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<th><strong>Title</strong></th>
<th>Boron Carbide-Based Nanostructured Composite by Spark Plasma Sintering</th>
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ABSTRACT: In the current paper, we present the use of nanostructured boron suboxide ($B_6O$) and in-situ synthesized hexagonal boron nitride (hBN) to form structured composites with commercially available boron carbide ($B_4C$). Taking advantage of the rapid heating rate of Spark Plasma Sintering (SPS), structured composite could be produced by limiting the grains growth and phase segregation. Characterisation of the composite structures and mechanical properties were carried out using electron microscopy techniques, X-ray diffraction and micro/nano-indentation test. Results have shown that the optimised mix of $B_4C$ sintered with nanostructured $B_6O$ could achieved a high hardness of 40 GPa and fracture toughness of 4.82 MPa·m$^{1/2}$. Using a reactive-SPS technique to sinter $B_4C$ in nitrogen gas environment, a unique core-shell structure of $B_4C$-hBN was produced. Nano-indentation test of the $B_4C$-hBN composite shows that an average high local hardness of 56.7 GPa was achieved.

INTRODUCTION

Superhard nanostructured ceramic materials are prized for their extreme mechanical robustness and are ideal candidates for the construction of nanocomposite with promising properties of high strength, high toughness and low density. Boron suboxide ($B_6O$) in recent years has received much attention as a novel superhard material with hardness comparable to cubic boron nitride (cBN) (Herrmann et al., 2013). In addition, $B_6O$ can be synthesized at or near ambient pressure, which makes it a more economical alternative as compared to other superhard material such as diamond and cBN. An approach to enhance mechanical robustness of superhard material is to use nanostructured materials as building blocks and organize them into a complex hierarchical structure (Su et al., 2011). In our research, we have studied the synthesis of nanostructured $B_6O$ and the consolidation of $B_4C$-$B_6O$ composites in varying mix ratios.

The study of biological material structures and systems has also gained significant interests among material scientists and researchers. Biological materials have undergone millions of years of evolution to form complex hierarchical structured composites whose outstanding mechanical properties could even exceed that of its constituent materials (Meyers et al., 2008). One example of such biocomposite is the nacreous layer of mollusc shell, which could achieve an impressive work of fracture that is 3000 times greater than its constituent material (Currey, 1977) with negligible loss in the modulus (Wegst and Ashby, 2004). Mechanical properties of conventional composites could be enhanced by mimicking biological material’s structured ‘hard’ core with ‘soft’ matrix, which allows the efficient transfer of mechanical stress, dissipate energy and resist cracking (Naslain et
al., 1991, Meyers et al., 2008, Chen et al., 2012). A method to produce a hard-soft structured composite is by reacting boron carbide (B$_4$C) powder with nitrogen gas to create a core-shell particle of B$_4$C-hBN follow by consolidation. The reaction and characterisation of the structures and properties would be discussed in this paper.

**EXPERIMENTAL SECTION**

Commercial boron carbide powder (1.5micron, 89-92% purity) from Sinopharm Chemical Reagent Co. Ltd. (China) was used in the current study. Boron suboxide (B$_6$O) was synthesized through a solid-liquid reaction between commercially available amorphous boron from Fluka (<0.1μm, purity 95-97%) and boron oxide from Sigma-Adrich (99.99%). The general reaction process could be found in equation 1 below.

$$\text{16 B (s) + B}_2\text{O}_3 (l) \text{ in excess } \rightarrow 3 \text{ B}_6\text{O (s)}$$

The synthesized B$_6$O and B$_4$C were mechanically mixed and consolidated using SPS machine produced by Sumitomo Coal Mining Co. Ltd (DR SINTER series SPS-1050, Japan), equipped with a 100 kN uniaxial press. Samples were prepared by mixing B$_6$O with different content of 0, 3, 5, 10, 20, 40 wt% B$_4$C. The samples were heated at elevating heating rates from 5 to 500 °C/min up to 1800 °C with a pressure of 80 MPa applied and holding time of 1 min in argon gas.

The chemical reaction process illustrated in equation 2 shows the reaction between B$_4$C and N$_2$ gas to form hexagonal boron nitride (hBN) and free carbon.

$$\text{B}_4\text{C (s) + 2 N}_2 (g) \rightarrow 4 \text{ BN (s)} + \text{C (s)}$$

The sintering was similarly conducted using the same SPS machine with continuous flow of N$_2$ gas at 2 L/min. Pressure was gradually applied uniaxially from 25 to 120 MPa during sintering. The samples were heated at elevating heating rates from 5 to 500 °C/min up to 1800 °C with a dwell time of 10 min. For comparative study, B$_4$C samples with 0.5-25 %wt of hexagonal boron nitride powder, produced by Wako Pure Chemicals (Japan), were also mechanically mixed and sintered under the same consolidation condition using inert argon gas.

**RESULTS AND DISCUSSION**

**Boron carbide – boron suboxide (B$_4$C-B$_6$O) composite**

Nanostructure of B$_6$O was grown using a controlled melt technique to limit the growth process. This was done by reacting amorphous boron in a viscous solution of boron acid melt which prevent the particles from agglomeration and aggregation throughout the reaction process. Figure 1 (a) shows the SEM image of the synthesized nanostructure of B$_6$O powder. The B$_6$O powder shows a star-like morphology with multiple re-entrant angles which would significant increase the amount of grain boundary after sintering. Figure 1 (b) shows the XRD patterns of the specimens with different mix ratio of B$_4$C-B$_6$O after SPS treatment at 1800°C for 1 min and uniaxial pressure of 80 MPa. Strong diffraction peaks for single phase B$_6$O could be observed without any addition of B$_4$C. Diffraction pattern for samples with 3 to 40 wt% B$_4$C shows increasing B$_4$C peaks intensity with respect to the B$_4$C mix ratio.
With the use of SPS technology, near-full dense of ≥98% were achieved for all samples as shown in Table 1. Result from Vickers indentation test of sintered pure B\textsubscript{6}O shows a hardness of 34 GPa and fracture toughness of 4 MPa.m\textsuperscript{1/2} was obtained. Furthermore, B\textsubscript{4}C with 90wt%B\textsubscript{6}O nanocomposite have hardness above than 40 GPa and fracture toughness of 4.82 MPa.m\textsuperscript{1/2}. Such high hardness and high toughness structured composite would not have been possible through conventional hot press method.

<table>
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<tr>
<th>Sample ID</th>
<th>B\textsubscript{4}C wt%</th>
<th>Temperature °C</th>
<th>Time min</th>
<th>Pressure MPa</th>
<th>Relative density %</th>
<th>Hardness GPa</th>
<th>Fracture toughness MPa.m\textsuperscript{1/2}</th>
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<tr>
<td>B\textsubscript{4}C-60%B\textsubscript{6}O</td>
<td>40</td>
<td>1800</td>
<td>1</td>
<td>80</td>
<td>97.9</td>
<td>35.35±0.95</td>
<td>5.32±0.22</td>
</tr>
<tr>
<td>B\textsubscript{4}C-80%B\textsubscript{6}O</td>
<td>20</td>
<td>1800</td>
<td>1</td>
<td>80</td>
<td>98.2</td>
<td>38.89±0.63</td>
<td>4.93±0.19</td>
</tr>
<tr>
<td>B\textsubscript{4}C-90%B\textsubscript{6}O</td>
<td>10</td>
<td>1800</td>
<td>1</td>
<td>80</td>
<td>98.5</td>
<td>40.75±1.27</td>
<td>4.82±0.20</td>
</tr>
<tr>
<td>B\textsubscript{4}C-95%B\textsubscript{6}O</td>
<td>5</td>
<td>1800</td>
<td>1</td>
<td>80</td>
<td>98.6</td>
<td>38.45±1.02</td>
<td>4.62±0.13</td>
</tr>
<tr>
<td>B\textsubscript{4}C-97%B\textsubscript{6}O</td>
<td>3</td>
<td>1800</td>
<td>1</td>
<td>80</td>
<td>98.6</td>
<td>35.41±0.73</td>
<td>4.56±0.18</td>
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**Boron carbide – boron nitride (B\textsubscript{4}C-hBN) composite**

Density of the B\textsubscript{4}C-hBN samples measured by Archimedes method shows that all samples have a relative densities of 96–98.6%. XRD patterns from figure 2 (a) shows the formation of hBN phase from B\textsubscript{4}C powder after nitridation in N\textsubscript{2} gas atmosphere as represented in equation 1. Apart from B\textsubscript{4}C, XRD of the initial commercial powder had shown the presence of B\textsubscript{2}O\textsubscript{3} phase which was a common residue from commercial B\textsubscript{4}C synthesis process. The B\textsubscript{2}O\textsubscript{3} peak after nitridation appears significantly reduced which could be attributed to formation of hBN as shown in equation 3 below.

\[
2 \text{B}_2\text{O}_3 (l) + 3 \text{C} (s) + 2 \text{N}_2 (g) \rightarrow 4 \text{BN} (s) + 3 \text{CO}_2 (g)
\]  

As both hBN and graphite shared very similar crystal structure, it was often difficult to identify the exact composition of each component from the XRD peaks. Elemental analysis by EDS as shown in figure 2 (b) revealed strong signal of nitrogen in the reactive-sintered composite which was evidential to the successful reaction of both B\textsubscript{2}O\textsubscript{3} and B\textsubscript{4}C to form hBN.
Figure 2. (a) XRD patterns of B₄C powder before and after nitridation in N₂ gas. (b) SEM image of sintered B₄C in N₂ gas with EDS analysis insert (bottom right) (Xie et al., 2013)

TEM image from figure 3 (a, b) show the B₄C powder after nitridation. Layers of hBN shell were found to encapsulate individual B₄C grains. In addition, the size of B₄C grains was found to be in the submicron range, which was smaller than the initial powder size of 1.5 micron. Crystallite size of hBN determined by Rietveld refinement of the XRD pattern was found to be fairly constant at 30-50nm for specimens with more than 3 %wt of hBN. TEM image from figure 3 (c, d) shows the cross section of the reactive-sintered B₄C in N₂ gas that was cut using Focused Ion Beam (FIB). The newly synthesized hBN was found to be located along the grains boundaries forming a continuous 3D matrix in the composite. The hBN layer in the composite could potentially provide a transitional region for stress redistribution, thus mitigate brittle-failure and increase fracture toughness.

Figure 3. TEM image of (a, b) nitrided B₄C powder and (c, d) cross section of sintered B₄C in N₂ gas cut by FIB.(Xie et al., 2013)

Mechanical properties of the core-shell B₄C-hBN ceramic matrix composite in figure 4 shows the results from the indentation test. The highest averaged hardness value for Vickers and Berkovich indentation achieved were 39.3 GPa and 56.0 GPa respectively at 0.4%wt of hBN. These results show that an optimum amount of hBN was required to achieve an equal redistribution of stress to the load-bearing material structure. However, excessive amount of hBN deteriorate the hardness due to grain boundary shearing.
Comparison with mechanical mixed sintered B₄C and hBN had shown that the micro-hardness does not have substantial difference with nitrided B₄C. However, the most significant result was achieved from the high localise hardness measured by Berkovich indenter tip. It was clear that the high value registered was not due to indentation size effect as the hardness of mechanically-mixed B₄C-hBN has comparatively lower value. This high hardness values were attributed to the structured configuration of B₄C and hBN at the nano-scale. The reasons that the material did not perform as well in the micro-hardness could possibly due phase segregation and porosity which could not be totally eliminated. Nevertheless, results from the TEM and Berkovich indentation have shown the capability of reactive-SPS to form complex structured B₄C-hBN with good mechanical properties which would not have been possible without the use of rapid sintering processing of SPS technology.

CONCLUSION
We have prepared two forms of nanostructured composites by using synthesized nanostructured materials as a precursor and also the using of a reactive-SPS technique to produce a core-shell structured material. The B₄C with 90wt% B₂O exhibits the highest hardness above 40 GPa with a fracture toughness of 4.8 MPa·m¹/₂. Such high hardness and high toughness structured composite would not be possible to be sintered through conventional hot press method. Boron carbide nitrided through a reactive-SPS process produced a unique core-shell structured composite consist of B₄C encapsulated by hBN. The highest hardness values measured at an optimum content of 0.4%wt of hBN, by both Vickers and Berkovich indentation were 39.3 GPa and 56.0 GPa respectively. Superior local hardness was measured by nano-indentation was observed in the core-shell structured B₄C-hBN but not in mechanically-mixed sintered B₄C-hBN. The hBN matrix provided a transitional region for effective redistribution of the load, thus it could mitigate brittle-failure and increase toughness of the composite. The application of nanostructured materials and SPS processing are a perfect combination to facilitate densification of difficult-to-consolidate ceramics and useful in the forming of a new class of high hardness and toughness structured nanocomposite materials.
ACKNOWLEDGMENTS
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REFERENCES