Consolidation of Nanocrystals of Detonation Nanodiamond under Thermobaric Sintering

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Abstract—The structural and physicomechanical properties of composite materials obtained by sintering detonation nanodiamonds under high pressures and temperatures ($P = 5$ GPa, $T = 1200$°C) have been investigated. There is a slight growth of diamond crystals after sintering from 4.5 to 5.2 nm. It is shown that the strength of the samples locally reaches 14 GPa. The high microhardness of the material is due to the consolidation of diamond nanocrystals into strong polycrystalline aggregates owing to the formation of covalent bonds between crystals under high pressure and temperature conditions.

INTRODUCTION

Research aimed at obtaining materials with a combination of physicomechanical and performance properties always received special attention.

Diamonds have unique physicochemical properties that are associated with the peculiarity of their crystal lattice. As a rule, high hardness and wear resistance are considered the most significant properties. Owing to these properties, diamonds are widely used in practice [1, 2]. One of the promising directions is creation of polycrystalline diamond materials, the hardness of which is commensurate with the hardness of natural diamonds. The sintering of synthetic diamond powders at high pressures and temperatures makes it possible to obtain compacts with high strength characteristics [3].

A high level of physicomechanical properties of a material depends on the grain size of polycrystals, which directly follows from the experimentally established dependence of the material hardness on the size of crystals [4].

Over the past decades, a direction has been formed in materials science with the creation and use of nanomaterials. In this regard, to obtain sintered high-strength diamond polycrystals, the use of diamond nanosized powders, for example, detonation nanodiamond, seems promising.

Detonation nanodiamond [5] is a complex system that includes a nanocrystalline diamond core and an impurity subsystem of various elements and compounds [6]. The quantitative and elemental composition of the impurity shell depends on the technological conditions of the synthesis. However, studies show that impurities are an integral component of diamond nanoparticles [7]. The nanodiamond core, the average size of which is 4.5 nm, has an ideal crystal structure, and there are no linear and flat defects in the crystal structure. Defects in the crystal structure in the form of packing defects, subgrains, etc., can be found only in large nanocrystals (more than 10 nm), which occur quite rarely [8].

Traditional pressing and sintering of detonation nanodiamonds under conditions of both dynamic and static loading is accompanied by a number of difficulties [9]. The main reasons for the low quality of compacts include the following: cluster structure and, as stated in some papers, the tendency of detonation nanodiamond powder to graphitization with low sintering parameters [9].

In addition, in the case of detonation nanodiamonds, where the proportion of impurities is significantly higher than that of other synthetic diamonds, their influence on the physicochemical properties of the powders is more pronounced [10, 11]. Therefore, it should be expected that the modification of the chemical and phase composition of the surface of nanodiamonds would have a significant impact on the sintering and consolidation of nanodiamonds under high pressure and temperature conditions.
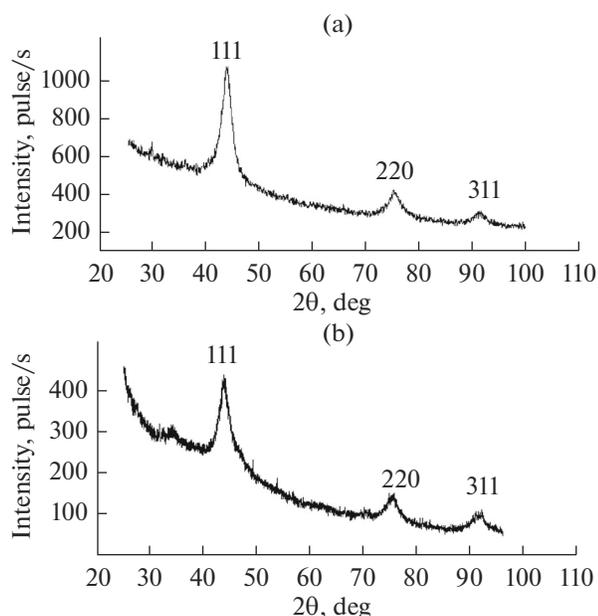
Fig. 1. X-ray diffraction pattern of detonation nanodiamond: (a) initial nanodiamond powder; (b) sintered at a pressure of $P = 5$ GPa and temperature of 1100°C. Numbers in parentheses indicate diamond reflexes.

Experiments show that the modification of detonation nanodiamond powders, which leads to a change in the chemical composition of the surface of diamond nanoparticles, contributes to the improvement of the physicomechanical properties of compacts. Desorption of gases adsorbed on the surface of particles by annealing compressed briquettes of nanodiamonds in vacuum for several hours leads to an increase in the density of the initial fabrications [12] and an increase in the strength and hardness of the sintered samples in comparison with the strength of samples that did not pass the stage of preliminary purification from adsorbed impurities [12, 13]. Modification of nanodiamonds with metal catalysts and carbide-forming elements, such as Co, Ti, B, and Si, in some cases leads to an improvement in the microstructure of composites and an increase in their strength [9, 14]. The hardness of such samples reached 30 GPa, and carbides of the corresponding metals were found in their structure [9].

The sintering of impurity-free nanodiamond powders with the surface of nanoparticles coated with a non-diamond nanoscale carbon sheath makes it possible to obtain a durable polycrystalline material [9]. It is argued that the non-diamond carbon shell possesses catalytic activity, ensuring the transfer of carbon to the diamond phase. As a result, during sintering, the formation of diamond polycrystals is observed, with single-crystal sizes reaching 150 nm.

Thus, it can be assumed that the physicomechanical properties of sintered detonation nanodiamonds compacts depend on the formation of covalent bonds between the carbon atoms of the adjacent diamond nanocrystals. In this regard, the purpose of this work is to investigate the processes of consolidation of nanocrystals of detonation nanodiamond into polycrystalline aggregates during sintering and the effect of the degree of connectivity of nanocrystals on the physicomechanical properties of the composite material.

EXPERIMENTAL

In this work, a detonation nanodiamond powder made by Federal Research and Production Technique Center Altai according to TU 84-112-87 was used for the study. Thermobaric sintering of nanodiamonds was carried out on the Cutting Sphere (BARS) nonpress apparatus [14] at the Institute of Geology and Mineralogy of the Siberian Branch of the Russian Academy of Sciences. Sintering was carried out at a pressure of 5 GPa and temperatures of 1100°C and 1200°C. When the maximum sintering parameters were reached, the time of thermobaric impact was 60 s. During the thermobaric action, the powder was placed in a semi-sintered MgO oxide sleeve. After sintering, the sample was placed in concentrated nitric acid until the bushing was dissolved.

The phase composition and structural state of nanocrystalline diamond composite materials were investigated using X-ray diffraction. The elemental composition of the samples was determined by X-ray microanalysis using a Quanta 200 3D scanning electron microscope combined with an energy-dispersive microanalysis system at the shared use center at Tomsk State University.

The study of hardness was carried out on a PMT-3 microhardness tester.

RESULTS

Figure 1 shows the X-ray diffraction pattern of the initial detonation nanodiamond (see Fig. 1a) and the X-ray diffraction pattern of the composite nanodiamond material obtained by sintering the nanodiamond powder (see Fig. 1b) at pressure $P = 5$ GPa and temperature $T = 1100$°C. The reflex system was identified as a carbon reflection system with a diamond crystal lattice.

As follows from the data in Fig. 1, the reflexes of the initial detonation nanodiamond and after thermobaric sintering have anomalous broadening. Analysis of the broadening of reflexes will make it possible to determine the sizes of the coherent scattering regions, i.e., to determine the size of detonation diamond nanocrystals in the initial powder and in sintered polycrystalline aggregates.

The results of X-ray structural analysis of detonation nanodiamond before and after sintering are presented in Table 1.

Table 1. The values of the physical broadening and the position of the main reflections of the initial powder nanodiamond and in the structure of the sintered samples

hkl	Sample of initial powder			Sintered sample at $P = 5$ GPa, $T = 1100°C$			Sintered sample at $P = 5$ GPa, $T = 1200°C$		
	2θ, degrees	d, Å	β, degrees	2θ, degrees	d, Å	β, degrees	2θ, degrees	d, Å	β, degrees
111	43.61	2.07	2.11	43.8	2.07	1.68	43.56	2.07	1.78
220	75.13	1.26	2.45	75.2	1.26	1.92	75.2	1.26	1.74
311	91.15	1.07	2.78	91.4	1.07	2.96	–	–	–

Table 2. The size of the initial detonation nanodiamond crystals and after thermobaric exposure

Sample	Initial nanodiamond	After thermobaric exposure	
		$P = 5$ GPa, $T = 1100°C$	$P = 5$ GPa, $T = 1200°C$
Size CSR, nm	4.5 ± 0.4	4.9 ± 0.3	5.2 ± 0.5

On the basis of the data given in Table 1, the sizes of the coherent scattering regions D were calculated. The calculation was performed using the Selyakov–Scherrer formula [16]. The broadening of the diffraction peaks may be due to the small size of the coherent scattering regions (crystallites). In addition, the lattice defects caused by the displacement of atoms from the sites of the crystal lattice lead to the broadening of X-ray maxima. The broadening value associated with the microdeformation of the lattice is determined by the value of $\Delta d_m/d$, where Δd_m is the average change in the interplanar distance and d is the interplanar spacing in an ideal crystal.

Owing to the fact that elastic moduli are large in diamond nanocrystals, $\Delta d_m/d$ cannot be large. Therefore, to determine the size of diamond crystals D, one can use the following simplified formula, according to which the broadening of X-ray reflexes is associated only with the small size of crystals:

$$D = \frac{\lambda}{\beta \cos \theta}. \tag{1}$$

The results of the calculations are presented in Table 2.

According to the data in Table 2, the size of the detonation nanodiamond crystals before sintering is 4.5 nm, which agrees well with the generally accepted data [17, 18]. After thermobaric exposure, a slight growth of crystals is observed. So, in a sample sintered at a pressure of 5 GPa and temperature of 1100°C, the size of nanodiamond crystals is 4.9 nm, and in a sample sintered at the same pressure value, but at a temperature of 1200°C, the size of nanodiamond crystals increases to 5.2 nm.

The observed growth can be associated with the transition to the diamond phase of carbon located on the surface of the nanodiamond core. This conclusion is confirmed by the results of a number of experimental studies in which an increase in the size of nanodiamond crystals was observed owing to the transition of graphite and "onion" carbon on the surface of nanocrystals to diamond by heating without applied external pressure [19, 20]. The growth can also be due to the interaction of nanocrystals along the boundaries during thermobaric sintering [21].

X-ray diffraction analysis of the samples did not reveal any carbon phase in the structure of composite materials, except for the diamond phase. Consequently, the thermobaric action with the selected sintering parameters of detonation nanodiamond does not lead to a significant reverse phase transition of diamond to graphite.

Table 3 presents the results of the elemental analysis of the initial detonation nanodiamond powder and after thermobaric sintering at a temperature of 1200°C.

Comparing the data in the Table 3, it can be noted that the elemental composition and content of elements in nanodiamond after sintering changed significantly. The amount of oxygen decreased by 4 times,

Table 3. The elemental composition of the initial powder of detonation nanodiamond and sintered polycrystalline diamond aggregate

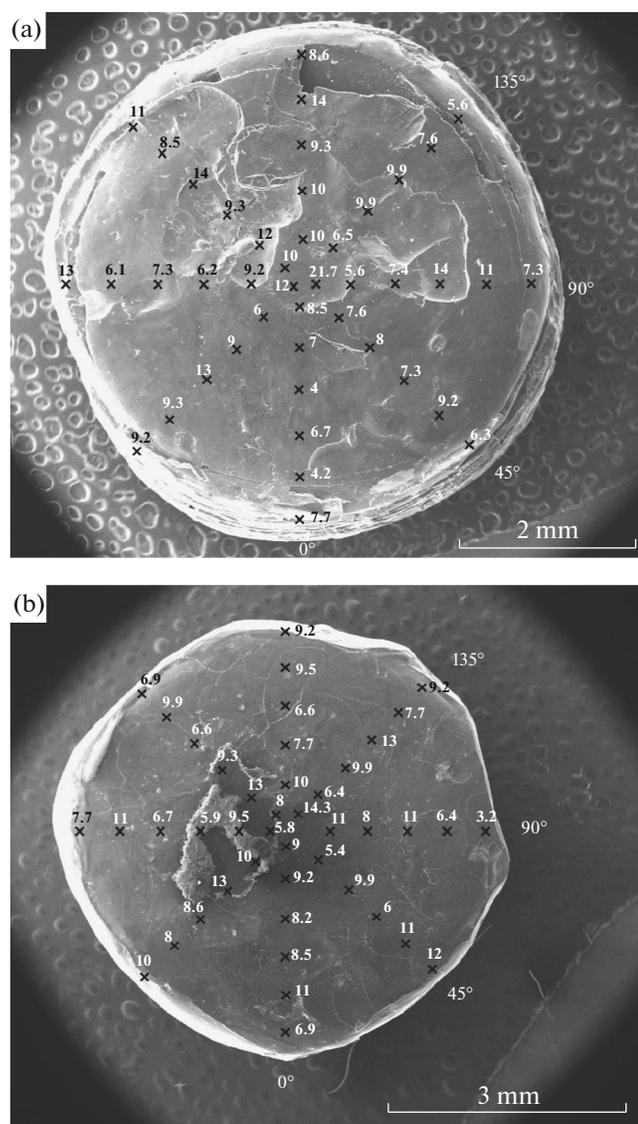| Element	C	O	Fe	S	Ca	Al	Cu	Cr	Si
Initial powder, wt %	82.28	4.93	4.52	4.33	1.92	1.27	0.61	0.56	0.40
Sintered at $P = 5$ GPa, $T = 1200°C$, wt %	94.60	1.26	0.76	1.91	0.37	0.66	–	–	0.45

Fig. 2. The microstructure of nanodiamond composite materials sintered at a pressure of 5 GPa and temperature of 1100°C (a) and 1200°C (b). Designated microhardness measurement points (microhardness values are indicated in GPa).

thermomechanical activation of diffusion processes, which apparently lead to the localization of metals along the interfaces of the crystals and a decrease in their concentration on the surface of the diamond core.

According to these data, in the sintering process, conditions are created that contribute to a decrease in the amount of impurities on the surface of the nanodiamond core.

Figure 2 shows images of the surface of sintered samples with an indication of the microhardness measurement sites and their magnitude.

As can be seen from Fig. 2, the microhardness values of the samples lie in a wide range. For a sample sintered at a temperature of 1100°C (see Fig. 2a), the minimum hardness value is 4 GPa, and the maximum is 14.3 GPa; for a sample sintered at 1200°C (see Fig. 2b), the values are 3.2 and 14 GPa, respectively. The scatter of data is not due to measurement error, but is due to the heterogeneity of the microstructure of the sintered specimens. It is possible to identify areas with high hardness, which, as can be seen, are located in the central part of the samples. It is also possible to identify areas with low strength, located mainly in the periphery. The heterogeneity of the structure of sintered nanodiamond materials means that the process of consolidation of diamond nanocrystals into a polycrystalline aggregate in the bulk of the material during sintering proceeds unevenly.

Table 4 shows the average microhardness for a sample obtained from the initial powder of nanodiamonds by annealing of a billet pressed in the form of a cylinder in vacuum at a temperature of 950°C and compacts obtained by thermobaric action at temperatures of 1100 and 1200°C and pressure 5 GPa.

As can be seen from the above data, the samples sintered without pressure have low strength characteristics (0.5 GPa). The microhardness of pressure-sintered samples is much higher. So, for a sample sintered at a temperature of 1100°C, the average value of hardness is 8.8 GPa, and for one sintered at a temperature of 1200°C, it is 8.9 GPa.

DISCUSSION

According to the experimental data, the sintering of detonation nanodiamonds in vacuum without applied external pressure does not lead to an increase in the sample hardness; i.e., the consolidation of nanocrystals into strong polycrystalline aggregates under low pressure conditions is absent. At the same time, the

iron by 6 times, aluminum by 2 times, sulfur by almost 3 times, and calcium by 6 times. The decrease in the content of volatile compounds is due to thermal desorption, resulting from the heating of the sample. A significant decrease in the concentration of metallic impurity elements is apparently associated with the

Table 4. Mechanical properties of nanodiamond samples before and after thermobaric exposure

Sample	Initial nanodiamond	After thermobaric exposure	
		$P = 5$ GPa, $T = 1100°C$	$P = 5$ GPa, $T = 1200°C$
Microhardness Hv, GPa	0.5 ± 0.1	8.8 ± 2.5	8.9 ± 2.4

sintering of nanodiamonds under high pressure and temperature conditions leads to an increase in the strength of the material by more than an order of magnitude.

An increase in hardness may be due to the formation of strong bonds between the carbon atoms of neighboring crystals during sintering. However, according to the elemental analysis data (see Table 3), in the detonation nanodiamond, there are atoms of iron, aluminum, calcium, etc., which can form strong covalent bonds with carbon. According to the experimental data, these metals and their compounds are located predominantly on the surface of the nanodiamond core [7]. Therefore, an increase in the strength of specimens hardened under conditions of high pressures and temperatures can also be due to the occurrence of strong bonds between the metal atoms and also between the metal and carbon atoms.

Calculations show a spherical particle 4.2 nm in size contains on average 7000 carbon atoms [22]. About 15−20% of the atoms are on the surface of the particle, which is about 1000 atoms. When the content of impurities in detonation nanodiamond is more than 15 wt %, its nanodiamond core is completely covered with impurity atoms, which prevent the interaction of nanocrystals with each other [23]. The structure of the impurity cover has a complex structure. The initial powder of nanodiamonds used in the experiments contains about 18 wt % of impurities (see Table 3). Annealing of nanodiamonds in vacuum allows one to get rid of a significant fraction of impurities, mainly volatile compounds [24]. When heated, up to 10 wt % of impurities may evaporate from the surface of the particles. After annealing, predominantly metal atoms and their compounds remain on the surface of nanodiamonds. However, as experiments show, the sintering of nanodiamonds in the absence of external pressure does not lead to an increase in the strength of the samples. In this connection, it can be argued that the formation of strong bonds between the impurity atoms of metals or metals and the carbon of neighboring crystals does not occur. Otherwise, an increase in the strength of the sample would be observed, at least in some of its areas.

Sintering of nanodiamonds under conditions of high external pressure is accompanied by a deeper cleaning of the surface of nanocrystals. According to the elemental analysis data (see Table 3), the residual content of impurities in the sintered samples is about 5 wt %. Such amount of impurity atoms is not enough to completely cover the nanodiamond core. As a result, regions free from impurity atoms appear on the surface of the nanonucleus, whose carbon atoms can interact with the atoms of neighboring crystals. An increase in the microhardness of the composite material indicates the consolidation of nanocrystals into a polycrystalline aggregate owing to the formation of strong covalent bonds between the carbon atoms of the adjacent crystals. An increase in the microhardness of samples to such values cannot be associated only with the formation of strong bonds between metal and carbon atoms. The microhardness of strong iron carbides does not exceed 10 GPa [25], while the microhardness of the sintered samples locally reaches 14 GPa.

The observed growth of nanodiamond crystals in sintered samples can be associated with the growth of regions of perfect crystal structure owing to the union of nanodiamond crystals along the boundaries with their successful conjugation. Such a process is quite likely if we consider that, during the thermobaric sintering of detonation nanodiamonds, conditions are created both for the deep purification of nanoparticles from impurities and for the consolidation of nanocrystals into a polycrystalline aggregate owing to covalent bonds.

CONCLUSIONS

According to the data obtained, thermobaric sintering of detonation nanodiamond at temperatures of 1100°C and 1200°C and pressure of 5 GPa is not accompanied by a significant increase in the size of nanocrystals.

At the same time, the sintering of detonation nanodiamond under these conditions allows for deep cleaning of the nanoparticles, as a result of which the formation of strong nanodiamond polycrystalline aggregates occurs. Polycrystalline aggregates are the volumes of detonation nanodiamond, which are formed predominantly by covalent bonds between diamond nanocrystals.

The observed growth of detonation diamond nanocrystals can also be the result of the interaction of the diamond nanocrystals purified from impurities when they are ideally conjugated during thermobaric sintering.

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