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Research of Influence of Carbon Nanotubes Content on the Electrical and Thermal Properties of Copper Matrix Composite Produced by Electrocontact Sintering Method

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Abstract
Composite materials on based powder systems "copper – carbon nanotubes" with different carbon nanotubes contents ranging from 0 to 0,1 wt. % were prepared by a electrocontact sintering. Its has shown that this composites have anisotropic thermal and electrical conductivity. It has been found that during uniaxial molding, in the process of electrocontact sintering, carbon nanotubes are oriented in one direction, which leads to a change in the values of the studied characteristics in this direction. Dependences of the change in the thermal conductivity, the electrical resistance and the specific electrical conductivity of the composites on the content of the nanostructured filler are established.

Keywords: carbon nanotubes, composite material, copper powder, specific electrical resistance, specific electrical conductivity, thermal conductivity coefficient, powder metallurgy, electrocontact sintering.

1. Introduction

Future technical needs will require the development not only of lightweight and strong materials but also, having high thermal and electrically conductive properties as compared to their conventional counterparts. Carbon nanotubes are a novel form of carbon that have the potential for spearheading exciting applications in the development of ultra strong nanocomposite materials, nanoelectronic devices, field electron emitters, nanoprobes, among others [1].

Carbon nanotubes (CNTs) are recognized as the ultimate carbon fiber for high performance, multifunctional composites [2]. Additionally, they can be used as potential reinforcements for composite materials due to their air stability, high aspect ratio, small diameter, lightweight, excellent mechanical, electrical, thermal and magnetic properties [8 and 9].

With the development of many low-cost synthetic routes for CNTs mass production of CNTs has proven to be less cost-prohibitive [3]. The matrices in which CNTs are incorporated to produce composites with improved electrical properties can be polymer, metal or metal oxide. Most composites containing CNTs are polymer based because of its flexibility in fabrication. Very few investigations have been focused on "metal – CNTs" composites.

Copper has been the dominating conductor materials during the past 100 years. In the high technology applications, Silver is sometimes used because its conductivity is approximately 5 percent larger than that of copper. However, Ag is a much more expensive material.

For comparison, the electrical conductivity and temperature coefficient of resistivity for copper is 59,88 MS/m and $3{,}886 \cdot 10^{-3}$ K^{-1}, respectively, for silver 63 MS/m and $3{,}8 \cdot 10^{-3}$ K^{-1}. For example, the specific electrical conductivity of structural steel is in the range of 1,5–7,6 MS/m [4].

The “copper – CNTs” composites prepared by the powder metallurgy technique [5] offers the possibility of obtaining a uniform product with a reduction in tedious and costly machining. However, this technique has the limitations of poor affinity between copper and CNTs, which has a detrimental effect on the structural, mechanical and electrical properties of the material [6]. Additionally, there are two important processing issues encountered in the fabrication of CNTs reinforced Cu matrix composite materials: a) acquiring a homogeneous distribution of CNTs and b) achieving high interfacial bonding between CNTs and the copper matrix [7].

Preliminary mechanical activation of the “copper – CNTs” powder system makes it possible to destroy CNTs agglomerates and redistribute CNTs over the volume of the metal matrix.

It should be noted that the interface between the initial components remains one of the main problem areas in which the properties of the composite material can be improved. Study [8] gives the value of the interfacial thermal resistance of a CNTs, which is $8{,}3 \cdot 10^{-8}$ $(m^2 \cdot K)/W$. This value is used in most publications at present.

Thus, the objective of the work was to investigate thermal and electrical properties of composite materials based on powder systems "copper – CNTs", that are obtained by electrocontact sintering.

2. Materials and investigation methods

In present work, we used multiwalled CNTs with an average outside diameter of 10 nm and average length of 800 nm. It should be noted that CNTs used in this work were not pre-treated with acid. Copper powder PMS-1, All-Union State Standard 4960-2017, was used without additional purification. Preparation of a powder mixture and dispersion of CNTs in a metal copper matrix were implemented in the process of mechanoactivation for 60 min in a special activator mixer.

Composite powder materials were obtained by electrocontact sintering. Samples were formed in a special mold through the molding at a pressure of 400 MPa and the sintering by passing an electric current of density 400 A/mm for 1,5 s under pressure.

For each percentage of CNTs in the copper matrix, 10 cubic workpeces of composite materials with a face size of 10 mm were fabricated. These workpeces were machanically treated subsequentlyand 5 specimens were prepared of each in the form of a parallelepiped with foundation sides of 10 mm and a height of 5 mm were prepared for investigation the termal and electrical properties in the direction of the axis of molding and in the direction perpendicular to the axis of molding. Parallel surfaces of the specimens were treated to a tolerance of ± 0,02 mm.

The thermal conductivity of composite materials in directions parallel and perpendicular to the axis of molding in sintering were determined using the measured values of thermal diffusivity, specific heat and density.

The thermal diffusivity was measured by the laser flash method, which is based on the unfocused laser beam absorption by a specimen's front surface. Experiments on investigation thermal diffusivity were conducted on an LFA-427 device from Netzsch Company (Germany). The specimen was installed in a holder inside a special chamber. Laser radiation was fed to the specimen at the bottom from a solid-state pulsed laser. The lens system ensured a uniform distribution of radiation intensity. The pulse duration was 0.7 ms, with the

maximum energy of a single pulse being no higher than 25 J. A temperature change of the specimen's upper surface was recorded by indium antimonide IR detector which was cooled with liquid nitrogen. To focus the radiation from the specimen's surface, a calcium fluoride (CaF_2) lens transparent to the IR spectrum was installed in front of the detector.
The thermal conductivity coefficient was calculated from the formula:

$$\lambda_k = \alpha_k \cdot \rho_k \cdot C_{pk} \tag{1}$$

where λ_k – the thermal conductivity coefficient of composite material, $W \cdot m^{-1} \cdot K^{-1}$;

α_k – the coefficient of thermal diffusivity of composite material, $m^2 \cdot s^{-1}$;

ρ_k – the density of the composite material, $kg \cdot m^{-3}$. The density of the composite was determined according to All-Union State Standard 25281-82 "Powder metallurgy. Method to determine the molding density";

C_{pk} – the specific heat of a composite material, $J \cdot kg^{-1} \cdot K^{-1}$.

The heat capacities of copper and CNTs were measured by differential scanning calorimetry on an apparatus of the PerkinElmer Inc (USA). The specific heat of the composite material was calculated from the formula for multicomponent composite materials:

$$C_{pk} = C_{p1} \cdot f_{i1} + C_{p2} \cdot f_{i2} \tag{2}$$

where f_i – the volumetric content of the i-th component,%;

C_{pi} – heat capacity of the i-th component, $J \cdot kg^{-1} \cdot K^{-1}$;

k – the number of composite components.

Electrical resistances of the specimens were measured on digital microohmmeter DLRO10X from Megger (Great Britain). The specific electrical resistances ρ and specific electrical conductivities g of the composite materials were calculated from formulas:

$$\rho = R \cdot S \cdot l^{-1} \tag{3}$$

$$g = \rho^{-1} \tag{4}$$

where R – measured electrical resistance of the specimen, Ohm;

s – the cross-sectional area of the specimen, m^2;

l – the length of specimen, m.

3. Results and discussion

3.1 Thermal properties

Analysis of the results of the carried-out investigations has shown that the values of thermal conductivity coefficients of composite materials which are based on powder systems "copper – CNTs" and are formed by electrocontact sintering in the direction of the axis of molding and in a direction perpendicular to this axis differ significantly. It has been established that the thermal conductivity coefficient of a sintered material based on copper powder PMS-1 is 363 $W \cdot m^{-1} \cdot K^{-1}$, which is much lower than the values of the thermal conductivity coefficient of copper which are 396–400 $W \cdot m^{-1} \cdot K^{-1}$ according to literature data [9].

If we take into account that the thermal conductivity of composite materials in the generally dependent on the thermal properties of the initial components, the amount and size of the filler and its distribution in the volume of the matrix, as also as the thermal resistance arising in the zones of contact interaction of the components, the reduction in the thermal conductivity of the specimens under study is attributable to the presence of interphase thermal the resistance arising between the CNTs and the matrix, contact resistance between the metal particles of the matrix due to the presence of oxide films and porosity which is present in the powder material, reduces the area of the contact between the composite particles, and acts as an internal thermal barrier in this case.

As can be seen from the Fig. 1, the material's anisotropy increases with CNTs concentration in the composite. Here, from the analyzing of the experimental results, it may be stated that upon the process of electrocontact sintering, CNTs in the copper matrix have a preferred orientation, which is, probably, due to the character of action of the electric current.

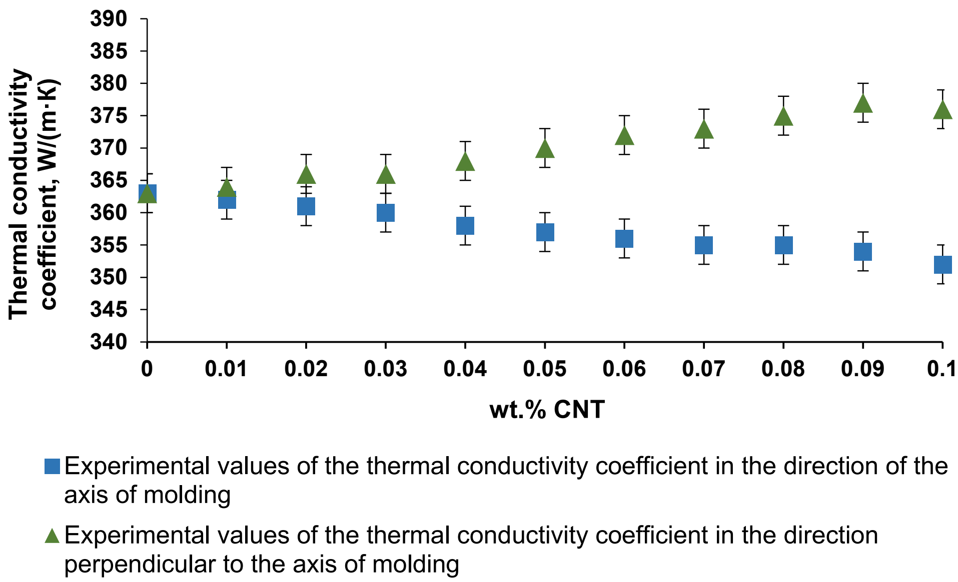

Fig. 1. Thermal conductivity coefficient of the composite materials “copper – CNTs”

As an analysis of the conducted experiments shows, the process of electrocontact sintering may lead to the orientation of the carbon nanofiller in the plane perpendicular to the axis of molding, which results in the anisotropy of thermal conductivity for the composite materials based on powder systems "copper – CNTs".

Thus, in the course of the carried-out investigation, it has been established that materials based on powder systems "copper – CNTs" possess anisotropic thermal conductivity, since the values in the direction parallel to the axis of molding differ from the values of thermal conductivity in the perpendicular direction, and experiments confirms that carbon nanotubes do not are randomly dispersed in the metal matrix.

Furthermore, the values of the thermal conductivity coefficients of composite materials in the perpendicular direction are 8% higher than those in the sintered pure powder copper, which shows the overall effect of the matrix and the filler and confirms the CNTs capacity for controlling the thermal properties of composites.

3.2 Electrical properties

Analysis of the results of the carried-out investigations has shown that the values of electrical conductivity of composite materials which are based on powder systems "copper – CNTs" in the direction of the axis of molding and in a direction perpendicular to this axis differ significantly.

As can be seen from Fig. 2 and Fig. 3, the electrical properties of the material's anisotropy increase with CNTs concentration in the composite that has to do with the preferred orientation of CNTs.

In accordance with the literature data, the electrical resistance of pure cast copper measured at a temperature of 20 °C is $1{,}67 \cdot 10^{-8}$ Ohm·m. However, the specific electrical resistance of a sample of material based on sintered powder PMS-1 is $1{,}92 \cdot 10^{-8}$ Ohm·m, which is 15% higher than that measured on a sample of pure cast copper. This difference in electrical properties can be explained in terms of the heterogeneity of the structure of powder composites and the presence of pore space. So porosity reduces the electrical conductivity of the material.

The dependences of the electrical resistance and electrical conductivity of composite materials based on "copper – CNT" powder systems on the CNT content are shown in Fig. 2 and Fig. 3. Figures show that the electrical resistance and electrical conductivity in the direction of the molding force and in the direction perpendicular to the pressing force differ.

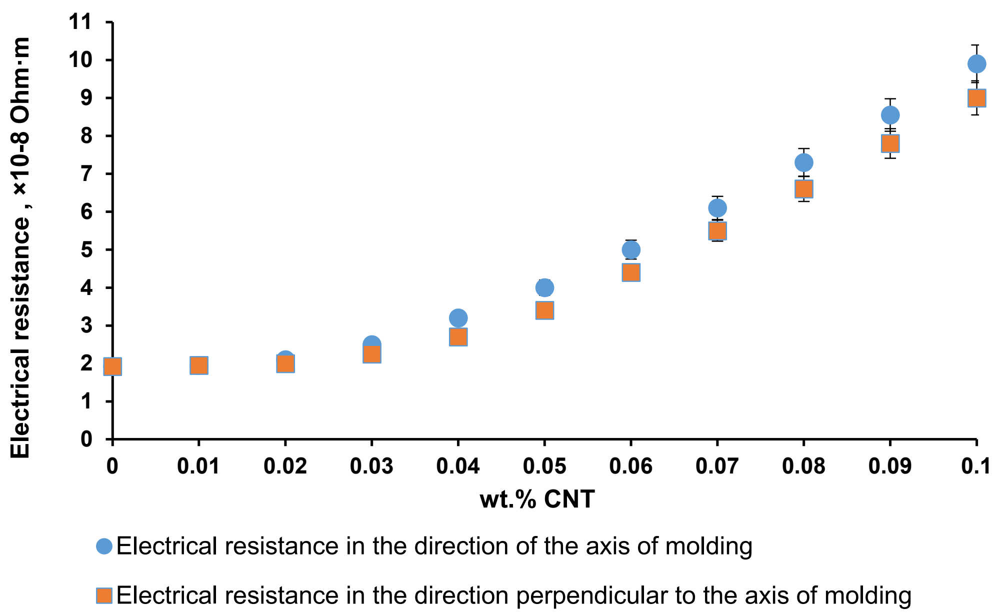

Fig. 2. Electrical resistance of the composite materials "copper – CNTs"

At the same time, with an increase in the concentration of CNTs in composites from 0.01 wt. % to 0.1 wt. % the values of the specific electrical resistance of composite materials increased: in the direction of the axis of molding from $1{,}95 \cdot 10^{-8}$ Ohm·m to $9{,}9 \cdot 10^{-8}$ Ohm·m; in the direction perpendicular to this axis from $1{,}95 \cdot 10^{-8}$ Ohm·m to $9 \cdot 10^{-8}$ Ohm·m. The electrical conductivity of these materials, determined in the direction of the molding, was in the range from $5{,}13 \cdot 10^{7}$ S/m to $1{,}01 \cdot 10^{7}$ S/m, and in the direction perpendicular to the molding, $5{,}13 \cdot 10^{7}$ S/m to $1{,}11 \cdot 10^{7}$ S/m. It should be noted that the anisotropy of the electrical properties of powder composites begins at a CNT content of 0,03 – 0,04 wt. %.

The deterioration of the electrical properties of composites is explained by the low electrical conductive properties of CNTs in comparison with the copper matrix. So the specific electrical resistance of CNT is $860 \cdot 10^{-6}$ Ohm·m that is two orders of magnitude larger than that of copper [16].

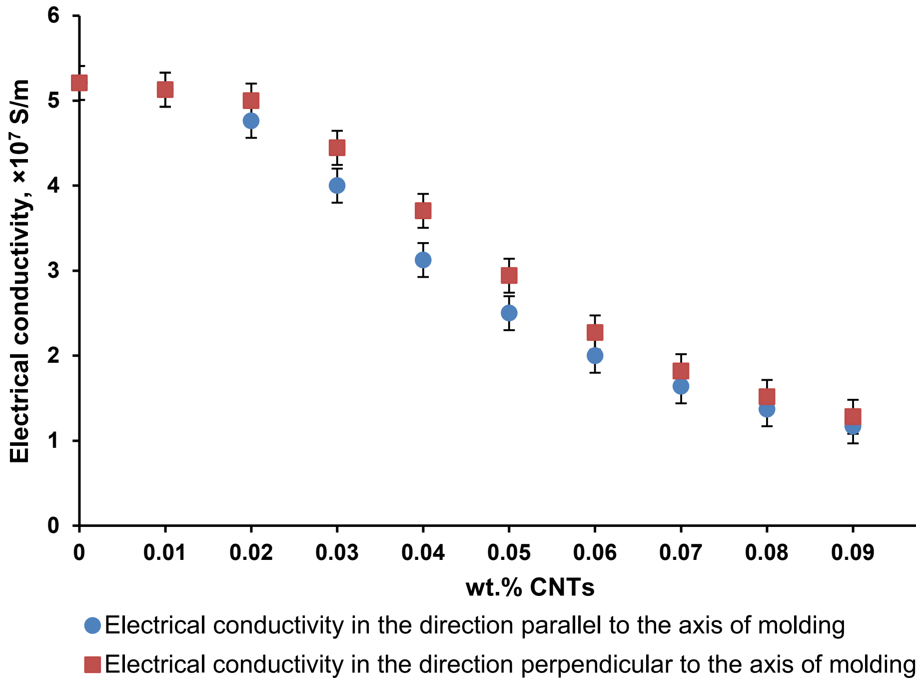

Fig. 3. Electrical conductivity of the composite materials "copper – CNTs"

4. Conclusions

In the present work demonstrated the obtaining the composite materials "copper – CNTs" with improved indices thermal properties compared to a sintered matrix containing no nanosized additions. It has been revealed that materials based on powder systems "copper – CNTs", which are obtained according to the powder metallurgy technology by electrocontact sintering, possess anisotropic thermal conductivity and electrical conductivity, since the values of the thermal conductivity coefficients and electrical conductivity measured in the direction parallel to the axis of molding differ from the values of the thermal conductivity coefficients and electrical conductivity measured in perpendicular direction to the indicated axis.

It is assumed that during uniaxial compression in the process of electrocontact sintering, the nanofiller in the form of CNTs is oriented in one direction, which leads to a change in the values of the studied characteristics of the composite materials in this direction.

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