

Electrophysical Properties of Carbon Nanocomposites Based on Nanodiamonds Irradiated with Fast Neutrons

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Abstract—The electrophysical properties of nanoporous carbon composites consisting of a nanometer-sized pyrolytic carbon matrix and nanodiamonds have been analyzed. It has been shown that the power-law dependence of the electrical resistivity on the thickness of the pyrolytic carbon layer D on a log–log scale has an inflection for $D = 1 \text{ \AA}$. It has been found that the temperature dependence of the electrical resistivity of the nanocomposite is described by an exponential function with an exponent of $1/4$ for both unirradiated samples and samples irradiated with fast neutrons. This is characteristic of variable-range hopping conductivity in the case of strong localization in systems with semiconductor conductivity in the presence of a local disorder. With an increase in the neutron fluence, the electrical resistivity of the studied material changes very significantly (by several hundred percent) and nonmonotonically. This result is associated with the transformation of the structure of the graphite-like matrix and with possible graphite–diamond phase transitions.

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1. INTRODUCTION

Interest in the study of nanodiamonds is associated primarily with the possibility of creating defects in the form of NV -centers in the diamond structure. These centers consist of a nitrogen atom substituting for a carbon atom in the crystal lattice of the diamond and a vacancy closely located to the nitrogen atom. The NV -centers are able to emit a flux of single photons; moreover, on such a center, the spin controlled by optical, radio-frequency, and microwave effects can be localized [1, 2]. The unique properties of NV -centers make them promising for many applications in biomedicine, magnetometry, quantum optics, and spintronics [3, 4]. The NV -centers can be considered as elements for information storage in quantum computers [5, 6].

Vacancies in the diamond structure can be created under well-controlled and metered irradiation with high-energy particles [3, 7]. However, it should be kept in mind that the kinetics of formation of radiation-induced defects in nanodiamonds can differ significantly from that in large-sized crystals. In a number of studies, it was found that nanostructured materials possess a high resistance to radiation and do not tend to rapid accumulation of defects due to the high density of interfaces that are effective sinks for radiation

defects [8–10]. In this respect, the purpose of the present work was to investigate the effect of neutron irradiation on the structure-sensitive electrophysical properties of the nanodiamond-based carbon composite.

2. OBJECTS AND METHODS OF INVESTIGATION

At present, we have developed a method for synthesizing bulk carbon materials based on nanodiamonds [11, 12]. The material is called Nanodiamond Composite (NDC). In this material, individual diamond particles are bound with each other via the pyrolytic carbon matrix, which is formed by the decomposition reaction of methane on the inner surface of the powder preform [11, 12]. The pyrolytic carbon matrix has a specific structure: the majority of its constituent atoms are in the sp^2 -hybridized state, like carbon atoms in graphite. The method proposed for synthesizing the NDC composite makes it possible to significantly vary (from 0 to 80%) the content of the graphite-like phase. Knowing the content of pyrolytic carbon in the composite and the specific surface area of the material, we can calculate the effective (average) thicknesses of graphite-like pyrolytic carbon layers. The results for

three composites of different compositions are presented in the table. As can be seen from the presented data, the effective thickness of the pyrolytic carbon layer reaches a few angstroms. Moreover, the material has a high open porosity.

Thus, in the NDC composite, there are three inter-related types of nanofragments: nanodiamonds, the nanometer-sized graphite-like matrix (pyrolytic carbon), and nanopores. On the macroscale, all three phases form a single composite which has a sufficiently high strength to retain a desired three-dimensional form.

We studied three samples labeled as NDC10, NDC30, and NDC40. The regularities of the accumulation of radiation defects were analyzed using the method for measuring electrical resistance. The resistance is a structure-sensitive characteristic, especially with respect to variations in the concentration of point defects. Furthermore, charge transfer processes in NDC are of independent interest. The character of the electronic spectrum of the composite can transform from semiconducting to semimetal depending on the contents of graphite and diamond-like phases in the composition of the material, as well as on the concentration of different defects, including those introduced under reactor neutron irradiation. The electrical resistivity was measured by the four-probe method in the temperature range from 77 to 400 K. In order to stabilize the electrical resistivity, all the samples were preliminarily annealed at a temperature of 770 K for 30 min in argon.

Irradiation was performed in vertical channels of the WWR-M research reactor (Konstantinov Petersburg Nuclear Physics Institute, National Research Centre "Kurchatov Institute," Gatchina, Russia) with fast neutrons ($E > 0.5$ MeV). For filtration of thermal neutrons producing impurities through transmutation, the samples were placed in a 0.5-mm-thick cadmium cover and an aluminum container with holes for cooling with water. To remove the heat due to absorption of γ -rays, the irradiation of samples in the reactor was carried out in an aqueous medium of experimental channels at a temperature of ~ 325 K. The NDC10 and NDC40 samples were irradiated in an aqueous medium. Additionally, a number of NDC10 samples were irradiated in quartz ampoules with helium. Irradiation was performed with fast neutron fluences in the range from 5×10^{16} to 5×10^{18} cm^{-2} .

3. EXPERIMENTAL RESULTS AND DISCUSSION

The structure of the studied material can be judged from the neutron diffraction pattern (Fig. 1). It contains reflections corresponding to the structure of cubic diamond with a unit cell size of $3.5570(5)$ Å, which is slightly smaller than that of single-crystal diamond (3.5668 Å). The average diffraction size of dia-

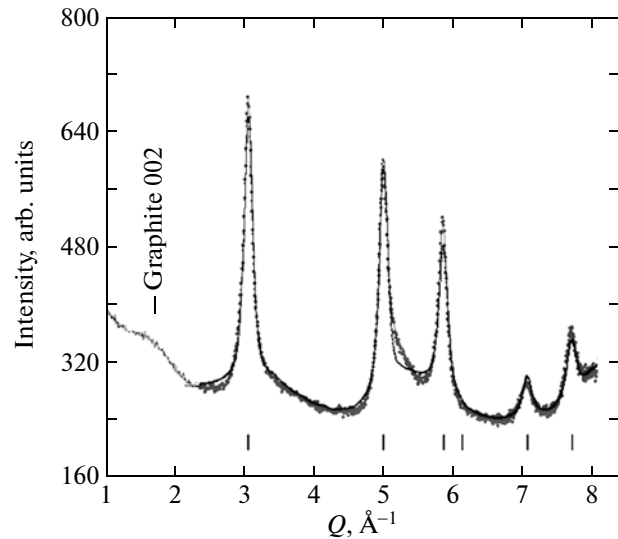


Fig. 1. Neutron diffraction pattern of the NDC30 sample. Points are experimental data. The solid line is the calculated curve. Vertical dashes show positions of the diffraction reflections. The neutron wavelength is 1.38 Å.

mond nanoparticles was calculated in the isotropic approximation and proved to be $3.1(1)$ nm. A highly diffuse reflection (002) from the graphite-like pyrolytic carbon layer suggests a very small characteristic size. The form of diffraction reflections from diamond nanoparticles is not described by a Gaussian profile: as can be seen from the figure, the neutron diffraction pattern has a characteristic "tail" on the right, which is typical of diffraction by quasi-two-dimensional objects [13]. This feature of the neutron diffraction can be explained by the difference in the structures of the surface layer of a diamond nanoparticle and its core. It should be emphasized that this thin surface layer has a crystal structure of diamond.

According to the available data, the electrical resistivity ρ of the NDC composites strongly depends on the pyrolytic carbon content [14]. Using the results obtained in [14, 15], we can construct the dependence of ρ on the effective thickness of the pyrolytic carbon layer D , which is shown in Fig. 2. It can be seen from

Parameters of the NDC samples

NDC type	Content of pyrolytic carbon, %	Porosity of the material, %	Content of nanodiamonds, %	Average thickness of the pyrolytic carbon layer, Å
NDC10	5	67	28	2
NDC30	15	57	28	6
NDC40	20	52	28	8

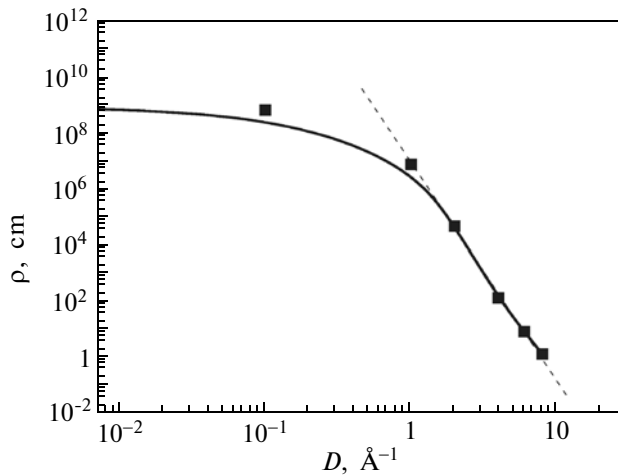


Fig. 2. Dependence of the electrical resistivity of the NDC composite on the thickness of pyrolytic carbon [14, 15].

this figure that the dependence $\rho = f(D)$ for $D > 1 \text{ \AA}$ has a power-law character:

$$\rho = CD^{-n}, \quad (1)$$

where $C = 6.97$ and $n = 7.65$. Obviously, the exponent n is anomalously high. When filling the volume with a conducting (for example, metallic) phase, the electrical resistivity should vary proportionally with the volume of the conducting phase; i.e., the exponent should satisfy the condition $n = 3$. In the case of NDC composites for $D > 1 \text{ \AA}$, the exponent n is larger by a factor of ~ 2.5 . It can also be seen from Fig. 2 that, when the effective thicknesses of the pyrolytic carbon layer are less than $\approx 1 \text{ \AA}$, the electrical resistivity depends very weakly on D , and the dependence of ρ on D has an inflection. The presence of an inflection in the dependence supports the assumption about the percolation character of the change in conductivity of the composite with increasing thickness D . Therefore, the transition to the power-law dependence of the electrical resistivity can be considered in terms of the percolation theory.

In order to explain the character of the dependence of the electrical resistivity of the NDC composite on the pyrolytic carbon content, it is necessary to take into account that the conductivity of NDC has a hopping character. This is confirmed both by the low Hall mobility at rather high values of the conductivity [12] and by the character of the temperature dependence of the electrical resistivity over a wide temperature range [15]. If the increase in the pyrolytic carbon content on the surface of nanodiamonds is considered as an increase in the concentration of charge carriers (localized at the expense of potential barriers) in proportion to the volume of pyrolytic carbon, the conductivity will vary depending on the thickness of the pyrolytic carbon layer with the exponent $n = 3$ (the third power of linear dimensions). It can be assumed that three

more unities in the exponent n are provided by a decrease in the distance between the localized centers proportionally with the volume of the introduced pyrolytic carbon. The rest of the exponent n (1.65 of 7.65), apparently, can be explained by a decrease of the potential barrier for charge carriers with an increase in the pyrolytic carbon content.

Thus, the value of $n = 7.65$ in the power-law dependence of the electrical resistivity on the pyrolytic carbon content, most likely, is determined by three processes: an increase in the concentration of localized carriers in proportion to the volume of pyrolytic carbon, a decrease in the distance between traps, and a decrease in the potential relief.

Let us consider the effect of neutron irradiation on the properties of NDC composites, for example, NDC10 irradiated in water. Figure 3 shows, on a log–log scale, the temperature dependences of the electrical resistivity of the NDC10 composite before irradiation and after irradiation in water with different neutron fluences. At once, we note that the presented dependences are best approximated by the power-law relationship

$$\rho(T) \sim \exp(-C/T)^{1/n} \quad (2)$$

with the exponent $n = 4$. As is known, relationship (2) is characteristic of variable-range hopping conductivity in the case of the so-called strong localization in systems with semiconductor conductivity in the presence of a local disorder [16].

In the analysis of the obtained results, primary attention is drawn to very large changes in magnitude of the electrical resistivity under irradiation, as well as to the nonmonotonic dependence of the electrical resistivity on the neutron fluence. Indeed, irradiation to a neutron fluence of $5 \times 10^{16} \text{ cm}^{-2}$ leads to a relative change of the electrical resistivity $\Delta\rho/\rho$ by 380% (Fig. 3a). If the neutron fluence is $1 \times 10^{17} \text{ cm}^{-2}$, the electrical resistivity changes by only 6% (Fig. 3b), whereas at a fluence of $5 \times 10^{17} \text{ cm}^{-2}$, the resistivity increases again already by 830% (Fig. 3c). This behavior is quite unusual. As a rule, the electrical resistivity of metals and semiconductors monotonically increases with increasing fluence due to the accumulation of radiation defects. However, the electrical resistivity of the NDC10 composite irradiated in helium and the resistivity of the NDC40 composite irradiated in water show qualitatively the same behavior as was described above. The only difference is that the change in the electrical resistivity of NDC40 is considerably less and does not exceed 37%.

The unambiguous physical interpretation of this behavior of the studied materials is very difficult because of the limited set of experimental data. We can only make some assumptions that do not contradict the experimental data. The change in the electrical resistivity of the material can be associated with two types of processes of its transformation: the diamond–

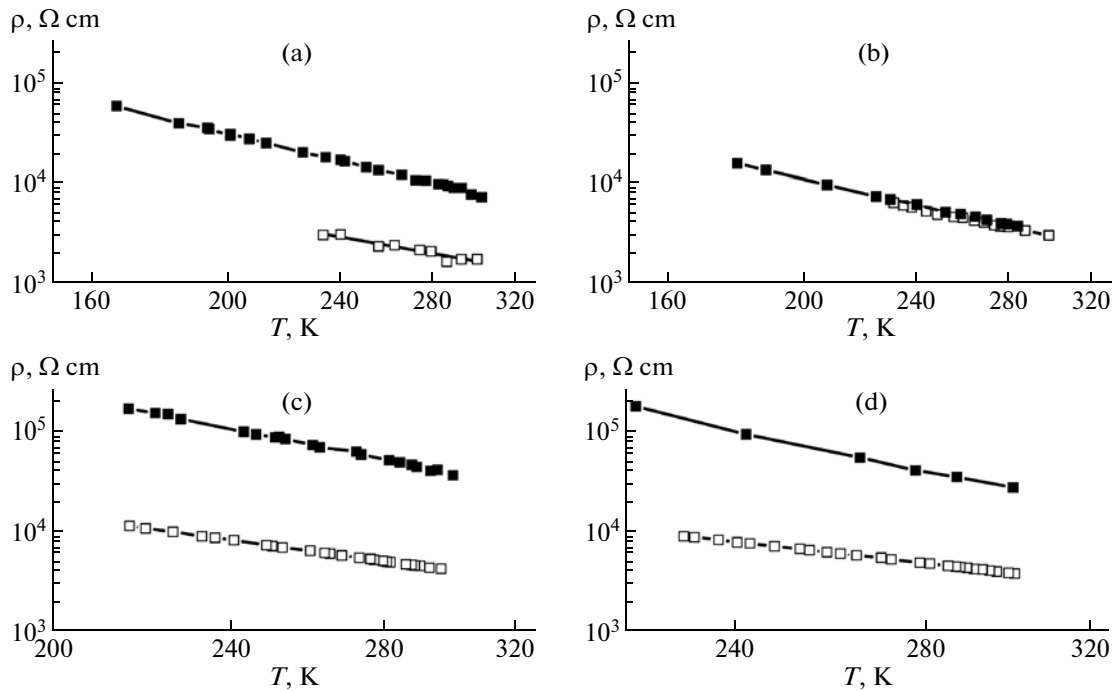


Fig. 3. Temperature dependences of the electrical resistivity of the NDC10 composite before irradiation (open symbols) and after irradiation in water (closed symbols) with fluences of (a) 5×10^{16} , (b) 1×10^{17} , (c) 5×10^{17} , and (d) $5 \times 10^{18} \text{ cm}^{-2}$.

graphite phase transition or structural (order–disorder) changes in the graphite-like matrix. The observed increase in the electrical resistivity can be explained by a partial transition of the graphite-like matrix into the diamond. This is possible if we take into account that, in the considered materials, because of the small thickness of the graphite-like matrix, even the transition of a part of its monolayer into the diamond will lead to a significant increase in the electrical resistivity. It is known that the nanodiamond with a size of 4–6 nm is thermodynamically more stable than graphite of the same size, so that the transition of a part of the graphite-like matrix layer adjacent to the surface of the nanodiamond particle into the diamond structure is possible. From the chemical point of view, the graphite–diamond transition is reduced to a change in the character of hybridization of the carbon atom and to its embedding into the tetrahedral environment.

When analyzing the above considerations and results, it can be assumed that, under irradiation of the NDC composite with low neutron fluences, there apparently occurs an ordering of the graphite-like component of the material. An increase in the neutron fluence leads to a partial transition of the graphite-like matrix into the diamond, which takes place at the interface of these phases. The fact that the process of diamond formation occurs after the ordering of the structure of the graphite-like matrix follows from the known data on the synthesis of diamonds at high pressures and high temperatures, because the use of crystalline graphites is preferable and makes it possible to

change conditions of diamond formation (to decrease the pressure and temperature). It can be expected that, in the considered case, too, the formation of diamond will occur after the ordering of the structure of the graphite-like matrix of the material.

4. CONCLUSIONS

The performed investigations have found that the temperature dependence of the electrical resistivity of the NDC nanocomposite is described by an exponential function with an exponent of 1/4 for both unirradiated samples and samples irradiated with fast neutrons in a helium atmosphere or in an aqueous medium. With an increase in the neutron fluence, the electrical resistivity changes nonmonotonically. The electrical resistivity can increase or decrease depending on the value of the fluence.

The unambiguous explanation of the obtained results is very difficult because there is no generally accepted model that completely describes charge transfer in nanodiamond-based structures. It can be assumed that, under neutron irradiation, a pyrolytic carbon–diamond transformation occurs at the interface between these structural components. At the same time, the possibility of the reverse transition occurring in the studied material should not be ruled out. Further experimental and theoretical investigations are necessary for the complete understanding of the nature of the electrophysical properties of the NDC nanocomposite and their dependence on the irradiation.

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