Composite Coatings in Copper Matrix with Graphite as Dispersed Phase obtained by Electrodeposition

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Composite copper coatings using graphite as dispersed phase were obtained by direct current electrodeposition. The structure of thin composite copper layers was studied by SEM, EDX and optical microscopy analysis. The percent of graphite particles in electrolyte and the applied current density was found to modify significantly the composite layers structure and properties.

Keywords: copper electrodeposition, graphite, composite coatings, self lubricated properties

Composite coatings obtained by including dispersed-phase particles in the matrix material have a wide technological interest for many applications. Copper is an environment friendly material with good electrical properties, maleability and corrosion resistance at ambient temperature; poor mechanical properties can be improved without changing its good electrical properties by creating composite coatings. The technologies often used for making composite coatings are physical vapour deposition, chemical vapour deposition, thermal spraying, laser cladding, electroless deposition and electro-deposition. The developing tendency for obtaining composite coatings by electrodeposition is driven by the following advantages: low cost, good reproductibility, uniform deposits and complexly shaped substrates also the process parameters can be easily tailored [1-3]. Using this technique can be obtained layers resistent to wear, layers with high hardness and with self lubricated properties; copper-graphite composite have self lubricated properties and they can replace the classical industrial bearing surfaces [4, 5]. The electrodeposition mechanism consists of five consecutive steps [6, 7]:

- the formation of ionic clouds on particles;
- convection towards the cathode;
- diffusion through the hydrodynamic boundary layer;
- diffusion through a concentration boundary layer;
- adsobtion of the particles on the cathode surface.

The quality of the deposit depends on a large number of variables such as dispersed phase (DP) characteristics, electrolyte composition, current density, *p*H etc. The amount of the embedded particles in matrix plays an important role in improving the new composite coating [8].

Copper-graphite composites obtained by electro-deposition have industrial applications for printed circuits, electrical contacts and automotive parts [9-16].

Experimental part

Since the copper-graphite composite coatings are entirely new, the electrochemical deposition technology was established [17, 18]. An SP-150 type potentiometer, a magnetic stirring machine and an electrolyte tank were used in order to obtain the copper composite coatings (fig. 1).

A volume of 250mL electrolyte was used and the experiments took place at 20°C.

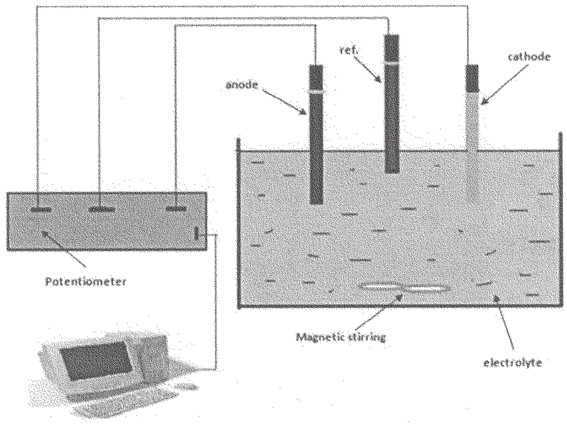

Fig.1. Experimental setup for electrodeposition

As for the copper layers in order to determin the optimal electrodeposition parameters there were used copper samples as base metal, substances for the preparation of electrolytic solutions, graphite powder as dispersed phases for the coatings and substances for preparation the surfaces. The active electrodes surfaces were degreased and polished [19-21]. The graphite particles (8-14μm size) were maintained in suspension in the electrolytic bath by continuous magnetic stirring of 250rpm for at least 100 minutes before deposition.

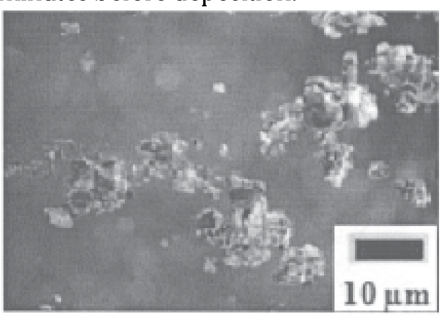

Fig. 2. Micrograph of the graphite dispersed phase (500X)

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For copper electrodeposition are commonly used cyanide plating baths, pyrophosphate plating bath and sulphate plating baths [9, 10, 22-24]. Because cyanide plating baths are toxic must be carefully used. There was used a strong acidic electrolyte (*p*H = 1) based on copper sulphate with the following chemical composition: $CuSO_4 \cdot 5H_2O$ - 200 $g \cdot dm^{-3}$ respectively H_2SO_4 – 50$g \cdot dm^{-3}$. Concentrations of graphite powder were 40$g \cdot dm^{-3}$, 60$g \cdot dm^{-3}$ and 80$g \cdot dm^{-3}$ in the electrolytic solution. The anodes are important for co-deposition; cast, extruded or rolled copper sheets are generally used for anodes. Copper anodes for high efficiency solutions must be free of oxide inclusions. Crystal structure of copper anodes is important for electrodeposition. In this work a high purity rolled copper anode (99.9%) and cathode of copper tape having an active area of 16cm^2 were used. The cathode face that did not come in direct contact with the anode was insulated. The working parameters of the deposition were as following: current density 1.5; 2.0 and 2.5$A \cdot dm^{-2}$, electrodeposition time of 120min. at magnetic stirring of 750rpm.

The surface morphology and EDX analysis of the copper composite coatings were performed by using FEI Quanta 200 Scanning Electron Microscope. The roughness of the samples was analyzed by a TR 100 roughness tester. The microscopic analysis of the composite layers was performed by Olympus PME3 optical microscope.

Results and discussions

The EDX analysis shows that graphite particles were embedded in the layers along with copper (table 1). Different graphite percentages embedded in the composite coatings depend on particles concentration in the electrolyte and applied current densities.

Table 1

VARIATION OF THE CURRENT DENSITIES ACCORDING TO THE PERCENT OF THE DP IN ELECTROLYTE AND EMBEDDED DP IN LAYERS FOR THE COPPER-GRAPHITE COMPOSITE COATINGS

Current density ($A \cdot dm^{-2}$)	Graphite particles in electrolyte ($g \cdot dm^{-3}$)	Graphite particles in layers (wt%)
1.5	40	29±1.2
2.0	60	57±1.5
2.5	80	37±1.3

It has been observed that the amount of the embedded graphite particles in layers increases with increasing the concentration of suspended graphite particles in the electrolyte. By increasing the DP particles in electrolyte of 80 $g \cdot dm^{-3}$, the amount of embedded particles decreases. The highest value for the embedded DP is 6 % obtained for

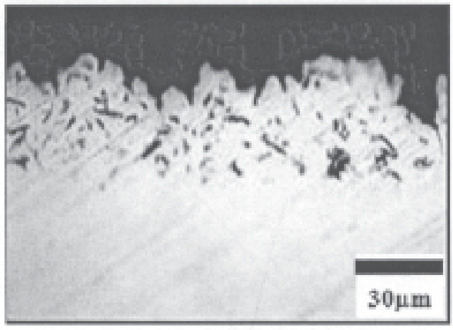


Fig. 3. Cross Optical Microscopy (500X) of the copper-graphite composite coatings obtained at 2$A \cdot dm^{-2}$, 60$g \cdot dm^{-3}$ DP in electrolyte, 750rpm, electrodeposition time of 120 min.

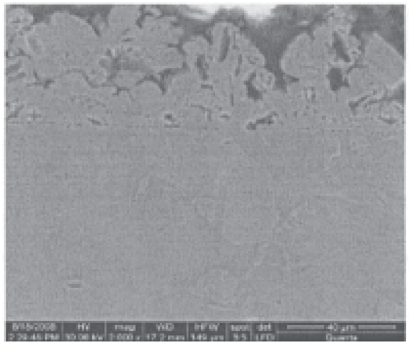


Fig. 4. Cross SEM micrographs of the copper-graphite composite coatings obtained at 2 $A \cdot dm^{-2}$, 60 $g \cdot dm^{-3}$ DP in electrolyte, 750 rpm, electrodeposition time of 120 min

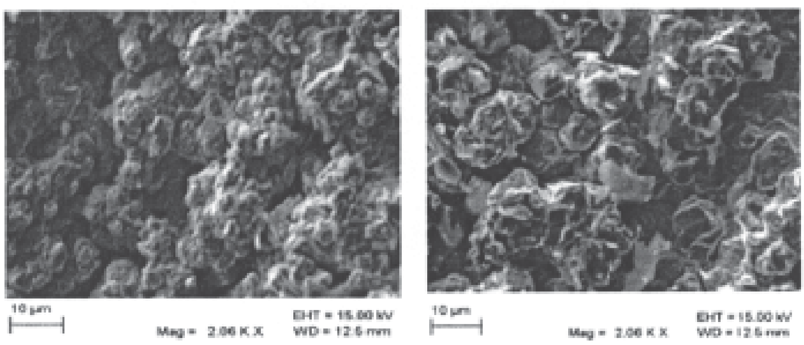
60 $g \cdot dm^{-3}$ DP in electrolyte, current density of 2$A \cdot dm^{-2}$, electrodeposition time of 120 min, stirring of 750 rpm and temperature of 20^{0}C (fig.3 and fig.4).

The figure 5a shows the copper-graphite composite coatings surface prepared at 2$A \cdot dm^{-2}$, 60 $g \cdot dm^{-3}$ graphite particles in electrolyte. Similarly, figure 5b shows the copper-graphite composite coatings prepared at 2.5$A \cdot dm^{-2}$ using 60$g \cdot dm^{-3}$ DP in electrolyte, 750rpm, electro-deposition time of 120 min.

SEM and optical microscopy analysis show homogeneous distribution of the additional phase-graphite- in the copper matrix especially for 2$A \cdot dm^{-2}$ current density, 60 $g \cdot dm^{-3}$ DP in electrolyte, stirring of 750 rpm and electrodeposition time of 120 min.

The figure 5 shows that composite coating surface is smoother at 2$A \cdot dm^{-2}$ than the composite coating surface prepared at 2.5$A \cdot dm^{-2}$ conditions also absence of cracks and dendrites.

The presence of graphite particles in the copper layers changed both structure and properties of the copper composite coatings. The layers thickness metallographic examinations were made in the middle of the samples on sections of 10mm. It can be observed an increase of the



a b

Fig. 5. Surface SEM micrographs of the coatings: a) copper-graphite composite coatings obtained at 2$A \cdot dm^{-2}$; b) copper-graphite composite coatings obtained at 2.5$A \cdot dm^{-2}$ using 60$g \cdot dm^{-3}$ DP in electrolyte, 750rpm, electrodeposition time of 120 min

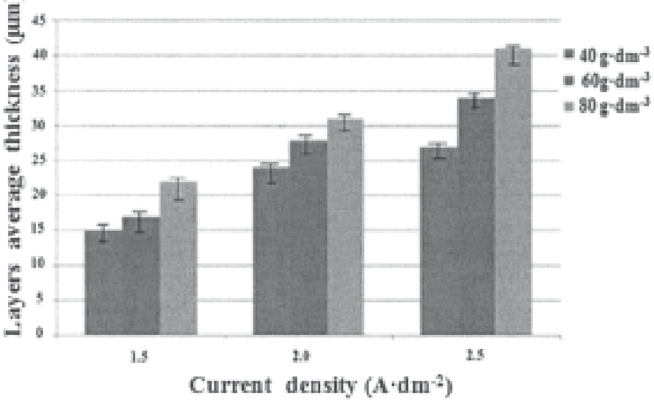


Fig. 6. The thickness variation of the composite layers with applied current densities and different DP concentrations in electrolyte

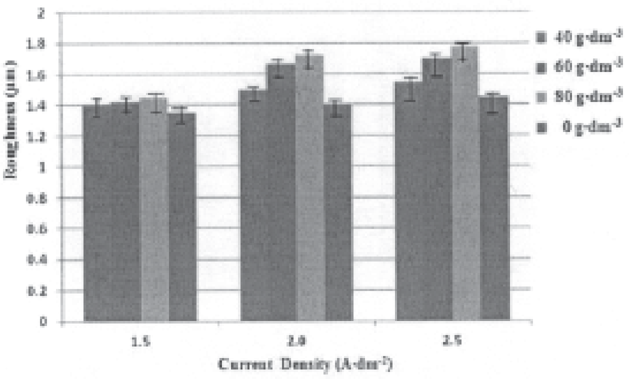


Fig. 7. The roughness variation of the composite layers with applied current densities and different DP concentrations in electrolyte

thickness of the layers by increasing the applied current density and by increasing the concentration of DP in electrolyte (fig. 6).

The most uniform structure for the composites is obtained for 2 A·dm^{-2} current density, 60 g·dm^{-3} DP in electrolyte, 750 rpm stirring and electrodeposition time of 120 min. Setting these parameters can be obtained the highest value (6%) for the embedded phase in the composite layer.

Roughness of the coatings obtained by adding graphite particles in the electrolyte solution have quite large variations for composites obtained under different conditions. The presence of graphite dispersed phase have a catalytic role in the copper reduction reaction. The immediate effect of this phenomenon is the modification of the matrix structure by increasing the size of the crystals which implicitly leads to higher surface roughness.

Also the current density had greatly influenced the crystal structure of the copper matrix. It is important the shape of the DP, too. The results for roughness variation of the composite layers for different applied current densities and different DP concentrations in electrolyte are presented in figure 7.

It is noted that the average roughness values varies from 1.40µm to 1.72µm for copper-graphite composites and 1.32-1.42µm for the pure copper layers. The particles concentration of 40-80 g·dm^{-3} in electrolyte makes the composite coatings surface rougher. The smoothest surface of Ra 1.32µm is obtained for the pure copper coatings. The experiments had in view also the influence of the distance between electrodes which is an important parameter for the composites layer quality; the distance anode-cathode was fixed at a range between 1-3cm. The

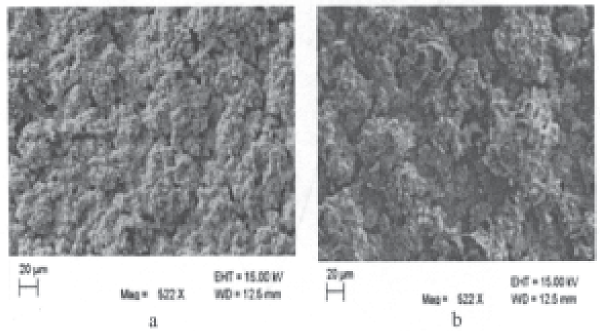


Fig. 8. SEM micrographs of the composite coatings for: a) copper-graphite composite coatings obtained at 2A·dm^{-2}, distance anode-cathode 2cm and b) copper-graphite composite coatings obtained at 2A·dm^{-2}and distance anode-cathode 1cm

results shows that the highest value for the embedded phase (6%) in the copper matrix is obtained for 2cm distance between electrodes.

SEM analysis indicates an uniform deposit accomplished for 2 cm distance between electrodes; if the distance anode-cathode is smaller or bigger than 2cm the composite deposit is patchy presenting low adhesion.

Conclusions

Electrochemical deposition is a suitable method for making composite coatings. Copper matrix composites with graphite particles as DP can be obtained by tailoring the electrodeposition parameters such as particles concentration in electrolyte, applied current density, electrodeposition time and electrolyte stirring. The presence of graphite DP in the copper matrix makes significant changes of the composite layers structure and properties such as surface roughness and layers thickness.

The most uniform structure for the composites is obtained for 2A·dm^{-2} current density, 60g·dm^{-3} DP in electrolyte, 750 rpm stirring and electrodeposition time of 120 min. Setting these parameters can be obtained 6% embedded DP in composite layer.

Average values for thickness of the layers varies between 15 to 41µm depending on the applied current densities and embedded DP in copper layers.

The particles concentration in electrolyte makes the composite coatings surface rougher. The smoothest surface is obtained for the pure copper coatings.

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