



Consolidation of cubic and hexagonal boron nitride composites



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ABSTRACT

Consolidating cubic boron nitride (cBN) typically requires either a matrix of metal bearing materials that are undesirable for certain applications, or very high pressures within the cBN phase stability field that are prohibitive to manufacturing size and cost. We present new methodology for consolidating high stiffness cBN composites within a hexagonal boron nitride (hBN) matrix (15–25 vol%) with the aid of a binder phase (0–6 vol%) at moderate pressures (0.5–1.0 GPa) and temperatures (900–1300 °C). The composites are demonstrated to be highly tailorable with a range of compositions and resulting physical/mechanical properties. Ultrasonic measurements indicate that in some cases these composites have elastic mechanical properties that exceed those of the highest strength steel alloys. Two methods were identified to prevent phase transformation of the metastable cBN phase into hBN during consolidation: 1. removal of hydrocarbons, and 2. increased cBN particle size. Lithium tetraborate worked better as a binder than boron oxide, aiding consolidation without enhancing cBN to hBN phase transformation kinetics. These powder mixtures consolidated within error of their full theoretical mass densities at 1 GPa, and had only slightly lower densities at 0.5 GPa. This shows potential for consolidation of these composites into larger parts, in a variety of shapes, at even lower pressures using more conventional manufacturing methods, such as hot-pressing.

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1. Introduction

The cubic and hexagonal structures of boron nitride both have vastly different physical and mechanical properties from one another that are both uniquely valuable for a number of applications. Boron and nitrogen are isoelectronic with carbon, leading to a phase diagram for boron nitride that is analogous to carbon [1–3]. Boron nitride has cubic and hexagonal structures with similar crystal structures and mechanical properties to diamond and graphite respectfully [2]. However, boron nitride has lower chemical reactivity and higher thermostability, which makes it more preferable over diamond and graphite for high temperature applications under oxidizing conditions [2,3].

Hexagonal boron nitride (hBN) has a layered structure, with strong, intra-layer covalent bonding and weak, inter-layer van der Waals bonding. As a result hBN has low overall hardness that allows it to be commonly utilized as a solid medium lubricant, often referred to as 'white graphite', under high temperature and highly oxidizing conditions [3]. hBN is sometimes mixed into ceramics to give them self-lubricating properties; and into oxides, borides, and carbides to increase resistance against thermal shock or corrosion [3]. It is commonly used in

experiments as a solid pressure media, because of its effectiveness at transmitting pressure. Boron and nitrogen are low Z elements making boron nitride transparent to x-ray radiation, so hBN is also commonly used as a crucible/capsule material in synchrotron studies. With properties similar to graphite, the hexagonal sheets of boron nitride can be disordered to form turbostratic phases, nanotubes, and aerogels [4–6].

Cubic boron nitride (cBN) occurs naturally as a rare mineral named qingsonite that was recently discovered in Tibet as microscopic inclusions inside Cr-rich rocks originating from deep earth [7]. cBN is a superhard material that is second only to diamond in hardness. Due to its hardness, strong covalent bonding, and stability it is commonly synthesized and used in many cutting and grinding applications [2,3]. However, these same properties present significant challenges for sintering cBN powders into dense, low porosity parts.

There are two commonly used processes for consolidating cBN. The first process transforms hBN within the cBN phase stability field, typically requiring very high pressures (≥ 5.8 GPa) and temperatures (≥ 1450 °C) [8]. These conditions are prohibitive to manufacturing size and cost. Also, cBN by itself is brittle and lacks the fracture toughness required for many commercial applications. Alternatively, cBN powder is consolidated within a matrix of other metal containing powders to create cermets for cutting tools [9–11]. These metals are potential sources of contamination that are undesirable for some machining procedures. All grinding processes will result in some degree of contamination in

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the finished product, so the choice and overall purity of grinding media are an important consideration for applications that are sensitive to even ppm or ppb levels [12–15]. Also phase transformation of cBN to hBN is a potential challenge when consolidating cBN outside of its stability field [16]. The current methods for consolidating cBN have limitations in size, shape, and potential for contamination.

Here we present the methods we have developed to combine cBN and hBN with a small amount of binder ($\text{Li}_2\text{B}_4\text{O}_7$ or B_2O_3) to create versatile, fully-dense, high purity boron nitride ceramics that utilize the unique properties of both BN phases for several advantages over existing BN ceramics and cermets. The presence of hBN lubricates impinging grain contacts during consolidation allowing for fully dense, high cBN content composites to be created at relatively lower pressures and temperatures in comparison to other methods. Despite the presence of hBN, the composites have high elastic stiffness that in some cases exceeds even the strongest steel alloys.

There are several potential applications that could benefit from utilization of cBN/hBN composites. These cBN composites can be machined, ground, or potentially pressed into specific shapes to match the needs of a variety of grinding applications. The presence of hBN would give the grinding tools self-lubricating properties [3], and could be used in grinding or polishing in applications where metal contamination is unacceptable [12–15]. Finally, there is a substantial difference between the densities of the two main components, hBN (2.1 g/cm^3) and cBN (3.45 g/cm^3), that allows mixtures of these phases to be tailored to a wide range of densities to match specific needs. Boron nitride crucibles have been used as crucibles in studies on metal sulfide systems [17,18], and serve as highly effective reducing agents [19]. These ceramics are highly transparent to x-ray radiation because they are composed entirely of low Z elements (B, N, Li, O), making them potentially useful materials as transparent crucibles or anvils in synchrotron studies [20,21]. The densities of cBN/hBN composites could be tailor-matched to the materials of interest to reduce reflections during radiographic or tomographic x-ray imaging.

2. Experimental techniques

Samples were composed of varying proportions of cBN (66–80 vol%), hBN (15–25 vol%) and binder (0–6 vol%). Two types of materials were explored for use as a binder and consolidation aid: lithium tetraborate – $\text{Li}_2\text{B}_4\text{O}_7$ (LTB) with a melting point of $930 \text{ }^\circ\text{C}$ and boron oxide – B_2O_3 with a melting point of $450 \text{ }^\circ\text{C}$ at 1 atm. Most runs used LTB (Alfa Aesar), one run used boron oxide B_2O_3 (Alfa Aesar), and several runs were performed without any binder phase present. The hBN (Alfa Aesar) was – 325 mesh powder ($<44 \mu\text{m}$), and the LTB (Alfa Aesar) was – 22 mesh powder ($<710 \mu\text{m}$). Several different size distributions of cBN were used by mixing sieved particle sizes of 0–2, 30–40 (Diamond Innovations), or 2–4 μm (Engis). Samples compositions are listed in Table 1. All powders were ground and mixed together for 30 min duration using a Retsch RM100 fitted with an agate mortar and a spring loaded pestle set to intermediate force.

The piston cylinder press technique has been proven useful for consolidation of both high hardness and metastable materials in previous studies [22]. Powder mixtures were consolidated using a piston cylinder press at pressures of either 0.5 or 1.0 GPa and temperatures between 900 and $1300 \text{ }^\circ\text{C}$. Approximately 1.2 g of these powder mixtures were loaded into fired pyrophyllite capsules (Rockland Research) by tamping down the powder with a drill blank. The loaded capsules were placed into an assembly with an alumina sheathed type C thermocouple, MgO rod that provided electrical insulation, a graphite furnace, a Pyrex sleeve that provided thermal insulation, and a salt sleeve that allowed effective transmission of pressure at the target run temperatures (Fig. 1). The assembly is inserted into a pressure plate with a carbide core that is end-loaded to increase its strength. A piston is driven by a separate ram to generate sample pressure. Samples were heated and

cooled at a rate of $100 \text{ }^\circ\text{C/min}$ to/from target temperatures where samples dwelled for 30 min (Fig. 2).

Phase transformation of cBN to hBN was an issue that affected our preliminary runs; however, methods to prevent this reaction from occurring were identified and incorporated into the procedure used in later runs. For our initial runs (referred to hereafter as ‘method 1’), assemblies loaded with sample powders were placed into a drying oven at $\sim 105 \text{ }^\circ\text{C}$ for durations of $\sim 20 \text{ min}$ for runs 1–3 and 15–30 h for runs 4–10. Based on our observations from method 1 runs, two procedural changes were made for subsequent runs 13–58 (referred to hereafter as ‘method 2’). First we eliminated the use of cBN powder that was $<2 \mu\text{m}$ in size from sample powder mixtures. Second, capsules loaded with sample powder mixtures and adjacent MgO and graphite assembly parts were then fired at $700 \text{ }^\circ\text{C}$ under 250 sccm of flowing N_2 gas for 4 h, and promptly transferred to the drying oven for $<8 \text{ h}$ prior to experiments.

High precision density measurements are ultimately the best way to confirm that full densification of powder mixtures was achieved while maintaining the same composition throughout experiments. Consolidated samples were machined into cylinders to simplify their geometries and enable accurate measurements. To calculate the geometric volume and densities, diameter and thickness of the cylindrical samples were measured by calipers with $25 \mu\text{m}$ accuracy, and weight was measured with 0.1 mg accuracy. These errors were propagated to calculate sample density errors. Geometric densities of consolidated samples were compared to the theoretical mass densities of the starting powder mixtures.

3. Analytical techniques

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed using a Netzch TG 449 F1 Jupiter with a silica carbide furnace to quantify the amount of volatile materials in powders. The instrument has $2.5 \times 10^{-8} \text{ g}$ TGA resolution. Approximately 100 mg of each individual constituent powder used in this study was heated at rate of $20 \text{ }^\circ\text{C/min}$ under 20 sccm of flowing N_2 gas to a temperature of $1500 \text{ }^\circ\text{C}$ for the hBN and cBN powders in Al_2O_3 crucibles, and to $1000 \text{ }^\circ\text{C}$ for the LTB powders in $\text{Pt}_{90}\text{Rh}_{10}$ crucibles to prevent sample/crucible reactions. Crucibles were burned out without powder beforehand using conditions identical to measurements. Powders were rerun using the same conditions to subtract background signals for TGA/DSC data. Powders were kept under continuous nitrogen flow between the first and second runs without exposing samples to air.

Scanning electron microscopy (SEM) was performed to verify grain size distribution, and purity of unmixed and mixed powders using an FEI XL30 S-FEG. Samples were viewed via Backscatter Electrons utilizing a solid state backscatter detector. The parameters used for imaging were: 20 kV voltage, 1.3 nm spot size, $\sim 148 \text{ pA}$ beam current, 1.4 μm depth.

X-ray diffraction (XRD) was performed before and after consolidation to verify composition using a Bruker AXS D8 ADVANCE X-ray diffractometer equipped with a LynxEye 1-dimensional linear Si strip detector. Samples were scanned from 2θ between $20\text{--}80^\circ$. The step scan parameters were 0.02° step and 1 s counting time per step with a 6 mm variable divergence slit and a 0.5° antiscatter slit. The sample was x-rayed with Ni-filter Cu radiation from a sealed tube operated at 40 kV and 40 mA. X-ray reference material (Bruker corundum standard) was analyzed before and after the samples to ensure goniometer alignment. No peak shift was observed in the reference material. Sample compositions were determined using the Rietveld refinement method, with $\pm \sim 5\%$ error [23].

Mechanical properties of consolidated samples were assessed by performing ultrasonic measurements with both ‘time of flight’ (TOF) and ‘resonant spectral ultrasound’ (RUS) methods. For TOF, one transducer was placed against samples producing ultrasonic waves and detecting their return echoes as they traversed to the other end of the

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