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CU/GRAPHENE COMPOSITE COATINGS PRODUCED BY ELECTROCHEMICAL REDUCTION METHOD UNDER SEMI-TECHNICAL LINE CONDITIONS ON ELECTRICAL EQUIPMENT COMPONENTS

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This paper presents a technological sequence of the fabrication process and test results of composite coatings with a nanocrystalline copper matrix including a dispersion phase in the form of graphene flakes deposited by electrochemical reduction on electrical equipment components. The conducted research included the development of solution compositions and process parameters for the deposition of Cu/graphene composite coatings, in addition to adaptation of the coating deposition process to a larger scale on a pilot electroplating line. The innovative aspect presented in the work (a key challenge) was the transfer of the positive results of the work from the laboratory scale to the semi-technical scale. The described work involved running the process in a plating drum and on hangers on a pilot plating line. The surface morphology, and roughness and the structure of the produced composite coatings were characterized. The thickness and bonding of the produced coatings to the substrate material were evaluated. Hardness tests of the produced coatings were carried out. The properties of the Cu/graphene composite coatings produced on the hangers and in the electroplating drum on the pilot electroplating line were compared. The key research challenge was the development of a technology for the fabrication of composite coatings on electrical equipment components, involving the application of Cu/graphene composite coatings by electroplating techniques at on a laboratory scale and then transferring the work to the pilot electroplating line.

Keywords: **composite coatings, copper matrix, dispersion phase, graphene, pilot plating line**

INTRODUCTION

The electrochemical reduction method is one of the basic techniques used in surface engineering to produce materials in the form of metallic coatings. This technology allows the parameters of the deposition process to be controlled, and thus enabling the production of materials with the desired properties. By controlling the deposition process, it is possible to produce materials with micro- and nanocrystalline structures [1]. The properties of coatings can also be modified by introducing dispersion phase particles into the metal matrix. Depending on the type of particles introduced, they can affect specific properties, improving corrosion resistance, abrasion resistance or hardness [2, 3, 4, 5].

In recent years, carbon materials suitable as a dispersion phase, which include graphene, have also gained popularity. The great interest in these types of materials is a direct result of their properties (thermal, electrical, mechanical, etc.), which are of particular interest from the point of view of potential applications in electronics. The use of carbon materials as dispersion phase embedded in a metal matrix can be found in works [6, 7, 8].

Cu-based materials are widely used in electronics due to their excellent electrical conductivity, thermal conductivity and ductility. Copper matrix composites have become increasingly popular in the last decade owing to their improved mechanical, electrical and thermal properties, allowing a variety of applications. In recent years, many copper matrix composites have been developed with various reinforcements in the form of carbon materials, such as carbon nanotubes [9], graphene [10] or diamond [11]. Among these, graphene has attracted considerable attention because of its unique properties and structure [12].

Composite materials constitute a group of materials that is currently being intensively researched and developed. They are being produced on a laboratory scale in many research centers around the world both as coatings and volumetric materials [6, 7, 8, 13], but it is still a major challenge to transfer the positive results of the work to the industrial scale. Attempts to produce composite coatings on a larger scale have been made, among others, by the authors of paper [14], presenting a process carried out by chemical reduction on a semi-technical scale.

This paper presents the technology for the production of Cu/graphene composite coatings by electrochemical reduction on a pilot electroplating line in 100 dm^3 baths. A process scheme for the production of the Cu/graphene coatings is presented and described. The structure and morphology of the composite coatings produced on the pilot electroplating line in an electroplating drum and for comparison on hangers were characterized. Selected properties of the coatings and their adhesion to the substrate were investigated.

The work consists of the development of a copper graphene coat (CGC) and a method for its industrial application to electrical appliance components, with applications in the automotive, electrical engineering and power generation industries. The aim of the work is to replace copper components with CGC-coated low-carbon steel in order to reduce the cost of manufacturing electrical appliance components that require copper. The proposed solution could contribute to reducing the consumption of this metal.

The work consists of selecting the parameters of the deposition processes on the electroplating line for each deposition mode, i.e. in the electroplating drum and on hangers. Initial trials were carried out in the laboratory and the deposition process parameters were selected. The positive results of the work from the laboratory scale were transferred to a larger semi-technical scale, the results of which are presented in this paper. Differentiation of the deposition process was made in terms of the processing method – on hangers and in a plating drum.

EXPERIMENTAL PROCEDURE

The first stage of the work was carried out on a laboratory scale to determine and select the optimal coating manufacturing parameters and choose the dispersion phase content. Then the work was transferred to the pilot electroplating line, which was the main challenge of the work.

As a result of the laboratory work, the electrolyte solution (bath) compositions and process parameters for the electrochemical deposition of the CGC composite coatings were selected. A bath with the composition shown in Table 1 was selected for the deposition of the CGC composite coatings.

TABLE 1. **Composition of baths for production of CGC coatings**

Component	Quantity
copper(II) sulfate(VI)	200 g/dm^3
sulfuric acid(VI)	50 g/dm^3
hydrochloric acid	1 ml/dm^3
Cu-189	6 ml/dm^3

The solution ensured good coverage of the components on a laboratory scale. A cationic surfactant compound (CTAB) was utilized to increase the dispersion of the graphene flakes in the bath and to increase the amount of embedded graphene in the metal matrix material. Graphene manufactured by Cheap Tubes (USA) was used for the study. The parameters according to the manufacturer's description are shown in Table 2.

The results of Raman spectroscopy studies of the graphene flakes used in the manufacture of the CGC composite coatings are shown in Figure 1. The Raman spectra show graphene's characteristic D (1350 cm-1), G (1580 cm-1) and 2D (2700 cm-1) bands. The intensity and shape of the 2D band indicate that it is not pure graphene. The 2D/G band intensity ratio of 0.36 proves that the material consists of several layers and may be a mixture of graphene and graphite. A micrograph of the graphene flakes obtained by scanning electron microscopy (SEM) is presented in Figure 1.

TABLE 2. **Characteristics of graphene used**

Name	**Graphene nano platelets grade 4**
Diameter of flakes	1-2 μm
Average thickness	<4 nm
Purity	>99%
Specific surface area	>500 m^2/g
Form	dry powder

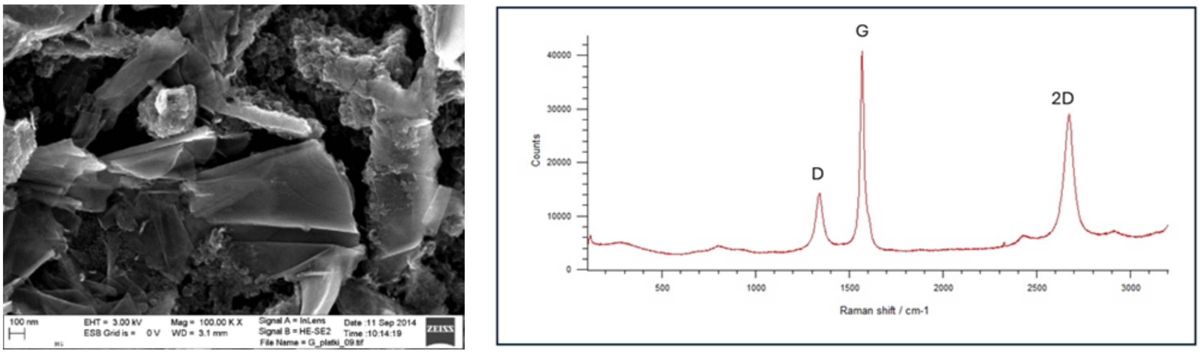


Fig. 1. Micrograph (SEM) and Raman spectrum of graphene used

For the bath of the given composition (Table 1), the current density for coating deposition was determined using a Hull cell. Based on observations of the coating surfaces obtained over a wide range of current densities in the Hull cell for the given bath, two current densities, 2 and 3 A/dm2, were selected for coating deposition. The coating deposited at the current density of 2 A/dm2 was smooth and glossy. In contrast, the coating deposited at the current density of 3 A/dm2 was characterized by dendritic growths on the edges of the sample (Figure 2). For further studies to produce the copper coatings, the current density of 2 A/dm2 was adopted for the process carried out on the hanger.

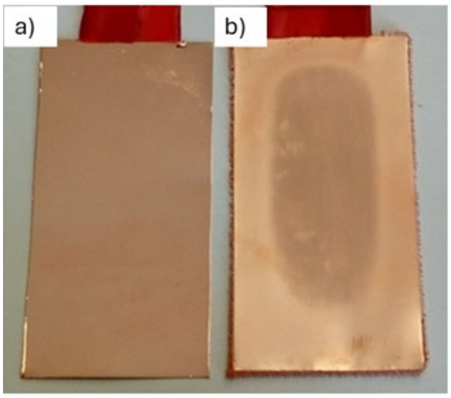


Fig. 2. Copper-coated samples deposited at current density of (a) 2 A/dm2 and (b) 3 A/dm2

To ensure a good bond between the composite coating and the substrate, the next step was to produce a thin nickel sublayer from a chloride bath consisting of nickel chloride and hydrochloric acid. The CGC composite coating was deposited onto the substrate thus prepared.

When depositing composite coatings, stirring of the bath during the process is an important parameter. This procedure is intended to evenly disperse the dispersion phase particles in the bath, as well as to ensure an even concentration of the bath components throughout the volume. Stirring can also be important to counteract pitting, which can form on the surface of the component to be coated (the cathode) due to the release of hydrogen during the process. The plating line employed in the second stage is supplied with compressed air. In addition, in the drum process, the electroplating drum rotating at 7 rpm was also responsible for mixing.

As part of the work carried out on the line, a technological sequence of the composite coating deposition process was developed. The technological sequence of the copper plating process for the deposition of the CGC composite coatings consisted of the following steps (Figure 3).

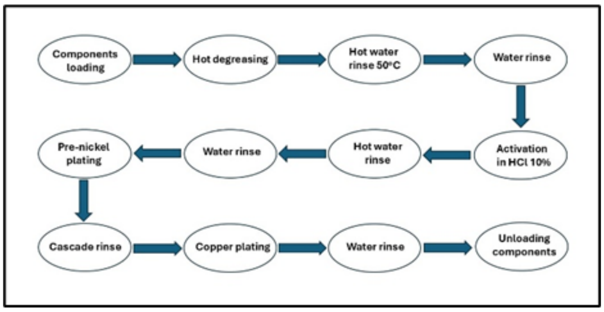


Fig. 3. Flowchart of CGC deposition process

Owing to the high specific surface area and low mass of graphene, the composite coatings were applied to the workpieces in baths with a graphene concentration of 0.1 g/dm3. The duration of the deposition process only affected the thickness of the produced coatings.

The deposition of coatings on the semi-technical line was carried out using the drum method (Figure 4) and, due to the shape of the workpieces with large flat surfaces, and for comparison purposes, additionally on hangers. The use of a drum makes it possible to coat a much larger number of components than on a hanger in a single process. In this case, a drum with a working volume of 2.1 dm3 and a maximum input of up to 1 kg was used. The method employing the electroplating drum generates a higher proportion of workpieces with defects; in the case of the hanger loss issues are practically eliminated. The most commonly observed problems with the drum method are: workpieces sticking together, scorching, uneven thickness of the deposited coating, and mechanical damage to the coated parts resulting from mutual impact of the workpieces. In part, these drawbacks have been eliminated or minimized by reducing the deposition current density to 1.5 A/dm2.

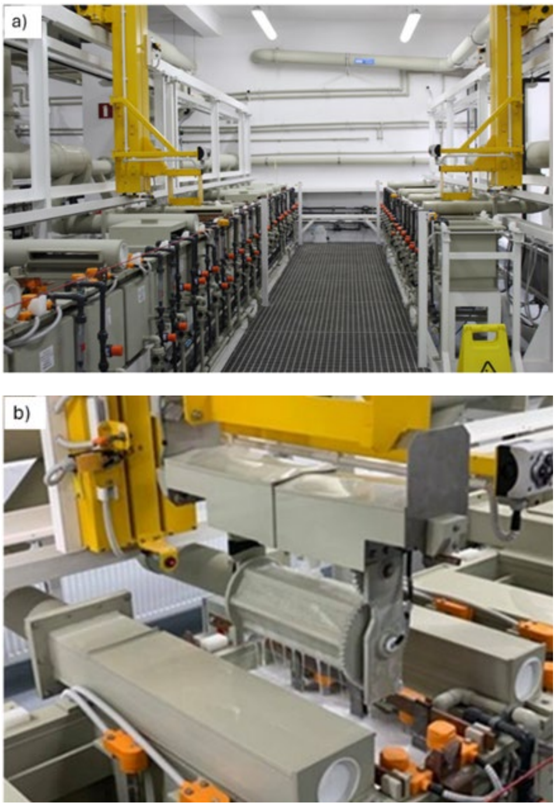


Fig. 4. Pilot electroplating line (a) and electroplating drum (b)

Literature reports indicate that the current density affects not only the rate of coating deposition, but also the structure, including the grain size of the matrix material. In addition, the structure has a very strong influence on the material properties, among others the hardness, corrosion resistance, and tribological properties [15-18]. Therefore, changes in the properties of the coatings produced on the pilot electroplating line are affected not only by the type of processing, but also by the modified conditions of the deposition process.

The morphology of the fabricated CGC coatings was studied using a Keyence VHX-5000 light microscope and a JEOL scanning electron microscope (SEM). A scratch-test was performed to test the bond between the coating and the substrate material. The scratch-test measurements of the coatings were made by means of a CSEM Revetest device. A progressive indenter load of 0-100 N was utilized; the speed of the indenter was 10 mm/min. Thickness measurements of the deposited coatings were made using a Fischer X-ray fluorescence spectrometer. Microhardness measurements were carried out by the Knoop method on cross sections of the samples employing a T1202 Wilson-Hardness tester (Buehler), with a 10 G load. Eight measurements were taken for each sample, from which the average microhardness of the coatings was calculated along with the standard deviation. On the surface of the workpieces with the composite coating, surface roughness tests were carried out with a Surftest SJ 210 profilometer from Mitutoyo.

Five measurements were taken for each workpiece, from which the average value was calculated along with the standard deviation. The tests were conducted on both sides of the sample – a and b (process specification).

Table 5 displays the results of the Ra roughness measurements for the CGC-coated workpieces. Owing to the shape of the workpieces and the holes present in them, the possibilities of the conducted tests were limited. For this reason, tribological tests were carried out on reference samples with the Cu/graphene coating and, for comparison purposes, with a Cu coating. The tests were performed by means of an Amsler A-135 machine in accordance with the PN-82/H-04332 standard. The friction tests were carried out at a load of 1 daN, at the rotational speed of 200 rpm, with a total test time of 30 minutes, using Lux-10 oil for immersion sliding friction. A heat-treated 40H steel ring was employed as the counter sample.

RESEARCH RESULTS AND DISCUSSION

Characterization of the surface morphology of the coatings produced on the pilot electroplating line was done using light microscopy and scanning electron microscopy (SEM). Example micrographs of the surface of the CGC coatings produced on the hanger (Figure 5) and in the electroplating drum (Figure 6), taken by light microscopy at different magnifications for selected components are shown in the following figures. The CGC composite coatings produced on the line differ in morphology depending on the processing method – drum or hangers (Figures 5–8).

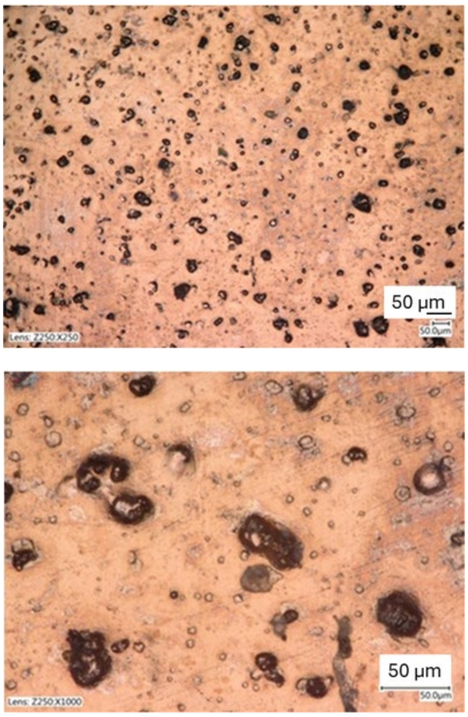


Fig. 5. Micrographs of surface morphology of CGC coating produced on hanger (light microscope)

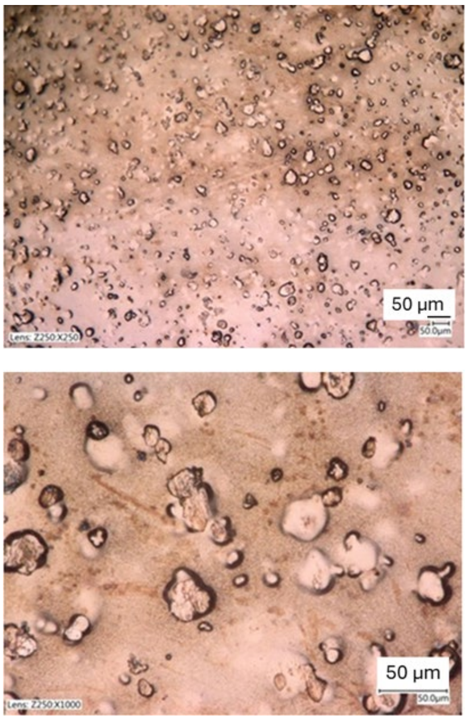


Fig. 6. Micrographs of surface morphology of CGC coating produced in electroplating drum (light microscope)

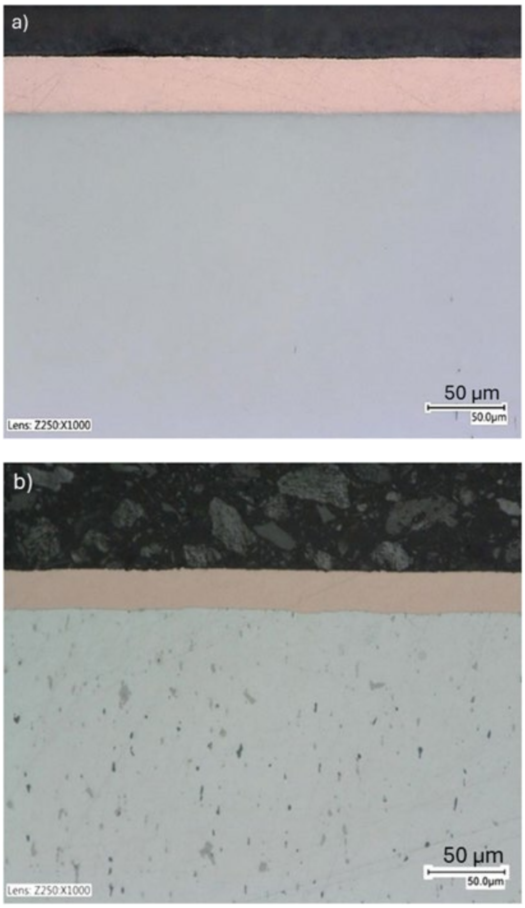
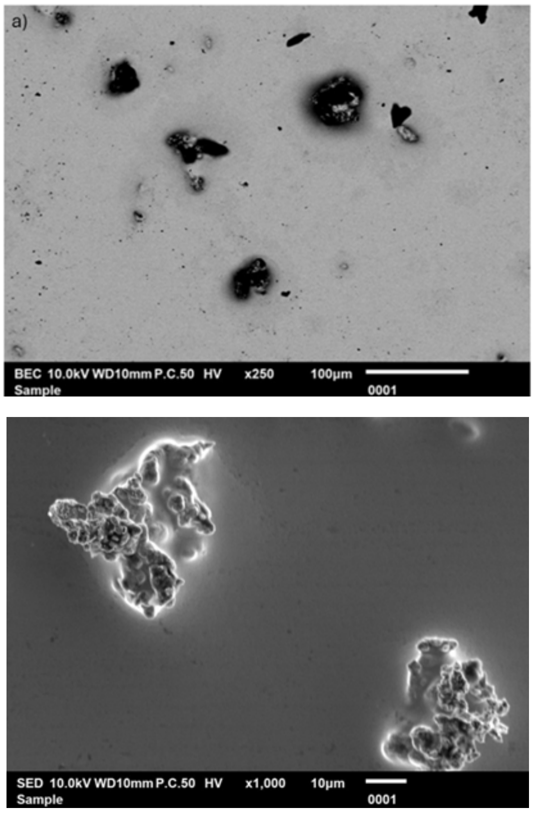


Fig. 7. Cross-section of CGC coatings produced (a) on hanger (b) in electroplating drum



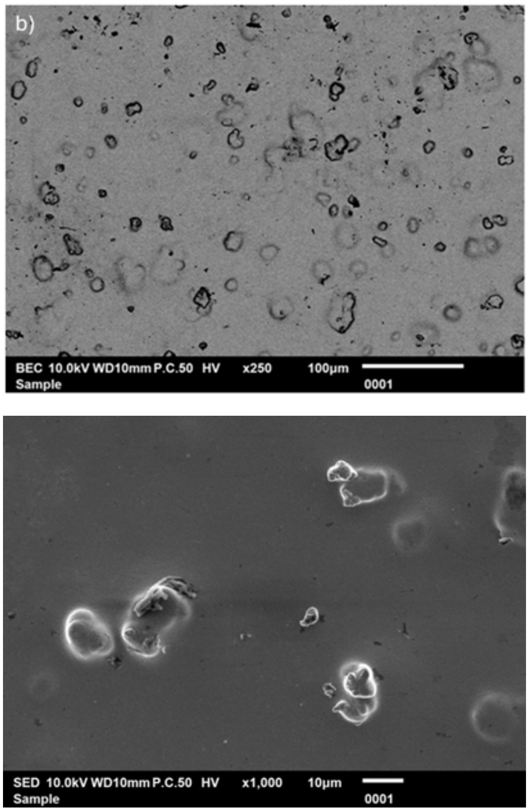


Fig. 8. Surface morphology of CGC composite coatings (SEM) (a) fabricated on hanger, (b) fabricated in electroplating drum

The composite coatings produced in the electroplating drum are characterized by a more uniform distribution of graphene on the coating surface than in the case of the hanger-deposited coatings. The described effect can be influenced by the additional movement of the bath generated by the rotation of the electroplating drum during the deposition process. In addition, larger particle agglomerates are formed on the surface of the hanger-deposited coatings.

The incorporation of the graphene into the copper matrix is confirmed by the results of studies performed using Raman spectroscopy (Fig. 9).

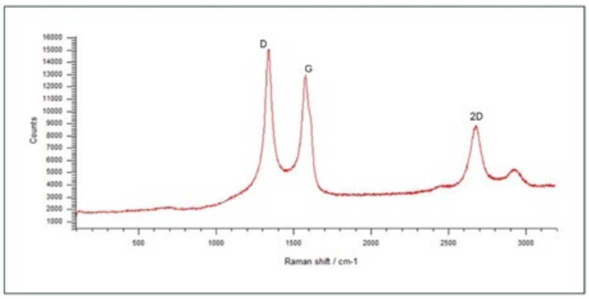


Fig. 9. Raman spectrum of CGC composite coating (hanger)

The Raman spectrum of the CGC composite coating shows D, G, and 2D bands, characteristic for graphene. These results confirm the incorporation of graphene into the copper coating material. The graphene particles embedded in the copper matrix exhibit a higher D band intensity compared to the G band, indicating less order in the dispersed phase material after incorporation into the Cu matrix. This may be due to the formation of agglomerates and the incorporation of graphene flakes into the CGC coating material at different angles and in different directions.

A scratch-test was conducted to test the bond between the coating and the substrate material. The test was performed on the surface of the sample. Example results of the scratch-test for the CGC coating are shown in Figure 10. Micrographs of the scratch and graphs with recorded: normal force, friction force, coefficient of friction and acoustic emission are shown.

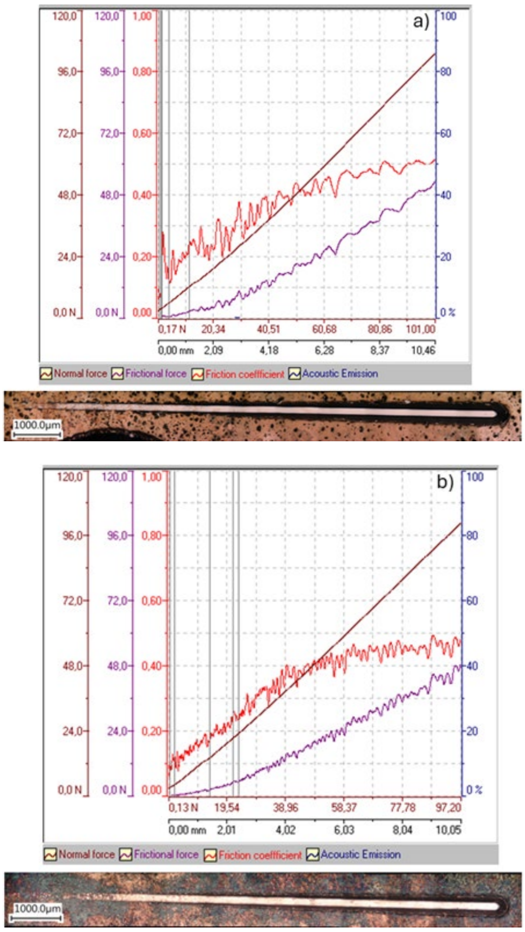


Fig. 10. Force diagrams from scratch test: a) coating produced on hanger and b) coating produced in electroplating drum. Micrographs of damage after scratch test of coatings: a) CGC (hanger) and b) CGC (drum)

The scratch tests conducted on the surface of the workpieces with the applied coatings did not show any delamination of the investigated CGC coatings from the substrates. Cohesive cracks formed resulting from the movement of the indenter with increasing force during the test were found.

A summary of the thickness measurement results for selected CGC coated samples is shown in Table 3.

TABLE 3. **Thickness of produced CGC coatings on hanger and in electroplating drum**

Sample	Coating thickness [µm]	Standard deviation [µm]
D – side a	24.46	3.17
D – side b	22.37	3.13
H – side a	30.18	7.03
H – side b	32.02	6.67

The results of thickness measurements by X-ray fluorescence spectroscopy is strongly influenced by the location of the measurement. Because of the different shapes of the test specimens and the two deposition methods (drum and hanger), different coating thicknesses were obtained in different areas of the sample, which is due to the orientation of the test surface to the flow of electric current during coating deposition. The results of the microhardness tests of the coatings, shown in Table 4, indicate that the hardness of the coatings deposited in the drum is significantly higher than that of the hangers. The copper coatings deposited in the drum have a hardness twice as high as that of the coatings deposited on the hangers.

TABLE 4. **Microhardness of CGC coatings deposited on hanger (H) and in electroplating drum (D)**

2	Substrate material	Microhardness HK0.01	Standard deviation
H	steel	179	3.7
D	steel	335	5.9

This phenomenon can be influenced by several factors: different current densities for the hangers and the drum, different positioning of the workpieces during the process forced by the specifics of the system, different hydrodynamic conditions, i.e. bath mixing, and current flow through the system during the deposition process. Tests of the roughness parameters (R_a, R_z) were carried out on the surfaces of the workpieces with the deposited CGC coatings for the process conducted on the hanger and in the electroplating drum. The results of the tests are presented in Table 5.

TABLE 5. **Roughness of coatings produced on hanger (H) and in electroplating drum (D)**

Workpiece designation (test side)	Roughness parameters [µm]			
	R_a		R_z	
	Average value	Standard deviation	Average value	Standard deviation
H (a)	2.38	0.96	17.15	5.69
H (b)	2.20	0.24	15.02	2.98
D (a)	1.37	0.33	7.92	2.07
D (b)	1.02	0.21	6.35	1.66

The results of the roughness parameters are strongly influenced by the initial surface on which the coatings are deposited. At the time of deposition, the growing coating replicates the surface on which it is deposited. In addition, the increase in roughness is also influenced by the graphene embedded in the metal matrix. Larger values of roughness parameters were obtained for the samples deposited by the hanger method.

The verification of the influence of the graphene dispersion phase on the abrasion resistance of the CGC composite coatings in the tribological process was carried out on reference samples with Cu and the CGC coatings deposited on a laboratory scale. The results of tribological tests in the form of graphs for the studied layers – copper and the CGC composite – are presented in Figure 11.

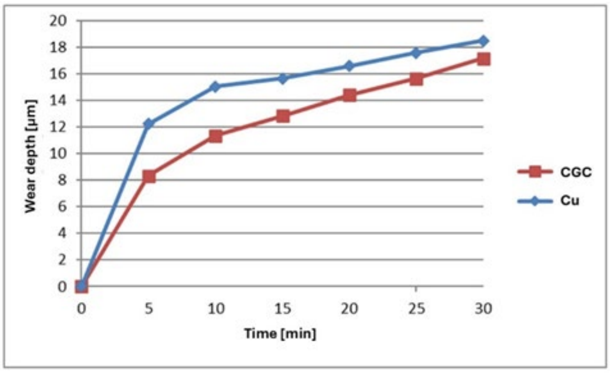


Fig. 11. Graph of tribological wear of Cu metal layer and CGC composite layer on reference samples

The intensity of layer wear depends on the hardness of the material. The harder the layer material, the more resistant it is to abrasion and, consequently, the lower the wear depth. The results of the tribological tests showed that incorporating graphene into Cu layers increases resistance to wear as a result of friction.

CONCLUSIONS

A technical solution was proposed to replace copper components with steel components coated with a CGC composite. The research presented here is one of the first attempts to deposit copper matrix composite coatings under industrial conditions. As part of the work, a pilot electroplating line was adapted to the requirements of the process of composite coating deposition by electrochemical reduction. A comparison was made between the properties of composite coatings differentiated by the deposition method, i.e. electroplating drum and hanger. The CGC composite coatings produced in both the drum and hanger were characterized by a compact structure and good adhesion to the steel substrate. In the case of the composite coatings produced on the hangers, larger agglomerates of the graphene dispersion phase can be observed. The CGC coatings produced in the electroplating drum have a more uniform morphology and are characterized by better dispersion of graphene in the Cu coating. In addition, the two treat ments require different conditions for the deposition process, with lower current densities required for the drum than for the hangers. In the case of the hangers, a major problem is the need to individually suspend each workpiece, while the method using the electroplating drum generates a higher incidence of surface defects.

Issues requiring further research for this type of material relate to the repeatability of the process and the conditions under which the deposition process is carried out, with particular attention to uniform conditions throughout the process bath. The results obtained in this study represent an important step toward gaining experience in adapting and adjusting the composite coating manufacturing process to industrial conditions and the commercial application of such materials.

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