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Hardness and thermal stability enhancement of polycrystalline diamond compact through additive hexagonal boron nitride

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ABSTRACT

Hexagonal boron nitride (hBN) was used as the additive in improving the hardness and thermal stability of polycrystalline diamond compact under high temperature and high pressure. Indentation testing on diamond/cubic boron nitride (cBN) composites indicated a Vickers hardness of 96 ± 7 GPa, rivaling the hardness of monocrystal diamond. Thermal gravimetric analysis (TGA) suggested that the composites of diamond/cBN are thermally stable in air up to ~910 °C which is higher than that of pure polycrystalline diamond compact (~750 °C). Raman, TGA, x-ray photoelectron spectroscopic and microstructure analyses all revealed the features of diamond/cBN composition beyond both diamond and cBN.

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Diamond is well known superhard materials with high hardness, large bulk moduli, high melting point and thermal conductivity [1–4]. Tools made of diamond are widely used for cutting and drilling, but poor thermal stability has limited its applications [5]. The onset oxidation temperature in air is about 800 °C for nature diamond [6,7] and <700 °C for synthetic diamond compacts [2], resulting in invalid of diamond tools at high temperature. Hence, in searching for novel superhard materials with both high hardness and thermal stability has long been desirable [5,8].

Conventionally, diamond composite materials were fabricated with some Fe, Co, Ni, Si and SiC etc. catalyst/solvent/additives. However, these diamond composite materials only possess one excellent performance of strength or chemical inertness owing to low melting point temperature of adhesives or relative infirm bonding between diamond and adhesives [9–12]. Therefore, these related diamond compacts having both high hardness over 75 GPa and thermostability of over 800 °C are hard to be prepared [13,14]. In consideration of the close propinquity of diamond and cBN in crystal structure and covalent bonding character, experimentally, BC_2N ternary phases, BC_4N solid solution and diamond-cBN alloy have been synthesized using various carbon materials and cubic boron nitride as raw materials at high temperature and high pressure (HPHT) [15–26]. Theoretical studies [27–30] also predict the existence of B—C—N phases or solid solution which has a hardness approaching that of diamond. However, the mechanical strength of these samples are variegated and the thermochemical stability of these phases did not achieve the desired effect as a result of technical obstacles and inappropriate binder in synthesizing well-sintered diamond composite materials. Here we attempt to improve the thermal stability of the diamond compacts and remain its high mechanical strengths by doping hexagonal boron nitride (hBN) as adhesives under HPHT. The hBN was chosen as an additive for two reasons: on the one hand, hBN is a "soft" phase and it could be easily squeezed under high pressure to fully fill the pores between the particles for obtaining a high-density sample. Another, hBN could convert to a superhard phase cBN under HPHT, and may form a B—C—N solid solution transition layer at the grain boundaries, leading to strengthening of grain boundary. Based on previous experiments and theoretical calculations [15,25,26,31], B-C-N phase or solid solution at grain boundaries between diamond and cBN grains were expected to be formed, which was in favour of resisting oxidation and graphitization of diamond compacts at higher temperatures, leading to acquire ultrahardness and superior thermal stability of diamond/cBN composite bulk materials which was able to be used to high-speed cut hardened-steel.

In quest of materials that have both prominent mechanical performance and thermochemical stability, mechanical alloying process was employed to treat mixture of diamond and hBN under simultaneous HPHT conditions. The homogeneous mixture of diamond (grain size: 0–1 μm, >99.9% purity, Zhongnan Jiete Super-abrasives Co., Ltd., Zhengzhou, China) and hBN (grain size: 50–300 nm, >99.9% purity, Aladdin Co., Ltd., Shanghai, China) powder was used as the starting materials. It well know that the porosity can reach 20–30% when the grains are densely packed [32]. In order to fill the pores, the weight ratio of 6: 1

mixture powder of diamond and hBN was used. The powders were treated in vacuum furnace of 3.0×10^{-3} Pa at 1000 °C for 1 h to get rid of impurity gases attached to the grain surface. After vacuum heat treatment, the mixtures were contained in an Pt capsule, and then were subjected to 15 GPa and 1900–2100 °C HPHT treatments in a two-stage (6–8 system) large volume multianvil apparatus [25,33]. A 10-mm MgO octahedron was used as pressure medium, a ZrO_2 sleeve as thermal insulator and a Re cylinder as heater. The pressure was calibrated by means of the well-known pressure-induced phase transitions and the cell temperature was measured directly using a WRe3%–WRe25% thermocouple. Samples were first compressed to a target pressure and then heated to the desired temperature with a heating rate of about 100 °C/min. After being maintained for a desired treatment time, the samples were quenched to ambient temperature with a cooling rate of about 50 °C/min and then decompressed to ambient pressure.

The recovered synthetic products were well-sintered bulk cylinder, about 3 mm in height and 2.5 mm in diameter, and were polished to a smooth mirror surface. X-ray diffraction analysis (XRD; DX-2700, Dandong, China) and Raman (Andor Shamrock SR-303i-B, ANDOR Newton DU970P-UVB, EU; RGB laser system, Germany) were performed on the polished surface to detect the composition of the samples. The thermal gravimetric and differential scanning calorimetry analysis (TGA-DSC; TG-Q600, TG-Q2000, USA) were carried out with a heating rate of 10 °C/min from 30 °C to 1400 °C for determining the oxidation resistance of the samples. The Vickers hardness (Model FV-700, Future-Tech., Japan) was tested with an applied loading force of 29.4 N and a fixed indenting time of 15 s. In order to observe the grain boundaries and bonding situation, scanning electron microscopy (SEM; JSM-6490, JEOL, Akishima, Japan), transmission electron microscopy (TEM; JEM-2100F, JEOL, Japan) and x-ray photoelectron spectroscopic (XPS; Thermo ESCALAB 250Xi, USA) were investigated.

The Vickers hardness of the sintered sample was measured with a standard diamond indenter. Fig. 1a showed the Vickers hardness of diamond-cBN bulk samples and polycrystalline diamond compacts prepared at 15 GPa/1900 °C–2100 °C. Five indentations were tested for each temperature point. The average Hv value of diamond-cBN bulk sample was 90 ± 5, 96 ± 7, and 92 ± 4 GPa under a load of 29.4 N, respectively. These values were slightly higher than the pure polycrystalline diamond (82 ± 5) and comparable to the hardness for single crystal diamond ($Hv \approx 75$–100 GPa). The thermal stability for well-sintered diamond-cBN bulk sample synthesized at 15 GPa/2000 °C were determined using TGA and differential scanning calorimetry (DSC) in air, as shown in Fig. 1b. For comparison, we also measured thermal stability of the bulk sample sintered with pure diamond at the same condition. The onset oxidation temperature (910 °C) of diamond-cBN bulk sample was higher than that of pure polycrystalline diamond (750 °C). Measurements by DSC yielded consistent TGA. The results indicated that the additive hBN apparently enhanced thermal stability of diamond without decreasing the hardness at the same time. We speculate that the significant enhanced thermal stability is attributed to the strengthened grain boundary between diamond particles.

To determine phase structures of the diamond-cBN sample, X-ray diffraction (XRD) pattern of starting materials and samples after HPHT treatment were shown in Fig.2a–b. Fig. 2 (a) was the XRD pattern for the starting mixture of diamond and hBN, and Fig. 2 (b) was the XRD pattern of the samples synthesized at different temperature. Only the diffraction peaks of diamond and cBN were detected in the diamond-cBN sample sintered at 15 GPa and 1900–2100 °C, implying that hBN has completely converted into cBN. In addition, the relative intensities of X-ray diffraction peaks changed with temperature, indicating the interaction between diamond and BN. There no new phase appeared according to the present X-ray diffraction result, while the Raman spectrum in Fig. 2c-d was different from that of XRD pattern. Fig. 2 (c) was the Raman spectrum for the starting mixture of diamond and hBN, and Fig. 2 (d) was Raman spectrum of the samples synthesized at 15 GPa/2000 °C. It has been found that it was dominated by broad features centered at ~450, ~700, ~1250 and ~1500 cm^{-1}. The peaks ~450, and ~1250 cm^{-1} were very similar to the spectrum of boron-doped diamond [34] and BC_5 [35]. The peaks ~450, ~700, and ~1500 cm^{-1} were also observed in nano-cBN [36] and nano-diamond [37], which are likely due to the scattering by grain boundaries in the nano-crystalline materials. The Raman spectrum suggested that new chemical bond B—C was presumably formed and nano-stucture existed in the sintered diamond-cBN sample.

The x-ray photoelectron spectroscopic (XPS) measurements were shown in Fig. 3. As a comparison, Fig. 3–c were the results of atmospheric conditions of diamond and cBN, and the Fig. 3d–f were the results of the diamond-cBN bulk sample synthesized at 15 GPa/2000 °C. It is obvious that the XPS peaks of the diamond-cBN sample after HPHT treatment are different from the peaks of the initial material. The diamond-cBN sample contained B, C, N and O element. O was absorbed from the atmosphere. XPS signal from B $1 s$ could be found that at binding energies of 190.3 eV and 191.8 eV, with a widening peak, consistent with B—C and B—N bonds. Simultaneously, the XPS peaks of the C $1 s$ and N $1 s$, located at 284.8 eV, 285.8 eV, 287.6 eV, 398.7 eV, and 399.7 eV, corresponding to B—C, C—N, C—O, B—N and C—N, respectively. The XPS results therefore confirmed that B—C and C—N bonds existed excepting B—N and C—C bonds in the diamond-cBN compact. The XPS measurements further revealed the existence of new bonds B—C and C—N. Combining Raman and XPS analysis, we
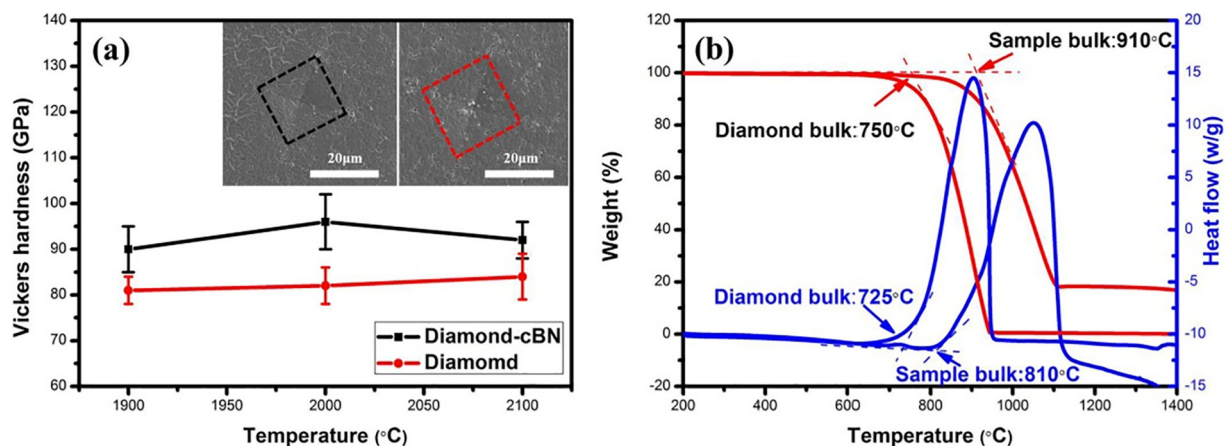
Fig. 1. (a) Effects of temperature on the Vickers hardness of the diamond-cBN samples and polycrystalline diamond compacts sintered at 15 GPa and the inset pictures are the indentations at an applied load of 29.4 N, respectively. The upper and lower bars represent the maximum and minimum values of each measurement. (b) The TGA-DSC comparison pattern of the diamond-cBN sample sintered at 15 GPa/2000 °C and the pure diamond bulk sintered at the same condition. Red line: the thermal gravimetric, blue line: differential scanning calorimetry. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)