CONFERENCES AND SYMPOSIA

Diamond-based superhard composites: new synthesis approaches and application prospects

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Abstract. We discuss experimental results on high-pressure and high-temperature (HPHT) synthesis of diamond-like cubic boron nitride (cBN) and diamond with a high concentration of point defects. The presence of active fluids allows obtaining cBN with a carbon content up to 10%. The concentration of boron in the diamond lattice is about 2%, and that of vacancies is two times higher. The concentration and positions of substitution atoms were determined by the Rietveld refinement method. Diamond micropowder reactive sintering with fluid phases was used to synthesize new superhard composites. The microstructure and grain boundaries were investigated by transmission and scanning electron microscopy. Tests of the wear resistance of the new diamond–cBN composites demonstrated that these materials offer good prospects for various applications.

1. Introduction

The first successful synthesis of diamond microcrystals under high-pressure and high-temperature (HPHT) conditions was carried out more than half a century ago. Since then, methods have been developed for producing single crystals with masses up to several dozen carats and diamond films and wafers using various techniques of carbon

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deposition from the gas phase. However, the industrial synthesis of diamonds in the form of particles up to 1 mm in size remains the most widespread. According to the report "Synthetic Diamond Market — Global Industry Analysis, Size, Share, Growth, Trends, and Forecast 2015–2023" (see https://www.transparencymarketresearch.com/synthetic-diamond-market.html), the global market of synthetic diamonds amounted to $15.7 billion in 2014 and is expected to grow to $28.8 billion by 2023.

Diamond micropowders can be used as loose abrasives or as materials for the fabrication of composites by sintering. The process of consolidation of diamond microparticles must be carried out at high pressures, where diamond is the thermodynamically stable phase. The range of pressures acceptable for mass reproduction in various kinds of apparatuses is 5–8 GPa. However, even under these conditions, binding microdiamonds into a firm compact (dense single-phase polycrystalline material) is impossible due to the graphitization of their surface. For this reason, diamond sintering is carried out with various additives. These can be divided into two groups, according to the mechanism of their action. The first group includes metals of the iron group (Fe, Co, Ni) and manganese, which catalyze the graphite-to-diamond phase transition. Because of the high solubility of carbon in the melts of these metals, the graphitized surface layer dissolves and becomes deposited again in the form of diamond, thus making strong bonds between particles. The basic methods for the fabrication of diamond composites with a metal binder are described in [1–3]. They were developed in two variants: sintering of homogeneous powder mixtures or infiltration of a metallic melt into a diamond layer from a cemented carbide (WC–Co) substrate. Physical and mechanical characteristics of these composites have been improved by decreasing the size of the diamond particles [4] and reducing the amount of metal binder [5].

In the second approach, components like silicon and titanium are added to diamond such that refractory carbides form as a result of chemical interaction. Silicon has become the most widespread because its melting temperature decreases under pressure, and silicon carbide has a diamond-like lattice. In their high thermal stability, diamond–silicon carbide composites are superior to diamond poly-

crystals with a metal binder. They can sustain temperatures as high as 1200 °C for several hours, while the stability of diamond–metal composites is restricted to temperatures of about 700 °C. However, because diamond–diamond bonds are nearly lacking in diamond–carbide ceramic materials, these feature increased brittleness and hence reduced wear resistance. The physical, mechanical, and performance characteristics of diamond–SiC composites can be enhanced by using source components and consolidation techniques providing the formation of nanostructure in these composites. For example, it was shown in [6] that after ball milling and sintering of powder mixtures of diamond with silicon, the fracture toughness of the diamond composite increases by 50% as the size of silicon carbide crystallites decreases from 10 μm to 20 nm.

Dense and entirely nanocrystalline diamond ceramics were synthesized in [7] by the infiltration of liquid silicon into a nanodiamond layer under a pressure of 8 GPa and temperatures up to 2000 °C. The hardness of this composite exceeded 50 GPa.

The properties of nanodiamond composites synthesized at a pressure of $\approx$ 8 GPa and a temperature of about 2070 K were described in [8]. Mixtures of diamond powders with silicon and titanium carbides were used as the starting material. Diamond crystals in the sintered composite were separated by thin binder layers with particle sizes smaller than 0.5 μm. Composites with a Ti_3SiC_2 binder proved to be the most suitable for applications, because they featured the highest wear resistance.

Diamond polycrystals with record-high hardness were obtained by the bulk conversion of the graphite starting material into diamond. Complete graphite-to-diamond phase transition yielded a transparent nanopolycrystalline compact whose hardness exceeds 100 GPa [9]. This material was obtained using a Kawai-type multi-anvil apparatus [10]. However, given the pressures ($\approx$ 15 GPa) and temperatures ($\geqslant$ 2000 °C) used in this process, only unique laboratory specimens can be synthesized in this way, with little opportunity for scaling up the technique.

The second superhard material is diamond-like boron nitride. It is inferior to diamond in hardness, but has certain advantages in thermal stability and chemical passivity to the iron-group metals. Direct transition of the graphite-like modification of boron nitride into the diamond-like modification occurs at lower pressures and temperatures. For example, the bulk conversion of cylinder specimens of pyrolytic boron nitride with a hexagonal lattice into the cubic structure occurs at a pressure of about 8 GPa and temperatures of 1600–1800 °C. With an increase in pressure, boron nitride grains in the compact decrease in size from submicrometers to nanometers. It was shown that boron nitride crystallites become about 50 nm in size when pressures of 18–20 GPa are used [11].

Superhard boron nitride compacts with no activator additives can also be obtained by sintering mixtures of ultrafine single-crystalline powders of the cubic phase (cBN) and nanopolycrystalline particles of the wurtzite phase (wBN) [12]. To attain the desirable strength, sintering has to be carried out at temperatures and pressures that prevent the reverse phase transition to a graphite-like phase at the grain boundaries and within the pores of the compact.

Because superhard materials can be obtained from diamond-like boron nitride at pressures of 6–8 GPa, it looks promising to use some variants of boron nitride additives as

binders for the sintering of microdiamonds. When synthesizing such composites, one needs to suppress graphitization and achieve the formation of strong bonds of diamond crystals both between them and with boron nitride. However, the fabrication of superhard diamond–boron nitride composites has not yet been implemented because of the low diffusivity of the components under sintering conditions.

Therefore, the aim of this study is to develop new approaches to the fabrication of diamond-based superhard composites in the B–C–N system. We present results of the synthesis and characterization of the powders of boron nitride with high concentrations of point defects and discuss their role in structure formation in sintering micro- and nanodiamonds.

2. Synthesis of diamond-like crystals in the B–C–N system

Synthesis was carried out in toroid-type high-pressure chambers representing two coaxial cemented-carbide anvils with a special profile fastened with steel rings [13]. A cell made of lithographic limestone was placed and compressed between the anvils. Pressure in the chambers was precalibrated by observing phase transitions in bismuth, and the temperature was measured by a chromel–alumel or a tungsten–rhenium thermocouple introduced into the chamber. The working volume was heated by passing alternating current through a tubular graphite heater. Synthesis was carried out using a specialized press unit delivering a force of 2000 tf and equipped with a system of programmable power controls based on the Advantech AWS-8129 workstation.

Powders of synthetic diamonds with sizes of about 10 and about 0.1 μm obtained by crushing larger crystals, as well as powders of boron, melamine ($C_3N_6H_6$), and carbon nitride with C_3N_4 stoichiometry, were used as the starting materials.

X-ray phase analysis of the samples was carried out using a Huber diffractometer ($CuK_{\alpha1}$ radiation). The source components and the cleaved-edge microstructure of the composites produced were studied using an FEI HELIOS NanoLab 660 scanning electron microscope (SEM) and JEM-2100 JEOL and FEI Tecnai G2 F20 transmission electron microscopes (TEMs).

Room-temperature Raman spectra were recorded using a TriVista 555 spectrometer.

It was established previously that the HPHT treatment of carbon nitride or melamine mixtures with boron leads to the formation of cBC_xN crystals with a diamond lattice. The cubic phase consisting of boron, nitrogen, and carbon has the sphalerite structure (space group F-43m). The lattice constant of cBC_xN crystals varies in a certain range. Crystals synthesized using melamine have a lattice constant close to that of boron nitride, while the unit cell in crystals produced from boron mixtures with carbon nitride can be 1% larger (Fig. 1a). Particle morphology and size (Fig. 1b) depend on the starting mixture composition and the synthesis temperature and pressure.

Structure refinement using X-ray data [14] demonstrated that boron and nitrogen atoms occupy different positions in the lattice, similarly to cubic boron nitride, while carbon is statistically distributed. The largest lattice constant (3.65515 Å) was observed in crystals grown from the nanospherical modification of C_3N_4. The results of structure refinement of these crystals according to the X-ray data are shown in the Table. For comparison, structure refinement
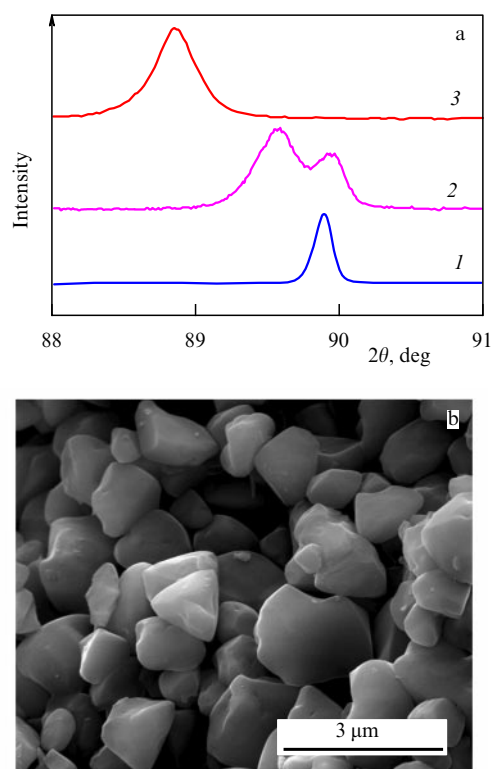
Figure 1. Analysis of diamond-like crystals synthesized in the B–C–N system. (a) Part of the X-ray diffraction pattern in the region of the 311 peak of diamond-like cBC$_x$N samples (θ is the X-ray diffraction angle): (*1*) boron nitride, (*2*) sample produced from a mixture of melamine with 50% boron, and (*3*) sample produced from a mixture of carbon nitride with 50% boron. (b) Morphology of cBC$_x$N crystals produced from a mixture of melamine with boron.

Table. Structure refinement data for crystals with a cBN lattice.

Chemical formula	BN	B$_{0.918}$C$_{0.139}$N$_{0.943}$
Space group	F-43m	F-43m
Number of atoms in the unit cell Z	4	4
Molecular weight	99.341	99.247
Lattice constant a, Å	3.616915(4)	3.65515(3)
Unit cell volume V, Å^3	47.317(0)	48.833(1)
Density d (calculated), g cm^{-3}	3.486	3.375
GSAS* full-profile analysis		
R_F	0.0112	0.0575
R_P	0.0363	0.033
R_{WP}	0.0607	0.0429

* GSAS — General Structure Analysis System [15].
R_F — structure reliability factor,
R_P — profile reliability factor,
R_{WP} — weighted profile reliability factor.

was also performed for cubic boron nitride obtained under similar $P-T$ parameters from a mixture of boron with sodium azide (NaN$_3$).

According to the structure refinement data, the composition of crystals of the diamond-like phase is described by the formula B$_{0.918}$C$_{0.139}$N$_{0.943}$. Because nanospherical carbon nitride contained about 15% chemisorbed oxygen, this element was also introduced in the refinement program. It was shown that oxygen cannot substitute boron, because a negative occupancy is obtained in this case, and can only reside in the nitrogen positions. The oxygen content in the lattice was about 4 at. %, which means that the actual composition of crystals with the largest unit cell must be described as B$_{0.92}$C$_{0.14}$N$_{0.86}$O$_{0.08}$.

To confirm the role of oxygen in the increase in the lattice constant, we carried out a series of experiments with varying compositions of the source mixtures. The results confirmed that oxygen is of decisive importance for the enlargement of the unit cell. Furthermore, the substantial incorporation of oxygen in the nitrogen positions within the basic boron nitride lattice requires two conditions: a high partial pressure of oxygen in the reaction volume of the high-pressure chamber and the simultaneous deficiency of nitrogen with respect to boron.

It was shown in [16] that the reactive interaction of melamine with boron initially leads to the formation of crystals with a graphite-like structure. It can be supposed that the substitution of boron and nitrogen with carbon and oxygen occurs already at this stage and persists upon the conversion of the lattice into a diamond-like one. This suggestion is corroborated by the results in [17], where the authors developed a technique for atom-by-atom TEM analysis. Studying a bilayer of doped boron nitride, they observed carbon in the form of pairs of neighboring atoms and of benzene rings (substitution for boron and nitrogen atoms), while oxygen was found only in the nitrogen positions.

When synthesis is carried out using mixtures with a high content of carbon nitride or melamine, the excess carbon crystallizes in the form of graphite disks or diamond crystals. Typically, the diamond particles are well faceted and their size is up to 20 μm (Fig. 2a). An X-ray analysis of several samples indicated that the lattice constant of these crystals is larger than 3.570 Å (to be compared with $a = 3.567$ Å for undoped diamond). The amount of diamond formed upon the synthesis of cBC$_x$N is fairly small, and the corresponding peaks in the X-ray diffraction patterns are broadened (Fig. 2b). For this reason, it is difficult to analyze the structural characteristics of the diamond phase using X-ray methods. The high concentration of boron in these diamond crystals is confirmed by the Raman spectra, which differ from those of conventional diamond by a strong shift of the diamond line (from 1332 to 1304–1305 cm^{-1}) and the presence of new broad bands (Fig. 2c) originating from the large number of point defects. The Raman spectra of heavily boron-doped diamond are analyzed in detail in [18].

It is known that a change in the lattice constant of diamond is caused by the substitution of carbon with boron. The largest increase in the size of the unit cell was observed in [5, 19], where polycrystals with lattice constants of 3.574–3.577 Å were formed upon the graphite-to-diamond phase transition. The boron content in the diamond lattice was estimated at the level of 3–4 at. %. We synthesized heavily boron-doped diamond microcrystals from mixtures of nano-size globular carbon with M-carborane (B$_{10}$H$_{16}$C$_4$O$_2$). Using full-profile X-ray analysis, we demonstrated for the first time that the lattice constant of boron-doped diamond can have two discrete values, 3.570 and 3.578 Å, with the respective boron contents of about 1% and 2% [20]. The concentration
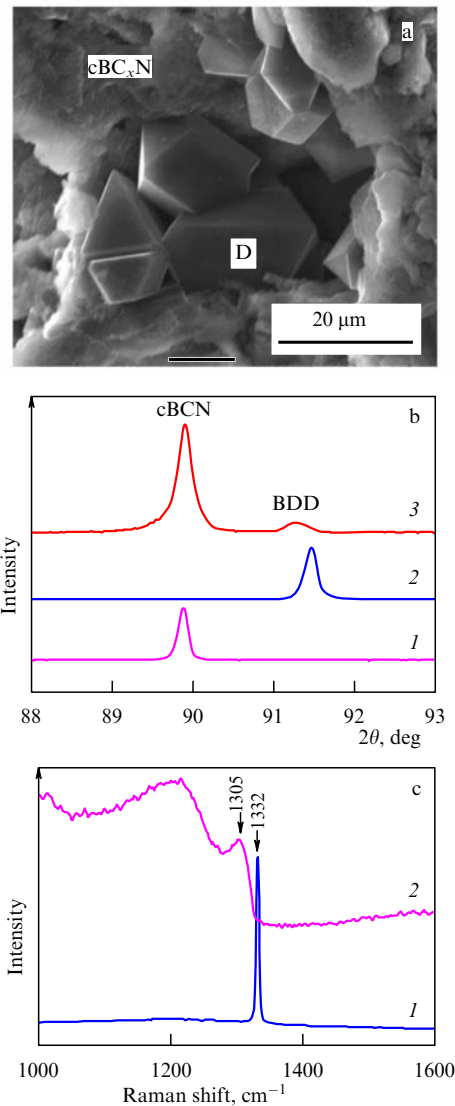
Figure 2. Analysis of boron-doped diamond (BDD) crystals. (a) Crystal morphology. (b) Powder X-ray diffraction patterns: (*1*) cBN, (*2*) diamond, and (*3*) powder synthesized from a mixture of melamine and boron. (c) Raman spectra: (*1*) diamond micropowder and (*2*) BDD.

of vacancies present in the diamond lattice exceeds that of boron by a factor of 2. Arguably, vacancies can form stable complexes with boron.

Diamonds with a high boron content feature metallic conductivity and undergo transition to a superconducting state at temperatures of 2–4 K [21]. But in the context of obtaining diamond composites by micropowder sintering, it is important that crystals of boron-doped diamond and $cBC_xN(O)$ crystals that form in the B–C–N system have high concentrations of point defects, which enable the activation of mass transfer and boundary readjustment.

The use of reactive mixtures with components that decompose upon HPHT treatment leads to the formation of active fluid phases. They contain nitrogen in the case of the destruction of carbon nitride or melamine and boron in the case of M-carborane. Individual heavily doped diamond and cubic boron nitride crystals form upon the interaction of fluids with solid components. These crystals can be used for sintering superhard compacts or for applications in various compositions.

3. Reactive sintering of diamond powders

Submicrometer (0.07–0.2 μm) powder of diamond with an added 30 wt. % mixture of melamine with boron was used as a model for studying the processes of reactive sintering. It was established that a period of 30 to 90 s is required for the efficient consolidation of particles at pressures of 7–8 GPa and sintering temperatures of 1600–1700 °C.

A very fine-grained structure reflecting the partial grinding of the source powders forms after the sintering of submicrodiamonds without additives (Fig. 3a). Analysis of these compacts demonstrated that even for short treatment durations, a graphite-like film appears on the surface of diamond particles. The presence of this film can be revealed by transmission microscopy or by the occurrence of the G mode in Raman spectra (Fig. 3b).
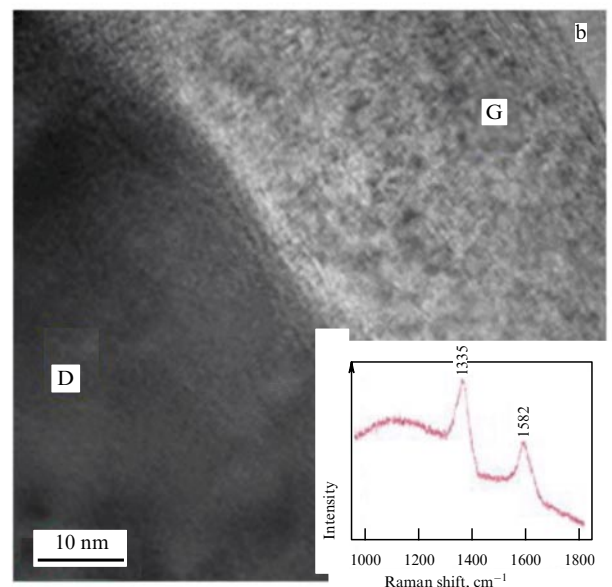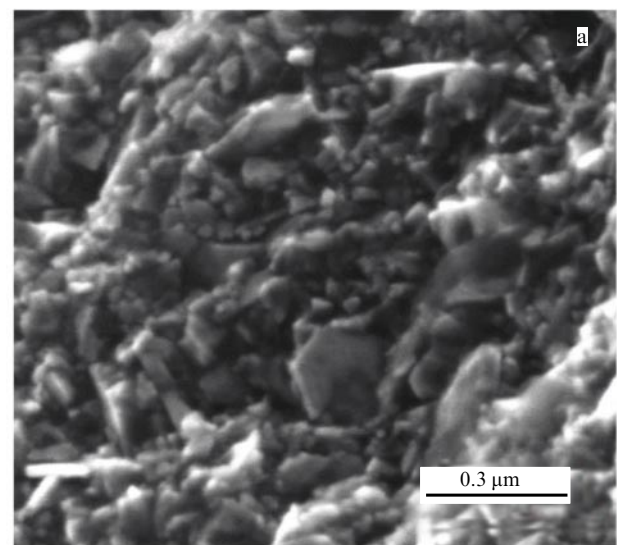

Figure 3. Microstructure of a compact produced from submicrometer diamond powder. (a) Cleaved-edge SEM image. (b) Graphite-like film on the surface of a diamond crystal. The inset shows the Raman spectrum recorded at the cleaved edge.
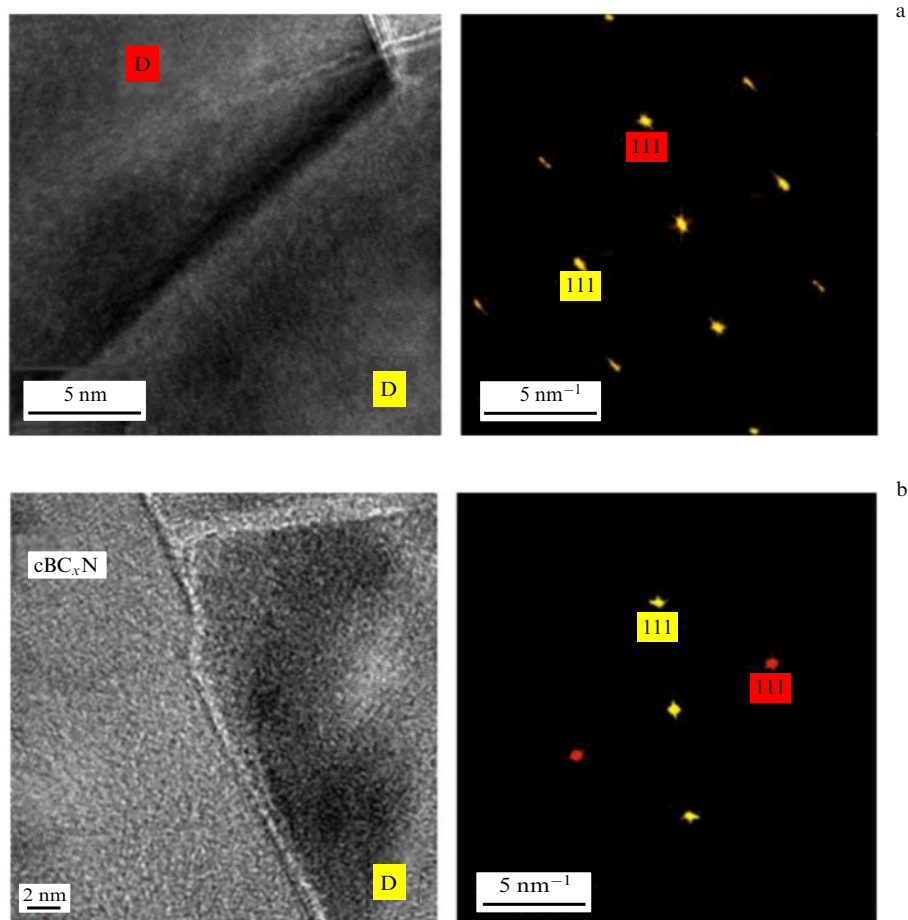
Figure 4. Fine structure and microdiffraction patterns of a diamond–cBC$_x$N composite. (a) Diamond–diamond twin boundary; the misorientation angle between the {111} directions is 90°. (b) Diamond–cBC$_x$N boundary; the misorientation angle between the {111} directions is 75°.

The addition of melamine with boron to diamond suppresses graphitization upon sintering due to the appearance of free hydrogen in the system upon the destruction of melamine. The sintering process involves reactive interaction between boron and the C–N fluid with the formation of crystals of carbon-doped diamond-like boron nitride and boron-doped diamond. TEM analysis of microfoil samples of this composite demonstrated the total absence of graphite-like phases and the high quality of boundaries between crystallites. Figure 4a presents an example of the formation of a twin boundary between diamond particles; Fig. 4b shows that the boundary layer between diamond and boron nitride grains has a width of 5–10 Å. Crystallites in the synthesized composites did not exceed 200 nm in size. The dimensions of the obtained composite specimens as a whole were 5 mm in diameter and 3 mm in height.

To scale up the dimensions of the composites, we used diamond micropowder with a particle size of about 10 μm as the basic component to which mixtures of submicrometer diamond with melamine and boron were added. Composite specimens up to 15 mm in diameter were obtained from these mixtures. Pieces of this size can be used in various applications, in particular, in drilling tools.

The wear resistance of the new superhard material was estimated by comparing it with that of commercial specimens of composites with ceramic (diamond–SiC) and cobalt-based metal binders when processing cylinder workpieces of a VK8 hard alloy [1] (without cooling) and of white granite (with cooling) in a turning lathe. The ratio of the volume of cut material to the volume loss of the composite was used as a measure of wear resistance. It was found that in the process of turning with no cooling, the new material has a wear resistance 30–50% higher than the diamond–SiC composite and two times higher than the commercial cobalt-based composite. The intense wearing of cobalt-based composites upon turning with no cooling is related to their low thermal stability. Upon turning white granite, the wear resistance of the diamond–cBN composite and the cobalt-bound composite was on the same level. The diamond–SiC composite showed poorer results because of its higher brittleness.

4. Conclusions

In summary, we have used HPHT synthesis involving fluid phases to obtain superhard composites from diamond micropowders. The new composites showed good results in test runs, which opens good prospects for exploiting reactive sintering at high pressures. Crystallization processes taking place in the course of sintering of boron nitride and diamond particles with a high concentration of point defects ensure a diffusive mobility sufficient for the formation of strong boundaries between particles. The composites consist of

[1] Tungsten carbide composite with cobalt binder.

only superhard components, and their characteristics can be enhanced considerably by optimizing the composition of starting mixtures and the regimes of sintering.

References

1. Katzman H, Libby W F *Science* **172** 1132 (1971)
2. Hibbs L E, Wentorf R H *High Temp.-High Press.* **6** 409 (1974)
3. Wentorf R H, DeVries R C, Bundy F P *Science* **20** 873 (1980)
4. Akaishi M, Ohsawa T, Yamaoka S *J. Am. Ceram. Soc.* **74** 5 (1991)
5. Ekimov E A, Ralchenko V, Popovich A *Diamond Related Mater.* **50** 15 (2014)
6. Zhao Y et al. *Appl. Phys. Lett.* **84** 1356 (2004)
7. Ekimov E A et al. *Appl. Phys. Lett.* **77** 954 (2000)
8. Jaworska L *High Press. Res.* **22** 531 (2002)
9. Sumiya H, Harano K *Diamond Related Mater.* **24** 44 (2012)
10. Kawai N, Endo S *Rev. Sci. Instrum.* **41** 1178 (1970)
11. Dubrovinskaia N et al. *Appl. Phys. Lett.* **90** 101912 (2007)
12. Filonenko V P et al. *Inorg. Mater. Appl. Res.* **8** 551 (2017); *Materialovedenie* (12) 30 (2016)
13. Khvostantsev L G, Vereshchagin L F, Novikov A P *High Temp.-High Press.* **9** 637 (1977)
14. Filonenko V P et al. *Diamond Related Mater.* **19** 541 (2010)
15. Larson A C, Von Dreele R B, Report LA-UR-86-748 (Los Alamos, NM: Los Alamos National Laboratory, 1987)
16. Filonenko V P et al. *Inorg. Mater.* **50** 349 (2014); *Neorg. Mater.* **50** 377 (2014)
17. Krivanek O L et al. *Nature* **464** 571 (2010)
18. Szirmai P et al. *Phys. Status Solidi B* **249** 2656 (2012)
19. Dubrovinskaia N et al. *J. Appl. Phys.* **99** 033903 (2006)
20. Zibrov I P, Filonenko V P *Crystals* **8** 297 (2018)
21. Ekimov E A et al. *Nature* **428** 542 (2004)