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CHARACTERISATION OF Cu-CNTs COMPOSITE ELECTRICAL PROPERTIES IN ELEVATED TEMPERATURES

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The current trend towards nanotechnology creates possibilities for its use in materials science as manufacturing material with extraordinary properties, and is one of the goals for scientists in this field. Carbon nanotubes in particular are promising due to their electrical, thermal and mechanical properties, which have been of interest for researchers around the world. This paper focuses on the manufacturing process of the Cu-CNT composite via powder metallurgy and KOBO extrusion process, its further cold drawing process, and electrical resistance test at an elevated temperature. As obtained data proved, the higher the CNT content the lower the electrical resistance.

Keywords: Cu-CNTs composite, billet, wire, electrical resistance at elevated temperature, temperature, coefficient of resistance

INTRODUCTION

High mechanical, thermal and electrical properties of carbon nanotube composites (CNTs) [1-5] are a direct reason for worldwide research concerning the synthesis of CNTs metal matrix composites in order to enhance exploitation properties of currently used materials [6-11]. Particular interest of performed studies is concentrated to improve electrical properties of metal matrix composites [12], which are most of the time synthesized with the use of copper and copper alloys [13]. An analysis of literature indicates that this goal was not achieved in ambient temperature. In [14] authors showed that addition of max. 3 wt. % of MWCNTs to copper increases room temperature resistivity of material from 3,9 up to $5,1 \cdot 10^{-8}$ W·m. This is in concord with research results showed in [15], which proved that with an increase of CNTs volume fraction up to 20 %, electrical conductivity is decreasing down to 45 % IACS.

Latest studies on the electrical properties of Cu-CNTs composites showed, by contrast, that nanotubes addition to copper can increase electrical properties of the composite in elevated temperature, which is directly connected to electrical/thermal properties of CNTs and also other carbon based materials like graphene. In [16] authors showed that due to the lower CNTs temperature coefficient of resistance, conductivity of the Cu-CNTs composite, measured at the temperature of 80 °C, was at the same level as for reference copper sample.

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Furthermore, increase of the temperature up to 227 °C resulted in doubling of the composite conductivity value.

In this paper authors conducted studies on characterization of Cu-CNTs wires obtained by powder metallurgy process with CNTs content up to 1 wt. %. The powder metallurgy route comprised the mixing of copper powder and MWCNTs (nano carbon materials were provided by the research partner, Dr Krzysztof K. Koziol from University of Cambridge), compacting of obtained mixtures and KOBO [17-18] SPD extrusion of compacted billets. Next, obtained by extrusion, 4 mm rods were cold drawn to 2,4 mm and analyzed for their electrical properties in ambient temperature and also in elevated temperatures reaching 900 °C.

EXPERIMENTAL METHODS

Wires subjected to the electrical conductivity measurements were obtained with the use of powder metallurgy and following cold drawing process. The powder metallurgy route included ultrasonic mixing of commercial, medium density, dendritic copper powder and prealigned MWCNTs with outer diameter of approximately 60 nm and inner diameter 8 nm. Addition of CNTs in prepared powders was at the level of 0,2 wt. % and 1 wt. %. Obtained mixtures of Cu and MWCNTs were next subjected to compacting process at a 35 atm compacting pressure without final sintering of compacts. Additionally a sample compacted only from the dendritic copper powder was prepared as well as a reference material for further tests. Used and described method enabled obtaining 3 different 40 mm diameter and approximately 60 mm long billets (Figure 1), which were a base material for following KOBO extrusion process.

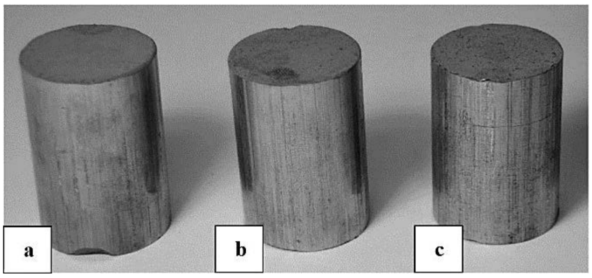

Figure 1 Billets (Ø40x60 mm) prepared for KOBO extrusion process; a) Pure dendritic Cu – reference sample, b) Cu + 0,2 wt. % of MWCNTs, c) Cu – 1 wt. % of MWCNTs

KOBO extrusion was conducted, after extended research on the optimization of all parameters, at an extrusion force of 1 000 kN, extrusion speed 0,5 mm/s, initial ingot temperature of 350 °C, and radial frequency of rotating die 5 Hz. Final diameter of extruded rods was set up at 4 mm, which translates into a strain coefficient of λ = 100. External surface of obtained wires was free of oxides due to use of secondary water cooling the extruded rod.

Scanning electron microscope (SEM) characterization (done on JEOL JEM-2 010 ARP microscope) of obtained wires, for fractures of rods (obtained in static tensile test), is shown in Figure 2. It can observe homogenous alignment of MWCNTs in copper – individual MWCNTs are visible within the matrix, and aligned in the axis of extrusion, and a static tensile test – which were the same. The above proves that both applied initial ultrasonic mixing of powders and SPD KOBO extrusion allowed even dispersion of carbon nanoparticles in a copper matrix.

The extruded rods were next cold drawn into 2,4 mm wires in order to improve surface quality and dimensional homogeneity of composites before electrical conductivity measurements. For this purpose, a new stand was designed and manufactured, which allowed to measure electrical resistance with the use of 4 point Kelvin resistance measurement system, in an argon atmosphere, up to the maximum working temperature of

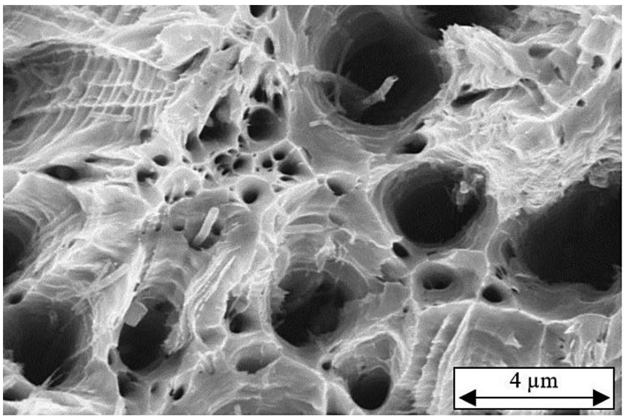

Figure 2 SEM characterization of Cu + 1 wt. % of MWCNTs rod fracture with visible homogenous dispersion of MWCNTs and alignment of carbon nanoparticles in extrusion direction

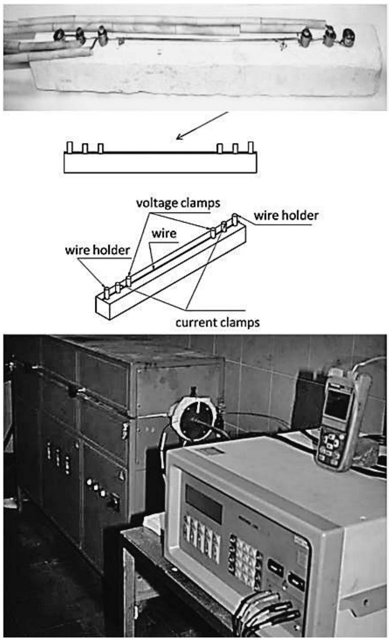

Figure 3 Stand for electrical resistance measurements in elevated temperatures

± 900 °C. The stand consisted of a tubular furnace, Buster RESISTOMAT device, a protective argon atmosphere installation, and a self-made wire holder made of Hakoplan insulating board (mixture of SiO_2 + CaO fibers), all shown below in Figure 3. The temperature of the wires during the tests was measured with the use of three separate type K thermocouples, installed in a furnace chamber (the furnace chamber was divided into three individual sections). For additional confirmation, a fourth external-type K thermocouple was used to measure the actual temperature of the tested samples during the tests.

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RESULTS AND DISCUSSION

Resistance measurements were conducted for wires of a total length of 500 mm and the measurement base was set up at 310 mm. the resistance of the wires was being evaluated approximately every 100 °C in a temperature range of 25 – 860 ^{o}C, after the stabilization of temperature 15 minutes before each measurement. The obtained resistance characteristics for all 3 types of materials are shown in Figure 4. An analysis of characteristics shows that reference copper sample and Cu + 0,2 wt. % of CNTs composite exhibit the same resistance in a function of temperature. A composite with 1 wt. % of CNTs up to 400 °C shows the same tendency, however at 400 °C resistance of Cu + 1 wt. % of CNTs sample starts to decrease in comparison to the other two materi-

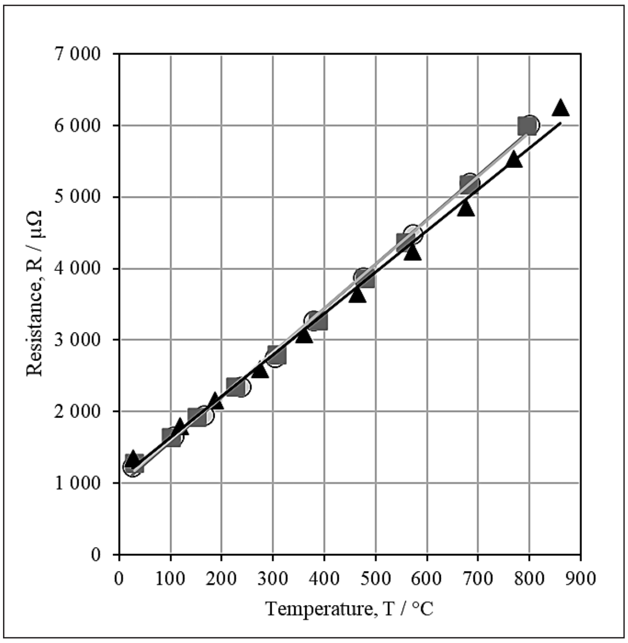

Figure 4 Resistance characteristics in function of temperature for tested materials

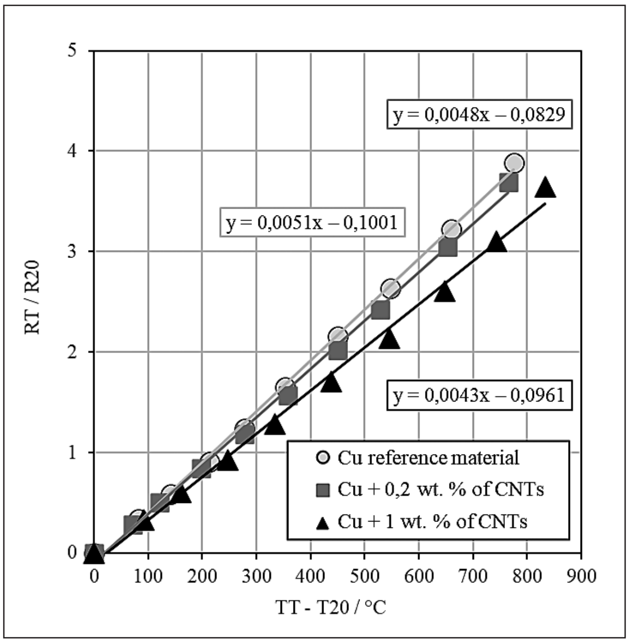

Figure 5 Graphical interpretation of thermal coefficient of resistance for analyzed materials

als. A further increase of temperature to approx. 800 °C resulted in continuous decrease of resistance with the maximal difference on final measurement at 800 °C at the level of 300 μΩ (5 700 μΩ for Cu + 1 wt. % of CNTs and 6 000 μΩ for pure copper and Cu + 0,2 wt. % of CNTs).

Based on the obtained resistance data, a graphical function was evaluated, according to the function presented below (1), in order to determine temperature coefficient of resistance for analyzed materials, which can be done by the determination of a linear curve and calculation of this curve inclination angle.

$$\left(\frac{R_t}{R_{20}}\right) - 1 = f(T_t - T_{20}) \qquad (1)$$

where:
R_t - resistance measured at given temperature,
R_{20}- resistance measured at ambient temperature (20 °C),
T_t - given temperature,
T_{20}- ambient temperature (20 °C).

The obtained research results in the form of resistance/temperature characteristic presented in Figure 5 allowed a confirmation that amounts of CNTs at the level of 1 wt. % and more, due to extremely low or even negative temperature coefficient of resistance of CNTs, in concord with the rule of mixture, will exhibit improved electrical properties at elevated temperatures.

CONCLUSION

Based on the conducted research it was empirically proved that electrical resistance of the Cu and Cu-CNT wires with the wt. % of nanotubes of 0,2 % and 1 % assumes a quasilinear nature at elevated temperatures.

Taking into consideration wires made of copper and Cu-CNT composite with 0,2 wt. % of nanotubes all the measured values appear to be very similar or even identical, however, the increase in content of nanotubes additive caused a significant decrease in the electrical resistance when measured over 400 °C up to 300 μΩ at the maximum measured temperature of 800 °C.

The calculated temperature coefficient of resistance, which for Cu-CNT composites is extremely low or even negative, explains the increased electrical conductivity at elevated temperatures.

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