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Polycrystalline cubic boron nitride prepared with cubic-hexagonal boron nitride under high pressure and high temperature

Ming Yang(杨鸣)[1], Zi-Li Kou(寇自力)[1,†], Teng Liu(刘腾)[1], Jing-Rui Lu(卢景瑞)[1], Fang-Ming Liu(刘方明)[2], Yin-Juan Liu(刘银娟)[1], Lei Qi(戚磊)[1], Wei Ding(丁未)[1], Hong-Xia Gong(龚红霞)[1], Xiao-Lin Ni(倪小林)[1], and Duan-Wei He(贺端威)[1]

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Polycrystalline cubic boron nitride (PcBN) compacts, using the mixture of submicron cubic boron nitride (cBN) powder and hexagonal BN (hBN) powder as starting materials, were sintered at pressures of 6.5–10.0 GPa and temperature of 1750 °C without additives. In this paper, the sintering behavior and mechanical properties of samples were investigated. The XRD patterns of samples reveal that single cubic phase was observed when the sintering pressure exceeded 7.5 GPa and hBN contents ranged from 20 vol.% to 24 vol.%, which is ascribed to like-internal pressure generated at grain-to-grain contact under high pressure. Transmission electron microscopy (TEM) analysis shows that after high pressure and high temperature (HPHT) treatments, the submicron cBN grains abounded with high-density nanotwins and stacking faults, and this contributed to the outstanding mechanical properties of PcBN. The pure bulk PcBN that was obtained at 7.7 GPa/1750 °C possessed the outstanding properties, including a high Vickers hardness (∼ 61.5 GPa), thermal stability (∼ 1290 °C in air), and high density (∼ 3.46 g/cm^3).

Keywords: PcBN compact, high temperature and high pressure sintering, PcBN without additive

PACS: 61.50.Ks, 61.72.Ff, 81.20.Ev **DOI:** 10.1088/1674-1056/27/5/056105

1. Introduction

Due to its high hardness, high chemical stability, extreme wear, and high thermal conductivity, polycrystalline cubic boron nitride (PcBN) is widely used in various industrial machining fields.[1–3] Traditionally, commercial cBN compacts are produced by sintering cBN powder with the addition of various binders (e.g., Co, Ti),[4,5], which reduces the experimental pressure and temperature requirements, whereas the additives affect the mechanical properties of the sintered PcBN composite,[6] and downgrade the mechanical properties. Therefore, the best way to obtain PcBN with excellent mechanical properties is free from additives, and the perfect additive is the material itself.[7]

In order to address this problem, more sintering methods have recently been adopted. For the sintering of PcBN without additives under HPHT treatment, the following two different methods are usually applied. One is to convert pure hBN to polycrystalline cBN directly without adding any catalysts.[8,9] However, phase transition from hBN to cBN in such a solid-state reaction process always needs high pressure (> 7.7 GPa) and high temperature (> 2000 °C),[10] which increases the cost for the industrial applications. The other method is called the direct sintering method. Owing to the Hall–Petch effect, the samples obtained by sintering pure nanocrystalline cBN powder under HPHT conditions show noticeable improvement of hardness.[11] However, the synthetic pressure for sintering of those nano-cBNs (∼ 20 GPa) is much higher than that for commercial cBN (∼ 5.5 GPa). As a result, the application of nano-cBN is limited.

Previous studies have shown that samples with submicron grains exhibit excellent mechanical properties.[12,13] The coherent twin boundaries (TBs) and stacking faults also promote properties of sintered samples.[14,15] However, the cBN-forming region and morphology relationship with P–T conditions in the cBN–hBN mixed system have not been studied. In this work, the mixture of commercial submicron cBN and hBN grains was used to sinter PcBN at a relatively low pressure and temperature. Through analyzing the phase, microstructure, Vickers hardness of sintered samples, our results demonstrated that under ultra-high deviatoric stress generated by grain-to-grain contact, original hBN particles fractured to fill pores among cBN grains, and then densified samples. Besides, the reconstructive phase transition from hBN to cBN under HPHT might generate numerous micro defects (e.g., twins and stacking faults) in the crystal. They would significantly improve the mechanical properties of the cBN samples.

2. Experimental procedures

The cBN powder (grain size: 0.4–1.0 μm, density: 3.47 g/cm^3, > 99.9% purity, purchased from the Zhongnan Jiete Superabrasives Co., Ltd, Zhengzhou China) and hBN powder (grain size: 0.2–1.5 μm, density: 2.29 g/cm^3, > 99.9%

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purity, purchased from Aladdin, Shanghai China) were used as starting materials in our investigation (Figs. 1(a)–1(c)). The powders were manually mixed with ethyl alcohol using a ceramic mortar and pestle for 3 h, and the hBN contents of the starting materials ranged from 16 vol.% to 28 vol.%. Additionally, in order to remove the impurities, the starting mixtures were degassed in vacuum of 3.0×10^{-2} Pa and temperature of 1250 °C for 1.5 h before HPHT sintering.

HPHT experiments were carried out in DS 6×14 MN cubic press and DS 6×8 MN cubic press machine, respectively.[16,17] The cell temperature was measured directly using a W–Re thermocouple, and the pressure was estimated by the well-known pressure-induced phase transition of Bi, ZnTe, ZnS.[18] As shown in Fig. 1(d), after cold compaction (7.5 GPa), the recovered cBN grains remained essentially the initial particle size, but most of the hBN grains fractured into small particles (∼ 0.17 μm). Samples were compressed to the desired pressure (6.5–10.0 GPa) values before heating to 1750°C for 10 min. After the HPHT treatment, the density of sintered samples reached approximately 3.46 g/cm^3 ($\rho_{\text{theory}} = 3.47$–$3.48$ g/cm^3).

To characterize the structural and determinate the phase of materials, x-ray diffraction (XRD) measurements were conducted in a DX-2500 x-ray diffractometer with Cu Kα radiation ($\lambda = 0.15406$ nm). The morphology and microstructure of samples were investigated by scanning electron microscopy (SEM Hitachi FE-SEM S4800, Japan) and TEM (JEM-2100F, JEOL, Japan). Oxidation–resistance studies were performed using a Mettler TGA/DSC11600 at 10 °C/min. Hardness values of the polished samples (using a polishing machine with 1.0–1.5 μm diamond paste) were measured by a Vickers hardness tester (FV-700B, Future-Tech, Japan).

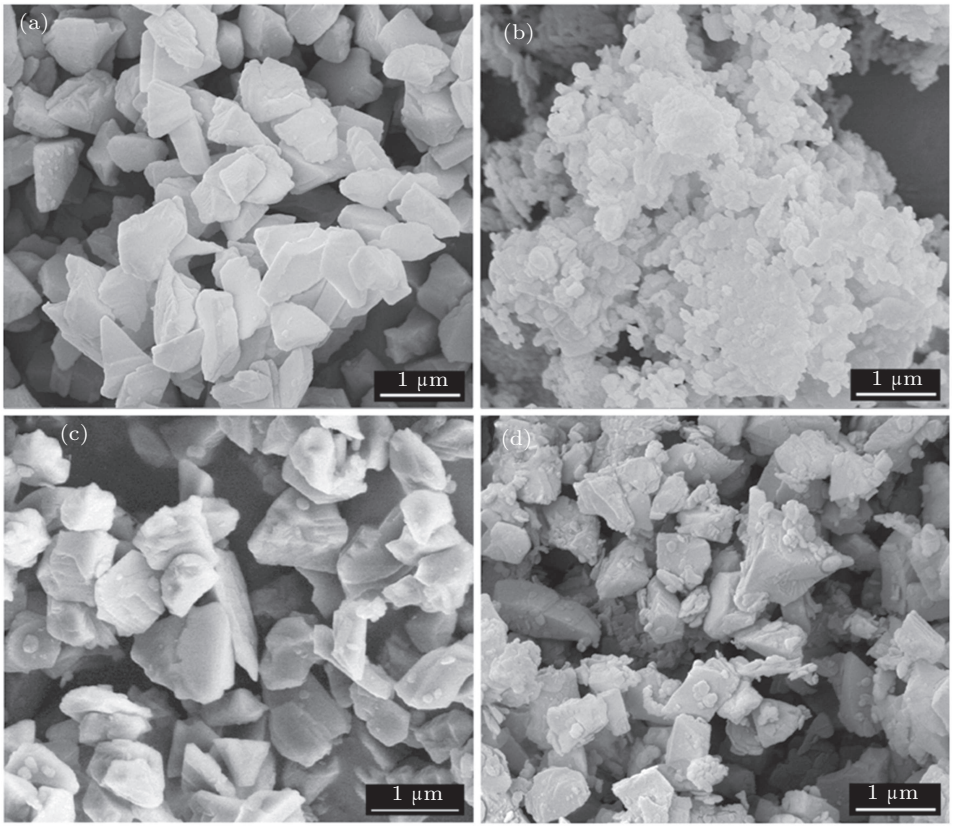


Fig. 1. SEM images of the starting materials. (a) Cubic BN powder and (b) hexagonal BN powder. (c) SEM image of mixed starting material. (d) SEM image of the recovered sample after cold compaction (7.5 GPa).

3. Results and discussion

3.1. XRD analysis

Figures 2(a) and 2(b) show the XRD patterns of samples sintered with different hBN contents and under different pressures at 1750 °C, respectively. Starting powders (hBN range from 16 vol.% to 28 vol.%) were sintered at 7.5 GPa/1750°C for 10 min. The concentrations of the hexagonal phases in samples were calculated from the intensities of the hBN (002) and hBN (100) lines in XRD patterns, which appeared at 26.7° and 41.6°. Figure 2(a) shows that the hBN XRD pattern did not appear in 20 vol.%-hBN and 24 vol.%-hBN. In addition, a certain amount of compressed hBN present has been found in 16 vol.%-hBN.[10] This further indicates that when hBN contents range from 20 vol.% to 24 vol.%, as shown in Fig. 2(a), the starting hBN powder utterly transformed into cBN phase after the HPHT treatment. For the samples with 20 vol.%-hBN sintered at 1750 °C under different pressures, the hBN appears when the sintering pressure is lower than 7.5 GPa, as shown

in Fig. 2(b). Once the pressure increases to about 10.0 GPa, all the samples consist of a single cBN phase. It is reasonable to consider that wurtzite boron nitride (wBN) may be involved in the phase transformation from hBN to cBN.[14,19,20] However, according to the x-ray diffraction result and following TEM observations, there is no wBN phase detected in XRD patterns.

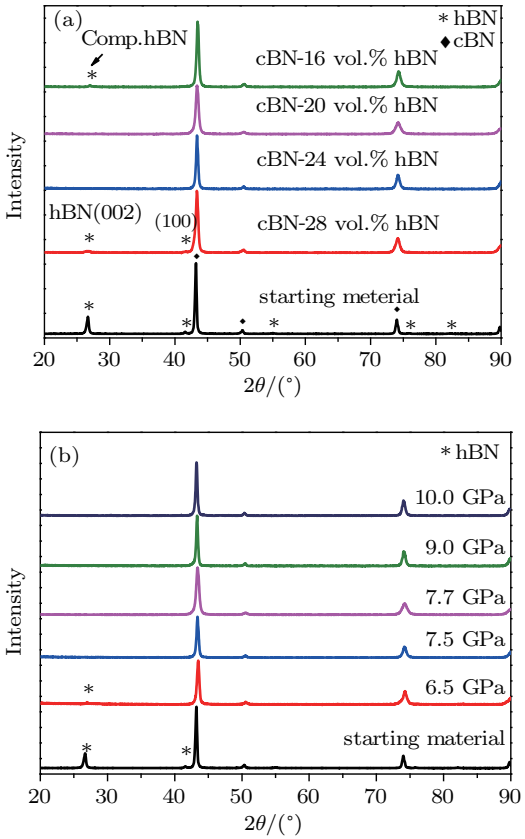


Fig. 2. (color online) (a) XRD patterns of starting material and samples hBN content of the starting materials (range from 16 vol.% to 28 vol.%) sintered at 7.5 GPa/1750 °C. (b) XRD patterns of starting material and samples (20 vol.%-hBN) sintered at 6.5–10.0 GPa/1750 °C.

3.2. Microstructure

Figure 3 exhibits the SEM images of the fractured surface of PcBN samples. The samples (hBN was mixed at 20 vol.%) were sintered under 6.5, 7.7, 9.0, and 10.0 GPa and at 1750 °C, respectively. From Fig. 3(a), as the pressure increased to 6.5 GPa, no obvious grain refinement occurred in cBN grains and most of the hBN grains (schistose texture) were crushed to tiny particles with an average size of 0.26 μm which was attached to the surface of cBN grains. The appearance of hBN is consistent with the XRD results in Fig. 2(b). In Fig. 3(b), with sintering pressure increasing to 7.7 GPa, the pure PcBN bulk sample was obtained and the shape of grains became angular. The small grains located among the large grains should be cBN crystals transformed from hBN during HPHT treatment, which filled the pores and enhanced the sample density. As can be seen from Fig. 3(c), when the sample was sintered at 9.0 GPa/1750 °C, most of cBN grains (∼ 0.46 μm) and a few tiny grains existed in the sample. The shape of grains is irregular and the interfacial bonding between small grains is not obvious. At a higher pressure (10.0 GPa), the submicron particle contains a considerable number of nano-sized grains (∼ 0.24 μm), while its grain boundary is not obvious. Furthermore, as shown in Fig. 3(d), a few pores and non-uniform grains still exist in the sample. There are many nucleation sites for the phase transformation within one respective hBN grain, and every original grain in the starting hBN powders might be fractured into a number of grains after sintering, which explained the small difference in grain size. And the amount of nano-sized cBN grains might need proper temperatures to bond with each other.[11]

Figure 4 shows the representative TEM and high-resolution transmission electron microscopy (HRTEM) images of the sample sintered at 7.7 GPa/1750 °C. It can be seen that the grain size was about 0.45 μm and the sample had a random distribution of grain orientation (Fig. 4(a)). In Fig. 4(b), the grain boundaries were observed as circular arcs, indicating that the grains have experienced a plastic deformation after HPHT treatment. As mentioned above, hexagonal phase BN transformed into cubic phase under ultra-high pressure and filled the gaps between large grains to promote pore closure (Fig. 4(a)).

Densely spaced twin boundaries and stacking faults (twin thickness: 3.8–10.7 nm) can be observed in grains (Figs. 4(c) and 4(d)), and the length between twin boundaries or stacking faults was predominantly in nanoscale. The corresponding selected area electron diffraction pattern confirmed that the sample was pure cBN (upper-right inset of Fig. 4(c)). In other words, original cBN crystals crashed into nanoscale dimensions along directions perpendicular to the twin boundaries or stacking faults and the much smaller twin width of the sample might be attributed to the remarkably ultra-high sintering pressure. Similar features can also be found in the recently reported cBN sample synthesized from specially prepared boron nitride precursor possessing onion-like nested structures.[21] The coherent twin boundary has excess energy of magnitude lower than that of the grain boundaries, so the coherent twin boundaries are more stable than the grain boundaries.[22–24] Owing to its special lamellar structure, the coherent twin boundary could accommodate more stacking faults, which can block crack propagation and ensure the high fracture toughness.[25] Therefore, nanotwins can improve the strength without reducing the malleability.[26] Furthermore, covalent material hardness can be defined microscopically as the combined resistance of each bond to the indenter, which is closely related to stacking faults initiation and motion, whereas the dislocation energy depends strongly on its position.[27] Because of the specific structure, the formation of an enormous nanotwin microstructure is an effective way to simultaneously

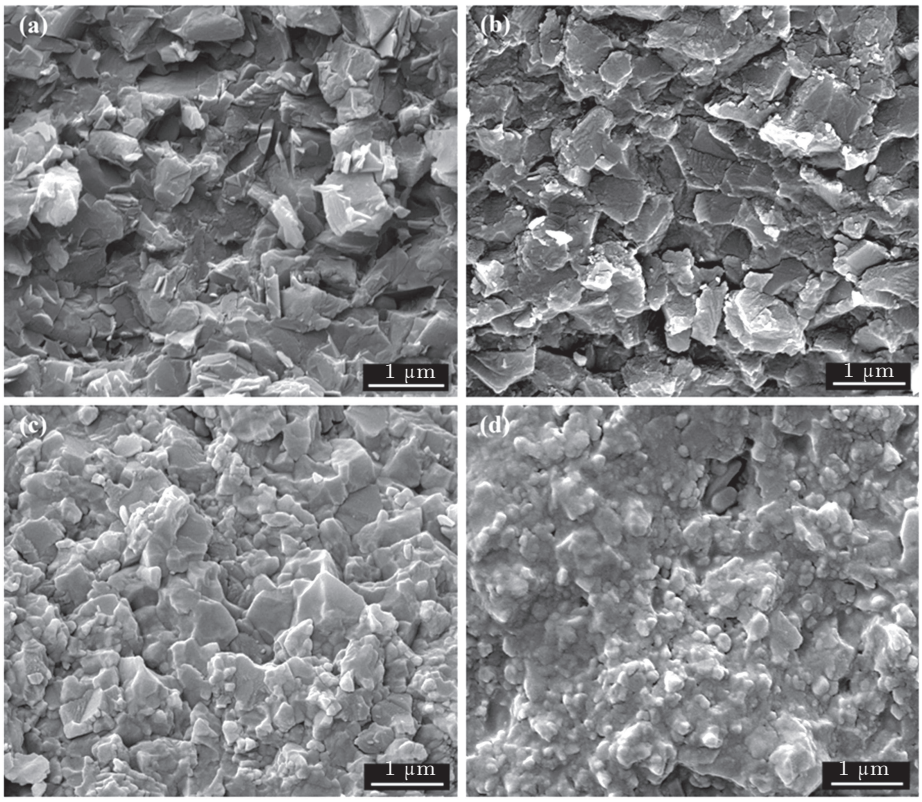


Fig. 3. SEM images of fracture surfaces of PcBN samples sintered at various *P*–*T* conditions. (a) 6.5 GPa/1750 °C. (b) 7.7 GPa/1750 °C. (c) 9.0 GPa/1750 °C. (d) 10.0 GPa/1750 °C.

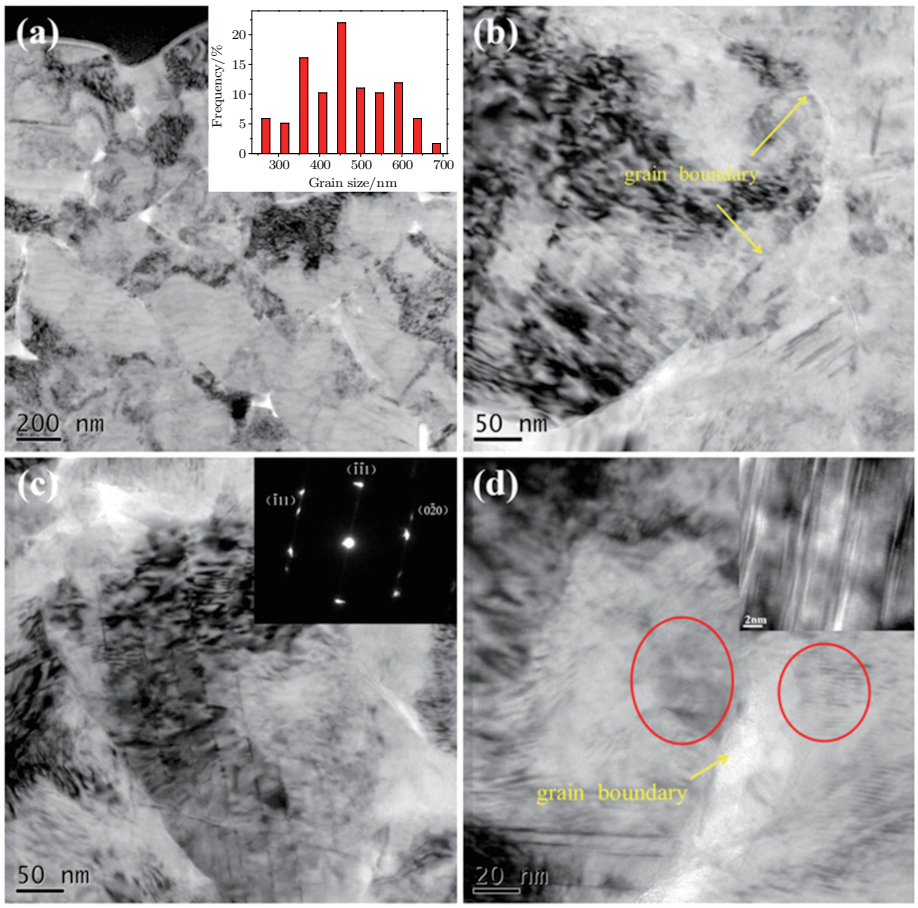


Fig. 4. (color online) TEM characterization of sample sintered at 7.7 GPa/1750 °C. (a) TEM image of the submicron cBN sample covers several grains. Upper-right inset: size distribution of grains measured from TEM images with an average grain size of ∼ 450 nm. (b) The grain boundary is observed as a circular arc. (c) TEM image of the interaction of a grain exhibiting numerous nanotwins. Upper-right inset: corresponding selected area electron diffraction pattern. (d) TEM image showing a large number of defects in the pure cBN sample. Upper-right inset: HRTEM image of stacking faults inside a grain.

enhance the hardness of superhard materials.[21,28,29]

Figure 4(d) reveals a high density of defects at the grain boundary. Compared with submicron cBN which was synthesized from pure cBN, we find that this submicron cBN synthesized from the special mixture of cBN and hBN precursor presented a large number of defects.[7] This may be attributed to the volume changes of grain which can cause numerous microstructural differences, during the reconstructive phase transition from hBN to cBN.[30] In particular, in the sintering process, the micro defects in crystallines should be generated during the nucleation and growth of a new phase. The peculiar morphology can be associated with plastic deformation between grains under HPHT treatment. The effect of stacking faults interacting with the TB boundary promotes the plastic deformation of grains to obtain samples with a high densification and grain refinement. In a word, when high-density nanometer-thick twins were introduced into sub-micrometer sized grains during the HPHT treatment, PcBN sample was strengthened.[14,31,32]

3.3. Thermal stability test

The thermal stability of the sample sintered at 7.7 GPa/1750 °C has been established by thermogravimetric analysis (TG). The temperature in the TG test ranged from 30 °C to 1500 °C at 10 °C/min, as shown in Fig. 5(a). The onset oxidation temperature was 1290 °C in air for the sintered sample, which was higher than those of single crystal cBN (∼ 1070 °C).[33] Furthermore, previous experiments have shown that the sample had a similar thermal stability (∼ 1273 °C), but the synthetic pressure for thee submicron cBN (∼ 11 GPa) was much higher than that we studied.[7]

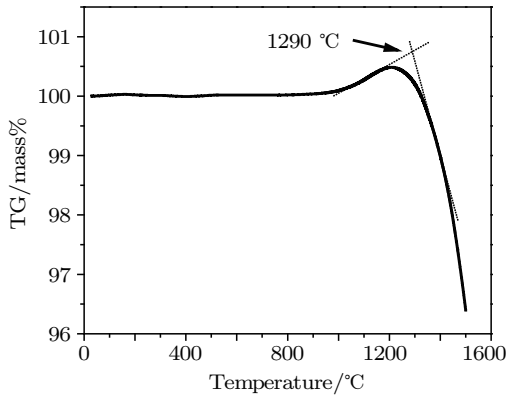


Fig. 5. Thermogravimetric curve for the PcBN sample sintered at 7.7 GPa/1750 °C.

3.4. Vickers hardness test

Figure 6(a) shows the Vickers hardness of sintered samples versus sintering pressure. The Vickers hardness of the sintered sample was measured with a standard square-pyramidal diamond indenter. Five Vickers indentations were made on each sintered sample, and the final hardness value was taken according to their average and standard deviation. The PcBN sintered at 7.7 GPa/1750 °C had a high hardness of $H_v = 61.5 \pm 3.0$ GPa at a 29.4 N load for 15 s. Variations in Vickers hardness at different applied loads were shown in Fig. 6(b). We also measured the Vickers hardness of single cBN (29–42 GPa), which is consistent with the previous studies.[34] The density of the sample sintered at 7.7 GPa/1750 °C was measured at room temperature. The sample density reached 3.46 g/cm^3, which was close to the cBN theoretical density. Combining with the TEM observations in Figs. 4(c) and 4(d) shown dense twins and stacking faults in grains, it can be concluded that deformation twin structures and stacking faults enhanced the hardness of PcBN. Under the cBN–hBN mixed system, hBN plays an important role in the transformation process of hexagonal to cubic, forcefully influencing the synthesis of PcBN.

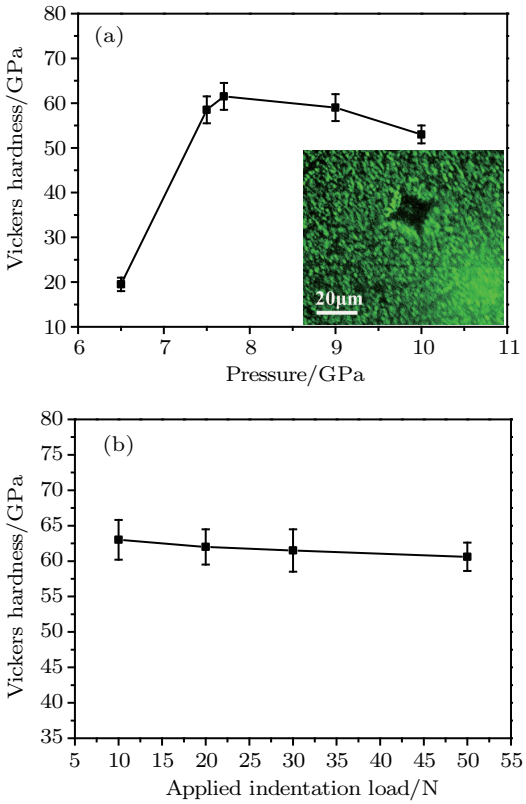


Fig. 6. (color online) (a) Vickers hardness of samples sintered at 6.5–10.0 GPa/1750 °C with an applied load of 29.4 N. Inset: micrograph of Vickers hardness indentation. (b) Applied load dependence of Vickers hardness of the sample sintered at 7.7 GPa/1750 °C.

4. Conclusions

In summary, using submicron cBN and hBN as the starting materials, PcBN without additives was sintered under a high pressure and at a relatively low temperature (6.5–10.0 GPa/1750 °C). The sample exhibited high hardness and thermal stability at 7.5 GPa and 1750 °C, which is attributed to numerous nanotwins and a large amount of stacking faults inside grains. Additionally, the hBN phase in the starting material completely transformed into the cBN phase at

7.5 GPa/1750 °C when hBN contents ranged from 20 vol.% to 24 vol.%. The transformed small cBN grains also act as a binder to sinter the original coarse cBN particles at a lower pressure than that direction conversion without additives. The affordable starting material and milder synthesis conditions could allow for the industrial application of this submicron cBN aggregate.

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