STRUCTURE AND PROPERTIES OF Cu/CARBON PHASE COMPOSITE COATINGS PRODUCED BY ELECTROCHEMICAL REDUCTION METHOD

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Abstract

This paper presents the results of a study on composite coatings with a copper matrix and embedded carbon dispersion phase particles. For comparative purposes, the study also includes copper coatings without embedded dispersion phase particles. The coatings were produced on steel substrates by electrochemical reduction from multicomponent electrolyte solutions using a current density of 3 A/dm2, magnetic stirring of 100 rpm at 298 K ± 2 K. Carbon allotropic varieties of carbon (graphene, diamond, carbon nanotubes) were used as carbon phases and characterised by scanning electron microscopy (SEM). The fabrication of Cu/carbon phase composite coatings is described. The results of the surface topography and morphology, structure and adhesion of the coatings to the steel substrate are presented.

Keywords: Copper, composite coatings, properties, carbon materials, CNT, Graphene, Diamond

1. INTRODUCTION

The electrochemical reduction method is one of the basic techniques used in surface engineering to produce materials in the form of metallic coatings. The relatively simple technology and the possibility to control the parameters of the deposition process make it possible to produce materials with different properties according to the needs. By controlling the parameters of the deposition process (current density, bath composition, temperature), it is possible to produce materials with micro- and nanocrystalline structures [1]. In addition, by introducing particles of dispersion phases into the metal matrix, it is possible to further influence the properties of the deposited coatings through synergy. Depending on the type of particles being incorporated, they can influence specific properties. Ceramic particles improve mechanical and corrosion properties [2], [3]. Soft particles such as MoS_2 or PTFE are used to improve tribological properties [4], [5]. In recent years, carbon materials such as carbon nanotubes, graphene, graphite and nanodiamond are also gaining 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 phases incorporated into metal matrices can be found in works [6], [7], [8].

This paper focuses on the potential use of graphene, nanodiamond and carbon nanotubes as reinforcing phases incorporated into a copper matrix. The choice of copper is due to its very good electrical properties. The fabrication of Cu/carbon phase composite coatings, the problems that can occur during the fabrication of this type of material are presented. The morphology and structure as well as the adhesion of the investigated coatings to the substrate were characterised. Copper matrix composite coatings produced by electrochemical reduction are not studied to the same extent as nickel coatings. The study of Cu/carbon phase coatings extends the state of the knowledge in this type of material and appears to be of interest for potential applications in electronics.

2. MATERIALS AND METHODS

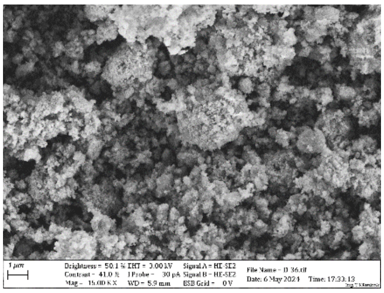
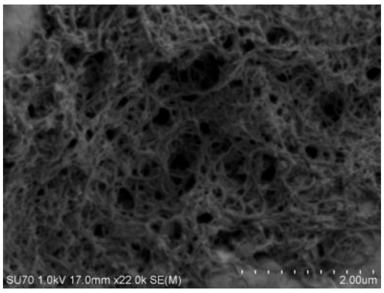
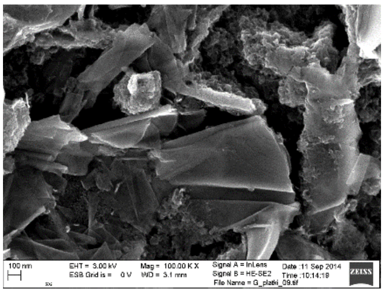
Copper (Cu) and Cu/carbon phase composite coatings with embedded dispersion phase particles in the form of nanodiamond particles, carbon nanotubes and graphene were deposited on a S355 carbon steel substrate. Prior to the process, the substrate, in the form of 60x20 mm plates, was mechanically grinded on 180-1200 grit sandpaper, then degreased with acetone, activated in 15% H2SO4 and nickel plated in a Watts-type bath. The nickel sublayer was intended to ensure good adhesion of the deposited copper coating to the substrate. The Cu or Cu/diamond coating was deposited onto the substrate prepared in this way. The copper plating process parameters are summarised in Table 1.

Table 1 Proces parameters

Matrix	**Cu**
Dispersion phase	CNT’s, graphene, diamond
Concentration of the dispersion phase [g/dm^3]	0.1 (CNTs, graphene) 1.0 (diamond)
Bath composition	$CuSO_4$, H_2SO_4, HCl, Cu-189
Proces time [min]	90
Current density [A/dm^2]	3
Mixing speed [rpm]	100

The chemical reagents used for the study were of high purity and were of production Chempur, Poland. A commercial Cu-189 additive was used to obtain the fine crystalline structure. Commercially available carbon materials shown in Table 2 were used.

Table 2 Carbon materials

Diamond (Sigma-Aldrich)	CNTs (Nanocryl)	Graphene (Cheaptubes)
		
• nanopowder • diameter <10 nm	• amine group • diameter 20-30 nm	• purity >99wt% • diameter 1-2 μm • surface area >700 m^2/g

The carbon materials used were characterised by varying particle shapes and sizes. The smallest and most regular particles were diamond particles. A current supplier and a magnetic stirrer were used to deposit the coatings. The coatings were deposited at a current density of 3 A/dm^2, a stirring rate of 100 rpm, the anodes were made of copper, and the coatings were deposited from a 298K ± 2K bath. The surface morphology of the produced coatings was characterised using a scanning electron microscope (Jeol JSM-IT100 LA). The surface topography was studied using a Keyence VHX-5000 light microscope. The structure of the coatings was investigated by X-ray diffraction (XRD) in the 2θ angle range of 20-120 degrees, using Cu-kα radiation (λ=1.5418Å) with a Rigaku Mini Flex II. The adhesion of the produced coatings to the substrate was tested by scratch test using a CSEM Revetest device with a progressive load of 0-100 N for 60 s at a Rockwell indenter speed of 10 mm/min.

3. RESULTS AND DISCUSSION

Images of the morphology, surface topography and diffractograms of the produced Cu and Cu/carbon phase composite coatings are shown in Figures 1-2.

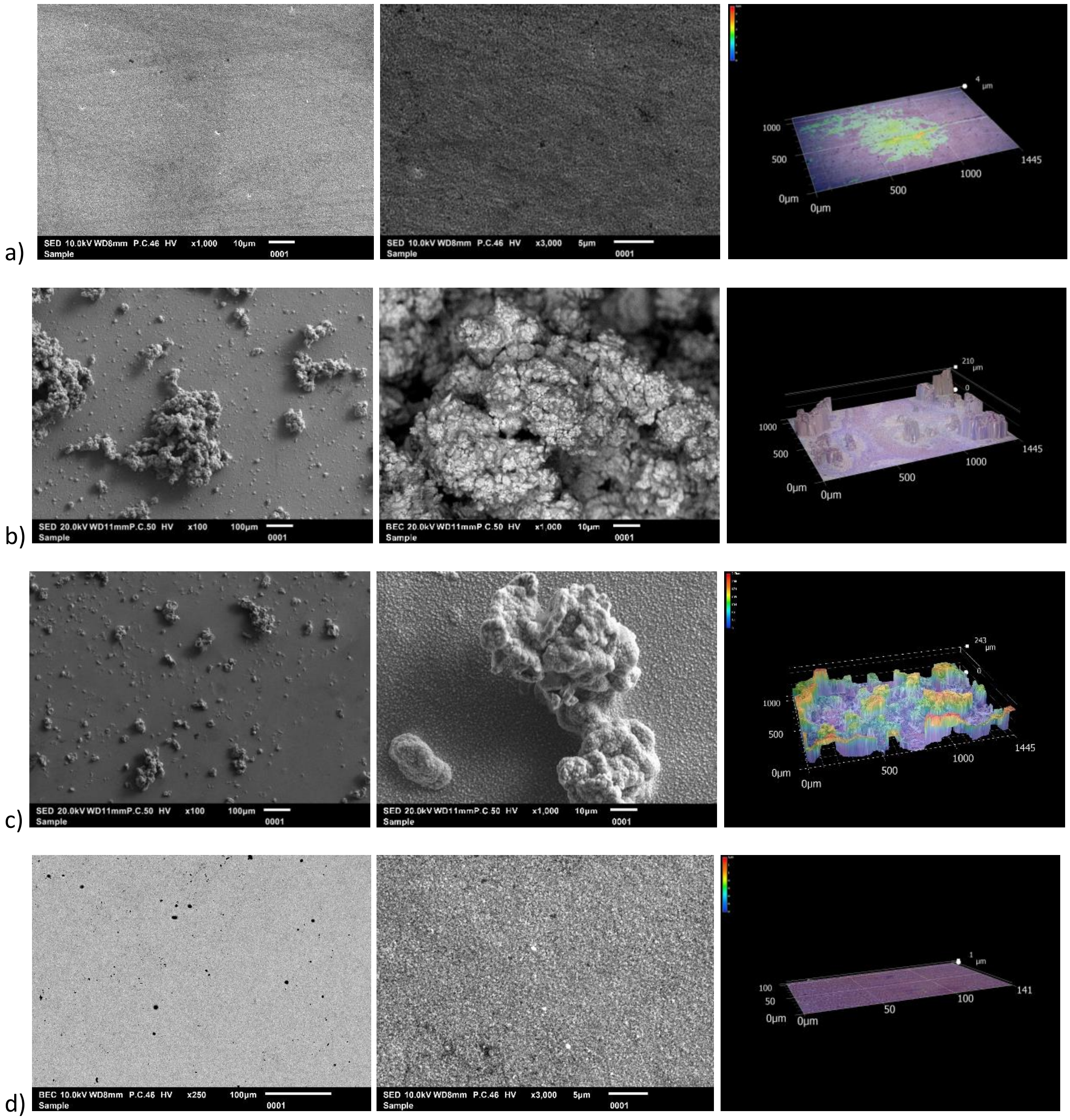


Figure 1 Morphology and surface topography of the produced coatings: a) Cu, b) Cu/CNTs, c) Cu/graphene, d) Cu/diamond

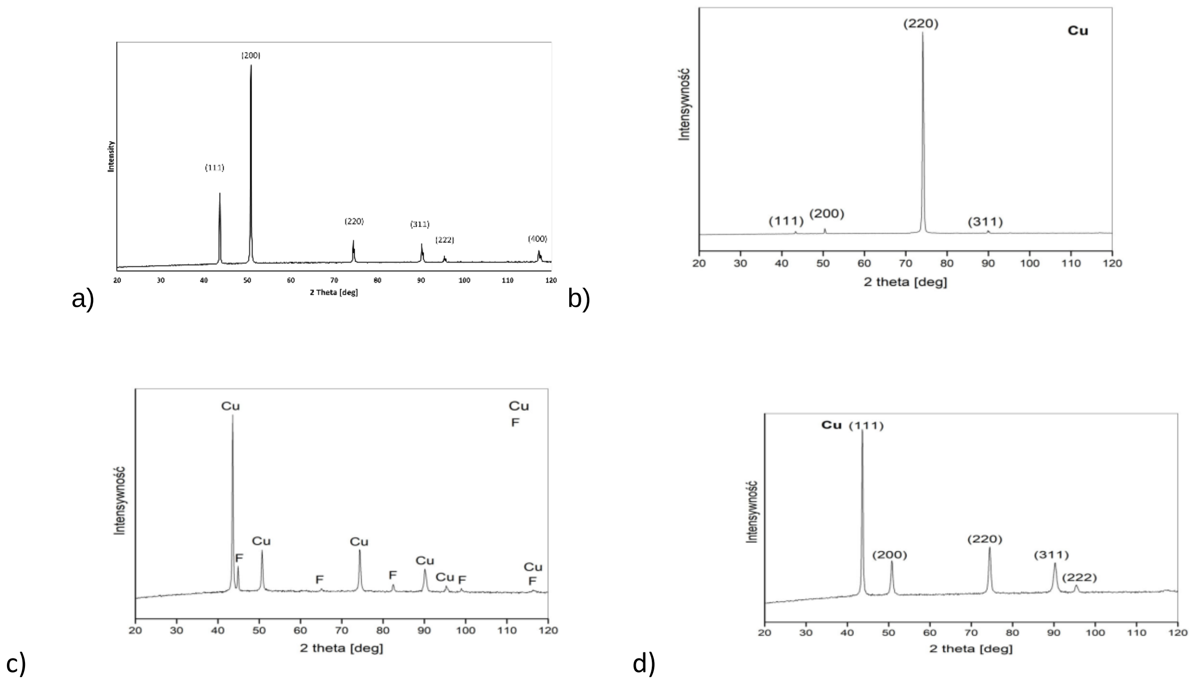


Figure 2 Diffractograms of the produced coatings: a) Cu, b) Cu/CNTs, c) Cu/graphene, d) Cu/diamond

The copper coating without embedded particles was smooth and shiny. This is characteristic of coatings deposited from baths containing organic compound additives [9]. The incorporation of a specific dispersion phase has a significant effect on the morphology and topography of the surface, as can be seen in Figure 1. The incorporation of a carbon phase with a large specific surface area (graphene) and a complex shape (carbon nanotubes) results in a significant degree of surface development of the coatings produced. This is a typical phenomenon and has been observed in many works [10], [11], [12]. One of the factors is the tendency of this type of material to agglomerate. Large particles, once anchored in a copper matrix, are gradually encapsulated by it. This phenomenon can be counteracted in various ways: by using different mixing methods (rotating electrode, ultrasound), by depositing coatings from baths containing additives of surfactants, or by using particles of different sizes and concentrations in bath solutions. In this respect, the use of nanometric and near-spherical (nanodiamond) particles appears to be much less problematic. The mechanism of co-deposition of the metal coating and incorporation of the dispersion phase particles into the coating is a complex phenomenon, depends on many factors and is not fully understood. The most important factors influencing it are the type and concentration of dispersion phase particles in the bath, the current density and the method and speed of mixing [13]. All the coatings produced were characterised by a crystalline structure. The incorporation of the dispersion phase influences the preferential growth direction of the crystallites (Figure 2). The diffractograms did not show the presence of reflections from the embedded carbon phases, which may be due to their small amount embedded in the matrix. For the graphene coating, reflections from the steel substrate are visible.

The results of adhesion tests of the produced Cu and Cu/carbon phase composite coatings to the steel substrate are shown in Figure 3.

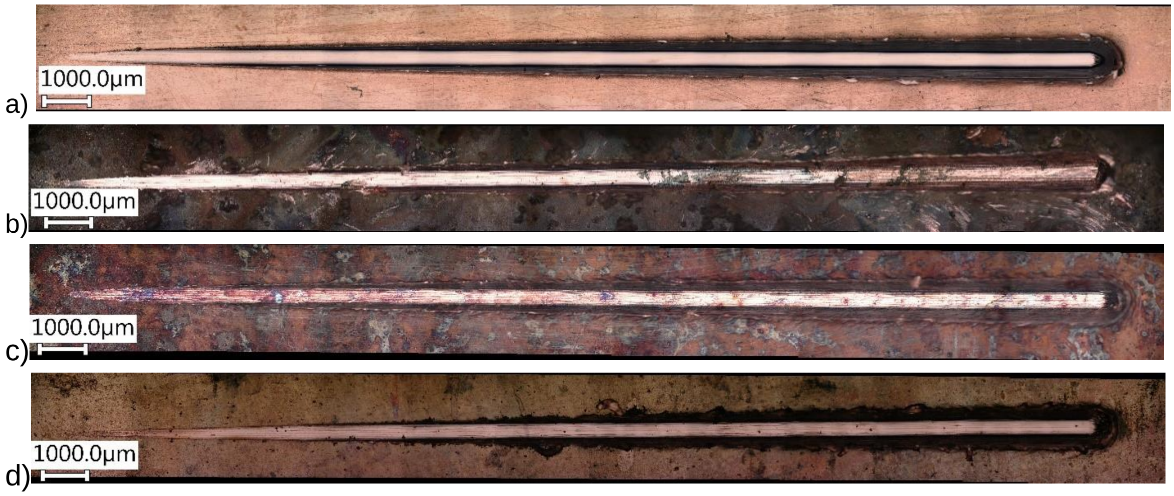


Figure 3 Damage images after scratch test of produced coatings: a) Cu, b) Cu/CNTs, c) Cu/graphene, d) Cu/diamond

All variants of the Cu and Cu/carbon phase composite coatings produced showed good adhesion to the steel substrate. No delamination was observed. Only cohesive damage caused by indenter displacement with increasing force during the test is present [14].

4. CONCLUSION

As a result of the research conducted, the following conclusions can be drawn:

- Electrochemical reduction methods can be used to produce composite materials in the form of Cu/carbon phase coatings
- The type of carbon phase has an influence on the structure and morphology of the coatings deposited
- The tendency to agglomerate and the irregular shapes of graphene and CNTs contribute to the high degree of surface development of composite coatings
- All variants of produced Cu and Cu/carbon phase coatings were characterised by compactness and good adhesion to the steel substrate. Conclusion contains no new data or findings.

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REFERENCES

[1] WASEKAR, N.P., HARIDOSS, P., SESHADRI, S.K., SUNDARARAJAN, G. Influence of mode of electrodeposition, current density and saccharin on the microstructure and hardness of electrodeposited nanocrystalline nickel coatings. Surface & Coatings Technology. 2016, 291, 130-140.

[2] LI, B., ZHANG, W., LI, D., Synthesis and properties of a novel NieCo and Ni-Co/ZrO2 compositecoating by DC electrodeposition. Journal of Alloys and Compounds. 2020, 821, 153258.

[3] WANG, C., SHEN, L., QIU, M., TIAN, Z., JIANG, W. Characterizations of Ni-CeO2 nanocomposite coating by interlaced jet electrodeposition. Journal of Alloys and Compounds. 2017, 727, 269-277.

[4] FURLAN, K.P, DE MELLO, J.D.B., KLEIN, A.N. Self-lubricating composites containing MoS2: A review. Tribology International. 2018. 120, 280-298.

[5] BALAJI, R., PUSHPAVANAM, M., KUMAR, K.Y., SUBRAMANIAN, K. Electrodeposition of bronze–PTFE composite coatings and study on their tribological characteristics. 2006, 201, 3205-3211.

[6] CHEN, J., LI, J., XIONG, D., HE, Y., JI, Y., QIN, Y. Preparation and tribological behavior of Ni-graphene compositecoating under room temperature. Applied Surface Science. 2016, 361, 49-56.

[7] LIU, J.H., LIU, Y.D., PEI, Z.L., LI, W.H., SHI, W.B., GONG, J., SUN, C. Influence of particle size and content on the friction and wear behaviors of as-annealed Ni–Mo/diamond composite coatings. Wear. 2020, 452-453, 203300.

[8] PRAVEEN, B.M., VENKATESHA, T.V. Electrodeposition and properties of Zn–Ni–CNT composite coatings. Journal of Alloys and Compounds. 2009, 482, 53-57.

[9] BUCZKO, Z.; GNIADEK, M.; OLKOWICZ, K.; OKUROWSKI, W. Copper/nanodiamond composite coatings obtained by electrochemical deposition. Inżynieria Materiałowa. 2016, 6, 306-309.

[10] JABBAR, A., YASIN, G., KHAN, W.Q., ANWAR, M.Y., KORAI, R.M., NIZAM, M.N., MUHYODIN, G. Electrochemical deposition of nickel graphene composite coatings: effect of deposition temperature on its surface morphology and corrosion resistance. RSC Advances. 2017, 7, 31100.

[11] CIEŚLAK, G., TRZASKA, M. Structure and properties of nanocomposite nickel/graphene oxide coatings produced by electrochemical reduction method. Archives of Metallurgy and Materials, 2019, 64, 4, 1479-1486.

[12] BARTOSZEK, W., TRZASKA, M. Hybrid nanocomposite layers ni/al2o3/cgraphite produced by electrocrystallization method. Archives of Metallurgy and Materials. 2019, 64,1, 167-173.

[13] HOVESTAD, A., JANSSEN, L.J.J. Electrochemical codeposition of inert particles in a metallic matrix. Journal of Applied Electrochemistry. 1995, 25, 6, 519-527. DOI 10.1007/BF00573209.

[14] CHRONOWSKA-PRZYWARA, K.; KOT, M. Effect of scratch test parameters on the deformation and fracture of coating-substrate systems. Tribologia. 2014, 254, 19-29.