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INVESTIGATION OF MAGNETIC PROPERTIES OF DIAMOND COMPOSITES WITH THE ADDITION OF N-LAYER GRAPHENE

ДОСЛІДЖЕННЯ МАГНІТНИХ ВЛАСТИВОСТЕЙ АЛМАЗНИХ КОМПОЗИТІВ З ДОБАВКОЮ N-ШАРОВОГО ГРАФЕНУ

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***Abstract**: The paper presents the results of studying the magnetic properties by magnetometry using a vibrating magnetometer "Vibrating Magnetometer 7404 VSM" of diamond polycrystals obtained by sintering diamond powders with the addition of n-layer graphene at high pressures. The presence of a hysteresis loop indicates ferromagnetic properties in the samples. The nature of these properties and the prospects for using such diamond composites with the addition of n-layer graphene in medicine and biology are discussed.*

***Key words**: diamond composite, graphene, high pressure, sintering, hysteresis, ferromagnetic properties*

Introduction

The development of modern science and technology requires the creation of materials that work reliably under the influence of force and temperature fields, aggressive media, deep vacuum and high pressure. One of the promising ways to improve materials for various functional purposes with the ability to adjust them in a wide range is the development and creation of composite materials, including nanostructured ones.

Due to the unique properties of diamond (hardness, high thermal conductivity and low coefficient of friction), the tool, equipped with working elements made of composite polycrystalline material based on diamond powders with sintering additives, has been actively implemented in many industries for more than half a century [1]. The study of the regularities of controlling the process of forming the structure of diamond polycrystalline composite materials opens up opportunities to create materials with the necessary combination of hardness, thermal conductivity, strength, wear resistance, and electrical resistance depending on the areas of their application. To produce such diamond polycrystalline composite materials, methods for their production under high pressure and temperature conditions using activating additives of various physico-chemical nature have been developed.

One of the directions of development of polycrystalline composite materials is the production of special-purpose composites, in particular with increased electromagnetic characteristics.

It is known that pure diamond in terms of electrical properties is an insulator and is diamagnetic (with the exception of varieties that have paramagnetic properties, as well as in some diamond crystals, magnetic properties are due to inclusions with increased magnetic permeability), which introduces restrictions on the scope of its application. But when sintering diamond powders with activating additives, it becomes possible to influence the electromagnetic properties of the polycrystal in a certain way. In particular, diamond composites with high electrical conductivity were obtained in [2]. This effect was achieved by adding graphene to the sintering charge, a material that has recently become one of the most attractive materials as a secondary phase in diamond polycrystalline composite materials.

The aim of this paper is to study the magnetic properties of a diamond polycrystalline material obtained by sintering diamond powders of various origins with the addition of n – layer graphene at high pressures.

Materials, equipment and research methods

For the production of diamond polycrystals, micro-powders of diamonds are used, which have two origins and origin: natural and obtained by synthesis using high-pressure technology (synthetic diamonds).

Micro-powders of natural diamonds are made by crushing low-grade natural diamonds. They consist of crystal fragments obtained as a result of diamond crushing (Figure 1) and are indicated by the letter index AM – micro-powders made from natural diamonds.

Figure 1- natural diamond micro-powder grains

Micro-powders of synthetic diamonds (Figure 2) are obtained by static or centrifugal sedimentation methods from the fine product remaining after the production of synthetic diamond grinding powders. Synthetic diamond micro-powder is indicated by the letter index DSM.

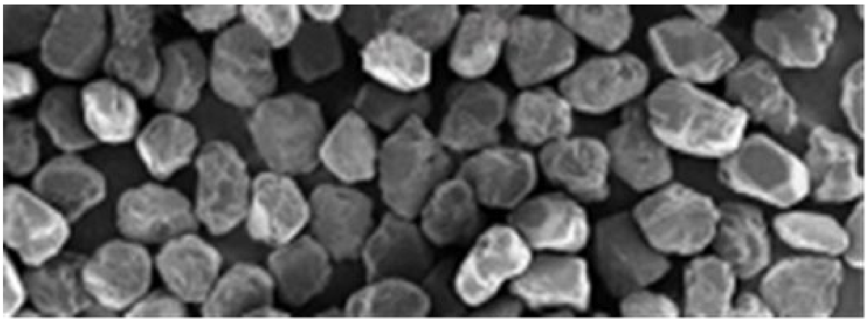


Figure 2 - DSM grade diamond micro-powder

In general, the grains of synthetic diamond micro-powders have a more developed surface. Their specific surface area is almost 1.5 times larger than that of natural ones.

In our sintering experiments, a micro-powder of synthetic diamond grade DSM with a grain size of 40/28 and a micro-powder of natural diamond with a grain size of 14/10 were used, and graphene of the Gn(4) brand (manufacturer Cheap Tubes Inc, USA) was used as an additive. Graphene of this brand is graphene nanoplates consisting of small stacks of graphene layers (less than four layers with a total thickness of less than 3 nm), which, depending on pretreatment, have a specific surface area of 700-2000 m^2/g (Figure 3).

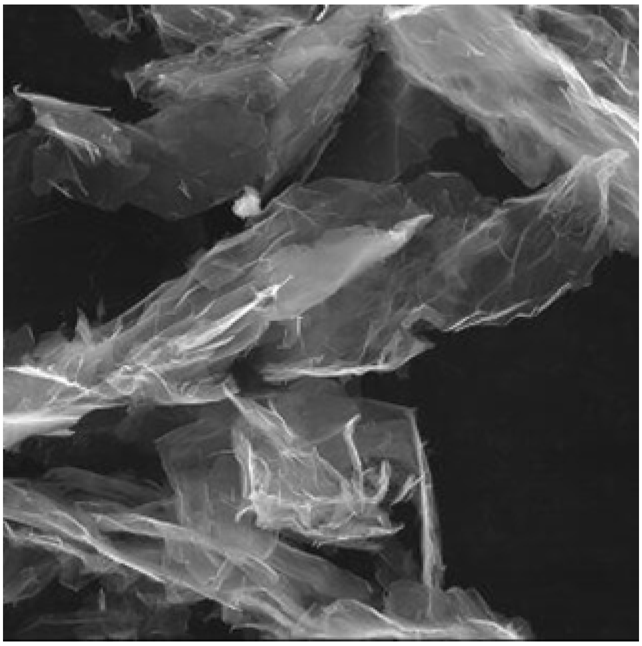


Figure 3 - Appearance of graphene scales of the Gn(4) brand

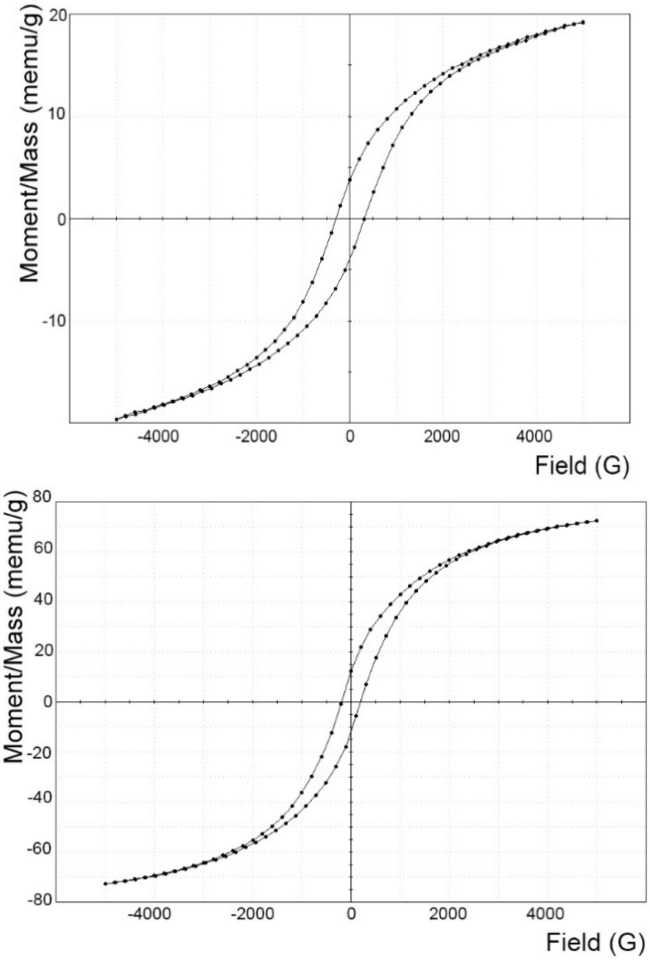
The choice of this type of graphene is because, as shown in [3], such graphene does not turn into diamond under high pressures and temperatures, even in the presence of metals that are carbon solvents and their alloys. In addition, it is known that the allotropic modification of carbon – graphene – has unique properties: the maximum electron mobility among all known materials (achieved carrier mobility of ~ $2 \cdot 10^5$ $cm^2 \cdot V^{-1} \cdot s^{-1}$), high electrical conductivity of films (1738 Sm/m), huge mechanical rigidity (young's modulus ~ 1 TPa), and a record high thermal conductivity of 3500-5500 $Wt \cdot m^{-1} \cdot K^{-1}$), high optical transparency (~ 97.7%). In this regard, graphene of various structures (monolayer and n-layer, where n = 1-20) and sizes (from micron to nanometers) are actively studied for the possibility of their use as a component capable of forming new properties of materials, while preserving or enhancing their other properties. For example, graphene's high ability to modify the surface of intergranular boundaries of composites, including diamond ones, was established. This property allows you to improve the performance characteristics of the composite and at the same time create new properties to increase wear resistance, reduce electrical resistance.

Polycrystals were sintered on a DO-043 press unit that develops a force of up to 20 MN using a high-pressure device (HPD) of the "toroid" type with a central recess diameter of 30 mm. Sintering of the charge was carried out at a pressure of 7.0–7.5 GPa, a temperature of 1250-1350 °C. The sintering duration was approximately 200 s. After sintering, the surface of the obtained samples of composite material with a diameter of 4 mm and a height of 4.5 mm was subjected to chemical treatment in order to clean it from graphite residues.

The magnetic characteristics of the samples were studied by magnetometry using a vibrating magnetometer "Vibrating Magnetometer 7404 VSM" (manufactured by Lake Shore Cryotronics, Inc.", USA) [4] in magnetic fields with a strength of up to 13 kE. The sensitivity of the magnetometer was 10^{-7} emo, which made it possible to measure the magnetic moment of samples weighing up to units of milligrams. The mass of the studied samples was determined using AB135-S / FACT electronic microweights from autocompensation (Mettler Toledo, Switzerland). The sensitivity of the scale was 10^{-5} g.

Research results and their discussion

The results of studying the magnetic properties of the obtained diamond composite samples are shown in Figure 3 and Table 1 are given.



a **b**

Figure 3 – Hysteresis loop in diamond composite samples of the following composition

a – *micro-powder of natural diamond am 14/10 and 0.3% (by weight) graphene Gn (4);* **b** – *micro-powder of synthetic diamond AFM 40/28 and 0.5% (by weight) graphene Gn (4)*

The hysteresis loop (Figure 3) indicates the presence of ferromagnetic properties in the samples. The magnetic field strength H_{ms}, at which the magnetic saturation moment m_S is achieved, in all cases is 5000 E. According to the coercive force (Table 1), the samples belong to magnetically solid materials, such as vikalla and kunife alloys, kuniko, Fe–Co–Cr, used for the manufacture of permanent magnets [5]. When the graphene content increases from 0.5% to 1.0% (by weight), the coercive force increases by about 14%; reducing the grain size of sintered diamond powders has a more significant effect: the coercive force increases by 1.4–1.6 times, while the magnetic losses determined by the area of the hysteresis loop decrease by 2.5–2.7 times

Table 1 – Magnetic properties of diamond polycrystalline composite samples of various compositions

Sample	Magnetic saturation moment m_S, emo/g	Coercive force Hc, e	Hysteresis loop area, erg/g
DSM 40/28 + 0.5% (by weight) graphene Gn (4)	$72.561\cdot10^{-3}$	189.79	39.66
DSM 40/28 + 1.0% (by weight) graphene Gn (4)	$75.435\cdot10^{-3}$	215.01	43.67
DM 10/14 + 0.3% (by weight) graphene Gn (4)	$19.423\cdot10^{-3}$	303.22	15.99

The nature of the manifestation of ferromagnetic properties in the studied samples can be determined by several reasons. As is known, a non-impurity diamond is a diamagnet, and the magnetic properties of real diamond powders, as well as electrical ones, depend on the presence of impurities and inclusions in them [6]. However, in recent decades, there have been publications devoted to the analysis of conditions under which carbon can exhibit ferromagnetic properties [7-9]. In particular, it has been shown that under certain extreme conditions, such as, for example, high temperatures, pressure, there is a special ordering of carbon atoms that is favorable for spontaneous magnetization.

Thus, the ferromagnetic properties of polycrystalline diamond composites obtained by us can be formed both due to the content of ferromagnetic impurities in natural diamond powders, as well as impurities and inclusions of carbon-solvent metals (Ni, Fe, Co) in synthetic diamond powders, and spontaneous magnetic ordering in nanographene layers, the appearance of which is regulated by Lattice distortions caused by electron-phonon interaction [9].

Conclusions

Consequently, the improvement of the technology for producing diamond polycrystalline composites with the addition of n-layer graphene with ferromagnetic properties will expand the scope of application of diamond composites, in particular, for creating permanent magnets.

In addition, if further experimental studies lead to reproducible results that would support the hypothesis of induced magnetism in n-layer graphene, this will open up prospects for the use of polycrystalline diamond composites with the addition of n-layer graphene in medicine and biology as unique biocompatible magnets.

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Анотація: *В роботі наведені результати дослідження магнітних властивостей методом магнітометрії за допомогою вібраційного магнітометра «Vibrating Magnetometer 7404 VSM» алмазних полікристалів, одержаних спіканням при високих тисках алмазних порошків з добавкою n-шарового графену. Наявність петлі гістерезису вказує на феромагнітні властивості в зразках. Обговорено природу цих властивостей і перспективи використання таких алмазних композитів з додаванням n-шарових графенів в медицині та біології.*

Ключові слова: *алмазний композит, графен, високий тиск, спікання, гістерезис, феромагнітні властивості*

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