

Superhard nanocomposite of dense polymorphs of boron nitride: Noncarbon material has reached diamond hardness

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The authors report a synthesis of unique superhard aggregated boron nitride nanocomposites (ABNNCs) showing the enhancement of hardness up to 100% in comparison with single crystal c-BN. Such a great hardness increase is due to the combination of the Hall-Petch and the quantum confinement effects. The decrease of the grain size down to 14 nm and the simultaneous formation of the two dense BN phases with hexagonal and cubic structures within the grains at nano- and subnanolevel result in enormous mechanical property enhancement with maximum hardness of 85(5) GPa. Thus, ABNNC is the first non-carbon-based bulk material with the value of hardness approaching that of single crystal and polycrystalline diamond and aggregated diamond nanorods. ABNNC also has an unusually high fracture toughness for superhard materials ($K_{IC}=15 \text{ MPa m}^{0.5}$) and wear resistance ($W_H=11$; compare, for industrial polycrystalline diamond, $W_H=3-4$), in combination with high thermal stability (above 1600 K in air), making it an exceptional superabrasive. © 2007 American Institute of Physics. [DOI: 10.1063/1.2711277]

High-pressure high-temperature (HPHT) synthesis of cubic boron nitride (c-BN) in 1957 (Ref. 1) opened a field of important technical applications similar to those of diamond. On thermal stability and reaction resistance, which reaches 1650 K, c-BN is superior to diamond² (the latter is thermally and chemically stable only up to 950 K), and it is the superabrasive of choice for machining hard ferrous steels.^{3,4} However, c-BN cannot completely replace diamond, while its hardness is twice as low (the hardest single crystal c-BN has Vickers hardness $H_v \sim 50$ GPa, while for single crystal diamond this value is ~ 100 GPa; for commercially used polycrystalline c-BN and diamond (PCD), corresponding values are lower⁴⁻⁷). Hardness of c-BN films measured using nanoindentation technique^{8,9} can reach ~ 70 GPa. Many researchers and industrialists are concentrated on the synthesis of superhard phases¹⁰ in the B-C-N ternary system as thin films^{11,12} and bulk materials^{13,14} to fill this “hardness gap.” Microcrystalline and nano-phases^{13,14} of boron carbonitrides c-BC₂N and c-BC₄N with Vickers hardness of 76 GPa (Ref. 13) (62 GPa (Ref. 14)) and 68 GPa,¹⁴ respectively, were claimed as the second to diamond hardest materials known. However, all these phases are thermodynamically unstable

and do not promise improvement in chemical stability of these phases in comparison with diamond. A real breakthrough in industrial technologies using superhard materials can be reached with designing of bulk materials, which are hard, tough, and thermally stable, that is ideal for cutting and drilling. However, so far, no one noncarbon material with hardness approaching that of diamond has been synthesized.

Experimental observations^{4,5,13-17} and simulations¹⁸⁻²¹ suggest that for many polycrystalline materials there is an optimal grain size (usually in the range of dozens of nanometers, i.e., nanocrystalline), which results in significant, up to 20%–30%, increase of hardness of the material in comparison with that of its coarse-grained counterpart. Nanocrystalline diamond and aggregated diamond nanorods have been synthesized at high pressure and temperature and demonstrate some noticeable improvement of hardness.^{3,4,22} Following this route, we conducted a series of experiments on the HPHT synthesis of nanocrystalline BN phases using a multianvil press and various precursors in a broad range of pressures and temperatures (Fig. 1). The technique of the synthesis is described elsewhere.^{3,22,23}

Figure 2 shows x-ray diffraction patterns and Raman spectra of the synthesis products obtained at 18(1) GPa and different temperatures from pyrolytic graphitelike boron nitride (p-BN) (GoodFellow Inc.). Characteristic x-ray and

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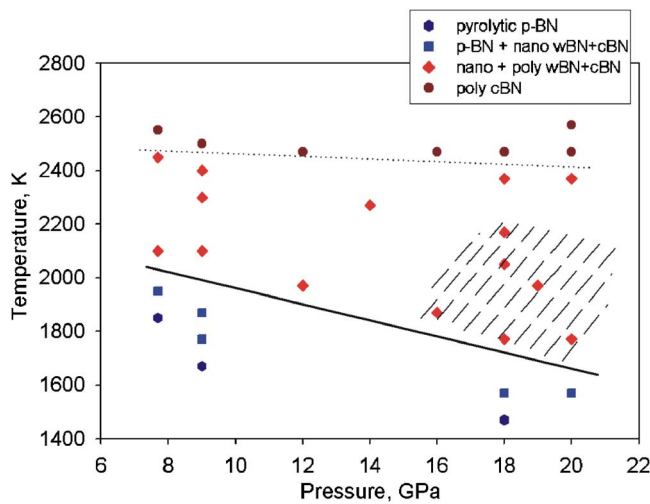


FIG. 1. (Color online) Transformation pressure-temperature diagram of p-BN (hexagons, p-BN; squares p-BN and nanocrystalline w-BN and c-BN; diamonds, polycrystalline and nanocrystalline w-BN and c-BN; circles, polycrystalline c-BN). The pressure-temperature field corresponding to ABNNC with smallest nanosize particles (14–25 nm) and highest hardness is shaded. Lines are given as guides for the eyes: solid line separates the field, where the precursor is present; dotted line separates the field of single-phase c-BN.

Raman spectra of initial p-BN are presented by the bottom curves (a). At temperatures below 1770 K no phase transformations are detected. At 1770 K very weak reflections of cBN [curve b, Fig. 2(a)] indicate the appearance of the new phase. When temperature increases up to 1870 K, the diffraction pattern changes drastically [curve c, Fig. 2(a)] and contains only reflections of dense sp^3 -bonded BN polymorphs: 3C (sphalerite structure) c-BN and 2H (wurtzite structure) w-BN, analogous to diamond and lonsdaleite, respectively. Raman spectrum also demonstrates a drastic change. While curves a and b [Fig. 2(b)] are dominated by the h-BN phonon modes²⁴ ($2E_g$), curve c significantly differs from the previous two: it is dominated by broad features centered at ~ 450 , ~ 750 , and ~ 1550 cm^{-1} , which are likely due to scattering by the numerous grain boundaries in the very fine

nanocrystalline material, as it was already observed for nanocrystalline diamonds.^{3,22} Such a Raman spectrum, which has never been reported so far for BN, can be considered as characteristic for this synthetic composite material. Further increase of synthesis temperature resulted in the disappearance of w-BN reflections in x-ray patterns. Single-phase c-BN was observed for samples synthesized at 2370 and 2570 K [curves d and e, Fig. 2(a)]. The two sharp Raman peaks at about 1057 and 1309 cm^{-1} [curves d and e, Fig. 2(b)] can be assigned to scattering by the transverse optical and longitudinal optical phonon modes²⁴ of c-BN. Thus, p-BN converts into both w-BN and c-BN at low temperatures,²⁵ and into single-phase c-BN at high temperatures.

In the diffraction patterns of the samples synthesized at moderate temperatures (1750–2200 K), all lines show considerable broadening that reflects changes in the size of blocks of coherent scattering as a function of the synthesis condition. In the case when structural defects contribute to the broadening of x-ray diffraction peaks, reflections must be asymmetric and/or full width at half maximum must be hkl dependent (see, for example, Ref. 26). We did not observe these effects and conclude that in studied samples reflection broadening is entirely due to the crystallite size. For the same pressure of synthesis of 18 GPa smallest crystallites of 14 nm are observed in samples obtained at 1870(50) K (Fig. S1 in Ref. 23).

The results of transmission electron microscopy (TEM)²³ are in good agreement with the x-ray data.

It has been found that the results of the HPHT synthesis in the BN system strongly depend on the precursor.^{5,23,26}

We measured the Vickers hardness of the samples.²³ As recommended for hard and brittle materials,²⁷ hardness is reported²³ in the asymptotic-hardness region. The results of hardness measurements are shown in Fig. 3. It is clear from the H_v versus crystallite size curve that with the decrease of the grain size, hardness of both ABNNC and c-BN increases, following, however, different paths. For c-BN hardness increases from ~ 40 GPa for polycrystalline material and reaches a maximum of 59(3) GPa at a crystallite size of

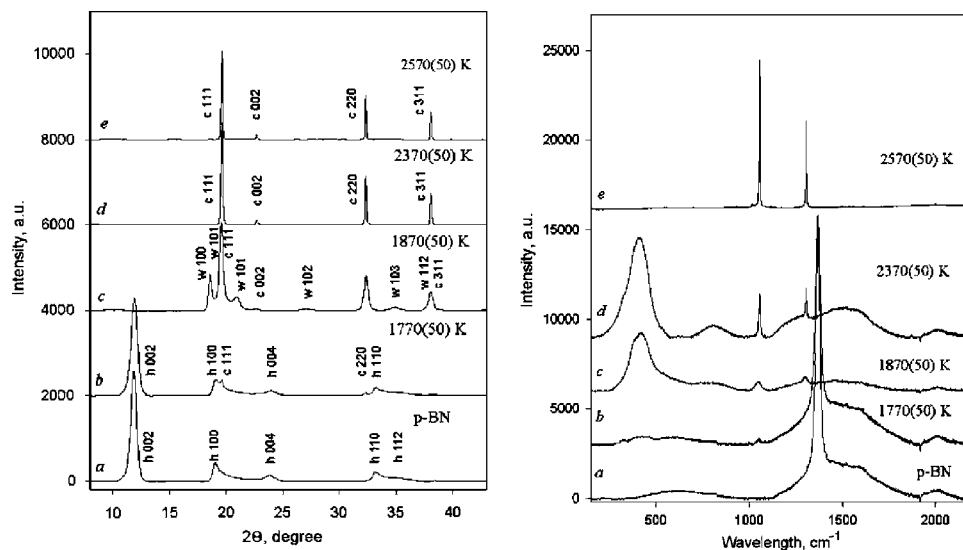


FIG. 2. (Color online) (a) X-ray diffraction patterns of the samples synthesized at 18 GPa and various temperatures from pyrolytic p-BN (curve a). Symbols “h,” “w,” and “c” before crystallographic indices of reflections denote hexagonal, wurtzite, and sphalerite (cubic) phases, respectively. (b) Raman spectra of the same samples.

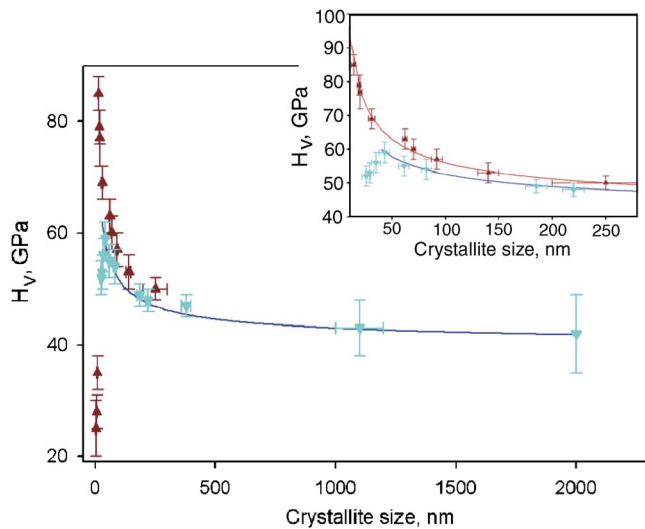


FIG. 3. (Color online) Vickers hardness (H_v) as a function of the crystallite size. Triangles correspond to the data for ABNNC; inverted triangles, c-BN.

~40 nm. In the case of ABNNC, hardness increases above 60 GPa, reaching its maximum of 85(5) GPa at a 14(2) nm crystallite size (Fig. 3). If the grain size decreases further up to a few nanometers, hardness drops down to 25 GPa. A transition from grain-size hardening (the Hall-Petch effect) to grain-size softening (the inverse Hall-Petch effect) in metals was reported^{20,21,28,29} and was attributed to intergranular deformation by grain boundary sliding.²¹ Note, however, that in our experiments the samples with smallest crystallite sizes (below 12 nm) were synthesized at relatively low temperatures (below 1800 K) and, hence, may contain some amount of nontransformed graphitelike material, which could be responsible for the hardness decrease.

The hardening effect of grain boundaries can be expressed through the Hall-Petch equation^{30,31} showing the grain-size (d) dependence of hardness (H): $H=H_0+K/\sqrt{d}$. With $H_0=39$ GPa and $K=126$ GPa nm^{1/2} this equation fully describes the dependence of c-BN hardness as a function of crystallite size (Fig. 3, and lower line in inset). For ABNNC, however, the simple inverse square root relationship is not adequate. Tse *et al.*,³² based on the results of *ab initio* calculations, suggested that hardness of nanocrystals depends on the “effective” band gap,³³ which, in turn, is inversely proportional to the size of crystallites. In other words, for the combined Hall-Petch and quantum confinement effects $H=H_0+K_1/\sqrt{d}+K_2/d$, and it perfectly describes the observed relations between hardness and crystallite size in ABNNC (Fig. 3, upper line in inset). Thus, the two-time increase of hardness of ABNNC ($H_v=85$ GPa), with respect to conventional polycrystalline c-BN ($H_v\sim 40$ GPa), is a result of the unique combination of two factors: (1) nanosize effect, which restricts dislocation propagation through the material, and (2) two-phase composition on nano- and subnanometer scales, which, due to the quantum confinement, increases hardness of individual crystallites.^{34,35} It makes ABNNC the first non-carbon-based bulk material with hardness higher than that of PCD and approaching that of single crystal and nanocrystalline diamonds and aggregated diamond nanorods. The fact that the gap of 50 GPa in hardness between the hardest known materials can be filled by BN nanocomposites

by tuning their properties through the grain size and the change of the constituent structure points out towards the synergetic effect of nanocrystallinity and the composite nature of materials in improving their mechanical properties.

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