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**PECULIARITIES OF FORMING A HYBRID DIAMOND
POLYCRYSTALLINE COMPOSITE REINFORCED WITH CVD DIAMOND
OF DIFFERENT STRUCTURAL PERFECTION AT HPHT CONDITIONS
ОСОБЛИВОСТІ ФОРМУВАННЯ В УМОВАХ HPHT ГІБРИДНОГО АЛМАЗНОГО
ПОЛІКРИСТАЛІЧНОГО КОМПЗИТУ, ЩО АРМОВАНИЙ CVD АЛМАЗОМ РІЗНОЇ
СТРУКТУРНОЇ ДОСКОНАЛОСТІ**

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Abstract. The influence of the structural perfection of reinforcing elements made of CVD diamond on the properties of a hybrid diamond polycrystalline material has been studied. After sintering under HPHT conditions of the material with coarse-grained CVD diamond, the structure of the composite is improved, dispersion strengthening of the composite as a whole occurs and its performance properties increase.

Key words: diamond, CVD diamond, composite, hybrid, high pressure, sintering

Introduction

The development of modern industry is impossible without the use of superhard materials, in particular, polycrystalline diamond composites. Their outstanding mechanical properties (Table 1) make these composites an advanced tool material for manufacturing high-performance cutting tools used for processing rocks, high-strength non-ferrous metal alloys, and carbon fiber-reinforced composites.

Table 1 - Basic properties of carbide (WC), polycrystalline cubic boron nitride (PCBN), and polycrystalline diamond (PCD) [1].

Material.	Physical and mechanical properties					
	HK, GPa	E, GPa	G, GPa	σ , GPa	μ	λ , W/(m K)
WC (K10)	13	620	258	4,5	0,22	100
CBN (Amorite)	28	680	279	3,8	0,22	100
PCD (CTB010)	50	776	363	7,6	0,07	560

Polycrystalline diamond composites are manufactured under high pressure and high temperature (HPHT) conditions similar to those used in the mass production of synthetic diamond powders [2]. In essence, a diamond composite is a completely dense mass of randomly oriented, fused together micron-sized diamond particles that are sintered together in the presence of sintering-activating phases [3]. It has also been found that during sintering, plastic deformation occurs in diamond particles, which results in the binding of diamond particles [4]. The hardness of the diamond



composite (Table 1) is close to that of natural diamond, but, unlike its single-crystal counterpart, it has no preferred bonding planes and is equally hard in all directions.

Currently, one of the most important areas of development of technologies for manufacturing diamond polycrystalline composites is research aimed at manufacturing hybrid diamond superhard materials. Such materials, in particular for drilling tools, represent an important area of research aimed at improving the efficiency and durability of drilling tools. These materials can increase drilling speeds, improve hole quality and reduce the time and cost of replacing worn-out tools.

One of the promising areas for obtaining hybrid polycrystalline composites based on diamond is sintering diamonds of different genesis to produce hybrid materials, which, in particular, will combine the high physical and mechanical characteristics of static synthesis diamond powders and CVD diamonds [5].

The aim of the article is to study the effect of the structural perfection of reinforcing elements made of diamond obtained by CVD on the properties of a hybrid diamond polycrystalline material.

Main text

Two CVD diamond samples with different structural perfection were prepared for the study, which were conventionally designated as CVDD-1 and CVDD-2 (Fig. 1, a-c and Fig. 1, d-f, respectively). The linear dimensions of the samples were $0.5 \times 0.5 \times 4.0$ mm.

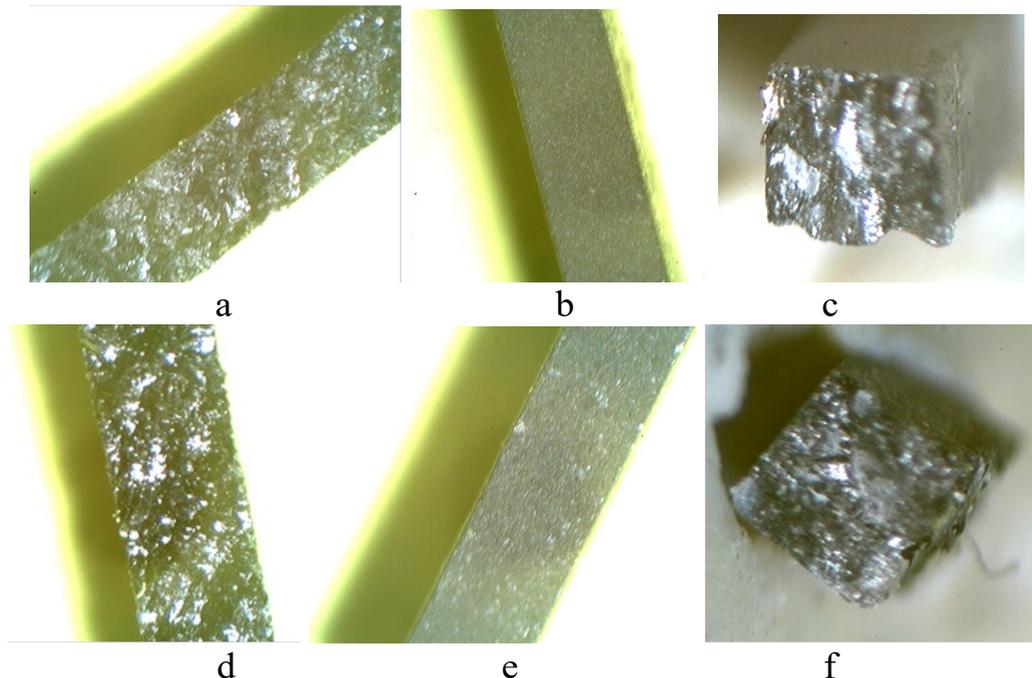


Figure 1 - CVDD-1 and CVDD-2 CVD diamond samples:
a, d - growth side; b, e - nucleation side; c, f - transverse fracture

A study by transmission electron microscopy in combination with microdiffraction on thin chipped plates of CVD diamond samples yielded the following results.

It was found that the particles of the original CVDD-1 sample contain three structural components that differ in phase composition (Fig. 2).

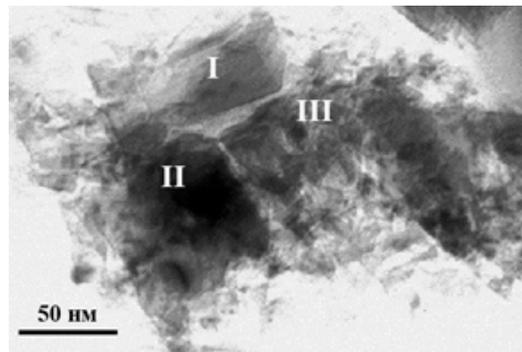


Figure 2 - Structural components of the CVDD-1 sample

The first component (the main one in terms of the quantitative share) is a cubic diamond, with small amounts of twins and packaging defects in its grains. Microelectron micrographs (MEMs) of the grains reveal Kikuchi lines, indicating their high crystalline perfection. The second component is fine-grained inclusions composed of cubic and hexagonal diamond phases. The range of grain sizes in such inclusions is 10–60 nm, and even in micro volumes, the grain sizes differ by a factor of 2–3. The approximate content of such inclusions by volume is 5–7%. In areas of inclusions with larger grain sizes, there is an admixture of a foreign phase. We were unable to identify this phase. The third component is disordered non-diamond carbon. It is contained in the form of inclusions in the cubic matrix component (the first component) and fine-grained inclusions (Fig. 2). Its approximate quantitative share by volume does not exceed 3–5%.

As in the previous case, the main component of the CVDD-2 sample is cubic diamond grains with individual defects, such as packing defects, twins, and dislocations (Fig. 3).

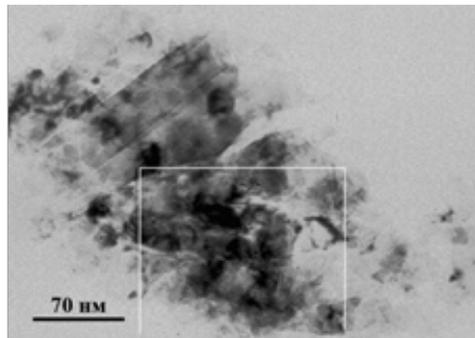


Figure 3 - Structural components of the CVDD-2 sample

The second component of the CVDD-2 sample (Fig. 3) is represented by fine-grained inclusions of the composition (cubic diamond + lonsdaleite) in combination with a non-diamond carbon component. The range of grain sizes in the inclusions is 10–20 nm. The approximate quantitative proportion of inclusions by volume is at least 10%.

To form the shell around the CVD diamond samples, a 40/28 grit micro-powder of synthetic diamond of the ASM grade was used.

The sintering of the composite material reinforced with CVD diamond was carried out in accordance with the heating mode of the diamond mass, which provides a contact area between the CVD diamond and the diamond shell [6]. This



method is implemented as follows. First, a diamond mass and a CVD diamond are formed in a multi-position cell with an impregnating layer of a mixture of silicon, graphite, and diamond nanopowder powders, followed by a two-stage sintering under high pressures and temperatures.

Sintering was performed in a high-pressure toroidal apparatus according to the silicon melting diagram and the equilibrium line $C_{gr} - C_{dia}$ (Fig. 3).

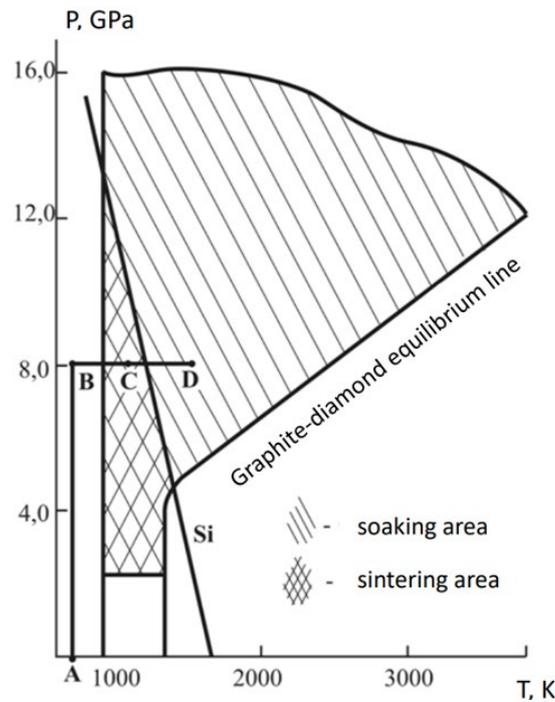
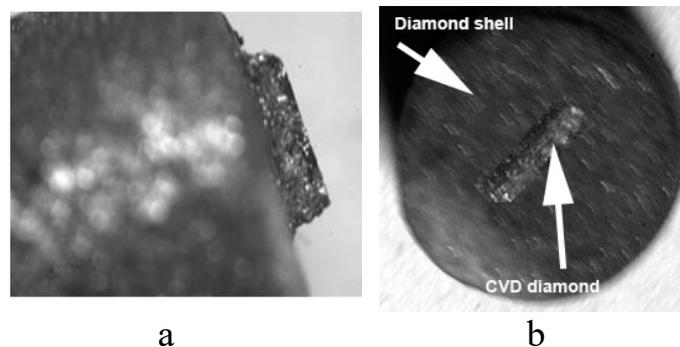


Figure 4 - Silicon melting diagram and equilibrium line $C_{gr} - C_{dia}$ [6].

First, the pressure was increased to 8 GPa, the distance from point A to point B. Then the system was heated to a temperature corresponding to the sintering zone of 600°C and held at this temperature (point C) for 30-45 s, followed by heating the system to a temperature of 1250-1300°C to melt silicon (point D) and held for 15-25 s. The appearance of the sample is shown in Fig. 5.



**Figure 5 - Sample of hybrid diamond composite material:
a - side view; b - top view**

After sintering, the samples of the hybrid diamond composite material were chemically cleaned of graphite residues by thermal oxidation with a chromium mixture.



A study by transmission electron microscopy has revealed that the main component of the CVDD-1 sample subjected to HPHT treatment during the sintering of a hybrid diamond polycrystalline composite is cubic diamond grains deformed to varying degrees (Fig. 6).

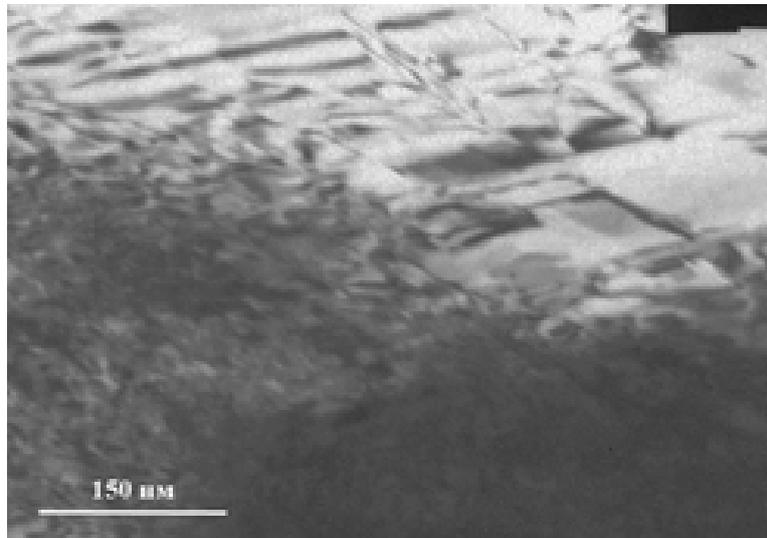


Figure 6 - View of the main component of the CVDD-1 sample subjected to HPHT treatment

The sample contains grains with groups of packing defects, microtwins along one or two non-parallel planes (111), groups of dislocations in combination with a high density of curved deformation contours. The presence of plane defects contributes to the structural disorder of the diamond.

After sintering at high pressure and temperature, the main component of the CVDD-2 sample is deformed cubic diamond grains. There are also fine-grained cubic diamond inclusions. The approximate proportion of such inclusions by volume does not exceed 2-3%. The main type of deformation substructure in cubic diamond grains of the matrix component is thin (20-40 nm) twins, the content of which varies greatly from grain to grain. Most of the grains contain only parallel twins, i.e., one plane of the (111) type (Fig. 7).

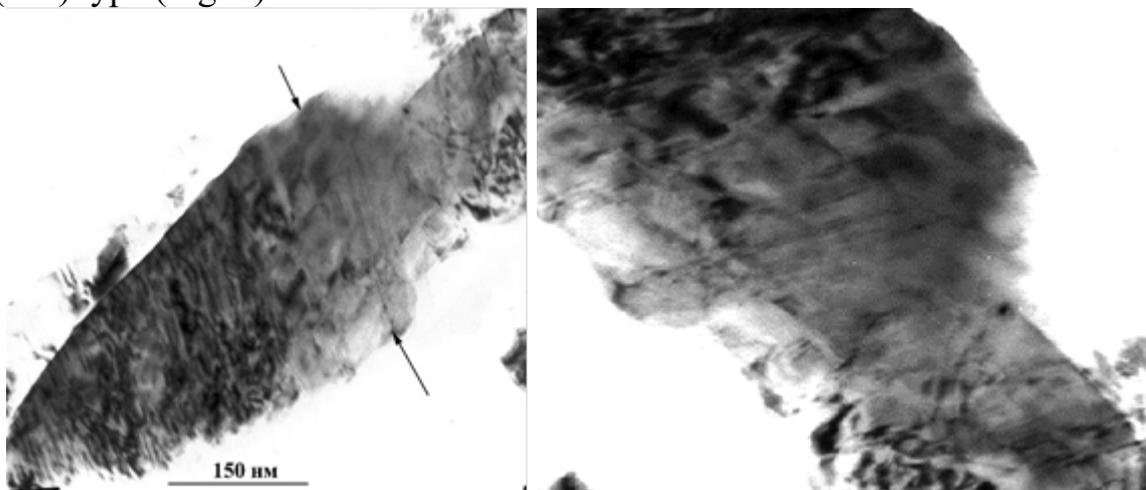


Figure 7 - View of the main component of the CVDD-2 sample subjected to HPHT treatment



Fig. 8 shows the spectra of Raman light scattering obtained from CVDD-1 and CVDD-2 samples before and after NRNT treatment during the sintering of a hybrid diamond polycrystalline material.

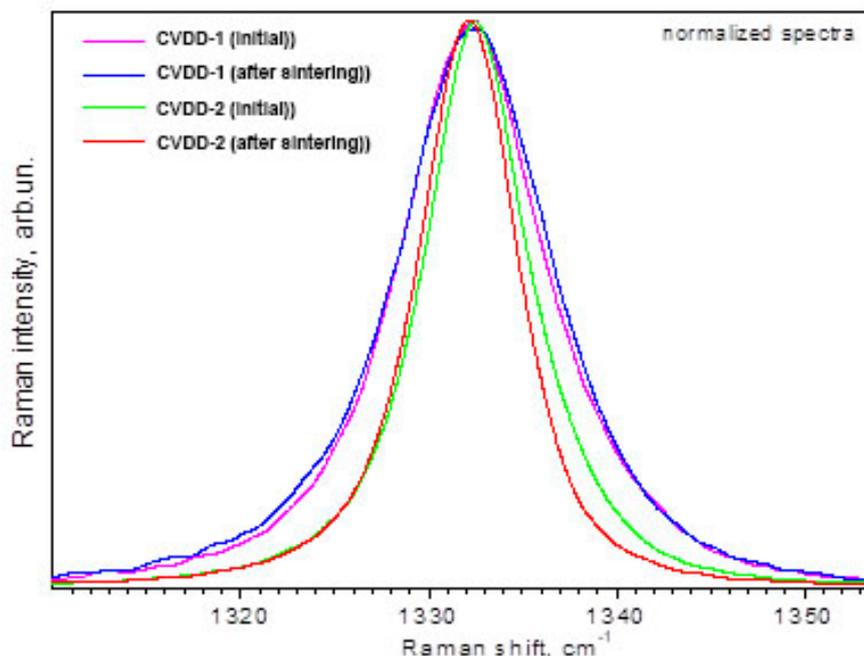


Figure 8 - Spectra of Raman scattering of the studied samples

The results of the study of the spectral position (ω) and half-width (G) of the oscillation band in the spectra of Raman light scattering of CVD diamond samples, both initial and after NRNT treatment, are presented in Table 2.

Table 2 - Spectral positions (ω) and half-widths (G) of vibration bands in the Raman spectra of CVD-diamond samples

Initial		
CVD diamond cipher	CVDD-1	CVDD-2
ω, cm^{-1}	1332,4	1332,5
G, cm^{-1}	9,3	6,6
After HPHT processing		
CVD diamond cipher	CVDD-1	CVDD-2
ω, cm^{-1}	1332,4	1332,1
G, cm^{-1}	9,8	6,2

The large value of the half-width (D) indicates a strong structural disorder of the CVD diamond material.

From the analysis of the obtained spectra, it can be concluded that the large-crystal CVD diamond (CVDD-1 sample) has a more perfect crystal structure. The increase in the half-width of the D-band as a result of HPHT treatment during the sintering of a hybrid polycrystalline material is a consequence of the formation of a complex stress state in the material during the sintering of a hybrid diamond polycrystalline material.

In the case of a fine-crystalline CVD diamond sample (CVDD-2 sample), a decrease in the half-width of the D-band is observed, which also indicates the



formation of a more perfect crystal structure, in particular, as a result of the transformation of a non-diamond form of carbon into diamond during NRNT treatment during sintering.

Taking into account the experimental data and electron microscopic studies, we conclude that in the case of CVDD-1, which is a polycrystal with a coarse-grained structure, a complex-stressed state is formed as a result of its HPHT treatment during the sintering of a hybrid polycrystalline material. At the same time, in the case of a fine-grained CVDD-2 sample containing a non-diamond carbon form, this effect is not observed. This result can be explained by the fact that the initial crystal structure is already stressed (the half-width ω in its initial spectrum of Raman light scattering is almost 1.6 times larger than in the case of CVDD-1) and the subsequent HPHT treatment in the process of manufacturing the hybrid material does not significantly affect the properties of CVD-diamond with a fine-grained structure.

Conclusion.

In the manufacture of a hybrid diamond polycrystalline material with CVD diamond with a coarse crystalline structure, a complex-stressed state is formed in it, which provides dispersion strengthening of the composite as a whole and improves its performance properties.

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Abstract. Вивчено вплив структурної досконалості армуючих елементів з алмазу, одержаного CVD методом, на властивості гібридного алмазного полікристалічного матеріалу. Після спікання в умовах HPHT матеріалу з крупнозернистим CVD алмазом структура композиту вдосконалюється, відбувається дисперсійне зміцнення композиту в цілому та підвищення його експлуатаційних властивостей.

Key words: алмаз, CVD алмаз, композит, гібрид, високий тиск, спікання.

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