

Superhard Superconductor Composites Obtained by Sintering of Diamond, *c*-BN and C₆₀ Powders with Superconductors

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Superhard superconducting samples with a critical temperature of $T_C = 10.5 - 12.6$ K were obtained by high-pressure / high-temperature sintering of synthetic diamond powders coated with a niobium film and in 50% – 50% composition with superhard C₆₀ fullerene. Superhard superconductors with $T_C = 9.3$ K were obtained when diamond and molybdenum powders were sintered at a pressure of 7.7 GPa and a temperature of 2173 K. Superconducting samples with $T_C = 36.1 - 37.5$ K have been obtained in the systems diamond-MgB₂ and cubic boron nitride-MgB₂.

Key words: Diamond, MgB₂, C₆₀, Superconductivity, High-pressure / High-temperature

Introduction

Superconductivity of heavily boron-doped diamonds was discovered recently [1, 2] and has attracted much attention. Superconducting diamonds are the hardest known superconductors. Their potential applications are broad, ranging from small anvils in research high-pressure apparatus [3] to large parts of industrial devices in power engineering. However, the highest value of the superconductivity onset temperature in boron-doped diamonds was found at just about 7 K in thin CVD-grown films [4] and at about 4 K in bulk diamonds grown at high pressure and high temperature [1, 2]. An alternative method for the creation of diamond superconductors was suggested using sintering of diamond powders with molybdenum for special research high-pressure anvils with $T_C \sim 10$ K [3]. Large-scale industrial diamonds manufacturing provides an easy opportunity to produce a wide range of superhard sintered superconductors with various mechanical and electronic properties.

In this work, superhard superconducting materials have been synthesized for the first time on the basis of the systems diamond-Nb, diamond-MgB₂, cubic boron nitride (*c*-BN)-MgB₂ and C₆₀-diamond-Nb. The microhardness, elastic modulus and superconducting properties of these materials have been investigated.

By sintering of diamond micropowders with metal powders (Nb, Mo) and using metal-coated diamond micropowders at high static pressure and temperature we obtained superhard superconductors with T_C substantially higher than in boron-doped diamonds. Interacting with diamond, Nb and Mo metals form carbides bonding diamond crystallites into a united compact material having relatively high critical temperatures of the transition to the superconducting state. Superconducting composites consisting of hard superconductors and normal metals that are in thermal and electrical contacts with each other make it possible to satisfy very conflicting requirements imposed on superconducting materials for the production of large superconducting magnetic systems [5].

We obtained and investigated for the first time very hard (50 ± 25 GPa) materials with $T_C = 36 - 37$ K by sintering diamond and *c*-BN micropowders with MgB₂. Various engineering applications of this set of new superhard superconductors are possible in power electronics and cryogenic electrical machines.

Samples and Experimental Methods

Samples of the materials were obtained at high static pressures and temperatures. The experiments were carried out using “anvils with cavity”-type high-pressure

apparatus. Pressure was calibrated by electrical resistance jumps in reference metals Ba (5.5 GPa), Bi (2.5, 2.7, 7.7 GPa), Pb (13 GPa) and ZnSe (13.7 GPa) at known phase transitions. The temperature graduation of the chambers was performed using Pt/Pt-10% Rh and W/Re thermocouples. Initial components were placed into a tantalum-foil shell of 0.1 mm thickness. Samples were heated by an ac current through a graphite heater with a tantalum shell as part of the sample system. The experiments were carried out at a pressure of 7.7 GPa and a temperature of 1373 K for diamond-MgB₂ and *c*-BN-MgB₂, 1973 K for diamond-niobium, 2173 K for diamond-molybdenum systems and 12.5 GPa, 1650 K for C₆₀-diamond-niobium systems. The heating time was 60–90 s. The samples were quenched under high pressure with a rate of 200 K per second. After pressure release the samples were extracted from the high-pressure cell. Small cylinder-shaped samples with a diameter of 4.5 mm and a height of 3.5 mm were obtained. After smoothing and polishing, 3.9 × 2.51 × 1.54 mm³ parallelepiped samples were obtained. The phase content of the samples was determined by X-ray diffraction using an HZG-4A diffractometer and monochromatic CuK α radiation ($\lambda = 0.1541$ nm). The resistance of the resulting samples was measured by the conventional four-probe method. Electrical contacts were produced using conducting silver paste. The temperature dependence of the resistance was measured in the interval 4.2 < T < 300 K.

The Vickers microhardness was measured using a PMT-3 device at an indenter load of 5.5 N. Sound velocities in 3 samples were measured using a wide-field pulse scanning microscope (WFPAM) in reflection mode (time-of-flight method) at a driving frequency of 50 MHz. The mean diameter of the acoustic beam in the specimen was about 0.1 mm. This experimental procedure was described in detail in [6].

Results and Discussion

Diamond-niobium system

Synthetic diamond with 80–100 μ m crystallites covered with a niobium film by sputtering in vacuum was used as the initial material. The total amount of niobium in the initial material was 24 wt %. The experiments were carried out at a pressure of 7.7 GPa and a temperature of 1973 K for 60 s. The diffraction patterns exhibited peaks associated with diamond and NbC monocarbide. A small fraction of Nb₂C was

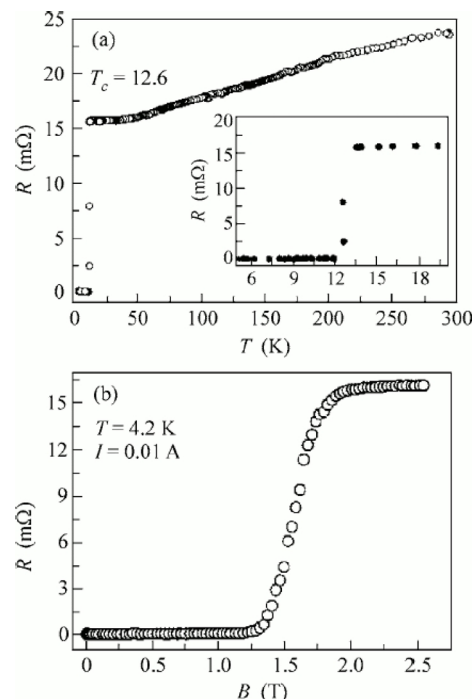


Fig. 1. Temperature (a) and magnetic field (b) dependences of the resistance for the sample obtained in the diamond-niobium system.

also found. The NbC monocarbide synthesized at the boundaries of the crystallites had a face-centered cubic lattice with the lattice parameter $a_0 = 0.447$ nm. This value is consistent with the data obtained for NbC by another method [7]. The carbide Nb₂C has a hexagonal structure with the lattice parameters $a_0 = 0.312$ nm and $c_0 = 0.492$ nm.

The critical temperature of the transition to the superconducting state in all the measurements was fixed at the onset of the transition. According to an analysis of the temperature dependence of the resistance, the critical temperature of the transition of the synthesized samples to the superconducting state was equal to $T_C \approx 12.6$ K (Fig. 1a), which is characteristic of a NbC compound with almost full carbon sites [8–10]. Carbon deficient NbC_{1-x} has a lower T_C or superconductivity is entirely absent. The characteristic feature of the synthesized samples is a quite narrow superconducting transition, $\Delta T \approx 1.5$ K. The measured dependence of the resistance of a sample on the external magnetic field (Fig. 1b) is characteristic of a compound the composition of which is very close to that of NbC. The value of the second critical field $H_{C2} = 1.25$ T (at $T = 4.2$ K) is consistent with H_{C2} for NbC films ob-

Table 1. Diamond-Nb density ρ , longitudinal and transverse sound velocities V_L , V_T , Young modulus E , bulk and shear elastic modules B , G and Poisson ratio σ .

	ρ g cm ⁻³	V_L km s ⁻¹	V_T km s ⁻¹	E GPa	B GPa	G GPa	σ
Diamond-Nb	4.1 ± 0.1	12.1 ± 0.5	6.9 ± 0.25	490 ± 95	340 ± 30	195 ± 14	0.26 ± 0.04

tained by the laser-evaporation method [9]. Thus, one can assume that on the surface of the sintered diamond crystallites NbC is formed with an almost perfect crystal structure and a low concentration of defects which also reduces the temperature of the superconducting transition [11].

The microhardness values are in the range of 35–95 GPa. According to [7], the Vickers hardness of NbC is approximately equal to 17 GPa. This value is significantly lower than the results obtained in our work for microdomains enriched in NbC. The hardness of such microdomains is high, apparently due to the effect of the boundaries of diamond crystallites, which have much higher hardness (100–150 GPa along different faces, depending on the quality of the crystals). The velocities of sound and the elastic modules are 30–40% less than in pure polycrystalline diamond (Table 1), nevertheless they are comparable with the values for the second very strong superhard material: cubic boron nitride (*c*-BN).

C₆₀-Diamond-niobium system

High-pressure / high-temperature treatment of C₆₀ and C₇₀ fullerenes leads to polymerization and transformation into new metastable carbon structures [12–14]. Among various polymeric forms, the 3D-polymeric ones are the hardest [12]. The density of superhard ($H_v > 50$ GPa) and ultrahard ($H_v > 120$ GPa) forms ranges from 2.5 to 3.3 g cm⁻³, intermediate between the densities of graphite and diamond. Mechanical, electrical and other properties of such materials strongly depend on their particular crystalline or disordered structure. A set of metal-C₆₀ compounds are superconducting with $T_C = 2–34$ K [15]. However, conventional fullerene superconductors are not hard and chemically active; they cannot be stored in air. We investigated the synthesis of composite superconductors on the basis of a 50%–50% mixture of C₆₀ powder with niobium coated diamond powder as described in the first part above. Sintering was carried out at a pressure of 12.5 GPa, at $T = 1650$ K. XRD analysis (Fig. 2) showed formation of a disordered superhard component on the basis of C₆₀ (broad diffraction peak) and

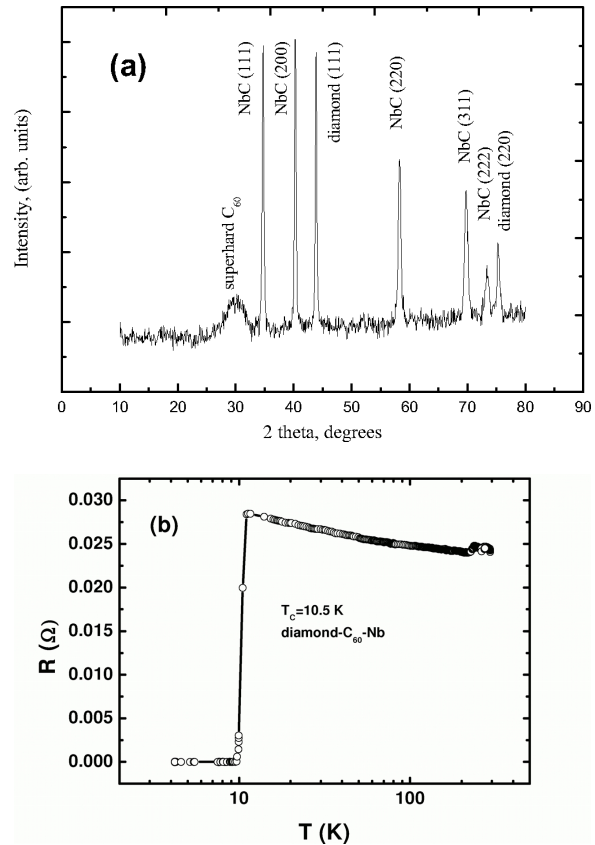


Fig. 2. X-ray diffraction pattern (a) and temperature dependence of the resistance (b) for the sample obtained in the C₆₀-diamond-niobium system.

niobium monocarbide with diamond crystals. The microhardness values of this composite material are 45–95 GPa. It is superconducting below 10.5 K (Fig. 2b).

Diamond-molybdenum system

In this system, a synthetic-diamond powder with a granularity of 40–100 μm and a molybdenum powder with a particle size of 1–5 μm were used as the initial materials consisting of 60 wt % of diamond and 40 wt % of molybdenum. A compact material was obtained by holding at a pressure of 7.7 GPa and a temperature of 2173 K for 90 s. The phase content of the samples was determined by the same method as for

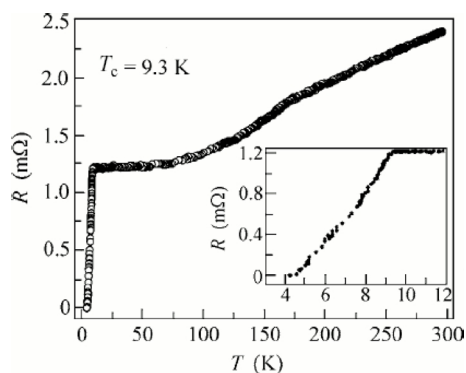


Fig. 3. Temperature dependence of the resistance for the sample obtained in the diamond-molybdenum system.

the diamond-Nb system. The following phases were identified in the samples: the α -MoC diamond phase with a cubic lattice with the parameter $a_0 = 0.427$ nm (B1 type), the η -MoC hexagonal phase with the lattice parameters $a_0 = 0.300$ and $c_0 = 1.452$ nm, and traces of the hexagonal γ -MoC phase (WC type) with the parameters $a_0 = 0.290$ and $c_0 = 0.282$ nm. The lattice parameters that were determined for molybdenum-carbon compounds are consistent with the data published in [7]. The Vickers microhardness of the samples lies in the range 27–83 GPa. The composites obtained in the reaction of diamonds with molybdenum are superconductors with characteristic features. First, the temperature of the transition to the superconducting state is $T_C = 9.3$ K, which is slightly lower than the T_C values for molybdenum carbide obtained by sintering powders of molybdenum and graphite [16]. Second, the transition width $T \approx 5$ K is larger than that for the diamond-niobium system. Fig. 3 shows the temperature dependence of the resistance of these composites.

The systems diamond-MgB₂ and c-BN-MgB₂

Magnesium diboride, whose bulk superconductivity was discovered recently [17, 18], has a higher critical temperature $T_C = 39$ K than niobium carbide and molybdenum carbide. Many investigations were devoted to the effect of the conditions under which MgB₂ was obtained and treated at high pressures and temperatures on the superconducting properties with various dopants [19–25]. It is of interest to obtain a superconducting composite material in which diamond or cubic boron nitride are used as the superhard components and MgB₂ is used as the superconducting component. As the initial material, we used industrial MgB₂ powders in which the content of the basic product was

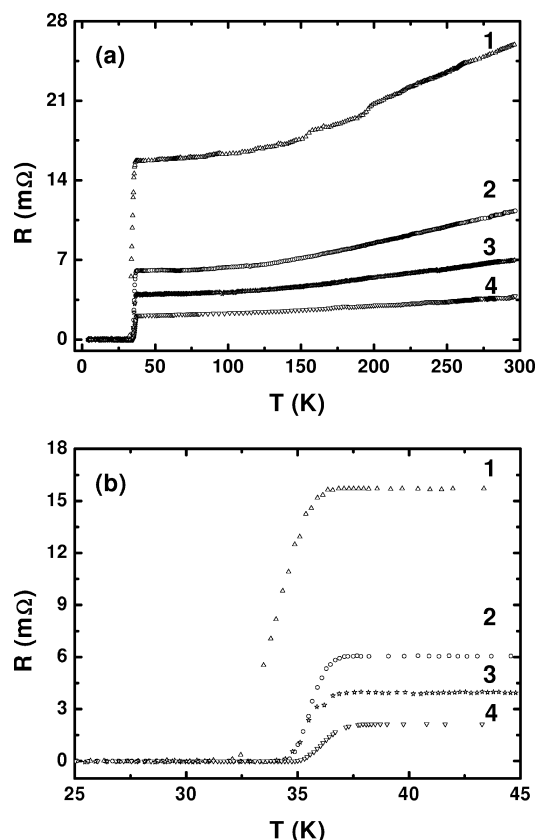


Fig. 4. Temperature dependence of the resistance (a) and transition range (b) for the composite samples obtained in the systems (1) cubic boron nitride-MgB₂, $T_C = 36.1$ K, (2) diamond-MgB₂, $T_C = 36.9$ K, (3) MgB₂, $T_C = 37$ K, and (4) diamond-niobium-MgB₂, $T_C = 37.5$ K.

equal to 98.5%. The particle size was reduced to 5–10 μm by additional powdering. The prepared mixtures consisted of 80 wt % of the superhard component and 20 wt % of MgB₂. The granularity of the diamond and cubic boron nitride powders was equal to 40–100 and 28–40 μm , respectively. The assembly of the high-pressure cells and the experimental procedure were the same as those used for the diamond-molybdenum system. In one of the experiments, a niobium-coated diamond powder was used. The samples were obtained by holding at a pressure of 7.7 GPa and a temperature of 1373 K for 60 s.

The temperature dependence of the resistance of the samples shows that the temperature of the transition to the superconducting state is $T_C \approx 37$ K, which is close to the value known for MgB₂ [17]. This closeness indicates that MgB₂ has a key role in the superconductivity of these composite materials, and the matrix con-

sisting of cubic boron nitride or diamond changes T_C insignificantly, while the hardness of such a superconducting material is much higher than the one of compacted MgB_2 . Fig. 4 shows the results.

The Vickers microhardness of the diamond- MgB_2 and $c\text{-BN-MgB}_2$ samples varies in the range of 25–78 and 24–57 GPa, respectively. According to [20], the microhardness of MgB_2 samples that were synthesized at 2 GPa and 1073 K from the elements with the addition of 2 wt % of a tantalum powder was 12.79 GPa. The values of densities, sound velocities and elastic modules are presented in Table 1. The respective values for both materials are very similar, but generally the velocities of sound and modules in diamond- MgB_2 are about 10% less than in the $c\text{-BN-MgB}_2$ system. We suppose that this is due to a smaller grain size of the initial $c\text{-BN}$ powder as compared to the diamond powder. The values for both types of materials are less than in superhard materials, they are superior to those of ordinary solids.

Conclusion

Composite superhard superconducting materials in the form of diamond and superhard fullerene-diamond matrices with superconducting NbC channels that have $T_C = 10.5\text{--}12.6$ K have been obtained in the diamond-niobium and C_{60} -diamond-niobium systems at high

pressures and temperatures. The microhardness and elastic modules of such materials correspond to very hard and superhard materials. A composite material consisting of a diamond matrix and superconducting channels of MoC with $T_C = 9.3$ K has been obtained in the diamond-molybdenum system. Parts of various devices can be made of such composites. Composite materials consisting of the superhard matrices (80 wt %) and superconducting channels of MgB_2 with $T_C = 36.1\text{--}37.5$ K have been obtained in the systems diamond- MgB_2 and $c\text{-BN-MgB}_2$. The microhardness of the samples indicates that the composite matrix (consisting of cubic boron nitride or diamond) occupying the major part of the body of the samples has a microhardness of 57–95 GPa. Such microhardness values are characteristic for superhard compact polycrystalline materials based on cubic boron nitride and diamond that are used to produce various abrasive and cutting tools [26]. Though the elastic modules are not very high, such materials have good prospects for applications. Generally, the method used in this work allows for the production of high-strength superconducting materials.

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- [1] E. A. Ekimov, V. A. Sidorov, E. D. Bauer, N. N. Mel'nik, N. J. Curro, J. D. Thompson, S. M. Stishov, *Nature* **428**, 542 (2004).
 - [2] V. A. Sidorov, E. A. Ekimov, S. M. Stishov, E. D. Bauer, J. D. Thomson, *Phys. Rev. B* **71**, 060602 (2005).
 - [3] V. N. Narozhny, G. N. Stepanov, G. A. Dubitski, E. E. Semenova, E. N. Yakovlev, *Fizika i Tekhnika Vysokih Davlenii* **27**, 88 (1988) (in Russian).
 - [4] Y. Takano, M. Nagao, I. Sakaguchi, M. Tachiki, T. Hatano, K. Kobayashi, H. Umezawa, H. Kawarada, *Appl. Phys. Lett.* **85**, 2851 (2004).
 - [5] A. V. Gurevich, R. G. Mints, A. L. Rakhmanov, *Physics of Composite Superconductors*, Nauka, Moscow (1987) (in Russian).
 - [6] V. M. Prokhorov, V. D. Blank, S. G. Buga, V. M. Levin, *Synth. Met.* **103**, 2439 (1999).
 - [7] L. Toth, *Transition Metal Carbides and Nitrides*, Academic Press, New York (1971); Russian translation: Mir, Moscow, 1974.
 - [8] Yu. S. Karimov and T. G. Utkina, *Pis'ma v Zh. Eksp. i Teor. Fiz.* **51**, 468 (1990); *JETP Lett.* **51**, 528 (1990).
 - [9] N. P. Shabanova, S. I. Krasnosvobodtsev, V. S. Nozdrin, A. I. Golovashkin, *Fiz. Tverd. Tela* **38**, 1085 (1996); *Phys. Solid State* **38**, 1085 (1996).
 - [10] S. I. Krasnosvobodtsev, N. P. Shabanova, E. V. Ekimov, V. S. Nozdrin, E. V. Pechen', *Zh. Eksp. Teor. Fiz.* **108**, 970 (1995); *J. Exp. Theor. Phys.* **81**, 534 (1995).
 - [11] W. E. Pickett, B. M. Klein, R. Zeller, *Phys. Rev. B* **34**, 2517 (1986).
 - [12] V. D. Blank, S. G. Buga, G. A. Dubitsky, N. R. Serebryanaya, M. Yu. Popov, B. Sundqvist, *Carbon* **36**, 319 (1998).
 - [13] V. D. Blank, N. R. Serebryanaya, G. A. Dubitsky, S. G. Buga, V. N. Denisov, B. N. Mavrin, A. N. Ivlev, S. N. Sulyanov, N. A. Lvova, *Phys. Lett. A* **248**, 415 (1998).
 - [14] V. D. Blank, S. G. Buga, G. A. Dubitsky, N. R. Serebryanaya, V. M. Prokhorov, B. N. Mavrin, V. N. Denisov, L. A. Chernozatonskii, S. Berezina, V. M. Levin, *Z. Naturforsch.* **61b**, 1547 (2006).
 - [15] K. Holczer, R. L. Whetten, in H. Kroto, J. E. Fischer, D. E. Cox (eds): *The Fullerenes*, Pergamon Press, Oxford (1993).

- [16] R. H. Willens, E. Buehler, B. T. Matthias, *Phys. Rev.* **159**, 327 (1967).
- [17] J. Nagamatsu, N. Nakagawa, T. Muranaka, Y. Zenitani, J. Akimitsu, *Nature* **410**, 63 (2001).
- [18] Y. Zenitani, J. Akimitsu, *AAPPS Bull.* **13**, 26 (2003).
- [19] C. U. Jung, M.-S. Park, W. N. Kang, M.-S. Kim, K. H. P. Kim, S. Y. Lee, S.-I. Lee, *Appl. Phys. Lett.* **78**, 4157 (2001).
- [20] T. A. Prikhna, W. Gawalek, A. B. Surzhenko, V. E. Moshchil, N. V. Sergienko, Ya. M. Savchuk, V. S. Melnikov, P. A. Nagorny, T. Habisreuther, S. N. Dub, M. Wendt, D. Litzkendorf, J. Dellith, Ch. Schmidt, G. Krabbes, A. V. Vlasenko, *Physica C* **372**, 1543 (2002).
- [21] W. Pachla, P. Kovac, R. Diduszko, A. Mazur, I. Huek, A. Morawski, A. Presz, *Supercond. Sci. Technol.* **16**, 7 (2003).
- [22] A. Tampieri, G. Celotti, S. Sprio, R. Caciuffo, D. Rinaldi, *Physica C* **400**, 97 (2004).
- [23] P. Toulemonde, N. Musolino, R. Flukiger, *Supercond. Sci. Technol.* **16**, 231 (2003).
- [24] Y. Zhao, C. H. Cheng, X. F. Rui, H. Zhang, P. Munroe, H. M. Zeng, N. Koshizuka, M. Murakami, *Appl. Phys. Lett.* **83**, 2916 (2003).
- [25] S. X. Dou, W. K. Yeoh, J. Horvat, M. Ionescu, *Appl. Phys. Lett.* **83**, 4996 (2003).
- [26] A. A. Shul'zhenko, B. I. Ginzburg, N. I. Khovakh, A. I. Pruss, *Sverkhtverd. Mater.* No. 1, 23 (1987) (in Russian).