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Silberschmidt, V.; Xie, Sky Shumao; Vasylykiv, Oleg; Tok, Alfred Ling Yoong

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Bio-inspired structured boron carbide-boron nitride composite by reactive spark plasma sintering

Sky Shumao Xie^{a,b}, Oleg Vasylykiv^{b,c}, Alfred I. Y. Tok^{a*}

^aSchool of Materials Science and Engineering, Nanyang Technological University, Singapore 639798, Singapore

^bTemasek Laboratories, Nanyang Technological University, Singapore 637553, Singapore

^cNational Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan

*Corresponding author: MIYTok@ntu.edu.sg

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Nature creates composite materials with complex hierarchical structure that possesses impressive mechanical properties enhancement capabilities. An approach to improve mechanical properties of conventional composites is to mimic biological material structured 'hard' core and 'soft' matrix system. This would allow the efficient transfer of load stress, dissipate energy and resist cracking in the composite. In the current study, reactive spark plasma sintering (SPS) of boron carbide B_4C was carried out in a nitrogen N_2 gas environment. The process created a unique core-shell structured material with the potential to form a high impact-resistant composite. Transmission electron microscopy observation of nitrated- B_4C revealed the encapsulation of B_4C grains by nano-layers of hexagonal-boron nitride (*h*-BN). Effect of the *h*-BN contents on hardness were measured using micro- and nano-indentation. Commercially available *h*-BN was also mechanically mixed and sintered with B_4C to compare the effectiveness of nitrated B_4C . Results have shown that nitrated B_4C have higher hardness value and the optimum content of *h*-BN from nitridation was 0.4% wt with the highest nano-indentation hardness of 56.7GPa. The high hardness was attributed to the *h*-BN matrix situated between the B_4C grain boundaries which provided a transitional region for effective redistribution of the stress in the material.

Keywords: boron carbide, boron nitride, structured composite, reactive spark plasma sintering, indentation test

Introduction

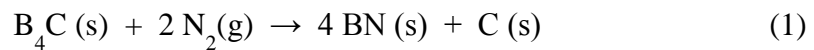
The study of biological material structures and systems has gained significant interests among material scientists and researchers in recent years. Biological materials have undergone millions of years of evolution to form complex hierarchical structure composites whose outstanding mechanical properties could even exceed that its constituent materials (Meyers et al., 2008). One example of such biocomposite is the nacreous layer of mollusc shell. The brick-and-mortar microstructure 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). An approach to enhance mechanical properties of conventional composites is to 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). High impact-resistant materials could be utilized in a wide range of functions such as protective equipment and impact-resistant apparatus in military and sports applications.

Similar work in biomimic of a structured 'hard-soft' material system were listed as follows: Tang et al. (2003) created a layered organic-inorganic composites made from montmorillonite clay platelets and polyelectrolytes by layer-by-layer assembly method; Bonderer et al. (2008) used alumina platelets and a chitosan polymer for the assembly of the building blocks with a colloidal-based technique; Munch et al. (2008) fabricated a ceramic/polymer hybrid material made up of alumina and polymethylmethacrylate by freeze casting of the ceramic suspension followed by polymer infiltration; and Kakisawa et al. (2010) used flake-like shaped glass powder coated with silver and fabricated the structured composite material using a 3D printing machine and hot-press to consolidate the powder. Most researches focused on ceramic-polymeric and ceramic-metallic approach to form structured composite materials, ceramic-based matrix composites however were seldom used. This was mainly due to inability of ceramics to flow and high melting temperature, which make it extremely difficult to control and form the desired structured materials. Therefore, it is essential to look into novel techniques to form light-weight, high hardness and high toughness ceramic-matrix composite.

Experimental Section

Commercial boron carbide powder (1.5micron, 89-92% purity) from Sinopharm Chemical Reagent Co. Ltd. (China) was used in the current study to form a core-shell structure of B₄C-BN. The chemical reaction process illustrated in Eqn. 1 shows the reaction between B₄C and N₂ gas to form hexagonal boron nitride (*h*-BN) and free carbon. Zhang et al. (2004) demonstrated that reaction between B₄C and N₂ was exothermic and was thermo-dynamically favourable to proceed .



B₄C powder was loaded into graphite die set for SPS consolidation. The graphite dies have an inner diameter of 10 mm and wrapped with 5 mm thick graphite felt to normalize the temperature distribution and reduce the heat loss by radiation. The SPS machine produced by Sumitomo Coal Mining Co. Ltd (DR SINTER series SPS-1050, Japan) was equipped with a 100 kN uniaxial press with the use of pulsed electric current to achieve densification. The sintering procedure was conducted with continuous flow of N₂ gas at 2 L/min. Pressure was gradually applied uniaxially from 25 to 120 MPa during sintering. After an intermediate heating of 900 °C for up to 40 min, the samples were further heated at elevating heating rates from 5 to 500 °C/min up to 1800 °C with a dwell time of 10 min. Each specimen was gradually cooled down to 600 °C at a cooling rate of 20°C/min and subsequently furnace-cooled to room temperature.

For comparative study, B₄C added with 0.5-25 %wt of hexagonal boron nitride powder, produced by Wako Pure Chemicals Industries. Ltd. (Japan), were processed by SPS under vacuum condition at 5 Pa. Reagent grade ethanol was used as a mixing medium. Homogenization was performed using ultrasonic apparatus fitted with a

titanium probe tip for 10–40 min until the slurries were dried under stirring conditions. A maximum temperature of up to 1800°C was similarly applied during sintering with 10 min of dwell time.

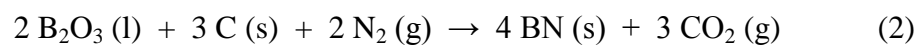
Field-Emission Scanning Electron Microscopy (FESEM) made by JEOL (JSM-7600F, Japan), equipped with Energy Dispersive X-ray Spectrometry (EDS) capability, was used to obtain micrographs and elemental analysis. Transmission electron microscopy (TEM) made by JEOL (JEM-2100F, Japan) was used to collect high resolution micrograph image. Phase composition was determined by powder X-ray diffraction (XRD) using reflection mode on a Bruker AXS diffractometer (D8 Advance, Germany) fitted with Cu-tube (CuK α radiation). The crystal structure of the B₄C was refined by Rietveld analysis using TOPAS software with fundamental parameters approach (Cheary and Coelho, 1992).

Hardness values were measured using a Vickers microhardness tester produced by Akashi Co. (MVK-E, Japan), using a load of 1 kgf with dwell time of 15 sec. Ten measurements were collected from each specimen polished surface. Localise hardness was also measured using nano-indentation by Micro Materials (NanoTest system, UK). Equipped with Berkovich diamond tip with a three-sided pyramid geometry $\gamma=70^\circ$, the diamond indenter was programmed to contact the surface of the samples at a loading rate of 1 mN/sec. The indentation load, ranging from 10 to 300 mN, was held at the maximum value in order to minimize the creep effect on unloading.

Results and Discussion

Density of the samples measured by Archimedes method shows that all samples have a relative densities of 96–98.6%. XRD patterns from Fig. 1 (a) shows the formation of *h*-BN phase from B₄C powder after nitridation in N₂ gas atmosphere as represented in Eqn. 1. Apart from B₄C, XRD of the initial commercial powder had shown the presence

of B₂O₃ phase which is a common residue of the precursor during B₄C synthesis. The B₂O₃ peak after nitridation appears to be significantly reduced which could be attributed to two possible explanations. The first reason is the sublimation of B₂O₃ above 1500°C (Patnaik, 2003) where solid B₂O₃ was vaporised and removed by the flow of nitrogen gas. Second reason is due to carbothermal reaction between B₂O₃ and simultaneous nitridation to form *h*-BN as shown in Eqn. 2 below (Aghayan et al., 2009, Bartnitskaya et al., 1986).



The latter was most likely the dominant process as earlier research have shown that the reaction between B₂O₃ and free carbon could proceed at relatively lower temperature from 1400°C (Xie et al., 2012). This was also supported by Bartnitskaya (1986) work in the synthesis of boron nitride between the temperature of 1000 to 1450°C using the same reaction process. Although B₂O₃ was known to form both B₄C and *h*-BN, the bulk of the *h*-BN observed in the XRD was form by the reacted B₄C powder as the amount of B₂O₃ could not have been sufficient to account for the *h*-BN form during through extensive heating duration.

As both *h*-BN 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 Fig 1(b), revealed strong signal of nitrogen in the reactive-sintered composite, evidential to the successful reaction of B₄C to form *h*-BN.

FIGURE 1

TEM image from Fig 2 (a, b) show the B₄C powder after nitridation. Layers of *h*-BN shell were found to encapsulate individual B₄C grains. In addition, the size of B₄C grains were found to be in the submicron range, which were smaller than the initial

powder size of 1.5 micron. This result was coherent with earlier research where the crystallite size of B_4C was found to decrease rapidly at the early stage of the nitridation process (Vasylykiv et al., 2012). Crystallite size of *h*-BN 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 BN. TEM image from Fig 2 (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 *h*-BN was found to be located along the grains boundaries forming a continuous 3D matrix in the composite. The *h*-BN layer in the composite could potentially provide a transitional region for stress redistribution, thus mitigate brittle-failure and increase fracture toughness.

FIGURE 2

Mechanical properties of the core-shell B_4C -BN ceramic matrix composite, in figure 3, also shows interesting 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 *h*-BN. These results show that an optimum amount of *h*-BN was required to achieve an equal redistribution of stress to the load-bearing material structure. However, excessive amount of *h*-BN deteriorate the hardness due to grain boundary shearing as observed in simulated and experimental materials studied by other researches (Carlton and Ferreira, 2007, Ivanov and Mishin, 2008). Some other hardness values of similar SPS of B_4C -based composites by other researcher were listed as follows, 41.8 GPa (Ye et al., 2010), 38.9 GPa (Grasso et al., 2011) and 32 GPa (Hayun et al., 2009).

FIGURE 3

Comparison with mechanical mixed sintered B_4C and *h*-BN had shown that the microhardness does not have substantial difference with nitrified 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 -BN has comparatively lower value. This high hardness could be attributed to the structured configuration of B_4C and h -BN at the nano-scale.

The reasons that material did not perform as well in the microhardness 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 -BN with good mechanical properties which would not have been possible without the fast sintering process of SPS.

Conclusion

Boron carbide nitrated through a reactive-SPS process produced a unique core-shell structured composite consist of both B_4C and h -BN. High resolution TEM revealed the h -BN located between the boundaries of B_4C grains forming a continuously 3D matrix. The highest hardness values measured, at an optimum content of 0.4%wt of h -BN, by both Vickers and Berkovich indentation were 39.3 GPa and 56.0 GPa respectively. Superior localise hardness by nano-indentation were observed in nitrated B_4C but not in mechanically-mixed sintered B_4C -BN. The structured core-shell composite which biomimic the unique structured 'hard' core with 'soft' matrix found in biological composite materials was credited for the high localise hardness. This structured composite was made possible by the fast sintering process of SPS with the use of pulsed electric current. The h -BN matrix provided a transitional region for effective redistribution of the stress, thus it could mitigate brittle-failure and increase toughness of the composite. The reactive SPS technique used to form the nano-layers of nitride-based composite could be applied in a wide range of other ceramics materials and create

a new class of mechanical properties-enhanced structured nanocomposite materials.

Acknowledgement

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Figure 1. (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)

Figure 2. TEM image of (a-b) nitrided B₄C powder and (c-d) cross section of sintered B₄C in N₂ gas cut by FIB.

Figure 3. Vickers/Berkovich hardness vs content of the BN in composite (Vasylykiv et al., 2012). For the SPS of mechanically-mixed B₄C and BN powders (B₄C+BN), the %wt of BN was the amount of commercial *h*-BN used in the mixture. For the reactive-SPS B₄C reacted with N₂(B₄C+N₂), the %wt of BN was the estimated value from the XRD Rietveld refinement analysis.

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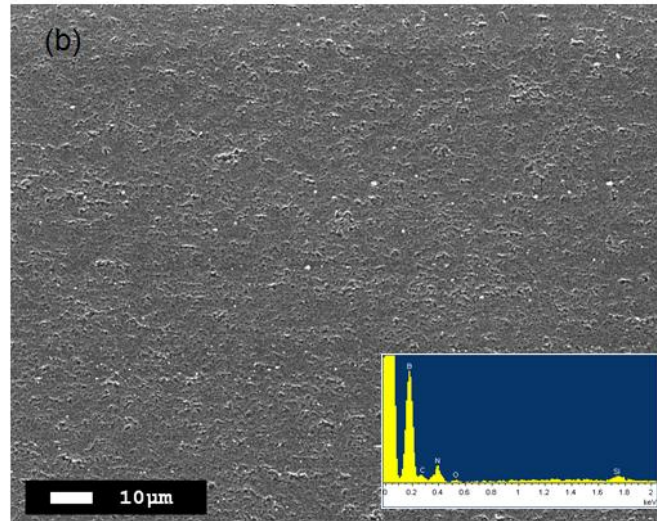
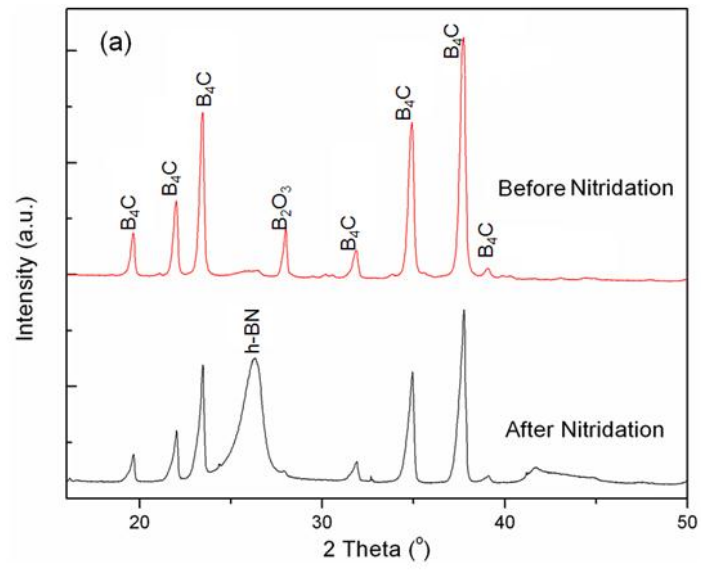


Figure 1

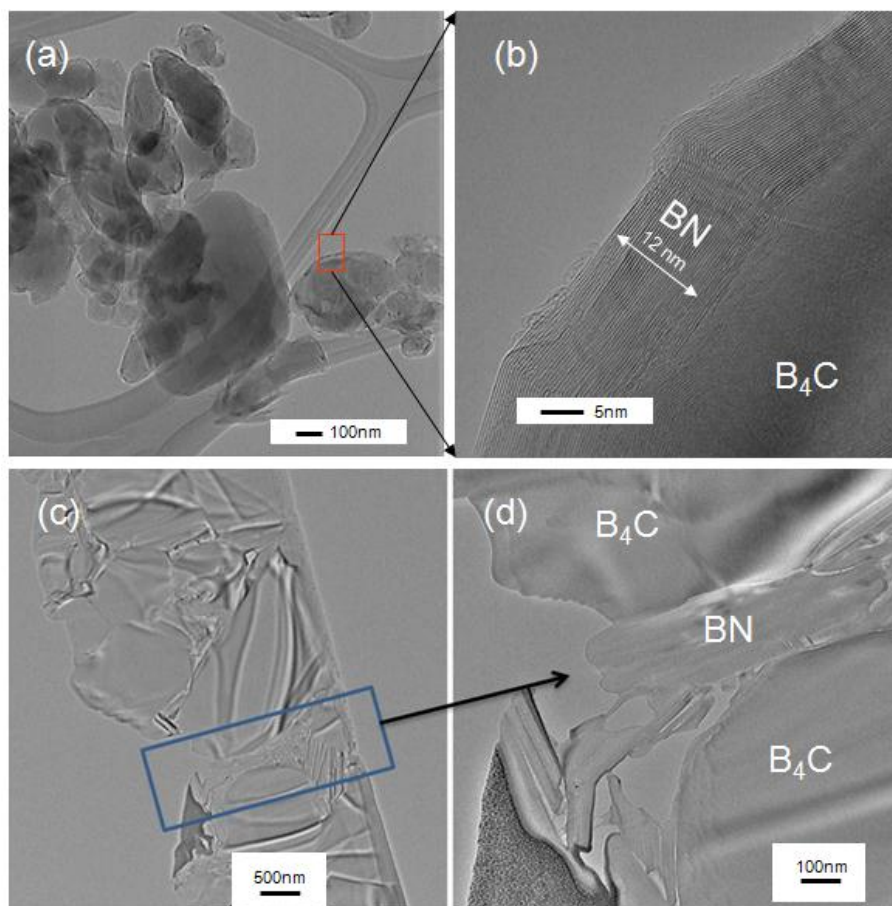


Figure 2

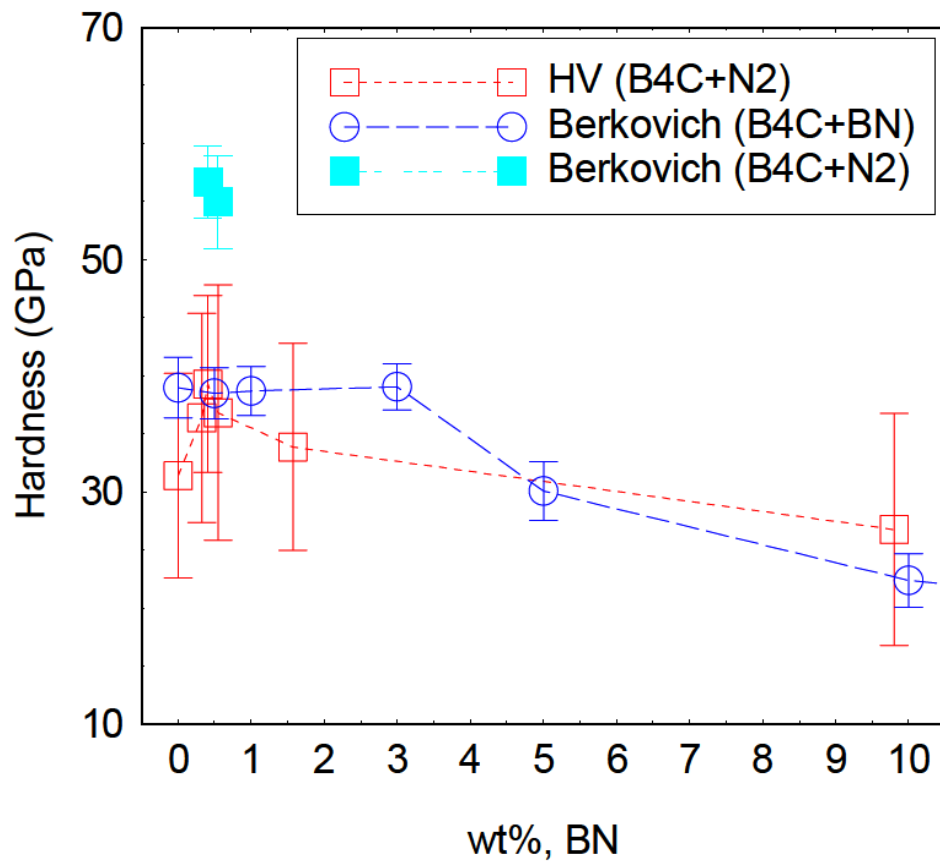


Figure 3