Mechanical Properties of Sintered B₆O-Alkaline Earth Metal Oxide Materials

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Abstract — Pure B₂O powder and B₂O powders admixed with 1.5 wt% of MgO, 1.4 wt% of CaO, and 0.7 wt% of CaCO₃ were sintered and the microstructure, phase composition and mechanical properties were investigated. Pure B₂O powders were sintered at a temperature of 1900°C and a load of 50 MPa for 20 minutes in an argon environment, while the B₂O-admixed powders were sintered at a temperature of 1850°C and loads from 50-80 MPa, under the same environment. The addition of the alkaline earth metal oxide additives resulted in the formation of boride and borate phases, depending on the oxide used. More than 96% of theoretical densities were achieved and the result indicates a good combination of hardness (between 31.6–32.1 GPa) and fracture toughness (between 6.1–6.8 MPa.m⁰.⁵) in the B₂O-alkaline earth oxide materials. The introduction of the additives enhances the improvement in the fracture toughness of the pure B₂O-materials. The fracture mode observed in the sintered materials is mainly transgranular.

Keywords — Alkaline earth oxide, boron suboxide, fracture toughness, hardness, transgranular.

I. INTRODUCTION

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. Research efforts by material scientists towards the development of materials with a combination of properties approaching or even improving on those of diamond have resulted in considerable results. Boron-rich compounds have proved good candidates for this type of materials. They give rise to a large family of materials with unique crystal structures and a range of interesting physical and chemical properties, which is related to their short interatomic bond lengths due to a strong covalent bonding [1]. Boron-rich compound with a structure based on a rigid three-dimensional, α-rhombohedra boron network include boron carbide (B₄C) and boron suboxide (B₆O₁₆, namely B₆O).

B₂O structure (space group R3m) consists of eight B₁₂ icosahedral units situated at the vertexes of a rhombohedra unit cell. The structure can be viewed as a distorted cubic close packing of B₁₂ icosahedra units [2] connected through oxygen. B₂O 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 [3]. In addition to this hardness, the fracture toughness of this material (B₂O single crystal) was found to be 4.5 MPa.m⁰.⁵, which approaches that of single crystal diamond at 5 MPa.m⁰.⁵ and is significantly better than that of single crystal cubic boron nitride (cBN) at 2.8 MPa.m⁰.⁵ [4]. The combination of high hardness, the possibility of cheaper production cost and production without the need for high pressure, unlike diamond and cBN, makes B₂O-based materials a good candidate for cutting tools and other applications where abrasive wear resistance is important.

The development of thermodynamic data for B₂O at high temperatures [5] has allowed prediction of the stability and crystalline phases in B₂O materials. This suggests that a careful selection of additives with controlled sintering conditions could result in the production of B₂O materials having unique combination of mechanical properties for industrial applications. Several attempts have been made to improve on the fracture toughness of B₂O through the addition of different materials. B₂O-material 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.m⁰.⁵ [6-7]. The addition of Al₂O₃ has been reported to increase the fracture toughness to a value of 3.1 MPa.m⁰.⁵ but with a slight reduction in hardness in comparison to pure B₂O material [8-9]. The addition of different cobalt containing additives resulted in a fracture toughness of between 3.2–3.9 MPa.m⁰.⁵ [10]. And recently, B₂O materials with different amount of rare-earth oxide additives reported a fracture toughness between 3.9–5.6 MPa.m⁰.⁵ [11]. This paper therefore aims to investigate the densification and mechanical properties of B₂O material sintered with alkaline earth metal oxide additives.

II. METHODOLOGY

B₂O powder (3 µm) produced and supplied by IKTS–Dresden, Germany was used for the hot pressing investigations. The powder was charged and milled in an attrition mill using steel balls (2.5 mm diameter) for 20 hours at 400 rpm, 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.
alkaline earth oxide materials were slightly higher than that presented by other researchers using ultra-high pressures. Material could not be determined. This agrees with the result of material fracturing. Hence, the fracture toughness of this material was measured under 1 kg load. Higher load resulted in a higher theoretical density. The Vickers hardness of this sample was also measured using indentation techniques under loads of 1 kg for pure B$_6$O and B$_6$O-CaO powders, and 5 kg for B$_6$O-MgO powder. 

Table 1: Mechanical properties of produced B$_6$O powders

<table>
<thead>
<tr>
<th>Applied load (MPa)</th>
<th>B$_6$O</th>
<th>B$_6$O-CaO</th>
<th>B$_6$O-MgO</th>
<th>B$_6$O-CaCO$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>30.5±2.1</td>
<td>32.1±1.9</td>
<td>31.6±2.1</td>
<td>Brittle</td>
</tr>
<tr>
<td>80</td>
<td>31.6±1.7</td>
<td>31.6±1.7</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* – represents a load of 1 kg; b – represents a load of 5 kg.

XRD phase analysis of the sintered pure B$_6$O sample and the sintered B6O-alkaline earth oxide materials are shown in Figure 1 (a-d). For pure B$_6$O material, only crystalline phases of B$_6$O were observed. In addition to the B$_6$O crystalline phases, the sintered B$_6$O-alkaline earth oxide materials also contain Mg$_2$B$_2$O$_6$ and MgO additive phases. CaB$_6$O$_4$ and CaO additives were also observed in the XRD patterns. The formation of CaB$_6$O$_4$ could be as a result of chemical reactions involving CaO and B$_6$O during sintering. The formation of CaB$_6$O$_4$ and CaO additives and the formation of boron carbide for stable oxide like CaO.

Figure 2 shows the SEM images with EDX of the hot-pressed pure B$_6$O and B$_6$O-alkaline earth oxide materials produced. Observations from the micrographs showed that a homogeneous distribution of the secondary (minority) phases was not obtained in these materials; rather there were segregations (pockets) in the microstructure. Pores which could be inherent in these materials due to decomposition reactions at the sintering temperature were seen as dark spots in the samples (at higher magnifications). There were no differences in the distribution of the additives between the centre and the near surface area of the sintered materials. No evidence of any grain growth was observed at higher magnifications in the sintered materials. The iron pickup in the EDX analysis of the additive-derived materials could have originated from the starting B$_6$O material. The segregation of the secondary phase in the B$_6$O-alkaline earth oxide materials (Figure 2 (c & d)) suggests variation in the properties of the materials at different points in the sample.
The EDX analysis of all the samples confirmed that the grey phase represents B₄O, while the white represents the boride and borate phases, in agreement with the phase analyses obtained from the XRD analysis. This is in agreement with the authors in [14–16]. The non-homogeneous distribution of the secondary phases on these materials could be a result of the poor wettability of the secondary phase with B₄O.

IV. DISCUSSION

A fully densified B₄O compact is difficult to sinter even when applying high pressure sintering techniques such as hot pressing [16], hence the need to develop an appropriate sintering aid is required. This is because B₄O is easily oxidized to form B₂O₃ with the mechanical strength of the resultant sintered compact degraded [7]. The degradation of mechanical properties by B₂O₃ has been corroborated by the work done by Andrews, 2008 [9]. The presence of B₂O₃ has also shown to lowers the theoretical density of B₄O [13].

Figure 1 XRD phase analysis of sintered B₄O-alkaline earth metal oxide (a) pure B₄O, (b) B₄O-MgO, (c) B₄O-CaO, and (d) B₄O-CaCO₃ materials respectively.

B₄O powders hot pressed either under vacuum or argon conditions at temperatures in the range of 1600°C–1900°C, have produced B₄O materials with densities in the range of 85–97% of the theoretical density [13,17–20]. This study produced a density of 2.45 g/cm³ for pure B₄O, which was about 96.1% of the theoretical density. The difference between the value obtained in this work and others is in the amount of porosity obtained in the sintered material. The presence of the pores has been attributed to the evaporation of B₂O₃ at high temperatures [14–16]. It is possible that small amount of B₂O present may have volatilized at high temperatures, partly acts as the source of small pores in the microstructure. As reported by Andrews, 2008 [9], the theoretical density of B₂O₃ is 2.46 g/cm³, which is less than that of pure B₄O; therefore a small amount of B₂O₃ in the samples will lower the overall theoretical density of a hot pressed B₄O sample.

This work assumed that all the additives in the powder completely transformed to their respective secondary phase(s) after sintering. And also 1 wt. % of B₂O₃ present in the starting material was made in the calculation of theoretical densities. The theoretical densities of the materials were calculated (based on the rule of mixture method) to ascertain the percentage densification obtained by the hot pressing process.

Figure 2 SEM images with EDX analysis of sintered (a & b) B₄O-MgO, (c & d) B₄O-CaO, and (e & f) B₄O-CaCO₃ materials.

Sintered B₄O-alkaline earth oxide additives resulted in higher densification as compared with that of pure B₄O (except for B₄O-CaO additive), even when same load was used. XRD patterns of the sintered materials show the
formation of a borate phase for MgO additive, a boride secondary phase for CaO additive, and carbide and boride phases for the CaCO$_3$ additive. There are two possible explanations for the improvement in the densities obtained for these materials; one is that the additives form a liquid phase in which B$_2$O partially dissolves, thus assisting in the densification of the materials at the sintering temperature and recrystallizing during cooling to form the respective secondary phase(s) at the grain boundaries as shown in the XRD patterns. On the other hand, the formation of B$_2$O as a result of the oxidation reaction occurring in most cases between the B$_2$O and the sintering additives, suggest that a more liquid phase is formed, thereby improving the densification behavior. Hence, a precise control of the oxygen content would be necessary for the reproducible densification of the materials.

In the B$_2$O-MgO material (Figure 2(a)), segregation of the secondary phase (Mg$_2$B$_2$O$_5$) was evident even though there was an increase in the density of the material. Two reasons could be attributed to this: the wettability of the additive with B$_2$O and the other can be understood from a thermodynamic point of view. To understand and properly explain the densification of this material, there is a need to consider the phase diagram of the MgO-B$_2$O$_3$-B$_2$O system. There is no known phase diagram for this system, but one can consider that of the MgO-B$_2$O$_3$ system (Figure 3).

From Figure 3, at the sintering temperature, there is enough liquid present which accelerates mass transport and therefore improves densification. The oxidation reaction between B$_2$O$_3$ and MgO resulted in liquid phase formation, which re-crystallized during cooling forming the borate phase (Mg$_2$B$_2$O$_5$) at the grain boundaries. Hence, the segregation could be a result of poor wettability of the MgO on B$_2$O.

For the B$_2$O-CaO and B$_2$O-CaCO$_3$ materials (Figure 2(c & e)), the segregation of liquid phase in the microstructure might be a result of poor wettability. At the sintering temperature, the existence of B$_2$O liquid which decomposed leaving pores within the material could be responsible for the decrease densification in the B$_2$O-CaO material (Figure 2(c)). This has a negative influence on the densification and is reflected at the measured porosity value of the material (Table 1). In the case of B$_2$O-CaCO$_3$ material (Figure 2(e)), the improved densification corroborates with the reduced porosity. The reactions for the sintered B$_2$O-CaO and B$_2$O-CaCO$_3$ materials can be represented in equations 1 and 2.

$$4CaO + 5B_2O \rightarrow 4CaB_6 + 3B_2O_3$$  \hspace{1cm} (1)

$$4CaCO_3 + 9B_2O \rightarrow 4CaB_6 + 4B_4C + 7B_2O_3$$  \hspace{1cm} (2)

Figure 4 showed a comparison of sintered pure B$_2$O material made by other authors. Although the values obtained by some authors [13,20–21] seems higher compared to this study, it should be advised however, that the porosity were either not reported or very high. In addition, variations in the sintering conditions (temperature, pressure, time and atmosphere) could affect the amount of porosity present which has a negative effect on hardness. It should however be noted that the hardness value obtained in this study is higher compared to those obtained by Andrews, 2008 [9] and Johnson 2008 [22], even at the same load. The hardness values obtained for the sintered B$_2$O-alkaline-earth metal oxide sintered material were higher than that of the pure B$_2$O compact. These values obtained show a similar range as seen from the error bars (Figure 5).

The variation in the hardness values obtained for these materials is also related to the better densifications as compared to the pure B$_2$O. And although full densification was not achieved in these materials, the average hardness value obtained was encouraging. This suggests that possible improvement in the densification of B$_2$O material with oxides from this group might result in better hardness values.
He et al., 2002 [23], at high pressure between 3–5 GPa made a single crystal of B$_6$O and recorded a fracture toughness ($K_{IC}$) of 4.5 MPa.m$^{0.5}$. Pure B$_6$O sintered compact is generally believed to be brittle and the reason for the very low toughness is not very clear. During the course of hardness measurement on a sintered pure B$_6$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 $K_{IC}$. Although it is not clear how fracture occurs in this material, but there were some evidence of transgranular fracture mode. The $K_{IC}$ values of the sintered B$_6$O-alkaline earth oxide additives reported in this study were measured using a load of 5kg and it ranged between 6.1 and 6.8 MPa.m$^{0.5}$. This showed a significant improvement in the $K_{IC}$ considering the fact that pure sintered B$_6$O compact is very brittle.

![Indentation crack path on sintered materials](image)

Figure 6 Indentation crack path on sintered (a) B$_6$O-MgO, (b) B$_6$O-CaO, and (c) B$_6$O-CaCO$_3$ materials.

Figure 6(a–c) shows the SEM images of the crack propagation on the polished surfaces of sintered B$_6$O-alkaline earth oxide materials. Crack propagations on these materials are predominantly transgranular mode and occasions of crack deflection with low deflection angles on the secondary phase (e.g., Figure 6(e)). Most of the crack deflections were either caused by the presence of the secondary phase and/or by the inherent pores. These deflections were reportedly caused by non-wetted grain boundary [5,23]. A similar findings was also observed by other authors [15,24]. In comparison to the pure B$_6$O, the crack path lengths of the B$_6$O-alkaline earth oxide materials are shorter. The deflection observed can be explained by the stresses that exist in the material. The B$_6$O matrix has a different thermal expansion coefficient (CTE) compared to the secondary phase(s). This could result in the formation of large internal stress when the material is cooled from the sintering temperature. This difference can induce a tangential compressive stress near the particle/matrix interface and thereby diverts the crack around the particle, making the material tough.

Bush 2011, reported that the effect of the additives on the fracture toughness of B$_6$O materials is not only dependent on the amount of additive present, as there is no evident relationship between measured fracture toughness and the additive content [25]. This 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 ceramic toughening mechanisms (crack deflection, internal stresses etc.) can unequivocally explain the increase in the $K_{IC}$ values. Hence, a detailed investigation of fracture behavior is necessary for an understanding and further development of these materials.

V. CONCLUSIONS

B$_6$O admixed with 1.5 wt% of MgO, 1.4 wt% of CaO, and 0.7 wt% of CaCO$_3$, were sintered and the mechanical properties evaluated. The addition of the alkaline earth metal oxide additives resulted in the formation of boride and borate phases, depending on the oxide used. More than 96% of theoretical densities were achieved for these materials. The result indicates a good combination of hardness (between 31.6–32.1 GPa) and fracture toughness (between 6.1–6.8 MPa.m$^{0.5}$) of the B$_6$O-alkaline earth oxide materials. The investigation indicates that the use of alkaline earth oxides as a sintering aid could be a promising way for the effective and reliable production of B$_6$O materials with improved hardness and fracture toughness for commercial application. Fracture toughness enhancement could be attributed to the introduction of secondary phases in the B$_6$O matrix and to bimetallic stresses induced between the matrix and the secondary phase or by many other mechanisms. The investigation showed that the additives used also had the potential of reacting with B$_6$O present to form other phases that cause bimetallic strain toughening at the grain boundaries. The cracks obtained in these materials showed mainly transgranular fracture mode. Although the fracture mechanism is not completely clear, further work is necessary to understand the mechanism.

ACKNOWLEDGEMENT

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