Modification of the properties of nanocomposites based on carbon nanostructures

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***Abstract**: The electrical and mechanical properties of nanocomposites based on carbon nanostructures has been studied. It is sown that a t a concentration of carbon nanotubes of 15-30 wt. %, the electrical resistance of the samples decreases to 1 order, while its mechanical properties change insignificantly, which is due to the transfer of free electrons from the metal to the CNT, which is comparable to the number of electrical contacts between the constituent elements of the composite and the competition between the numbers of tu nneling and ohmic contacts.*

***KEY WORDS:** CARBON NANOTUBES, ELECTRICAL RESISTIVITY, COMPOSITE, MECHANICAL PROPERTIES*

Introduction

Carbon nanotubes (CNTs) attract the attention of scientists from many countries of the world last 30 years. This interest is due to their unusual properties: they combine high strength and elasticity, heat and electrical conductivity. Mechanical deformation and defects influence the electronic structure, concentration of charge carriers, electrical, emission and other properties of CNT. Defects arise both in the process of synthesis (growth and gas admixtures) of CNT, and with external influences, especially in radiation. They reject the form of CNT from the rectilinear, change the conditions of passage of current, affect the concentration of charge carriers, Fermi energy and electrical conductivity.

The properties of the array of CNTs, as well and materials that containing its, differ from the properties of individual nanotubes. Individual CNT may have a metallic type of conductivity, array of CNTs may not be conductivity. This is due to the fact that in the initial array of CNTs, the distances between adjacent nanotubes can be very large, the contacts between them are small and mostly tunnel, that is no formed the conductive network. It can be achieved by increasing the area of contacts between adjacent tubes (reducing the volume between them) or adding of a small amount of CNT to the dielectric matrix promotes the appearance of the electrical conductivity of the composite [1-6], the value of which can vary in a wide range of values. This variation in the value of electrical conductivity is due to the complex interaction of various factors, the most important of which - the presence of CNTs with different types of intrinsic conductivity, their concentration and types and magnitudes of contact resistance between CNTs.

Nanostructured composite materials are characterized by adjustable anisotropy and gradient structure of properties due to a certain orientation of the fibers in the matrix, which can be achieved by using mainly powder technologies. Nanofibers, carbon nanotubes, including those functionalized by metals, oxidation and hydroxidation, nanoparticles of irregular or spherical shape, including metal particles and feet, are used as nanosized fillers of composite materials.

The main factors influencing the properties of metal-matrix composites, which are reinforced with CNT, are the following: differences in the properties of CNT, the degree of decoupling of agglomerates and the uniform distribution of CNT in the metal; method and degree of compaction of a mixture of metal powder and CNT; wide variation of the ratio of length to diameter of CNT (aspect ratio); possible chemical reactions between carbon and metal, leading to the formation of carbides [7].

Metal-based composites have the potential to replace traditional materials in the automotive, aerospace and other industries. This is facilitated by their excellent mechanical, physical, thermal properties, the ratio of their strength to weight, which is important for the different industry [8, 9].

Composite materials such as metal-CNT acquire new qualities that were not present in any of their original pure components, it allows the use of such composites in the creation, for example, materials for "cold" cathodes of photothermal converters, for which are important as high conductivity and surface geometry, namely, the presence of separately located elements of the composite surface in the form of sharp CNT needles, around which the electric field strength can increase by several orders of magnitude, which increases the proportion of electrons leaving the cathode not due to thermal emission but tunneling. through reduced by the electric field potential barriers at the tips of CNTs. The possibility of realizing the effect of "cold" emission requires a more careful study of promising for these purposes metal-nanocarbon composites, in particular their mechanical and electrical properties.

Experiment

In bulk, carbon nanotubes do not form a conductive environment. However, under compressed, they become conductive due to the increase in the number and density of electrical contacts both between adjacent nanotubes and between them and the electrodes. It is necessary to distinguish between the electrical conductivity of individual CNTs and the material of which they are elements. Peculiarities of the atomic structure and its defects are decisive for the electrical conductivity of individual CNTs, and for the case of the CNT array, in addition to the existing types of CNT defects and impurities, the number and density (type) of contacts between adjacent nanotubes are important [10, 11, 12].

In this work, the electrical conductivity of the CNT ensemble was measured according to the original method [13]. The electrical characteristics of the sample were taken by using a device consisting of an insulating framework, a press matrix, two electrodes, one of which is movable. When the piston is lowered, the sample is loaded, its volume decreases, the density of the powder material increases and conductive paths are created in it, while the electrical conductivity increases rapidly (by orders of magnitude), which is accompanied by the transition of the CNT array to the conductive state. This occurs at a certain density of the powder sample containing the amount of CNTs greater than the threshold, when the contacts between the CNTs form percolation pathways that ensure the conductivity of the material. After the maximum achievable under the conditions of this experiment compression of such material, the piston was gradually raised, the material was partially relaxed, and simultaneously with the unloading also measured the electrical conductivity. The cessation of the relaxation expansion of the material during the lifting of the piston was recorded by a sharp decrease in electrical conductivity, which accompanied the opening of the electrical circuit due to the loss of contact of the powder with the moving electrode.

Nanosystems appeared at the brightness of the sparks, which were deposited from metal particles of cuprum and multy wall carbon nanotubes with different amount of residues (Cu + c% wt. CNT). Particles of Cu powder are small linearly sized from 20 nm to 1 micron. CNT was received by the method of CVD from the gas phase on catalysts containing Al/Fe/Mo transition metals in propylene vapors at a temperature of 923-1023 K, according to mass spectrometry contain water. The nanocomposites of the Cu – CNT system have been adjusted to the mechanical mixing in the primary components in the different proportions.

Results

Figure 1 shows the dependence of the electrical resistivity Ω of samples in processes of compression the bulk mass of particles Cu (a), MCNT (b) and their mechanical mixture containing 65 wt.

% CNT (*b*) in load and unload deformation. All curves Ω(ρ) have hysteresis, which indicates the course of inelastic processes. The minimum value of Ω(ρ) is fixed at a density of ρ = 0.07 g/cm^3 and is equal 2.38 (Ohm · cm), then, with increasing ρ to 0.09 g/cm^3, decreases by half and than practically does not change as a result of the partial orientation of the CNT in the plane of the electrodes and the increase in the contribution to the electrical conductivity of the tunnel current. Its proceed by formation of a three-dimensional grid of CNT - ways of transferring electric charges along the axis of nanotubes, and tunneling through the Van der Waals gap between adjacent nanotubes.

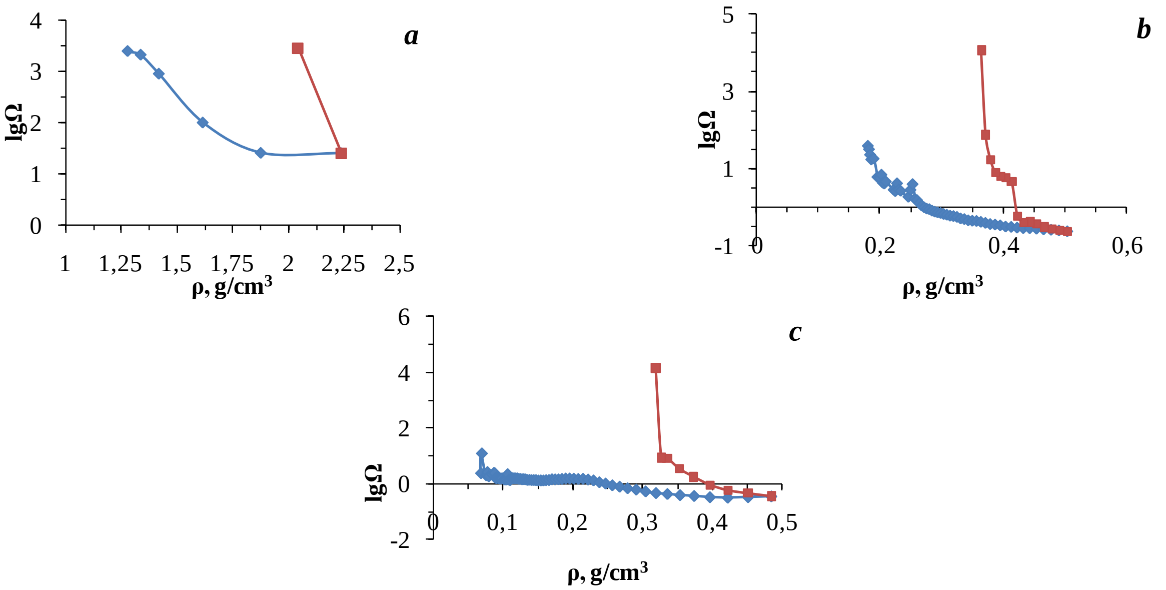

Fig. 1. *Dependences of electrical resistivity Ω of metal–carbon composites with different content of carbon nanostructures on the density ρ of the material in the process of loading–unloading.*

As the process of unloading the volume filled with nanotubes increases, the electrical contacts between the CNT and with the electrodes are maintained due to the elastic relaxation (Fig. 1, *c*) of the pre-compressed simple. The reverse type of the curve Ω(ρ) practically repeats the direct course in the part ρ, after which a rapid increase in the value of Ω by 5 orders of magnitude at ρ = 0.32 g/cm^3, apparently due to a decrease the total area of contacts between nanotubes and with electrodes, the process ends with a break in the electrical circuit (Ω = ∞). Nanocomposites with different percentages of CNT were investigated. The thermo-EMF for these composites has also been adjusted, it is shown that the increase in the carbon component has been increased for the growth of the Seebeck's efficiency. The results are presented in table 1.

Increased concentration of CNT up to 3,92 wt. almost does not affectto the electrical resistivity, but adding of 16 wt. % change it for 8 times compared to the original copper powder. The efficiency of the increase in the concentration of electrical power at the CNT, the degradation of its products, with the indicated concentration. These effects are due to the increase in the concentration of conduction electrons in CNTs, where their mobility is higher, at these concentrations. Increasing the concentration of CNT up to 60 wt. % reduces the electrical resistance by 2 orders of magnitude (table 1), after which it is practically not eliminated. The latter is due to the presence of water in CNT.

It is known that CNTs have a low concentration of conduction electrons (n_e=1.3·10^{19} cm^{-3}), which have a high mobility (μ_{CNT}~10 m2/V·s) [14], and metals, have a high concentration of electrons (~ 10^{22}) with very low mobility. This means that the rapid decrease in the resistivity in the nanosystem is due to an increase in the concentration of electrons in the CNT with a slight change in mobility. During the contact of copper particles with CNTs ($\varphi_{Cu} \approx \varphi_{CNT}$), electrons will pass from the metal to the CNT and increase their concentration in it.

Table 1. Electrophysical parameters of nanocomposites Cu + c wt.% CNT

	Ω, Ohmcm	α, μV/K	ε, %
0	25		43
3,92	23,80	18	63
16,16	3,38	29,9	63
26,26	1,50	25,71	68
40	0,82	27,5	72
50	0,46	27,57	60
60	0,25	28,02	65
64,4	0,23	28,5	64
70,5	0,28	28,86	71
75	0,27	28,56	70
77,5	0,30	28,6	53
80,4	0,28	28,29	72
90	0,29	24,75	69
100	0,32	37,77	86

The increase in the concentration of current carriers in the CNT due to the transfer of charge from the metal should lead to a decrease in resistance. a decrease in resistance by an order of magnitude during the establishment of electrical contacts between CNTs and metal is observed only at a certain concentration of CNTs. Charge transfer means that CNTs have an excess of charge and metal particles lack them. As a result, CNTs and metallic particles must have a Coulomb attraction. It is obvious that at concentrations 60 wt. % and more the mechanism of electron transfer from metal to CNT works most effectively.

Conclusions

Adding to the CNT metal particles resistivity increases more than an order of magnitude, as a result of the transition of electrons from metal to CNT, the mobility of which is greater than in metals, leading to Coulomb interaction between different components and streamlining the system.

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