Conductivity of a Mechanical Mixture $\text{LaNi}_5 + c \text{ wt. \% CNT}$

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Abstract The specific electrical conductivity (σ) of mechanical mixture consisting of particles LaNi_5 and multi-walled carbon nanotubes was studied under compression. Found that the conductivity of mechanical mixture with micro particles LaNi_5 (diameter $28 \pm 6 \text{ mkm}$) and 51 wt. % CNT is executed to the order of magnitude σ of CNT. Growth mechanism of specific electrical conductivity of mechanical mixture LaNi_5 with CNTs is due the process of ordering and the transfer electrons from the metal to CNTs. At this concentration, the mechanism of electron transfer from the metal particles to the CNT is most optimal.

Keywords Carbon Nanotubes, the Electrical Conductivity, Deformation, Mechanical Mixture

1. Introduction

Carbon nanotubes have unique properties: mechanical, electrical, thermal, and emission that contribute to their effective realization in different fields of science and technology [1].

The deformation of the carbon nanotube (CNT) is affected its electronic structure, particularly the gap width and the concentration of charge carriers [2].

It was detected that single-walled CNTs along its axis – conductors, and in the transverse direction – insulators. Therefore, its have a wide range of properties [3].

The surface area of filler particles of nanocomposite materials are much more developed (by several orders of magnitude) than conventional materials. This increases the surface energy and the properties of nanocomposites are greatly dependent on the morphology of the filler, and nature of the interaction of components at the interface. It is important for many applications create conditions under which the properties of the composite with carbon nanotubes, especially electrical conductivity, reaches higher values compared to the corresponding properties of each separate component. Using CNT in practice requires the development of technologies for their consolidation. However, the

properties of compacted CNT due to their interaction will be different from those of the initial nanotubes.

This paper is devoted to researching the electrical properties of the nanocomposite LaNi_5 with multi-walled carbon nanotubes during deformation by compression, which leads to the establishment of electrical contact between the nanotubes, an increase in their total area, the change in orientation and geometry of the nanotubes, and thus properties.

2. Materials and Methods

Multi-walled CNT and metallic microparticles of LaNi_5 were used in research. CNTs were grown by chemical vapor deposition (CVD) with catalyst $\text{Al}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-MoO}_3$, vapor propylene at a temperature of 650°C , identified by transmission electron microscopy (JEM-100CX11, Japan), the average diameter is $d = 10 \pm 2 \text{ nm}$. LaNi_5 particles were synthesized by an electric discharge in toluene, average diameter is $d = 28 \pm 6 \text{ nm}$.

LaNi_5 have a low work function ($\phi = 3,6 \text{ eV}$) than CNT ($\phi = 4,7 \text{ eV}$).

CNTs in bulk state aren't conductive, but in small compression they pass to the electrically conductive state. Therefore, the electrical conductivity was measured in the dielectric tube under the piston, where the bottom and piston were metallic and served as electrodes. The electrical conductivity of the mechanical mixture was measured at the forward (compression) and reverse (decompression) motion of the piston. Conduct pathways created by lowering of the piston and decreasing the volume with mechanical mixture $\text{LaNi}_5\text{-CNT}$ and electrical conductivity sharply by several orders of magnitude increases.

The mechanical mixture was compressed to a density $\rho \sim 1 \text{ g/cm}^3$, then the piston rises and the material experienced relaxation; and simultaneously measured electric conductivity in the direction of movement of the piston. The establishment of contacts between the individual particles of mixture and electrodes under compression led to the transition of a mechanical mixture $\text{LaNi}_5\text{-CNT}$ array of

nonconductive to the conductive state (insulator - conductor) at a density ρ_1 . The moment of complete relaxation of the mechanical mixture LaNi_5 -CNT during the return stroke of the piston was fixed for electrical disconnection [4].

3. Results and Discussion

Fig. 1 presents electron micrographs of multi-walled carbon nanotubes. Catalyst particles are observed at the ends of the nanotube.

Figure 1. Multi-walled carbon nanotubes

Statistical analysis of the pictures showed that the average diameter of multiwalled CNTs is 10 ± 2 nm (Fig. 2). The wall thickness varies from 0,6 to 3,6 nm, which corresponds to 2-10 graphene layers.

Fig. 3 shows the dependence of the logarithm of the conductivity $\sigma(\rho)$ mechanical mixture LaNi_5 + c wt % CNT on their density in the compression and decompression process. A sharp peak of $\sigma(n)$ is observed for 51 wt. % CNT, and the conductivity value is equal $\sigma = 10,65 (\text{Ohm} \cdot \text{sm})^{-1}$. The conductivity of the original compacted components is much lower: for particles LaNi_5 $\sigma = 0,7 (\text{Ohm} \cdot \text{sm})^{-1}$, and array CNT – $\sigma = 1,04 (\text{Ohm} \cdot \text{sm})^{-1}$.

Figure 2. The statistical distribution of the nanotubes in the outer diameter

a)

b)

c)

Figure 3. The dependence of the logarithm of conductivity $\lg(\sigma)$ to the density ρ for: a) microparticles LaNi_5 , the average diameter is $d = 28$ nm; b) mechanical mixture LaNi_5 + 51 wt. % CNT; c) CNT. (1 – compression, 2 – decompression)

Elastic relaxation is observed in process of decompression, and is minimum for microparticles LaNi_5 and maximum for CNTs. A sharp drop in $\sigma(\rho)$ indicative of completion of the elastic relaxation, reduction of the total area of contact between the nanotubes, particles LaNi_5 with CNTs and the electrodes and the electrical disconnection. This process occurs for LaNi_5 when $\rho = 4,60 \text{ g/cm}^3$, for LaNi_5 + 51 wt. % CNT $\rho = 0,40 \text{ g/cm}^3$ and CNT $\rho = 0,22 \text{ g/cm}^3$. It points out that among the most resilient of the samples are CNTs.

Figure 4. The dependence of conductivity (σ) of the mechanical mixture $\text{LaNi}_5 + c$ wt. % CNT from (n) CNT concentration. ■ – maximum conductivity, ○ – conductivity at maximum compression

Fig. 4 shows the dependence of the logarithm of the conductivity $\sigma(p)$ mechanical mixture $\text{LaNi}_5 + c$ wt. % CNT on their density in the compression and decompression process. A sharp peak of $\sigma(c)$ is observed for 51 wt. % CNT, and the conductivity value is equal $\sigma = 10,65 (\text{Ohm} \cdot \text{cm})^{-1}$. The conductivity of the original compacted components is much lower: for particles LaNi_5 $\sigma = 0,7 (\text{Ohm} \cdot \text{cm})^{-1}$, and array CNT – $\sigma = 1,04 (\text{Ohm} \cdot \text{cm})^{-1}$.

It is known [5] that CNTs have low concentration of conduction electrons ($n_e = 1,3 \cdot 10^{19} \text{ cm}^{-3}$), but have a higher mobility ($\mu = 10 \text{ m}^2/\text{V} \cdot \text{s}$), and metals, conversely, have a high concentration of conduction electrons ($\sim 10^{28}$) and very low mobility (for LaNi_5 $\mu = 0,0072 \text{ m}^2/\text{V} \cdot \text{s}$).

According to the classical electron theory of the electric conductivity of metals conductivity is

$$\sigma = en_e \mu,$$

where n_e – concentration of conduction electron, μ – the mobility of electrons.

Experimental evidence suggests that a sharp increase in conductivity in the mechanical mixture (Fig. 4) due to increased concentration of electrons in a slight change in nanotube mobility.

Upon contact with the metal LaNi_5 with CNT ($\varphi_{\text{LaNi}_5} < \varphi_{\text{CNT}}$), electrons will move from the metal to the CNT, increasing their concentration. According to [6], with an increase in the mobility of the charge carrier concentration falls $\mu \sim 1/n^{1/2}$. Therefore, the current density (conductivity) will grow $\sim n^{1/2}$. Increasing the concentration of charge carriers in the nanotubes in the charge transfer from the metal should lead to an increase in conductivity. In this experiment, there is a tenfold increase in conductivity in establishing electrical contact between the nanotube and the metal, but only if it is certain CNT concentration (51 wt.%). The charge transfer means that CNTs have an excess of electrons, and their lack of metal particles. As a result, they should experience the Coulomb attraction. Indeed, in the most effective compression mechanical compaction mixture LaNi_5 -CNT happened for the above optimal composition and the sample was transformed into a tablet. Obviously, with 51 wt. % CNT most effective mechanisms for the transfer of electrons from the metal particles LaNi_5 to CNT.

The subsequent increase in concentration of up to $c = 56,8$ wt. % CNT leads to a drop in the electrical conductivity of the nanocomposite to $3 (\text{Ohm} \cdot \text{cm})^{-1}$. This is due to a decrease in the average concentration of electrons in the nanotube due to the presence of a dense layer of CNT around the metal particles LaNi_5 , thereby reducing electrical conductivity, since the mechanism of electron transfer from the metal to the CNT, which are farther from the particles LaNi_5 , will be less effective.

Fig. 5 shows the dependence of the transition to the conducting state ρ_1 and relaxation transition ρ_{rel} for mechanical mixture $\text{LaNi}_5 + c$ weight. % CNT from CNT concentration (c), which are also seen small peaks at the same concentrations (≈ 50 wt.%). Adding to the powder LaNi_5 2,20 wt. % CNT reduces ρ_1 and a half times (Fig. 5). This means that highly anisotropic nanotube axis which is preferably the current is connected between the particles and thereby reduce ρ_1 . This conductivity does not change when the load changes (Fig. 2).

Small maximum two transitions at this concentration is associated with a slight reduction in the ordering of CNTs and the elasticity of the composite, apparently due to an increase in the maximum concentration of electrons in the nanotube. Therefore, all three peaks are observed at the same concentration (51 wt. % CNT), which may indicate the relationship of different physical parameters, is shown. At high concentrations, the CNT and ρ_1 , ρ_{rel} reduced due to a violation of the procedure, increase elasticity and substantial reduction in electrical conductivity.

Figure 5. The dependence of the percolation threshold concentration CNT in the mechanical mixture (1) and moment of complete relaxation (2)

The Seebeck coefficient α depending on the density ρ of mechanical mixture with different CNT concentrations is shown on the Fig. 6.

It is seen that the lowest value of 1.8 mV/K for the array of particles observed LaNi_5 , and entering it only weights 1.24. % CNT growth factor leads to 27 mV/K. Anisotropic particles LaNi_5 nanotubes connect with each other, provide electrical contact, reduce 2.7 times the transition to a leading position. The concentration of nanotubes to 5 wt. %. Did not significantly affect the electrical conductivity, but defines nanocomposite thermoelectric characteristics. When

nanocomposite powder compressed under the piston Seebeck coefficient decreases rapidly and reaches values of particles of LaNi_5 . This may be due to the fact that particles under compression piston they are together in electrical contact and shunts contribution from carbon nanotubes, as evidenced by data on conductivity. With increasing concentration of CNTs most important (at minimum density) the Seebeck coefficient does not change, but the maximum compression observed, first, a significant drop coefficient α with increasing ρ , and, secondly, the gradual increase in the minimum value (Fig. 6).

For all samples of LaNi_5 -CNT for all values of ρ α has a positive sign. That indicating hole conductivity. The rapid decline in the value of α deformation associated with an increase in the proportion of NTDs that have come into electrical contact with metal particles LaNi_5 , which leads to an increase in the concentration of electrons in nanotubes.

They cause the fall in order coefficient α at low concentrations (<5 wt. %) Nanotubes (Fig. 6).

Figure 6. The dependence of the Seebeck coefficient of the nanocomposite density at reduced volume under the piston. 1 - LaNi_5 ; 2 - LaNi_5 + 1,24 wt. % CNT; 3 - LaNi_5 + 5,3 wt. % CNT; 4 - LaNi_5 + 11,43 wt. % CNT; 5 - LaNi_5 + 14,48 wt. % CNT; 6 – CNT

Rising concentrations of conduction electrons is confirmed by the fact that the value of the coefficient α (27-31 mV/K) with a minimum density for all samples nanocomposite remain below the values α (37-39 mV/K) for an array of nanotubes.

With increasing concentration of carbon nanotubes nanocomposites drop coefficient α decreases due to increase in the proportion of CNTs that are not in contact with the particles LaNi_5 .

4. Conclusions

1. It is found that in the composite the microparticles LaNi_5 ($d = 28 \pm 6$ nm) and 51 wt. % CNT conductivity (σ) in the order of magnitude higher compared to σ CNT array.
2. The mechanism of growth of the electrical conductivity of the mechanical mixture LaNi_5 + CNT due to streamlining processes in establishing electrical contact between the components and transfer of conduction electrons from the metal to the CNT

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