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BORON CARBIDE-BASED NANOSTRUCTURED COMPOSITE BY SPARK PLASMA SINTERING

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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 to 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 B4C 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 56.7GPa 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 make 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 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 lost in the modulus (Wegst and Ashby, 2004). Mechanical properties of conventional composites could be enhanced by mimic 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_4C) powder with nitrogen gas to create a core-shell particle of B_4C-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_6O) 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.

$$16\ B\ (s)\ \ +\ \ B_2O_3\ (l)\ \text{in excess}\ \ \rightarrow\ \ 3\ B_6O\ (s) \tag{1}$$
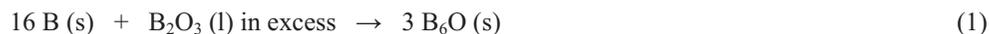
The synthesized B_6O and B_4C were mechanically mixed and consolidated using SPS machine produced by Sumitomo Coal Mining Co. Ltd (DR SINTER series SPS-1050, Japan), equipped with a 100 kN uniaxial press. Samples were prepared by mixing B_6O with different content of 0, 3, 5, 10, 20, 40 wt% B_4C. The 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_4C and N_2 gas to form hexagonal boron nitride (hBN) and free carbon.

$$B_4C\ (s)\ \ +\ \ 2\ N_2\ (g)\ \ \rightarrow\ \ 4\ BN\ (s)\ \ +\ \ C\ (s) \tag{2}$$
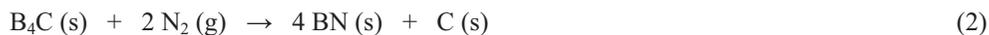
The sintering was similarly conducted using the same SPS machine with continuous flow of N_2 gas at 2 L/min. Pressure was gradually applied uniaxially from 25 to 120 MPa during sintering. The samples were heated at elevating heating rates from 5 to 500 °C/min up to 1800 °C with a dwell time of 10 min. For comparative study, B_4C 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_4C-B_6O) composite

Nanostructure of B_6O 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_6O powder. The B_6O 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_4C-B_6O after SPS treatment at 1800˚C for 1 min and uniaxial pressure of 80 MPa. Strong diffraction peaks for single phase B_6O could be observed without any addition of B_4C. Diffraction pattern for samples with 3 to 40 wt% B_4C shows increasing B_4C peaks intensity with respect to the B_4C mix ratio.
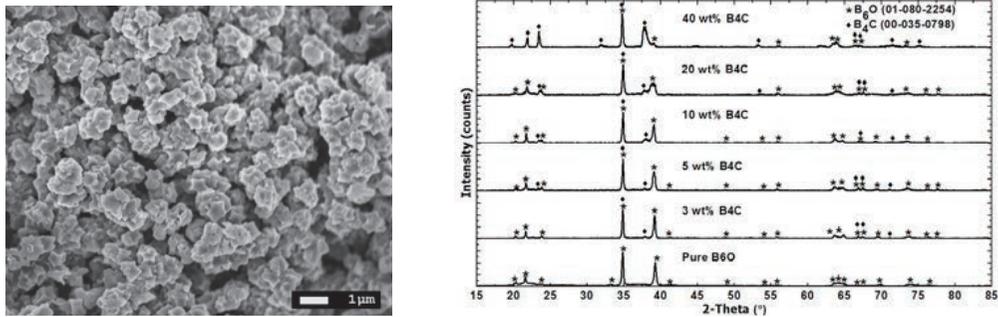
Figure 1. (a) SEM image of nanostructured B_6O powder. (b) XRD patterns of B_4C-B_6O composites fabricated via SPS (Solodkyi et al., 2013). Phases and ICSD files as indicated.

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_6O shows a hardness of 34 GPa and fracture toughness of 4 MPa.m$^{1/2}$ was obtained. Furthermore, B_4C with 90wt%B_6O nanocomposite have hardness above than 40 GPa and fracture toughness of 4.82 MPa·m$^{1/2}$. Such high hardness and high toughness structured composite would not have been possible through conventional hot press method.

Table 1. Sintering conditions and properties of SPS B_4C-B_6O composites (Solodkyi et al., 2013).

Sample ID	B_4C wt%	Temperature °C	Time min	Pressure MPa	Relative density %	Hardness GPa	Fracture toughness MPa.m$^{1/2}$
B_4C-60%B_6O	40	1800	1	80	97.9	35.35±0.95	5.32±0.22
B_4C-80%B_6O	20	1800	1	80	98.2	38.89±0.63	4.93±0.19
B_4C-90%B_6O	10	1800	1	80	98.5	40.75±1.27	4.82±0.20
B_4C-95%B_6O	5	1800	1	80	98.6	38.45±1.02	4.62±0.13
B_4C-97%B_6O	3	1800	1	80	98.6	35.41±0.73	4.56±0.18

Boron carbide – boron nitride (B_4C-hBN) composite
Density of the B_4C-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_4C powder after nitridation in N_2 gas atmosphere as represented in equation 1. Apart from B_4C, XRD of the initial commercial powder had shown the presence of B_2O_3 phase which was a common residue from commercial B_4C synthesis process. The B_2O_3 peak after nitridation appears significantly reduced which could be attributed to formation of hBN as shown in equation 3 below.

$$2\,B_2O_3\,(l)\ +\ 3\,C\,(s)\ +\ 2\,N_2\,(g)\ \rightarrow\ 4\,BN\,(s)\ +\ 3\,CO_2\,(g) \hspace{2cm} (3)$$
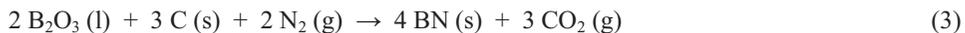
As both hBN and graphite shared very similar crystal structure, it was often difficult to identify the exact composition of each component from the XRD peaks. Elemental analysis by EDS as shown in figure 2 (b) revealed strong signal of nitrogen in the reactive-sintered composite which was evidential to the successful reaction of both B_2O_3 and B_4C to form hBN.
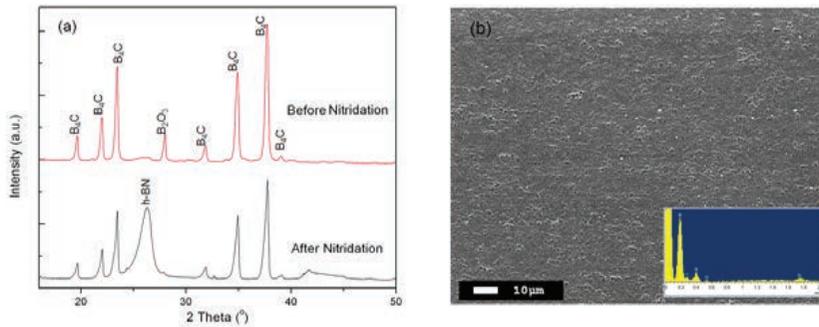
Figure 2. (a) XRD patterns of B_4C powder before and after nitridation in N_2 gas. (b) SEM image of sintered B_4C in N_2 gas with EDS analysis insert (bottom right) (Xie et al., 2013)

TEM image from figure 3 (a, b) show the B_4C powder after nitridation. Layers of hBN shell were found to encapsulate individual B_4C grains. In addition, the size of B_4C 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 B_4C in N_2 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.
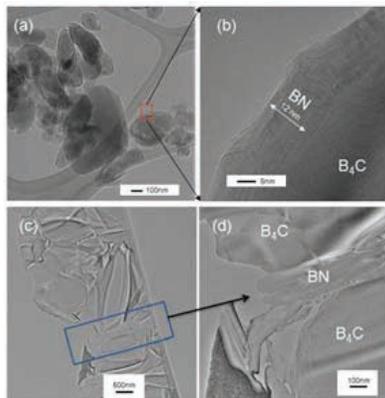

Figure 3. TEM image of (a, b) nitrided B_4C powder and (c, d) cross section of sintered B_4C in N_2 gas cut by FIB.(Xie et al., 2013)

Mechanical properties of the core-shell B_4C-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.
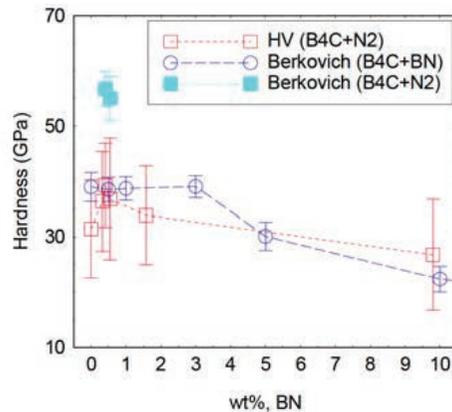
Figure 4. Vickers/Berkovich hardness vs. content of BN in composite (Xie et al., 2013). For the SPS of mechanically-mixed B_4C and hBN powders (B_4C+BN), the %wt of hBN was the amount of commercial hBN used in the mixture. For the reactive-SPS B_4C reacted with N_2 (B_4C+N_2), the %wt of hBN was the estimated value from the XRD Rietveld refinement analysis.

Comparison with mechanical mixed sintered B_4C and hBN had shown that the micro-hardness does not have substantial difference with nitrided B_4C. 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 B_4C-hBN has comparatively lower value. This high hardness values were attributed to the structured configuration of B_4C 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 B_4C-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 B_4C with 90wt% B_6O exhibits the highest hardness above 40 GPa with a fracture toughness of 4.8 MPa·m$^{1/2}$. 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 B_4C 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 B_4C-hBN but not in mechanically-mixed sintered B_4C-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.

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