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**DIAMOND-CONTAINING POLYCRYSTALLINE COMPOSITE  
MATERIALS AND METHODS OF THEIR PRODUCTION  
АЛМАЗОВМІСНІ ПОЛІКРИСТАЛІЧНІ КОМПОЗИЦІЙНІ МАТЕРІАЛИ  
ТА ШЛЯХИ ЇХ ОДЕРЖАННЯ**

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**Abstract.** *This text discusses the production of diamond polycrystalline materials, factors that contribute to the strength of the diamond-diamond bond, conditions for forming a dense and finely dispersed material structure, and the resulting composite with improved performance characteristics.*

**Key words:** *diamond, composite, high pressure, sintering, activating additive.*

### **Introduction**

The advancement of science and technology necessitates the creation of materials that can function dependably under the influence of force and temperature fields, harsh environments, deep vacuum, and high pressure. Developing and creating composite materials, including nanostructured ones, is a promising way to improve the physical and mechanical properties of materials for structural and functional purposes.

Composites must meet specific requirements, such as high strength, hardness, wear, and corrosion resistance, to be used as materials for tooling or other functional purposes. Only a few composite materials currently meet these requirements to a sufficient degree due to factors such as low strength, hardness, thermal and electrical conductivity, and reduced physical and mechanical properties at extreme temperatures or in a vacuum.

During the 1960s and 1970s, there was a significant development in the production of diamond polycrystals using high-pressure techniques [1]. These materials are characterized by a rigid framework of fused diamond grains, which gives them isotropic properties. This results in improved mechanical properties, particularly impact strength, when compared to single crystals. Diamond's unique properties, such as its hardness, high thermal conductivity, and low friction coefficient, make it a valuable material for tools in various industries [2]. These tools often use composite polycrystalline materials with diamond powders and sintering-activating additives. It is important to maintain consistency in the use of specific terms and units throughout the document.

Diamond-based superhard materials are 2-5 times harder than the materials they process, making them ideal for cutting tools used in processing non-ferrous metals



and alloys, ceramics, metal-ceramics, wood chips, plastics, polymeric materials, granite, and sandstone products.

### **Main text**

The manufacturing of diamond polycrystals is based on two processes: the transformation of non-diamond carbon, usually graphite, into diamond through high static pressures and temperatures or the use of the CVD method [3]. Alternatively, diamond micropowders can be sintered within their thermodynamic stability region [4].

These impurities and inclusions can significantly affect the quality of the polycrystals. Polycrystals obtained through phase transformations often contain impurities and inclusions of graphite or solvent metals, which can be located both inside crystallites and at their boundaries, often forming a second phase. Therefore, when synthesizing carbon materials using carbon solvent alloys, the resulting polycrystals are composed of diamond, metal phases (both through and isolated inclusions), and residual graphite. This composition leads to low heat resistance, which ultimately limits their performance in tools.

During the direct phase transformation of carbonaceous materials into diamond, non-diamond carbon remains in the final product, reducing its physical and mechanical properties as well as thermal stability.

To address these issues, diamond powders are often sintered at high pressures and temperatures. Polycrystalline diamond material is produced by sintering diamond powders under high pressures and temperatures in the presence of additives that activate the sintering process. This technology involves the use of additives to activate the sintering process, resulting in the production of polycrystalline diamond material. In most cases, sintering technology involves a liquid phase. According to sintering practice, the sealing process has four stages: cold compaction, liquid flow, dissolution-precipitation, and solid-phase sintering.

The cold compaction stage involves compressing the diamond without temperature to seal the composite. As pressure increases, the powder compacts due to the sliding of the grains. With further pressure, intensive powder crushing occurs, although not all grains are crushed. Initially, the more defective grains are destroyed. If the operating pressure is slowly released without heating the charge, it is evident that the solid phase particles are surrounded by fine particles (powder) of the same phase.

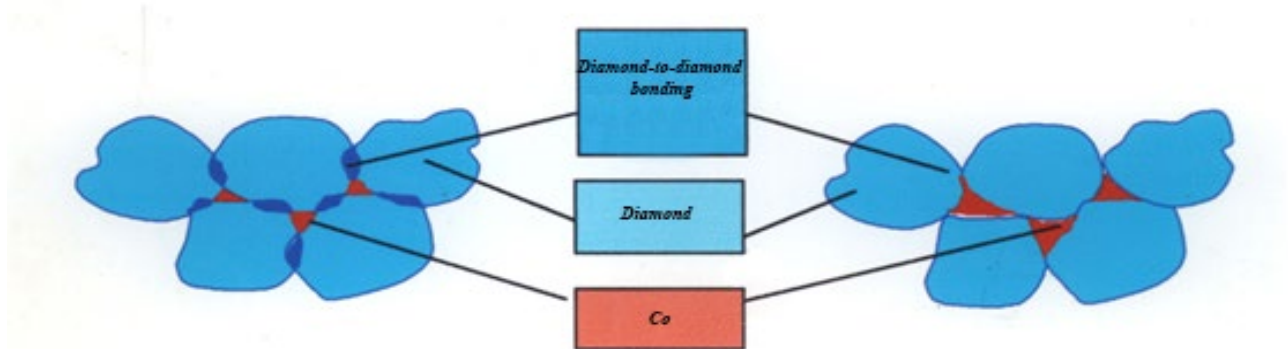
The liquid phase activates the movement of solid particles, causing pores and capillaries to quickly fill with substance. When the solid particles are well wetted by the liquid, menisci, or curved liquid surfaces, form between them. These menisci are subject to capillary forces that bring the particles closer together, resulting in shrinkage. When there is a layer of liquid at the particle contacts (with good wetting), it reduces friction and jamming between solid particles. This increases the mobility of the particles, allowing them to regroup.

The dissolution-precipitation stage is observed in systems where the solid phase is sufficiently soluble in the liquid phase. The process mechanism involves grain growth resulting from the dissolution of small particles in the liquid and their subsequent deposition on larger particles. Shrinkage occurs due to the presence of



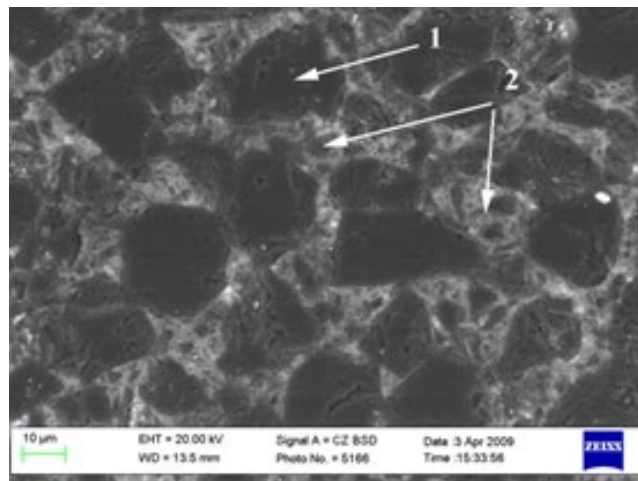
compressive forces in the contact areas, which increases the chemical potential of the components in the solid phase and their solubility in these areas compared to other areas of the solid phase. During sintering, the solid phase moves from the contact points to the free surface, causing shrinkage as the distance between particles decreases.

If solid particles are in direct contact without a liquid phase layer, they fuse together, known as solid-phase sintering. In the case of diamond polycrystalline composite materials, this results in the fusion of diamond particles, as shown in Fig. 1. The final stage of sintering produces solid phases with a rigid, strong framework.



**Figure 1 - Elements of the structure of diamond polycrystalline composite material**

The material obtained through this method contains a second phase, as shown in Figures 1 and 2.



**Figure 2 - The structure of the polycrystalline diamond shell (1 - grains of diamond; 2 - destroyed small grains of diamond and sintering additive)**

The sintering of diamond powders is influenced by the formation of polycrystalline structures during barothermic treatment. Diamond micropowders experience plastic deformation at a temperature of 1230 K and a pressure of 7 GPa. Graphite is formed in the pores between diamond particles where the sintering pressure is lower. When using additives to activate the sintering process, such as cobalt, nickel, or iron, the graphite formed in the pores transforms into diamond.

When sintering a composite material with increased wear resistance based on diamond powders and additives, it is important to consider that the material's hardness



has the greatest influence on its physical and mechanical properties. The relationship between wear resistance and hardness is determined by the formula:

$$S = (HV)^{1/2} \cdot K_{1C}^{3/4}.$$

The wear resistance parameter is represented by  $S$ , while material hardness is represented by  $HV$ , and crack resistance is represented by  $K_{1C}$  [5].

The physical and mechanical properties of polycrystals are determined by the presence of a continuous framework of diamond particles. This is due to the formation of diamond-diamond bonds and a dense, highly dispersed grain structure. The plastic deformation of diamond particles plays a significant role in the formation of diamond-diamond bonds. It has been established that in order for plastic deformation to effectively consolidate diamonds, high pressures and temperatures corresponding to the thermodynamic stability of diamond are necessary [4]. Additionally, the formation of interdiamond boundaries is mainly determined by the development of mass transfer in the areas where grains indent each other. To strengthen the intergranular boundaries in a polycrystal, sintering process-activating additives are added to the sintering charge. Initially, metals and alloys of the iron group (Fe, Co, Ni) were proposed as additives to activate the sintering process of diamond polycrystals. However, it should be noted that the materials produced using such additives have limitations that restrict their applications. The additives' adhesive activity causes them to interact with the workpiece's surface during smoothing, resulting in tears and a significant decline in roughness.

To ensure high hardness and strength of a diamond composite, a fine-grained dense structure can be achieved by using nanocrystalline diamond powders, advanced methods of preliminary formation and activation of starting materials, and the introduction of sintering-activating additives, grain growth inhibitors, carbon, nitrogen, and oxygen getters into the charge. For instance, cobalt oxide was proposed as an additive that activates the process of diamond sintering in [6]. It was discovered that this substance inhibits grain growth and acts as both a carbon and oxygen heterogeneous agent. It forms various compounds when interacting with metal oxides. The charge was prepared using a special technology that involved submicron powders of diamond grade ASM5 0.1/0 and cobalt oxide. The sintering process was carried out at a pressure of 8.0 GPa and a temperature of 2000 K for 20-30 seconds. The study of sintered composites [7] has shown that combining preliminary mechanical activation of the initial charge with the introduction of activating additives can significantly improve the physical and mechanical characteristics of the diamond nanocomposite sintered under high pressure and temperature. Hardness can be increased by 1.7 times and crack resistance by almost 2 times. The homogeneity of the sintered composite microstructure and the suppression of growth and recrystallization processes during sintering are the primary factors contributing to this result.

Composite polycrystalline materials based on diamond and silicon carbide, such as geothermal and sindax-3, are currently used in tools for drilling, straightening, and smoothing various materials. These materials are produced by impregnating diamond powder with silicon under HPHT conditions, resulting in polycrystals with high thermal stability (~1500 K). The composites in this case consist of a framework of diamond particles (80-85% of the total volume), with silicon carbide and a small



amount of unbound crystalline silicon interspersed between them. Experimental evidence has shown that the strength of this material can be increased by introducing a mixture of silicon and graphite powders, diamond nanopowders, or silicon carbide into the impregnating layer [8].

A two-stage sintering method was proposed [9] to enhance the quality and strength of diamond composites. During the first stage, diamonds are sintered to the melting point of silicon, which increases the contact area between diamond particles and strengthens the diamond-diamond bond. During the second stage, silicon is melted to impregnate the diamond framework and bind free carbon formed in the pores of the material into silicon carbide. This approach improves the physical and mechanical properties of the diamond composite heat-resistant material, resulting in a compressive strength approximately 25% higher than that of the material obtained through one-stage sintering.

Thus, summarizing the above, we can conclude that, in accordance with the tasks set, the sintering process-activating additive should:

- to act as grain growth inhibitors, i.e. to help preserve the fine-grained component of the composite;
- moisten the diamond, helping to reduce inter-particle friction;
- under the thermobaric parameters of sintering, dissolve graphite formed during sintering or present in the diamond powder as an impurity.

Meeting these requirements will help to create favourable conditions for achieving a dense and finely dispersed material structure, resulting in a composite with improved performance characteristics.

When sintering diamond powders to obtain polycrystalline composites with predetermined performance properties, it is recommended to control the structure and properties of polycrystals using the following means [10]: controlling the sintering process parameters such as pressure, temperature, and sintering time. Controlling the sintering parameters allows to produce polycrystals with varying inclusion contents (such as Co and Si), intense grain fusion, and controlled fracture patterns (either transcrySTALLINE or intercrySTALLINE), resulting in increased wear resistance.

Other important factors include selecting the appropriate diamond particle size, ensuring proper grain surface condition (including thermochemical cleaning), adding sintering process-activating additives, and choosing the appropriate schemes for equipping the reaction volume.

The hardening of the material can be achieved by introducing finely dispersed impurities that prevent the movement of dislocations and cracks. Additionally, the introduction of extra crystallization centers, such as nanodiamonds when impregnating diamond powders with silicon, can also be effective.

**Conclusion.** The scientific and technological foundations for creating diamond polycrystals with activating additives of various physical and chemical natures under high pressures and temperatures have been developed. The physical, mechanical, and operational properties of the diamond composite are influenced by the composition, properties, and structure of its components. This provides a scientific basis for obtaining new superhard diamond materials for various functional purposes under high pressure and temperature.



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**Анотація.** Розглянуто способи одержання алмазних полікристалічних матеріалів, фактори, що сприяють підвищенню міцності зв'язку алмаз–алмаз, умови формування щільної, мілкодисперсної структури матеріалу і, як наслідок, одержання композиту з підвищеними експлуатаційними характеристиками.

**Ключові слова:** алмаз, композит, високий тиск, спікання, активуюча добавка

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