Electrical properties of Ag-C and Cu-C contact materials

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Abstract: Industrial production of various forms of carbon, including graphene, nanotubes, and fullerenes, expanded the range of composite materials for which they constitute the reinforcing phase of metallic matrices. It was expected that the graphene form (GF) reinforcing phase would improve the electrical, thermal, and mechanical properties of such composites. Composites with Cu and Ag matrices, having a wide range of applications in micro- and optoelectronics, aerospace and automotive industries, proved to be particularly promising. A specific group of these composites is used in a variety of electrical circuits for electrical switches, contactors, circuit breakers, voltage regulators, and arcing tips. Among others, this group includes composites such as Ag-W, Ag-WC, Ag-WC-C, or Cu-W. The presented results of electrical tests performed for the Cu (Ag) /GF composites extend the number of properties of materials used in air and vacuum electrical contacts.

Key words: contact materials, composite materials, graphene form

Właściwości elektryczne materiałów stykowych Ag-C i Cu-C

Streszczenie: Przemysłowe otrzymywanie rozmaitych form węgla – grafenu, nanorurek, fulerenów – rozszerzyło gamę materiałów kompozytowych, w których stanowią one fazę wzmacniającą matryc metalicznych. Oczekiwano, że grafenowa faza wzmacniająca polepszy cechy elektryczne, cieplne i wytrzymałościowe takich kompozytów. Szczególnie obiecującymi są kompozyty z matrycami Cu lub Ag znajdujące zastosowania w mikroelektronice i optoelektronice, przemysłach lotniczym i samochodowym. Specyficzna grupa tych kompozytów stosowana jest w rozmaitych elementach układów elektrycznych jako wyłączniki etc. Do grupy tej należą między innymi kompozyty Ag-W; Ag-WC, Ag-WC-C lub Cu-W. Prezentowane wyniki badań elektrycznych kompozytów Cu(Ag)/GF poszerzają zbiór właściwości materiałów stosowanych w powietrznych i próżniowych stykach elektrycznych.

Słowa kluczowe: materiały stykowe, materiały kompozytowe, formy grafenowe

1. Introduction

Composite materials with Cu and Ag matrices are used as electrical contacts in a number of applications such as electrical switches, residual current circuit breakers, contactors, automatic circuit breakers, voltage regulators, relays and current dividers, as well as blade electrodes. Depending on the target application, the incorporation of reinforcing phases of contact materials can be different, e.g. W[1], WC [2], Ni [3], SnO_2 [4], and C [5 - 6]. Until now, carbon forms used in contact composite materials included diverse allotropic carbon structures [7 - 8], e.g. graphite in the form of fibers, grains, and flakes [9]. Materials found in electrical contacts require both coexistence and complementarity of qualities such as good thermal conductivity, resistance to wear and deformation, erosion and welding resistance, as well as low and stable electrical resistance. Ag-C composites with the carbon content of around (3 ÷ 5)% wt. are used in air-connectors. They are characterized by high resistance to welding, as well as low contact and corrosion resistance in the air environment. Cu-C (3 ÷ 5)% wt. composite materials are used in welding-resistant contacts for currents in the 30 - 100 kA range. The relatively low hardness and strength of these materials make them easy to separate when serving as contacts. They also oxidize copper easily and, in consequence, are most frequently used either in vacuum or oily electrical systems. Experimental work on graphene (G) [10 - 11] and its geometrical forms (GF), i.e. nanotubes (CNT) [12] and graphene powder (GP) [13], and Cu(Ag)/CNT(GP) composite materials [14 - 15], as well as a strong commercial market of graphene materials, make it possible to carry out research work focused on the application of Ag-GF and Cu-GF contacts. There are several reasons, why the introduction of carbon based nanofillers (nanofibers, nanotubes) into metallic matrices is a difficult task [16]. The results presented in this paper are closely related to the research into arc erosion and electrical resistance of the Cu-3% v CNT(GP) and Ag-3% v CNT(GP) contacts. The volume share of 3% v CNT(GF) was derived from the correlation between thermal conductivity and hardness of the tested composite materials. More extensively, the problems regarding the preparation and properties of composites reinforced with nanostuctures are shown in [8].

This sequence of the procedures for preparing the composites, helped to obtain materials with high density, hardness and thermal conductivity. The features that are important for contact materials.

2. Experimental procedure

2.1. Materials

The granulometric characteristics of the starting materials are shown in Tab. 1, whereas Fig. 1 presents the Raman spectra of both graphene forms used before sonication process. Results coming from Renishaw inVia Confocal Raman Microscope with laser ND:YAG of 532 nm line.

The analysis of the spectra proved MWNTs to be a material variation of reduced graphene oxide, while GP is a collection of objects consisting of several individual flakes of defected graphene. Both forms of graphene used in the study were dry forms of carbon. Multi-walled carbon nanotubes (MWNTs) appeared as heavily entangled balls with diameters larger than 30 microns. Graphene nanopowder showed up in the form of aggregated clusters of more than 5 microns in diameter. It can be assumed from the analyses that the planes of carbon are strongly defected, as evidenced by the high intensity of modules D and D '. Activation mode D" is related to the concentration of sp3 hybridized atoms and is proportional to the number of defects in the planes of carbon. 2D a single band, extended (compared to the SLG) indicates the material thickness of layers 4 - 6 different than the Bernal arrangement (ABAB, as in graphite). Intensity ratio I2D / IG is in the range 0.4 - 0.6. Intensity ratio ID / IG is in the range 0.4 - 0.8. The distance between the defects ranges from 50 to 25 nm, with a substantial edge defects (mod D '). Shift modes at positions G and 2D indicate the stress occurring in the sample.

On average, the thermal conductivity of an aggregated or entangled graphene material is two orders lower than for pure graphene – ~ 5500 $W(mK)^{-1}$. Its electrical conductivity is reduced to a lesser, but equally important extent when compared to pure graphene – ~ 10^7 Sm^{-1}. To produce a composite contact material, it was therefore necessery to adopt procedures entailing detangling and separation of carbon forms. These procedures consisted in breaking up large concentrations of carbon forms in the sound field. The pulse sound field working in the 1 sec/1 sec ON/OFF mode for 4 minutes exerted influence on MWNTs in the aqueous micellar solution of Triton X-100 as well as GP in pure isopropyl alcohol. The solutions were then centrifuged at 5000 rpm, at intervals from 10 to 20 minutes. The concentrations of the solutions after centrifugation were determined spectrophotometrically by comparing the transmission of light for the known GF masses to the transmission for respective solutions after centrifugation. MWNTs solutions were filtered through a layer of Cu or Ag powders, and washed several times with deionized

Tab. 1. Details of raw materials.
Tab. 1. Charakterystyka materiałów wyjściowych.

Materials		Producer	Geometric characteristics of materials (data of producers)
Ag	Ag (1000)	Innovator	10 μm
Cu	Cu	Aldrich	10 μm
C	Multiwalls nanotubes (MWNTs)	Aldrich	Φ 110 - 170 nm, length 5 - 9 μm
	Graphene nanopowder (GP)	Skayspring Nanomaterials Inc.	1 - 5 nm Surface area 750 m^2/g

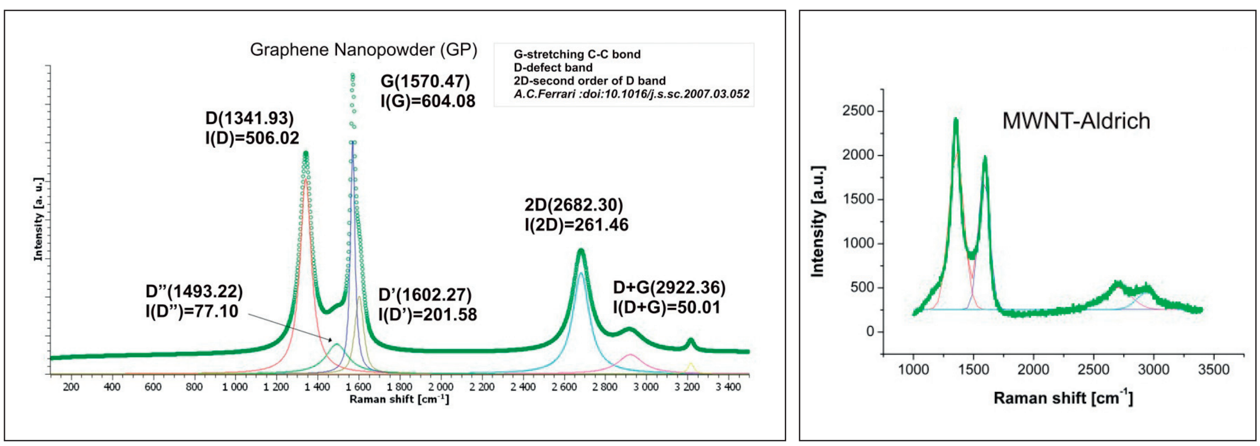

Fig. 1. Raman spectrum of graphene materials.
Rys. 1. Ramanowskie widma materiałów grafenowych.

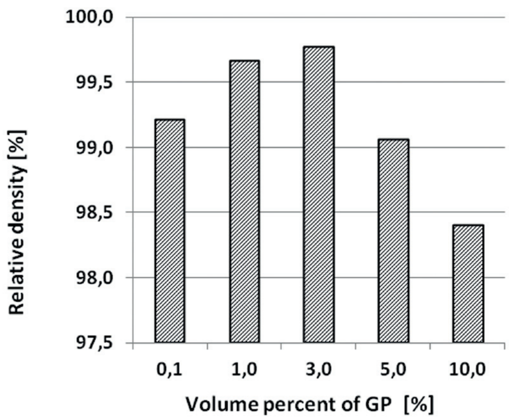

Fig. 2. Density of Cu-GP composites with different GP content.
Rys. 2. Gęstość kompozytów Cu-GP o różnej zawartości GP.

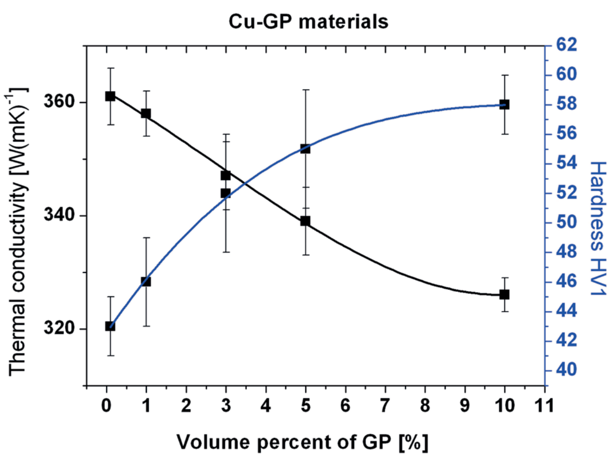

Fig. 3. Correlation of thermal conductivity and hardness for composites with different content of GP.
Rys. 3. Korelacje pomiędzy przewodnictwem cieplnym i twardością kompozytów o różnej zawartości GP.

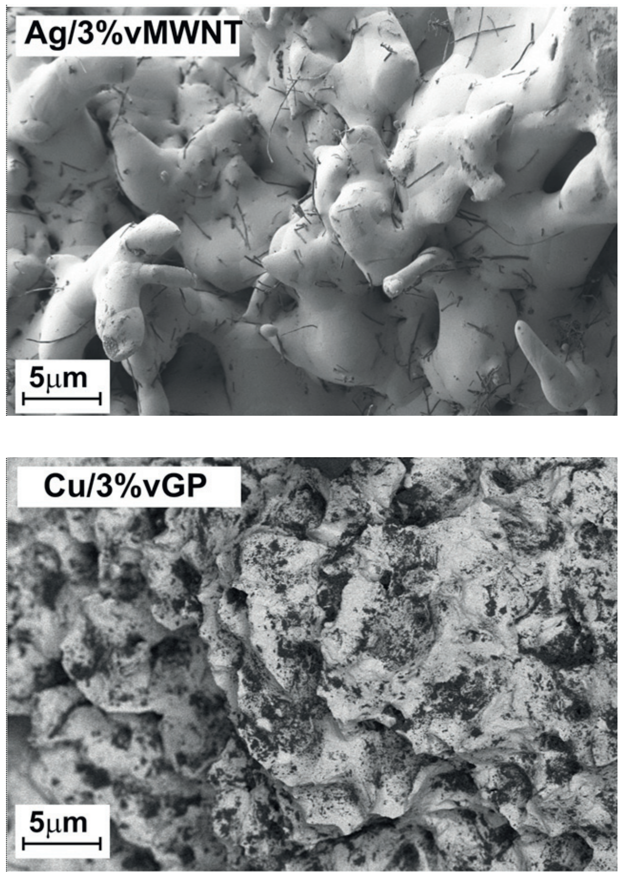

Fig. 4. SEM images of the composite fractures of Ag/3%v MWNTs and Cu/3% v GP.
Rys. 4. Obrazy SEM przełomów kompozytów Ag/3%v MWNTs and Cu/3% v GP.

water. GP solutions in ethanol were mixed with the powder and evaporated. The resultant composite powders with Ag and Cu matrices, in the (0.1 ÷ 10)% v GP and (0.1 ÷ 5)% v MWNTs range, were sintered by the Spark Plasma Sintering (SPS) method. The sintering conditions were as follows: pressure 50 MPa; time 15 min; vacuum 10^{-5} hPa, and temperatures Ag/GF-850°C; Cu/GF-950°C. The density of composite materials reached 99% of the theoretical density (Fig. 2). Thermal conductivity and hardness were measured for the obtained composites. Fig. 3 shows the interrelationship between the thermal conductivity of the Cu-GP composite and its hardness as a function of the percentage share of the graphene form.

The analysis of the graph shows that for this particular relationship the optimum conditions are offered by the Cu3.5% v GP composite. The results of similar analyses performed for the Cu MWNTs and Ag-GP(MWNTs) turned out to be a set of values in the (2.7 ÷ 4.3)% v GP (MWNTs) range for both Cu or Ag matrices. Therefore, electrical contacts were tested using Cu and Ag composites containing 3% of the volumetric reinforcing phases of the GP and MWNTs. The representative images showing the structures of Ag/3% v MWNTs and Cu/3% v GP composite can be found in Fig. 4. Embedded in the matrix the nanometric carbon structures were invisible on metallographic cross section but could be seen on composite fractures. It should be noted that there is good adhesion and uniform distribution of MWNTs in the silver matrix. A similar character was observed for graphene nanopowder. In the copper matrix flake clusters can be observed, decorating the grain boundaries of copper. Also, the nanotubes in the copper matrix form bunches with distinctive pores on the copper-MWNT interfaces.

2.1. Electrical test

Plates in the form of cylinders having a diameter of 8 mm and a height of 1 mm, sintered by SPS, were used for the electrical tests. Research into arc erosion and contact resistance was carried out using the original computer test system, designed and built in the Department of Electrical Apparatus of the Lodz University of Technology [7, 16]. The current path of the tester is equipped with two contact handles. A single, 3-second cycle of the experiment consists in switching the contact tips on and off. The device has 10 identical yet independent current paths.

Tab. 2. Mechanical and electrical parameters of testing device.
Tab. 2. Mechaniczne i elektryczne parametry testera.

Mechanical parameters	**Unit**	**Value**
Contact diameter	mm	8
Contact gap	mm	5
Contact tilt	mm	2
Contact tip pressure force	N	10
Opening spring force	N	30
Electrical parameters	**Unit**	**Value**
Test voltage	V, Hz	230, 50
Test current (peak value)	A (AC)	60
Circuit power coefficient	-	1
Operating frequency	cycles/h	1200

The whole system is controlled with copyright software in the automatic mode. The testing device is based on a computer system for measurement data (current, voltage) acquisition. Basic parameters of mechanical and electrical tests are provided in Tab. 2.

The parameter determining the level of arc erosion is the weight loss of the contacts. In general, the energy of an electric arc and mechanical opening cause detachment of the material from the surface of the contacts. The loss of weight as a function of the number of cycles is a measure of the electrical and mechanical resistance of the contact to the electric arc. The measurement of contact resistance indicates changes in the subsurface layer of the contact material, affecting the contact resistance. The voltage drop over the electrical contact as well as its resistance have an influence on the circuit operation, and consequently on the temperature and the safety of electrical devices that operate in this circuit. Contact resistance was measured experimentally based on the voltage drop across a pair of closed contacts and the flow of the 5 A electric current amperage. This measurement was carried out as a function of the number of cycles.

3. Results

In total, the number of the performed switching cycles for the Ag-matrix composite was $N = 10^5$. For Cu-matrix composites the number of $N = 10^4$ cycles was the upper limit from the point of view of arc erosion resistance. The representative images of tip surfaces after the end of the test with the maximum number of cycles are presented in Fig. 5. Differences in tip surface morphology are clearly seen in Fig. 5a. The contact surface of the Ag3% v GP composite has numerous small craters and is significantly developed. The tip based on the Ag3% v MWNTs composite has a much less developed surface, with many ovoid hills on top. The morphology of the Cu-tip surfaces is very much alike. Numerous craters and areas with oxidized layers are observable in Fig. 5b.

The edges are decorated by the drops of the composite material. In all SEM images of the contact surface, presented in Fig. 6, the influence of the arc's high temperature is visible. The drops of molten composite material appear on the surfaces of silver tips, whereas granules with extended surfaces are observed for the Cu tip. Additionally, cracks on the surfaces of both types of GP-reinforced matrices are clearly visible. The surface cracks are imperceptible for MWNT-reinforced composites. The analysis of SEM images showing the tips' microsection in Fig. 7 indicates differences in the composite structures with nanotubes and nanopowders. The highly loosened centers of zone overheating are formed for GP-reinforced Ag-matrix composites. They are seen as pores, from which the composite material is poured. Gray overheating channels, with a subtle nanocrystalline structure, are visible for the Ag/3% v MWNT composites. The edge zone of the tips forms a solid, but very fine-grained structure. In the case of the Cu3% v GP composite, vast gray centers of copper oxide mixtures can be observed in the superficial zone. For the Cu matrix reinforced with nanotubes, the width

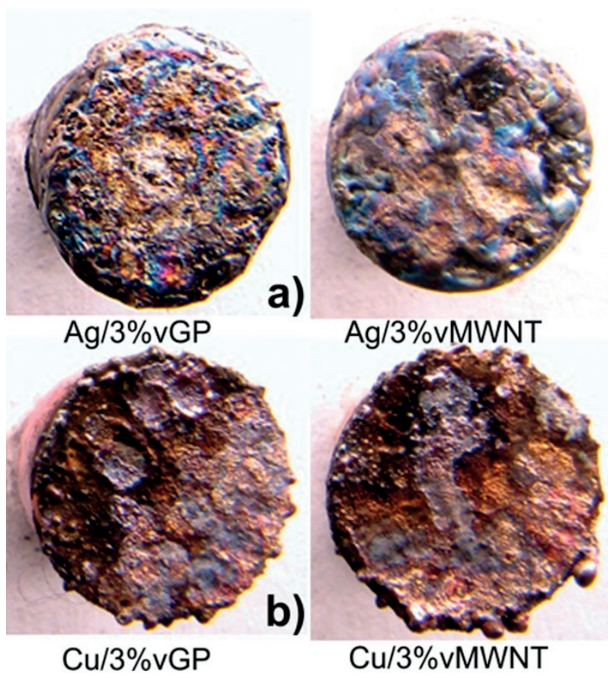

Fig. 5. The surface images of contact tips after the end of tests; a) with Ag matrices, b) with Cu matrices.
Rys. 5. Obrazy powierzchni nakładek stykowych po zakończeniu testu: a) z osnową Ag, b) z osnową Cu.

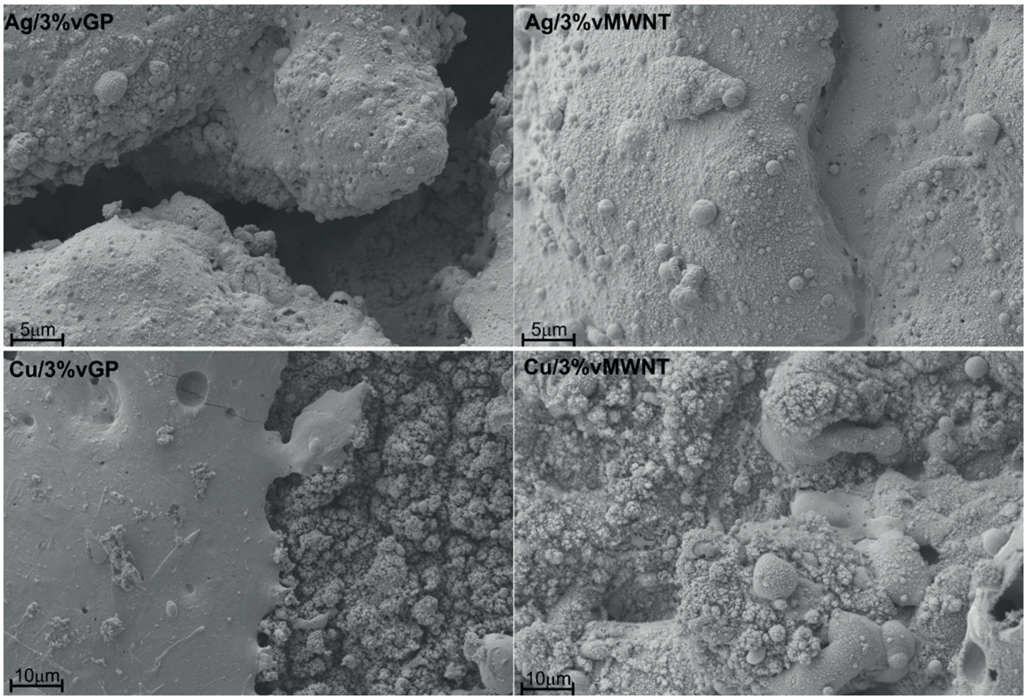

Fig. 6. The SEM images of contact tips surfaces after the end of tests.
Rys. 6. Obrazy SEM powierzchni nakładek stykowych po zakończeniu testu.

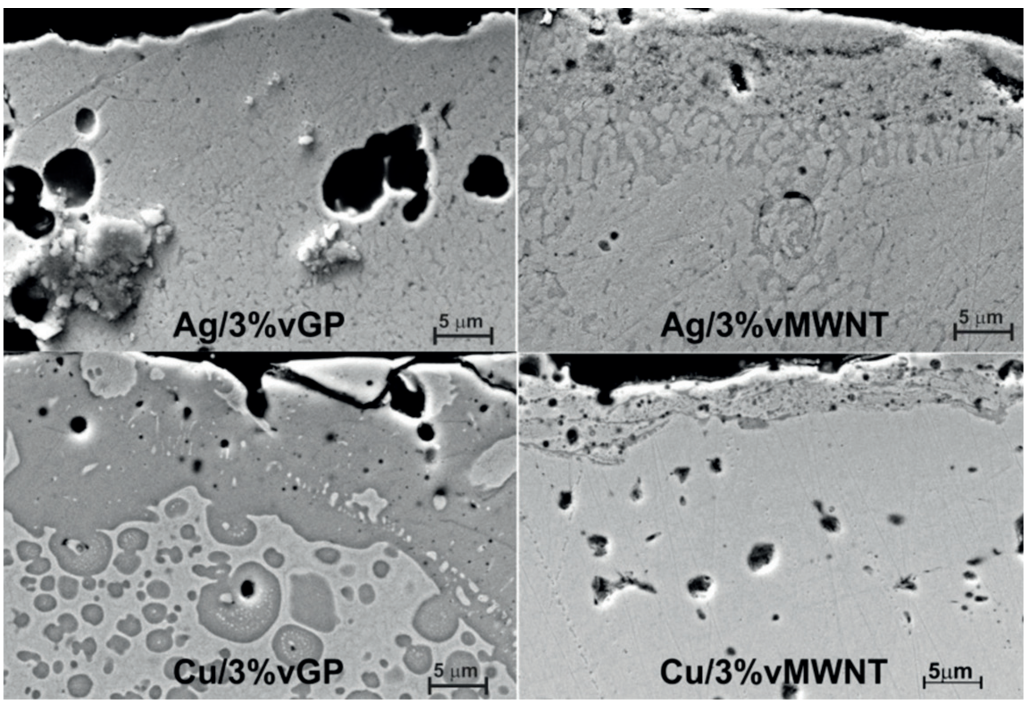

Fig. 7. SEM images of the metallographic sections of contact tips with different matrices and reinforcement phases.
Rys. 7. Obrazy SEM zgładów nakładek stykowych o różnych osnowach i fazach wzmacniających.

of the oxidized layer is many times smaller and quite well separated from the core tip.

The measurement results of the weight loss of the contact tips and their contact resistance are shown in Fig. 8.

The left-hand axes on the charts in Fig. 8 indicate the mass losses of the tips, while the right-hand Y-axes show contact resistance. It should be noted that contact resistance for both types of matrices is not dependent on the used reinforcing phase. Moreover, the absolute values of contact resistance for two kinds of materials differ significantly. For Ag matrices, resistance after N = 100 k operating cycles amounts to ~ 150 μΩ as presented in Fig. 8a. On the other hand, Fig. 8b shows that for Cu matrices it reaches 400 μΩ only after 20 k cycles. Depending on the

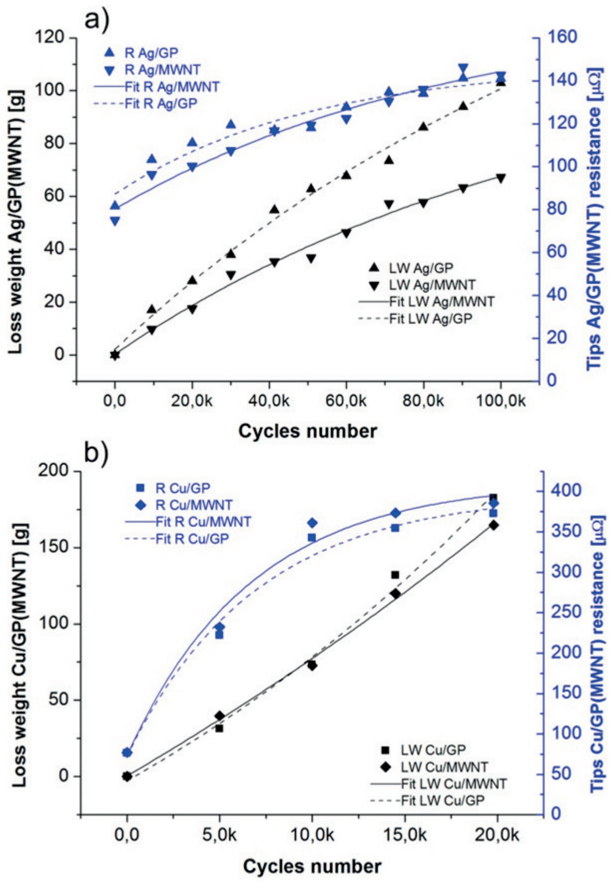

Fig. 8. The loss of mass and electrical resistance of contact materials vs. number of switching cycles: a) Ag/3% v GP(MWNTs), b) Cu/3% v GP(MWNTs) materials.
Rys. 8. Ubytek masy i opór elektryczny materiałów stykowych w funkcji liczby cykli łączeniowych: a) Ag/3% v GP(MWNTs), b) Cu/3% v GP(MWNTs) materials.

type of the reinforcing phase, mass losses are significant in contacts with the silver matrix. The loss of weight for silver contacts with nanotubes is two times lower than for those reinforced with GP (see Fig. 8a). The weight loss percentage for Cu/3%v GP composite (MWNTs) contacts is about 40%., for Ag/3% v MWNTs contacts it reaches the level of 10% of the starting material, and for the Ag/3% v GP composite it equals 20%.

4. Summary and conclusions

Correlation studies of thermal conductivity and hardness demonstrated that the optimal volume fraction of graphene forms for composite contact materials is around 3%. The performed electrical tests showed that:

- Surfaces of contacts made of cupreous composites are rapidly oxidized when exposed to electrical arc in atmospheric air. The addition of graphene forms does not protect the contact material against this type of corrosion. No protective effect can be observed when using graphene forms, unlike in the case of composites coated with graphene or exposed only to the slow action of air.
- After the arc action, contact materials based on silver revealed the existence of clear structural differences between composites with the GP and MWNTs. The Ag/3% v MWNTs composite turned out to be tougher in operation, with its weight loss being two times lower than for Ag/3% v GP contacts. In contrast, the electrical resistance of both composites was comparable in the whole range of cycles.

Acknowledgment

The results presented in this paper were obtained as part of the "GRAMCOM" project (Contract No Graftech/NCBiR/10/29/2013 with the National Centre for Research and Development) within the framework of the GRAF--TECH program.

References

[1] Bukhanovsky V. V., Grechanyuk N. I., Minakova R. V., Mamuzich I., Kharchenko V. V., Rudnitsky N. P.: Production technology, structure and properties of Cu–W layered composite condensed materials for electrical contacts. *International Journal of Refractory Metals and Hard Materials*, 2011, 29, 5, 573 – 58

[2] Findik F., Uzun H.: Microstructure, hardnes and electrical properties of silver - based refractory contact materials, *Materials & Design*, 2003, 24, 489 – 492

[3] Wu C., Weng D. Yi, W., Li S., Zhou J., Zheng F.: Arc erosion behavior of Ag/Ni electrical contact materials, *Materials & Design,* 2015, 85, 511 – 519

[4] Xu W., Canfield N. L., Wang D., Xiao J., Nie Z., Zhang J. - G.: A three-dimensional macroporous Cu/SnO_2 composite anode sheet prepared via a novel method, *Journal of Power Sources*, 2010, 195, 21, 7403 – 7408

[5] Kaczmar J. W., Pietrzak K., Włosiński W.: The production and application of metal matrix composite materials, *Journal of Materials Processing Technology*, 2000, 106, 1 – 3, 58 – 67

[6] Berner A., Mundim K .C., Ellis D. E., Dorfman S., Fuks D., Evenhaim R.: Microstructure of Cu–C interface in Cu-based metal matrix composite, *Sensors and Actuators A: Physical*, 1999, 74, 1 – 3, 86 – 90

[7] Borkowski P., Walczuk E., Wójcik-Grzybek D., Frydman K.: Electrical properties of Ag-C contact materials containing different allotropes of carbon, 25th International Conference on Electrical Contacts and 56th IEEE Holm Conference on Electrical Contacts, 2010, Charleston, 167 - 175

[8] Pietrzak K., Sobczak N., Chmielewski M., Homa M., Gazda A., Zybala R., Strojny-Nedza A.: Effect of carbon allotropic forms on microstructure and thermal properties of Cu-C composites produced by SPS, *Journal of Materials Engineering and Performance*, 2016, 25(8), 3077 - 3083

[9] Kováčik J., Bielek J.: Electrical conductivity of Cu/graphite composite material as a function of structural characteristics, *Scripta Materialia*, 1996, 35(2), 239 - 246

[10] Novoselov K. S., Geim A. K., Morozov S. V., Jiang D.: Two-dimensional gas of massless Dirac Fermions in graphene, *Nature*, 2005, 438 (7065), 197 - 200

[11] Bonaccorso F., Lombardo A., Tawfique H., Zhipei S., Colombo L., Ferrari A. C.: Production and processing of graphene and 2d crystals, *Materials Today*, 2012, 15(12), 564 - 589

[12] Lehman J. H., Terrones M., Mansfield E. et al.: Evaluating the characteristics of multiwall carbon nanotubes, *Carbon*, 2011, 49, 2581 – 2602

[13] Pop E. V., Varshney A., Roy K.: Thermal properties of graphene, *Fundamentals and Applications MRS Bull*, 2012, 37, 1273

[14] Wejrzanowski T., Grybczuk M., Chmielewski M., Pietrzak K., Kurzydlowski K. J., Strojny-Nedza A.: Thermal conductivity of metal-graphene composites, *Materials and Design*, 2016, 99, 163 – 173

[15] Chen F., Ying J., Wang Y. et al.: Effect of graphene content on the microstructure and properties of copper matrix composites, *Carbon*, 2016, 96, 836 - 842

[16] Neubauer E. , Kitzmantel M., Hulman M., Angerer P.: Potential and challenges of metal-matrix-composites reinforced with carbon nanofibers and carbon nanotubes, *Composite Science and Technology*, 2010, 70, 2228 - 2236