardness and fracture toughness of the sintered materials. Although the pure B<sub>6</sub>O material is brittle, the B<sub>6</sub>O-Ni compound additive showed improved fracture toughness values, when compared with the pure B<sub>6</sub>O material, there were significant increases in fracture toughness. The fracture toughness sharply increased with a small addition of each additive. Values of 6.4, and 6.1 MPa.m<sup>0.5</sup> were obtained for B<sub>6</sub>O-Ni and B<sub>6</sub>O-NiO additives respectively. The increase in the values could be due to the similarity in grain sizes and grain boundary chemistry in the sintered materials. Although the secondary phase was not evenly distributed in these materials, as seen by the segregation of the boride phase, yet there was no evidence of grain growth observed (Figure 2).

The segregation of the boride secondary phase was evident even though there was an increase in the density of the material. For the B<sub>6</sub>O-Ni and B<sub>6</sub>O-NiO materials (Figure 2(a & c)), the segregation of liquid phase in the microstructure might be a result of poor wettability. At the sintering temperature, the existence of B<sub>2</sub>O<sub>3</sub> liquid which decomposed leaving pores within the material could be responsible for the decrease hardness in the B<sub>6</sub>O-NiO

material. This has a negative influence on the densification and is reflected at the measured porosity value of the material (Table 1).

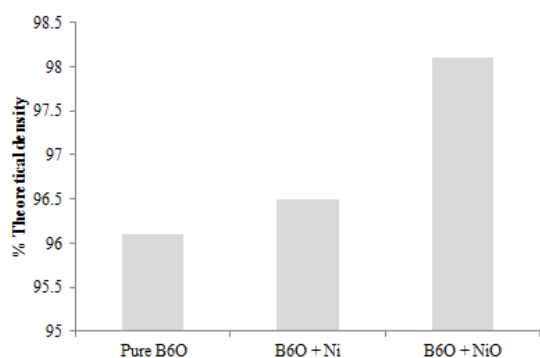


Figure 3 Comparison of the percentage theoretical density of the sintered B<sub>6</sub>O and B<sub>6</sub>O-Ni compounds.

Pure B<sub>6</sub>O sintered material is generally believed to be brittle and the reason for the very low toughness is not very clear. In this study, for hardness measurement on a sintered pure B<sub>6</sub>O compact in this study, on increasing the load above 1kg, the material showed a high scattering property with chipping during indentation. It was thus concluded that the material had low K<sub>IC</sub>. Although it is not clear how fracture occurs in this material, but there were some evidence of transgranular fracture mode. The K<sub>IC</sub> values of the sintered B<sub>6</sub>O-alkaline earth oxide additives reported in this study were measured using a load of 5 kg.

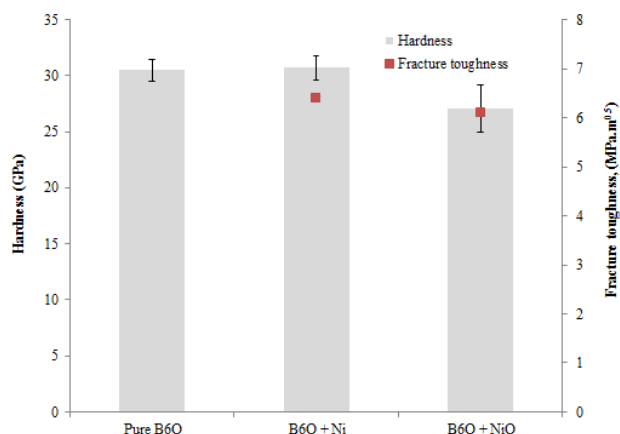


Figure 4 A comparisons of sintered pure B<sub>6</sub>O materials made by other authors with this study.

The high fracture toughness values obtained for the B<sub>6</sub>O-Ni compound materials were enhanced by a combination of toughening mechanisms. A combination of crack deflections and bowing, which are caused by bimetallic stresses. The difference between the thermal expansion of the B<sub>6</sub>O matrix and the boride secondary phase induces a tangential compressive stress near the particle/matrix interface and diverts the cracks around a particle. Also, pores in the B<sub>6</sub>O-NiO material helped to reduce the energy of the propagating cracks, thereby causing improvement in the fracture toughness in the material.

SEM images of the crack propagation on the polished surfaces of the B<sub>6</sub>O-Ni compound materials shows a straight-line crack which cut across the grains of B<sub>6</sub>O was observed mainly in the materials, indicating a transgranular

fracturing mode (Figure 5). In addition, some deflections were observed in the B<sub>6</sub>O-Ni material. Most of the crack deflections were either caused by the presence of the secondary phase and/or by the inherent pores. These deflections was reportedly caused by non-wetted grain boundary [4, 19]. Therefore, the formation of the boride secondary phase caused the improvement in the fracture toughness of the materials.

There is no evident relationship between measured fracture toughness and the amount of the additive present [20], which means that the properties of the final phases of the additives have some effect on the fracture toughness of the materials and none of the toughening mechanisms can unequivocally explain the increase in the K<sub>IC</sub> values. Hence, a detailed investigation of fracture behavior is necessary for an understanding and further development of these materials.

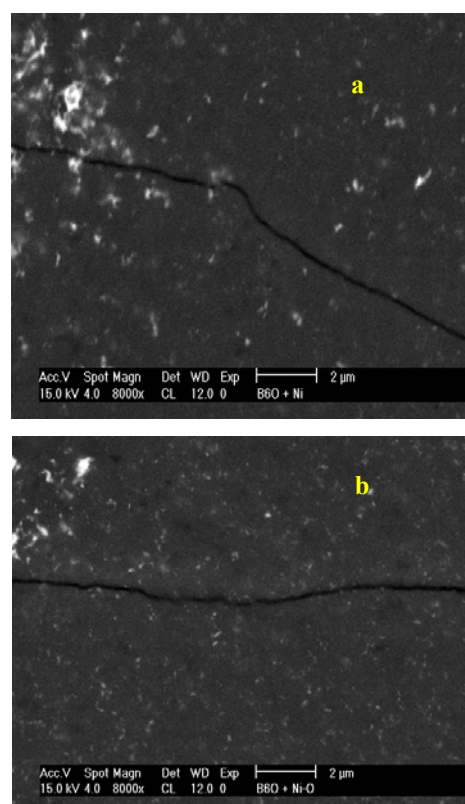


Figure 5 Indentation crack path on sintered (a) B<sub>6</sub>O-MgO, (b) B<sub>6</sub>O-CaO, and (c) B<sub>6</sub>O-CaCO<sub>3</sub> materials.

## V. CONCLUSIONS

B<sub>6</sub>O with 1.10 vol% of Ni and NiO, additive were sintered using hot pressing techniques at 1850°C for 20 minutes, with an applied pressure of 80 MPa. More than 96% of the theoretical density was attained for the materials. The phase relationship, microstructure and mechanical properties were examined. Fracture toughness as high as 6.1 and 6.4 MPa.m<sup>0.5</sup> were obtained in these materials. It was concluded that the significant improvement in the fracture toughness of the materials was due to the introduction of the boride secondary phase at the grain boundary interface. This suggested that suitably prepared B<sub>6</sub>O materials could be used as cutting tools and other wear applications.

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