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MECHANICAL PROPERTIES OF GRAPHENE OXIDE–COPPER COMPOSITES

Due to their characteristics, sintered Cu-C composites are materials used in electrical equipment. These characteristics include high electrical conductivity, thermal conductivity and excellent resistance to abrasion. Currently, graphite nanopowder is used successfully as a carbon material. Metal-graphite, which is created on its basis, exists in different proportions of graphite to metal. A larger graphite content has a positive effect on smaller wear of commutators and rings. In contrast, a material with a higher copper content is used at high current densities. An example of such machines is a DC motor starter characterized by low voltage and large current.

Tribological properties of Cu-C composites depend on the form of carbon they include. Owing to the capability to manufacture graphene, it has become possible to produce composites with its content. The present study tested the effect of a graphene oxide content on tribological properties in contact with steel. Tests were conducted on a ball-on-disk apparatus in conditions of dry friction. Microscopic observation was performed on the Hitachi SU70 field emission electron microscope. EDS analyses were performed using the Thermo Scientific X-ray Microanalysis system. Disk wear and surface geometrical structure parameters (SGP) of the samples after tribological tests were determined on the basis of measurements made on the Talysurf 3D contact profilometer from Taylor Hobson.

Keywords: composites of copper, graphene oxide, surface microgeomety, tribological properties

1. Introduction

The energy, electronic and electrical markets determine the use of new species of copper (i.e. oxygen free copper of the following types: Cu-OFE (Oxygen Free Electronic Copper) and Cu-ETP (Electrolytic Tough Pitch Copper)) or Cu-C composites (where graphite, carbon nanotubes, graphene oxide or glassy carbon are used as carbon) which are responsible for high electrical and thermal conductivity, mechanical strength, corrosion and hydrogen resistance [1-2]. Copper, depending on the way it is obtained, is divided into:
- raw (blister or anode)
- refined and remelted (oxygen free, oxygen and deoxygenated) used mainly in energy and rail industry in the production of cables, wires [1].

Oxygen free copper is used for structural elements of vacuum tubes and vacuum apparatus, in electrical wires and so on. The other types of copper, depending on purity, are used in the preparation of various structural components and are processed into alloys or galvanized coatings [3]. Copper used in abrasive composite materials belongs to the group of enhancers and is used in the form of fibres and powder. It is responsible for both the mechanical strength of such materials and, at the same time, a temperature decrease in the contact area, which are connected indirectly with good thermal conductivity properties [4,5]. In the process of composite manufacturing, the type of raw materials used and the degree of their dispersing in the whole volume as well as the way of combining the ingredients are of great importance [2]. Constructing metal composites that contain carbon particles poses technological problems due to their poor wettability and lack of interaction with the matrix. Internal stresses are generated during production which result from mechanical and thermal differences in the properties of the used raw materials [2,6].

2. Experimental

Tribological and stereometric tests were carried out on a graphene-copper material. Composites were based on dendritic copper with a grain size of approx. 40 µm and subsequently included 0 (sample base), 0.5 and 1% of rGO (thermally reduced graphene oxide). Samples with rGO were mixed in a static mixer with the remaining amount of base for about 3-4 hours and then transferred into the hydraulic press mold. Thus prepared moldings were sintered at max. 800 °C using soot as backfill. For the obtained composite samples, bulk density, resistivity and Shore hardness were determined. The results are given in Table 1. The hardness was measured using Shore method due to plasticity of the obtained materials.

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Characteristics of the obtained composites

	Bulk density [g/cm³]	Relative density 20°C	Resistivity, r 10-6 [Ω·m]	Shore hardness, [Sh]
Cu + 0% rGO	7.59±0.15	7.60±0.15	1.71±0.06	11±0.25
Cu + 0.5% rGO	7.15±0.15	7.16±0.15	2.80±0.06	11±0.25
Cu + 1.0% rGO	6.85±0.15	6.86±0.15	3.40±0.06	14±0.25

T-01 apparatus, ball-on-disk type, was used in order to carry out tribological tests. Tribological characteristics were recorded under conditions of dry friction with the following parameters: slip of 0.1 m/s, load of 10 N, friction distance of 1000 m. The diameter of the friction track amounted to 24 mm. 52100 steel balls with a diameter of 10 mm were the tribological partner material. Room conditions were maintained in accordance with the recommendations of the VAMAS technical note [7]: humidity - 50±10%, the ambient temperature - 23±1°C.

The intensity of volume consumption of the samples (shields) and geometrical structure parameters of the SGP surface of the samples after tribological tests were determined on the basis of 3D measurements made on the Talysurf Series II contact profilometer from Taylor Hobson. Surface microscopic analysis of composites was performed using images taken with the Hitachi SU 70 electron microscope with a field emission together with the Thermo Scientific X-ray microanalysis system, on which EDS analyses were conducted.

3. Results and discussion

Microscopic observation was performed in order to confirm the presence of rGO on the composite surface. Sample images of the surface prepared for cooperation together with the arrangement of graphene oxide flakes are provided in Fig. 1. The distribution of small cavities and holes is stochastic. During observation no rGO flakes protruding from the composite were noticed. This proves that there occurred large forces during the polishing process, which was necessary to prepare the samples. The only evidence of the occurrence of graphene visible on SEM observations were cracked fragments (looked like a flaky shell) on the surfaces of the samples (Fig. 2).
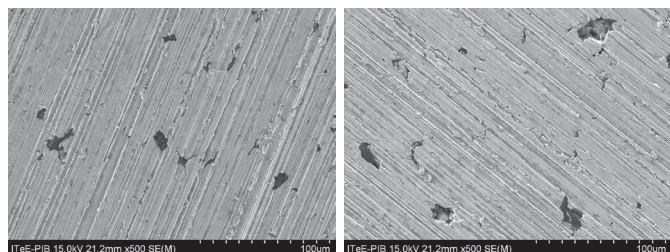

Fig. 1. SEM images of the composite surfaces with the distribution of graphene oxide particles. Visible microcraters in the matrix material

Darker places occurring randomly in Fig. 1 are losses in the matrix material. Closer observation revealed that there was no copper material separation only in a small number of cases of edge alignment of the particles. EDS analysis enabled to confirm the presence of graphene oxide.
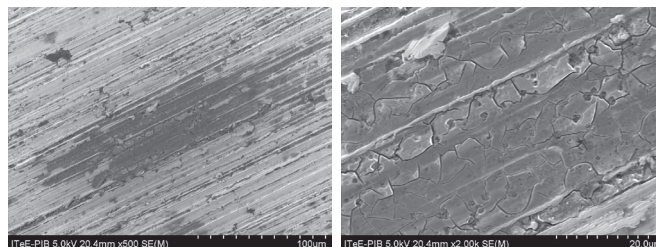

Fig. 2. SEM images of samples prepared for tribological tests. In this example can be noted graphene oxide particles arranged parallel to the surface

There was no need to identify a graphene oxide flakes because the samples were compacted and sintered from known materials only. Fig. 3 shows the analysis of a sample cavity resulting from plucking the matrix material. The results clearly show the carbonaceous material located on the cavity walls. Additionally, there followed point analyses (Fig. 4a) of the elemental composition of the surface of similar cavities and flakes present on the surface (as in Fig. 2). The tests performed on the matrix material showed a different elemental composition and a low carbon content (Fig. 4b).
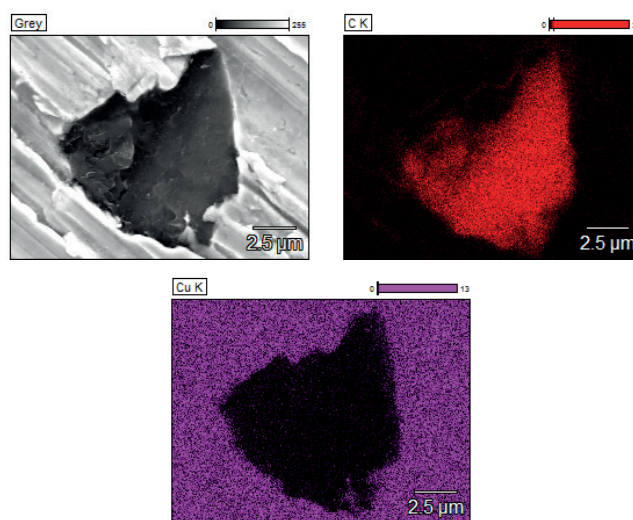

Fig. 3. Distribution of copper and carbon elements in the hole

Tribological tests were preceded by the surface geometric texture study. Mainly amplitude parameters were analysed. No significant differences in excess of 20% of the value between individual samples are observed on the graphs of the parameters: Sa (arithmetic mean deviation of the surface), Sq (root-mean-square deviation of the surface), Sp (maximum height of summits) (Fig. 5). Only in the case of the base material there was a greater value of Sp with respect to the composites. Since this parameter is strongly dependent on the individual summits

in the material, it does not prove any significant differences between the surfaces prepared for the test.
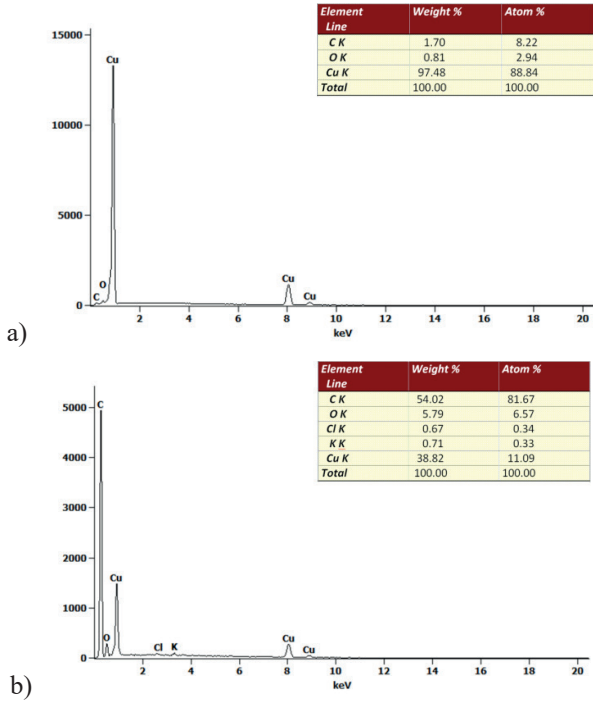

Element Line	Weight %	Atom %
C K	1.70	8.22
O K	0.81	2.94
Cu K	97.48	88.84
Total	100.00	100.00

Element Line	Weight %	Atom %
C K	54.02	81.67
O K	5.79	6.57
Cl K	0.67	0.34
K K	0.71	0.33
Cu K	38.82	11.09
Total	100.00	100.00

Fig. 4. Analysis of the elemental composition a) on the matrix material surface; b) on the side surface of the hole
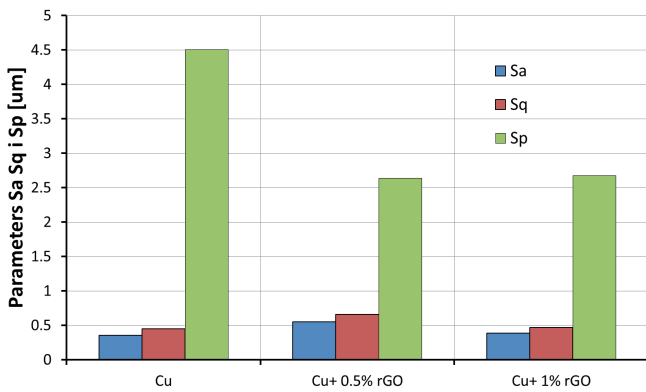
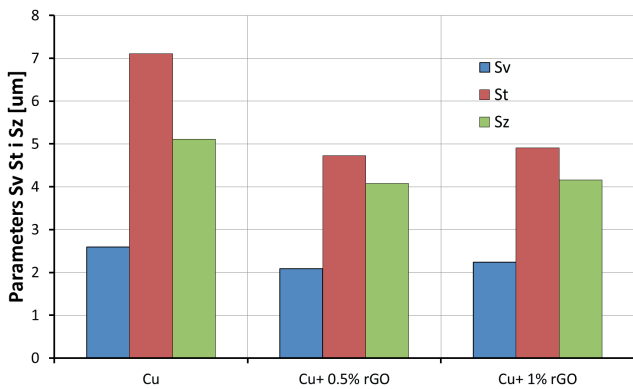Fig. 5. Values of the parameters Sa, Sq and Sp for the top layer

Fig. 6. Values of the parameters Sv, St and Sz for the top layer

When analysing the other parameters such as: Sv (maximum depth of valleys), St (total height of the surface), Sz (ten point height of the surface), similar conclusions are drawn as in the case of the previously analysed parameters (Fig. 6). Since the parameters Sp and St are strongly correlated, the relationship between them was observed in the analysed case. The parameter St for the base material has a higher value than for the composites.

The parameters Ssk (skewness of the topography height distribution) and Sku (kurtosis of the topography height distribution) are important because of their low correlation with the other amplitude parameters [8]. They are sensitive to the characteristic peaks and cavities, thus allowing for detailing the information on the test surface shape. The values of Ssk oscillating around zero and the low value of Sku for composites indicate an area with distinct periodicity of traces (Fig. 7). In the case of the base material, it can be said that the sample surface is smooth with flat peaks and small dominant cavities.
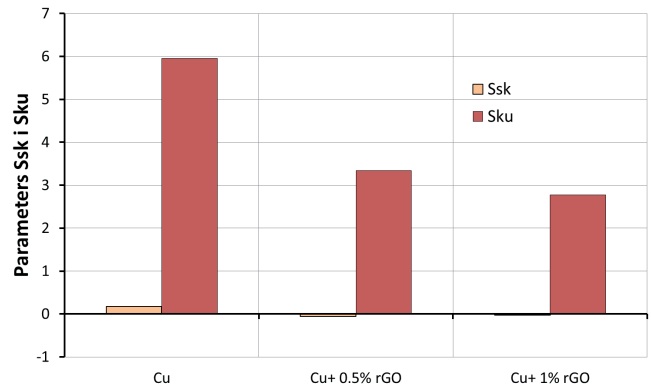

Fig. 7. Values of the parameters Ssk and Sku for the top layer

Tribological tests were conducted to determine the changes in tribological characteristics when modifying dendritic copper by introducing thermally reduced graphene oxide. The appearance of samples after the first series of measurements is shown in Fig. 8. Clear traces of friction tracks on the test shields and low wear observed on the surface of 52100 steel balls testify to the significantly lower abrasive wear resistance of composite materials in comparison to the base material. The longitudinal trace of cooperation present on the balls (Fig. 9) and their unregisterable mass wear confirm that copper-based materials are the weak material in this type of friction nodes.

The wear characteristics of the shield material were determined based on the friction track by measuring its width in several places perpendicular to the cooperation trace. An example of the measurement is presented in Fig. 10. When analysing the friction track width values for each material, it can be said that they differ considerably (Fig. 11). In order to improve the quality of results, at least a dozen repetitions should be performed for the different options along with the elimination of extreme values. The friction track width, which characterizes the intensity of the shield material wear, does not indicate very significant differences between

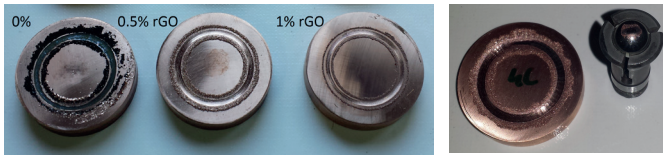the materials. Slightly greater friction track width can be observed for the composite containing 0.5% of rGO.

Fig. 8. Shields after the first series of tribological tests

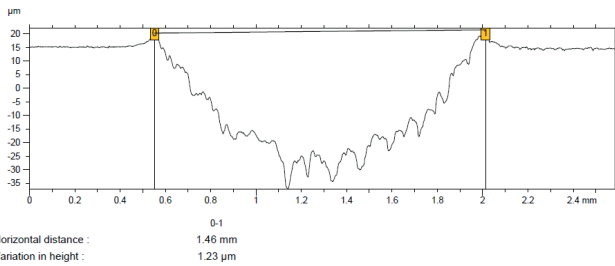Fig. 9. Appearance of the shield and ball after a tribological test

Horizontal distance :   1.46 mm
Variation in height :   1.23 µm

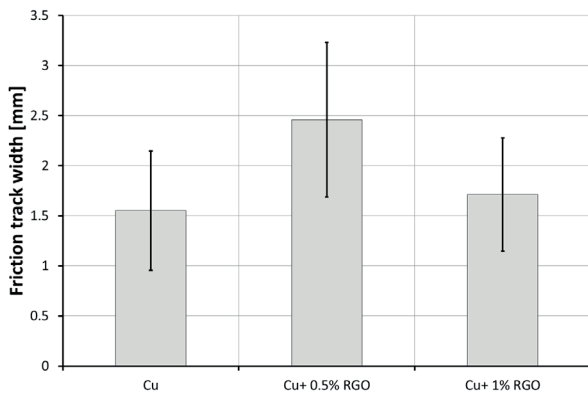Fig. 10. Measurement of the wear track width

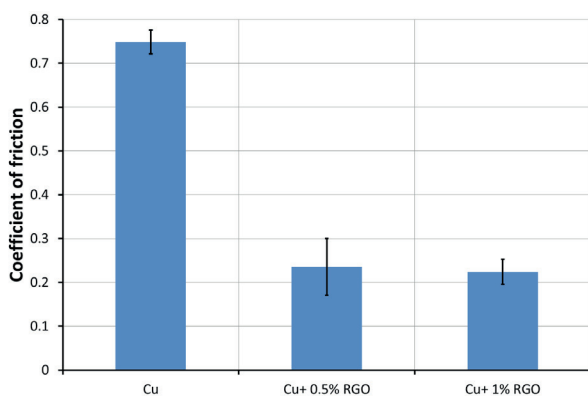Fig. 11. Friction track width depending on the material type

Fig. 12. Mean values of the coefficient of friction for the tested options

Significant differences between the base material and materials containing rGO are observed in the case of the coefficient of friction (Fig. 12). Tribological pairs with composites containing thermally reduced graphene oxide were characterized by almost three times lower coefficient of friction than the base material in cooperation with the steel balls. A similar conclusion can be reached by analyzing the graphs of friction force as a function of cooperation time (Fig. 13).

The friction force value for almost the entire tribological test of the base combination (copper-steel) is three times greater than for the combination of the composite and rGO. It follows that rGO, like other carbonaceous materials, e.g. graphite, can be used to reduce frictional resistance in the kinematic nodes consisting of copper composites and steel partners.
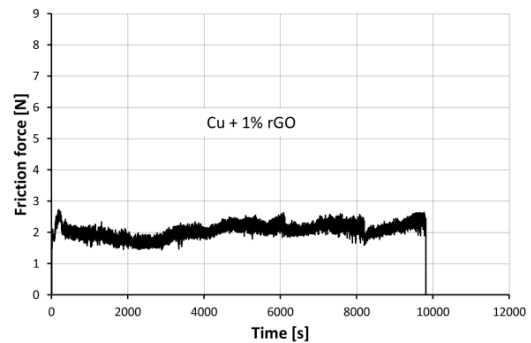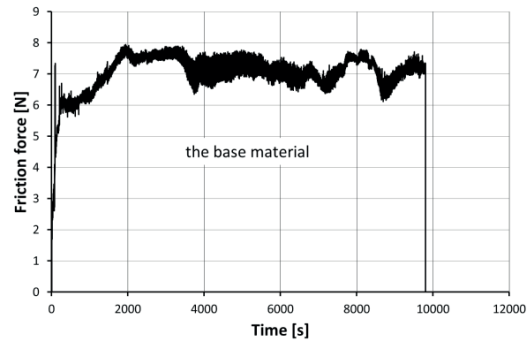

Fig. 13. Characteristics of the friction force for the base material and 1% of rGO as a function of cooperation time

4. Conclusions

The composites based on dendritic copper and thermally reduced graphene oxide presented in this paper are characterized by the stochastic distribution of the reinforcing material flakes. It is this characteristic structure that causes, during surface preparation, plucking of the matrix material fragments contained between the graphene oxide and the material surface. EDS analysis confirms the presence of the carbonaceous material on the walls of the holes in the material surface and on the technically prepared top layer.

The geometric structure of the top layer of all materials is similar, which the analysed amplitude parameters confirm. Further analysis of the parameters indicates that the composites have a surface with clear periodicity of traces. In the case of the base material, it can be said that the sample surface is smooth with flat peaks and small dominant cavities.

The tribological tests performed under standardized parameters have shown that the copper-based composites modified by the addition of 0.5 and 1% of rGO have the coefficient of friction which is almost three times smaller than for the matrix material without reinforcement. Unfortunately, the intensity of shield material wear changes to the disadvantage of the composites. For the rGO content of 0.5% there is even slightly greater width of the cooperation trace. Reduction in

the coefficient of friction and maintenance of the similar wear intensity are obtained in the case of the composite containing 1% of rGO.

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