1. Introduction

After the discovery of graphene and nanotubes, which possess unprecedented properties, an idea to combine different metals with new forms of carbon was established. The purpose was to increase the operating properties of obtained material (composite) compared to materials used so far. There are various methods for the synthesis of metallic materials with carbon, e.g. metallurgical method, powder metallurgy, thermal spray, electrochemical deposition and others [1-8, 10]. However, there is a significant difficulty in synthesis of metallic materials with carbon. In the case of metallurgical synthesis with copper, nanotubes and graphene are poorly wettable by liquid copper and refuse to integrate within its structure. A similar situation occurs in the process of electrochemical deposition of copper on the carbon material. Additionally the solubility of carbon in copper is very low, which makes further difficulties insynthesis processes of this type of materials [12]. Examined carbon materials have low density compared to the copper and they are high-melting, therefore they don’t react with the metal to form a composite. In recent years several papers describing and characterizing a metal-carbon composites were published. TH Nayfeh, AM Wiederholt claim in their patent that it is possible to increase the conductivity of carbon composites compared to pure copper by more than 10%. K.Jagannadham writes in his work about the increase of electrical conductivity of the obtained composite by 15% compared to copper [9]. TS Koltsova and his team postulate that the electrical properties of Cu–graphene and Cu-nanotubes composites may increase twice in the coming years [4]. As the literature and own...
researches show, there is a possibility to increase the quantity of carbon in copper. This is possible by using metallurgical method with appropriate process conditions for producing the copper-carbon composites [7,8,14]. Unfortunately, these researches did not show the results of electrical conductivity increase in the obtained composites in relation to the reference material.

Research of powder metallurgy of copper powders with graphene and carbon nanotubes using classic compression method showed no significant changes in properties of composites compared to the reference material [13]. The process of copper synthesis with different variety of carbon is still not well understood and knowledge of this subject is lacking.

The paper presents results of research on the possibility to obtain copper-graphene and copper-carbon nanotubes composites by mechanical alloying in the process of cold drawing of previously prepared graded materials. The paper presents the results of the electrical conductivity and structural analysis of fracture surfaces, obtained from tensile test for materials developed by a cold drawing process.

2. Experiment details

The research included mechanical synthesis of copper with carbon and copper with CNT’s. In the research authors used CuETP copper, graphene flakes and SWeNT SMW200 carbon nanotubes. Graphene flakes used for the mechanical synthesis were manufactured by Institute of Electronic Materials Technology and SWeNT SMW200 carbon nanotubes were purchased in SouthWest NanoTechnologies company. To obtain desired composites the following process was used: a rod with 200 mm length and diameter of 10 mm, was drilled axially to the depth of 60 mm with a 5 mm diameter of used drill. Carbon material was placed in the hole, filling 40 mm of it. During the filling process, carbon material was gradually compressed. At the end of the rod, copper chock with length of 50 mm was placed to prevent carbon material from displacing (superfluous chock part was cut after the process). Next obtained rods with Cu-graphene and Cu-CNT were hermetically closed (ends of rod were cold rolled) and then subjected to cold drawing process. Within the process 13 draws were conducted with average elongation factor of 1,2 resulting in a final wire with diameter of 2,953 mm. For drawing process, Petrofer Isolube lubricant was used.

Fig. 1. Copper rods with a carbon material

Figure 1. shows a rod with carbon material, subjected to drawing process.

For a comparison, solid CuETP copper rod was subjected to the same procedure.

Properties of carbon materials used for synthesis are shown in Table 1.

Copper used for synthesis as base material was in CuETP grade (electrolytic tough pitch copper) and it was obtained in classic Contirod process.

Structures of used carbon materials are shown in Figure 2.

![Fig. 1. Copper rods with a carbon material](image)

![Fig. 2. SEM structures of materials used for mechanical synthesis](image)

a) SWenT SMW200 nanotubes b) graphene

<table>
<thead>
<tr>
<th>Type of carbon</th>
<th>Graining/ tube length [µm]</th>
<th>Bucky Paper Resistance [Ω/□]</th>
<th>Specific surface area [m²/g]</th>
<th>Bulk Density [g/dm³]</th>
<th>Carbon content [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphene</td>
<td>0.283</td>
<td>0.101</td>
<td>-</td>
<td>-</td>
<td>99.7</td>
</tr>
<tr>
<td>CNT’s SWenT SMW 200</td>
<td>~4</td>
<td>~600</td>
<td>350</td>
<td>0.08</td>
<td>≥98</td>
</tr>
</tbody>
</table>

TABLE 1

Properties of graphene and SWenT SMW200 nanotubes
3. Research results and analysis

Obtained rods with 2,953mm diameter were prepared for SEM and optical microscopy analysis. Figure 3. shows cross-section and longitudinal section of the rods. From the analysis we can see that tube with 10mm diameter and wall thickness of 2,5 mm has undergone plastic deformation to diameter of 2,953 mm and wall thickness approx. 1 mm (total elongation factor of copper matrix = 9,7). Carbon material core was deformed from initial 5 mm diameter to 1 mm. After drawing process lengths of composite rods containing carbon material were approx. 400 mm.

Both Cu-graphene and Cu-CNT rods were subjected to electrical conductivity tests. Studies of electrical properties were performed using 4-wire Kelvin Thomson bridge with the use of High-Precision Automatic Inspection and Test Unit for Electrical Resistance Testing RESISTOMAT Model 2304-Buster. Table 2. shows results of conducted electrical properties measurements for both composite rods and base material. The analysis has shown that rod with graphene has the lowest conductivity - 46,3 MS/m. A Cu-CNT rod has electrical conductivity of 51,17 MS/m, which is 5MS/m more than Cu-graphene rod. Pure CuETP copper rod conductivity is exceeding 58M/m which is a typical result for material in this grade. Performed tests showed that carbon material causes differences in electrical conductivity of obtained composites, depending on used carbon material.

If we assume that carbon core does not influence electrical current conduction then conductivity of Cu matrix should be the same for Cu-graphene and Cu-CNT rods, and it should be greater than 58MS/m, since both of them have the same wall thickness and diameter. Calculation has shown that mentioned property does not hold, since electrical conductivity of Cu tube in Cu-graphene composite is 52,3MS/m and conductivity of Cu-CNT is 57,8 MS/m being close to pure copper conductivity. It means that in the process of sample deforming, non-conductive carbon material particles were built into Cu-graphene composite matrix material, decreasing the electrical conductivity of the matrix.

It is probably caused by lack of electrical contact between copper and graphene surfaces of built-into copper (pressed) graphene particles, where preferential flow of electrons should occur.

Both Cu-graphene and Cu-CNT rods were subjected to tensile test using material testing machine to obtain clean fractures, which were next subjected to microstructure analysis. SEM analysis has shown that significant areas of graphene particles pressed into the matrix can be found in copper structure of Cu-CNT composite. Figure 4. shows structure of Cu-graphene composite with visible graphene particle pressed into copper matrix. It is a confirmation of graphene particles presence in copper structure, however without any improve in electrical conductivity of composite. To make it happen, electrical contact of copper atoms with graphene atoms is required. This contact may be possible by using surface activated carbon material with copper particles. High pressure of copper matrix on surface activated carbon material makes connection of copper matrix and atoms of surface activated carbon material particles possible. As a result (assuming that carbon material has higher electrical conductivity than copper matrix) we can get better

<table>
<thead>
<tr>
<th>Material</th>
<th>Resistivity of the wire (nΩm)</th>
<th>Electrical conductivity of the wire (MS/m)</th>
<th>Calculated electrical conductivity of matrix (MS/m)</th>
<th>Wire diameter (mm)</th>
<th>Wire cross-section (mm²)</th>
<th>Resistance of the wire (µΩ)</th>
<th>Length of the measurement base (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-CNT's</td>
<td>19,544</td>
<td>51,17</td>
<td>57,8</td>
<td>2,953</td>
<td>6,8453</td>
<td>571</td>
<td>0,2</td>
</tr>
<tr>
<td>Cu-grafen</td>
<td>21,597</td>
<td>46,30</td>
<td>52,3</td>
<td>2,953</td>
<td>6,8453</td>
<td>631</td>
<td>0,2</td>
</tr>
<tr>
<td>Based material Cu</td>
<td>17,113</td>
<td>58,43</td>
<td>-</td>
<td>2,953</td>
<td>6,8453</td>
<td>500</td>
<td>0,2</td>
</tr>
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</table>
electrical properties of a composite. In Cu-CNT composite case, nanotubes particles pressed into copper structure cannot be observed. Figure 5. shows microstructure of Cu-CNT composite. It explains the observation that electrical conductivity of copper part of composite is close to the value for pure copper.

4. Conclusion

1. The research has shown that during the cold drawing process of copper-graphene and copper-CNT’s graded materials simultaneous deformation of copper matrix and carbon components occurs, resulting in wires with core made from carbon material and copper in the form of tube with homogeneous diameter and wall thickness.

2. Obtained composites have lower electrical properties in comparison to tested CuETP base material.

3. The scanning electron microscopy research have shown that in the copper matrix of Cu-graphene composite, graphene particles are pressed and solid with Cu matrix. It is postulated that these particles have no electrical connection with matrix thus constituting barriers to conduction of electricity, although, as it is generally known, graphene is an excellent electrical conductor.

4. In the Cu-CNT’s composite no nanotubes particles solid with Cu matrix were detected, which results - as seen from the calculations - in high (close to pure copper) electrical conductivity of the matrix.

5. Increase in the electrical properties of copper by mechanical alloying can occur by insertion of vocationally activated (by a copper atoms) graphene or nanotubes particles in its structure. At high pressures occurring during the drawing process it allows to create a solid connection of Cu matrix with copper atoms present on the surface of carbon materials.

Acknowledgements

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REFERENCES


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