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СТРОЕНИЕ И СВОЙСТВА НАНОРАЗМЕРНЫХ И МЕЗОСКОПИЧЕСКИХ МАТЕРИАЛОВ

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Peculiarities of Electrical Conductivity of Metal/Carbon Nanotubes Array

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A study of the electrical conductivity of mechanical mixture of both the carbon nanotubes (CNTs) (with work function of ≅ 4.7 eV) and the Cu and Al metal microparticles (with lower work functions of 4.2 and 4.0 eV, respectively) under compression is provided. As shown, the electrical conductivity of the Al and Cu powders is essentially increased with addition of the CNTs (up to 30 wt.%). The electrical conductivity dependence on the density of a powder mixture of Al with CNTs is characterized by a deep minimum observed at the concentration of 9.6 wt.% CNTs. This feature is a result of the electrons' localization in the Al_2O_3 film formed on a sample surface. A number of factors, in particular, a shift of the Fermi level of the CNTs deep into the valence band, explain the sharp decrease in the electrical conductivity of the Al + CNTs composite, unlike the Cu-based composite.

Key words: carbon nanotube, nanocomposite, electrical conductivity.

Досліджено електропровідність механічної суміші вуглецевих нанотрубок (ВНТ) (робота виходу ≅ 4,7 еВ) і металевих мікрочастинок Cu та Al (з меншими роботами виходу: 4,2 та 4,0 еВ відповідно) в процесі деформації

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стисканням. Показано, що електрична провідність порошків Al та Cu істотно збільшується за рахунок додавання ВНТ (до 30% ваг.). Залежність електропровідности від густини порошкової суміші Al з ВНТ характеризується глибоким мінімумом, що спостерігається на одержаній кривій за концентрації вуглецевих нанотрубок у 9,6% ваг. Ця особливість є результатом локалізації електронів у плівці Al_2O_3, що утворюється на поверхні зразків. Різке зменшення електропровідности композиції Al + ВНТ, на відміну від композиції на основі Cu, пояснюється низкою чинників, зокрема, зміщенням рівня Фермі ВНТ глибоко у валентну зону.

Ключові слова: вуглецева нанотрубка, нанокомпозит, електрична провідність.

Исследована электропроводность механической смеси углеродных нанотрубок (УНТ) (работа выхода ≅ 4,7 эВ) и металлических микрочастиц Cu и Al (с меньшими работами выхода: 4,2 и 4,0 эВ соответственно) в процессе деформации сжатием. Показано, что электрическая проводимость порошков Al и Cu существенно увеличивается за счёт увеличения количества нанотрубок в смеси (до 30% вес.). Зависимость электропроводности от плотности порошковой смеси Al с УНТ характеризуется глубоким минимумом, наблюдающимся на полученной кривой при концентрации углеродных нанотрубок 9,6% вес. Эта особенность является результатом локализации электронов в плёнке Al_2O_3, образующейся на поверхности образцов. Резкое уменьшение электропроводности композиции Al + УНТ, в отличие от композиции на основе Cu, объясняется рядом факторов, в частности, смещением уровня Ферми УНТ глубоко в валентную зону.

Ключевые слова: углеродная нанотрубка, нанокомпозит, электрическая проводимость.

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1. INTRODUCTION

Carbon nanotubes (CNTs) have received significant attention as a material for the production of advanced engineering composites due to their unprecedented mechanical and thermal properties like ultra-high elastic modulus (≅ 1 TPa), tensile strength (≅ 150 GPa) and thermal conductivity (3000–6000 W/mK) in combination with an extraordinarily low coefficient of thermal expansion ($\sim 10^{-6}$ K^{-1}), which may offer high mechanical, electrical and thermal performances unattainable for common materials [1–3]. Extensive researches have shown that the CNTs have proven themselves as cold field emitters [4–6], supercapacitors [7], solar cells [8], sensors [9], *etc.*

The carbon nanotube has a high anisotropy of properties, for example, it is a good conductor of charge carriers and phonons in the direction of the axis, but the potential barrier at the surface in transverse direction limits their movement. This means that, depending on the distribution and degree of orientational ordering of CNTs in the array or composite, the material can have a wide range of properties [9–13].

The properties of an individual nanotube are well studied, but additional factors appear for CNTs in a bulk state, namely, the nature and magnitude of the bond between CNTs, spatial orientation, the packing degree, *etc*. CNTs do not conduct electric current in a bulk state, but under a small compression, they become a conductor, on the contrary. Moreover, the geometry of nanotubes is changed resulting in a change of their properties. An important role in this case is played by defects that arise both during the synthesis (growth) and under external influences (deformation, radiation irradiation, *etc*.). They deflect the shape of nanotubes from linear, change the concentration of charge carriers, and the position of the Fermi level as well as the conditions of current passing [14]. In the case of CNTs contact with a metal, it becomes possible to transfer electrons between the components, which affects the electrical conductivity of nanotubes and the composite on their basis, since the contribution of each of the components will depend on the carrier concentration and their mobility. Metals are characterized by high carrier concentration but low mobility, and in CNTs, on the contrary, a low concentration of charge carriers is combined with extremely high mobility, which is three orders of magnitude higher than in metals. This, on the one hand, can lead to an increase in the electrical conductivity of CNTs. On the other hand, a low concentration of electrons in the CNTs makes it possible to easily control the position of the Fermi level: to shift it deep into the valence band with a decrease in the conduction electron concentration or, conversely, into the conduction band, if the metal work function is lower than the work function of CNTs. Methodical point of our investigation [14, 15] consists in the use of the CNTs/metal array (mechanical mixture of nanotubes and powder metal, which has the work function smaller than the work function of CNTs). As a result, the electrical conductivity σ of an array has reached higher values than the corresponding value of each of the components separately.

Here, we present a study of the electrical conductivity of an array of CNTs (with work function of $\cong 4.7$ eV) with Cu and Al metal particles (having lower work functions of 4.2 and 4.0 eV, respectively). In this case, it is expected that an amount of charge transferred from the metal to the CNTs will depend on the structure, geometric parameters and the defectiveness of the nanotubes, which will affect the electrical conductivity of the composite.

2. EXPERIMENTAL DETAILS

Multiwall carbon nanotubes used in this study were synthesized by the catalytic chemical vapour deposition method (CVD) using Al_2O_3–

Fe_2O_3–MoO_3 as the catalyst. Figure 1 represents a transmission electron microscope (TEM) image of the CNTs used. Statistical processing of the images has revealed that the diameter of the CNT is within 8–28 nm, and the wall thickness is 4–5 nm. The appearance of electrical conductivity has been detected at a density of 0.11 g/cm^3 under one-dimensional compression of nanotubes (under the piston).

The mixture of initial CNTs powders and metallic Cu and Al microparticles was subjected to mechanical milling in a high-energy planetary ball mill to obtain nanocomposites. Elemental Cu powder (99.6% purity, particle sizes of 20 and 40 μm), Al chips (containing 3 at.% of Li, particle size of ≅ 60 μm), and multiwall CNTs were mixed to give the desired average composition and sealed in a vial under an argon atmosphere. High-energy planetary ball mill used for mechanical milling is a custom-made model developed at the Metal Physics and Ceramics Laboratory of Taras Shevchenko National University of Kyiv [16]. Hardened stainless steel balls (15 units of 15 mm diameter) and a vial (70 mm height, 50 mm diameter) with a ball-to-powder weight ratio of 20:1 were used. The vial temperature was held at below 375 K during the experiments by air-cooling. The milling process was cyclic with 15 min of treatment and 30 min of cooling time. The rotation speed was equal to 1480 rpm; the acceleration was about 50 g: the pressure for a substance particle reached 5 GPa. An energy-dispersive X-ray spectroscopy (EDS) method using a JEOL JSM-840 microscope operated at 10 kV shows that no additional Fe powder due to wear debris from the steel balls and vial is introduced into the powders after milling. The quality of milling (average particle diameter) and the stability of the process were monitored using an optical microscope AXIO Observer A1m (Carl Zeiss), the maximum magnification of which is ×1000.

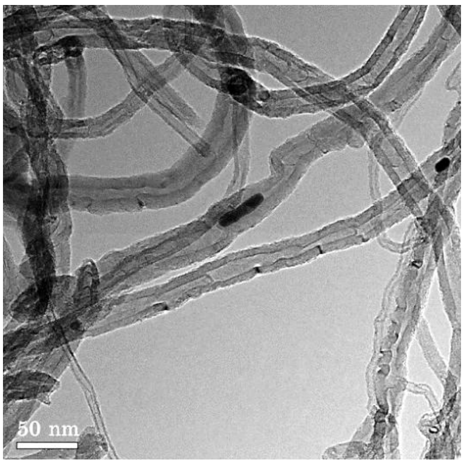

Fig. 1. TEM image of initial CNTs.

The electrical conductivity and thermopower of the initial components and their mechanical mixture have been measured in a dielectric cylinder under the piston on the forward and reverse motion under compression to density $\rho = 1$–1.3 g/cm^3 and subsequent unloading. When the piston goes down and volume decreases, the conductive paths are created in CNTs array and the electrical conductivity increases by many orders of magnitude. When the piston goes up and volume, where the CNTs are located, increases, the elastic relaxation of nanotubes occurs. Due to this relaxation, the electrical contacts are kept between both CNTs and between CNTs and electrodes. This allows keeping an eye on a process, and its completion was recorded by breaking the electrical circuit.

3. RESULTS AND DISCUSSION

Figure 2 shows the dependence of electrical conductivity σ on the density ρ of a bulk array of Al powder compressed under the piston (Fig. 2, *a*), multiwall CNTs (Fig. 2, *b*) and Al + CNTs (9.6 wt.%) nanocomposite (mechanical mixture) (Fig. 2, *c*) at forward and reverse stroke of the piston. All $\sigma(\rho)$ curves are characterized by a hysteresis, which indicates the occurrence of inelastic processes. When the CNTs are compressed under the piston, the minimum value of $\sigma(\rho)$ is equal to $\sigma \sim 10^{-6}$ $(\Omega\cdot\text{cm})^{-1}$ at density $\rho = 0.11$ g/cm^3, and then, it rapidly rises to $\sigma \approx 1$ $(\Omega\cdot\text{cm})^{-1}$ with ρ increases up to 0.19 g/cm^3. This phenomenon could be explained by the formation of a three-dimensional grid of CNTs (the paths of electric charge transfer) along the axis of nanotubes and the tunnelling through the Van der Waals gap between neighbouring nanotubes. The subsequent compression of the CNTs array to $\rho = 1.1$ g/cm^3 monotonically decreases σ value because of the partial orientation of CNTs in the plane of electrodes and due to the enhanced contribution of tunnelling current to electrical conductivity. With the return piston stroke and the increase in the volume filled with nanotubes, the electrical contacts between nanotubes and the electrodes are preserved due to elastic relaxation of the precompressed CNTs array (Fig. 2). The reverse of σ (ρ) curve practically repeats the forward motion in the ρ range from 1.1 to 0.35 g/cm^3, after which a rapid decrease (by 7 orders of magnitude) in the value of σ is detected at $\rho = 0.34$ g/cm^3, due to a decrease in the total area of contacts between CNTs and with the electrodes. The process is completed by breaking the electrical circuit ($\sigma = 0$). The $\sigma(\rho)$ curve for the CNTs array demonstrates the smallest hysteresis value equal to $\Delta\rho = 0.23$ g/cm^3 (Fig. 2, *c*) that is caused by high elasticity of nanotubes. The hysteresis value $\Delta\rho$ is approximately equal to 0.5 g/cm^3 for Al and $\Delta\rho \approx 0.8$ g/cm^3 for mechanical Al + CNTs (9.6 wt.%) mixture (Table 1).

A qualitatively similar behaviour of $\sigma(\rho)$ is observed for two other

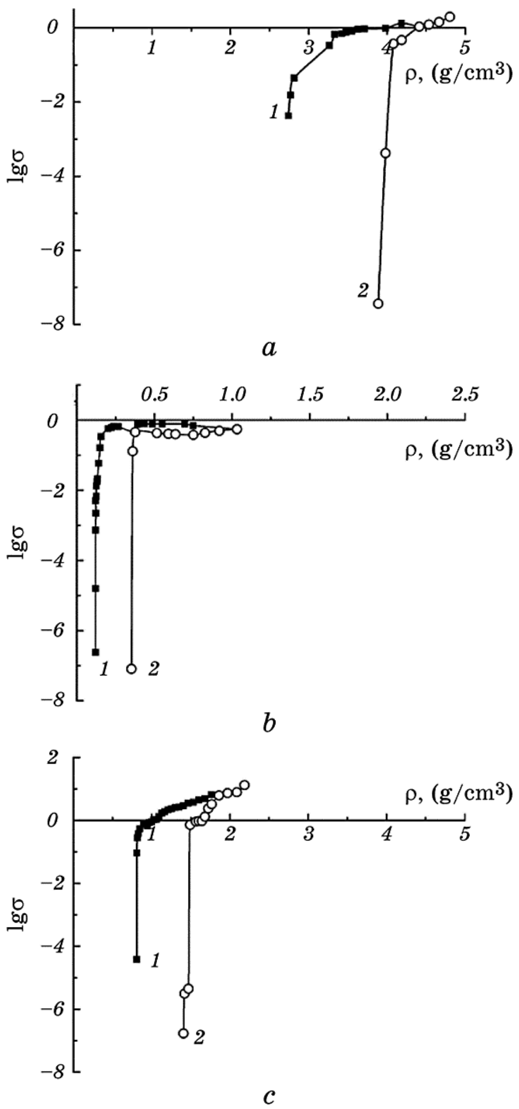

Fig. 2. Dependences of electrical conductivity logarithm lg(σ) on density ρ for: *a*—Al particles, *b*—carbon nanotubes, *c*—Al + 9,6 wt.% CNTs (*1*—forward and *2*—back stroke of the piston.

samples obtained from Cu powders of different dispersity (20 and 40 μm) and their mixture with CNTs.

Table 2 lists the abnormally high values of σ for the CNTs content at which they are detected. It is seen that the density of the CNTs array, at which it transforms to the electrically conducting state (ρ_{cr}) under compression and relaxation transition (ρ_{rel}) detected when the load is removed, has the smallest values (Table 1).

The dependences of the maximum values of σ_{max} for copper particles of different dispersity and Al particles on the concentration c of CNTs are presented at Fig. 3. Table 2 summarizes σ_{max} values both of the initial powders and their mechanical mixtures with CNTs.

As seen, the electrical conductivity σ for mechanical mixture of Cu (20 μm) + CNTs (9 wt.%) reaches 1.76 $(\Omega\cdot cm)^{-1}$ and at c(CNTs) = 26 wt.% it increases up to 2.3 $(\Omega\cdot cm)^{-1}$ (Table 2), which is approximately 4–5 times higher than σ for copper powder. For mechanical mixture of Cu (40 μm) + CNTs (17 wt.%) the electrical conductivity undergoes the rise to 1.64 $(\Omega\cdot cm)^{-1}$, so σ value increases by 40 times in comparison with σ of copper powder (Table 2). The observed electrical conductivity

TABLE 1. Densities of mechanical mixture measured under compression (ρ_{cond}) when the electrical conductivity appears and under decompression (ρ_{rel}), at which the electrical open is detected. Hysteresis value $\Delta\rho$ is defined as $\rho_{rel}-\rho_{cond}$.

Materials	Particle size, μm	Carbon nanotubes content (c, wt.%)	Density under compression (ρ_{cond}, g/cm^3)	Density under decompression (ρ_{rel}, g/cm^3)	Hysteresis ($\Delta\rho$, g/cm^3)
CNTs	–	100.0	0.11	0.34	0.23
Al	60	–	0.68	1.16	0.48
Al + CNTs	60	9.6	0.41	1.14	0.83
Cu	40	–	1.27	2.00	0.73
Cu + CNTs	40	29.6	0.53	1.17	0.64
Cu	20	–	1.23	1.46	0.23
Cu + CNTs	20	26.0	0.47	1.01	0.54

TABLE 2. Electrical conductivity of the initial components (σ_0) and its maximum values for mechanical mixture of metal powders with the carbon nanotubes.

Materials	Particle size, μm	Carbon nanotubes content (c, wt.%)	Electrical conductivity, $(\Omega\cdot cm)^{-1}$		
			Value for source materials, σ_0	Maximum values for composites σ_1^{max}	Maximum values for composites σ_2^{max}
CNTs	–	100.0	0.3–0.6	–	–
Al	60	–	0.52	–	–
Al + CNTs	60	9.6	–	0.01	–
Cu	20	–	0.40	–	–
Cu + CNTs	20	9.0	–	1.76	–
Cu + CNTs	20	26.0	–	–	2.30
Cu	40	–	0.04	–	–
Cu + CNTs	40	29.6	–	–	1.06

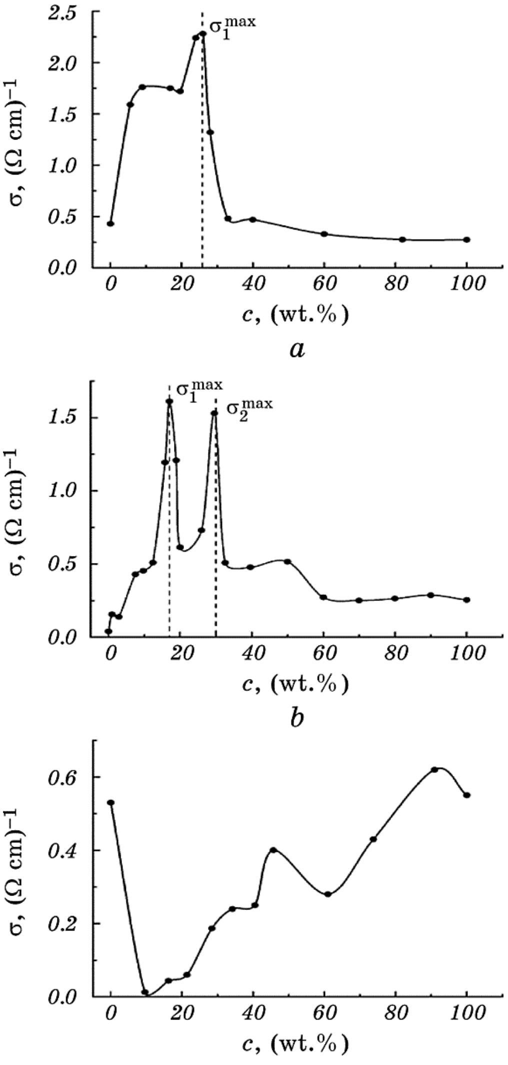

Fig. 3. Dependences of electrical conductivity on CNT content of Cu- and Al-based arrays: *a*—Cu (20 μm), *b*—Cu (40 μm) + CNTs, *c*—Al + CNTs.

increasing is explained by an increase in the concentration of charge carriers in CNTs because of their transition from the contacting metal. Besides, redistribution of the charges between components leads to their electrostatic attraction and compaction.

The 'resonance' form of $\sigma(\rho)$ curves with resolved and unresolved peaks and the order of their distribution on the concentration dependence $\sigma(c)$ can be associated with a shift of the Fermi level in multiwall carbon nanotubes occurring if the electron concentration of CNTs is changed and a variation of the tunnelling conditions (Fig. 3, *b*).

The concentration dependence $\sigma(c)$ of the Al + CNTs nanocomposite is presented at Fig. 3, *c*. As seen, the electric conductivity decreases with CNTs content increase up to 9.6 wt.% and then increases with further CNTs content increasing because of the growth of the electrically conductive paths along nanotubes.

The drop in σ is attributed to the presence of a nonstoichiometric Al_2O_3 oxide film on surface of the Al powder. It contains aprotic (acidic) Lewis centres, whose role is played by the Al^{3+} ions on the surface with an uncompensated charge due to the lack of O^{2-} surrounding anions. The sharp decrease in the electrical conductivity of the Al composite upon addition of CNTs, in contrast to the Cu-based composite, is explained by the effective capture of electrons by Al^{3+} acceptor centres (Lewis centres). This leads to a decrease of the concentration of conduction electrons in the CNTs and to a shift of their Fermi level deep into the valence band.

4. CONCLUSIONS

The CNTs/Cu mixture was allowed to compact in a concentration region with the electrical conductivity maxima because of the Coulomb interaction that occurs between dissimilar particles with the most efficient electron transfer from the copper to the CNTs.

With addition of the carbon nanotubes, which has the work function higher than that of metals, to metal particles, the radial electrical conductivity essentially increases due to the transition of electrons from metal to CNTs, where their mobility is orders of magnitude higher than in metals. This results in the Coulomb interaction between components and the ordering of a system.

For a mechanical mixture of Al with CNTs, a deep minimum is observed on $\sigma(\rho)$ curve at the concentration of 9.6 wt.% CNTs. The existence of such feature is caused by the localization of electrons in the Al_2O_3 film formed on a sample surface. The sharp decrease in the electrical conductivity of the Al + CNTs composite, unlike the Cu-based composite, is explained by several factors, namely: the effective capture of electrons by Al^{3+} Lewis acceptor centres, a decrease in the concentration of conduction electrons in CNTs, and a shift of the Fermi level of the CNTs deep into the valence band.

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