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# COMPOSITE COATING IN COPPER MATRIX WITH MOLYBDENUM IN DISPERSION PHASE OBTAINED BY ELECTROCHEMICAL METHODS

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## ABSTRACT

*The paper describes reviews referring to determination of working parameters of the development processes of composites in copper matrix, obtained by electrochemical deposition methods.*

*The molybdenum particles having particle sizes of 3µm, respective 7µm have been used as a complementary phase. The optimal conditions for codeposition were determined, the structure and chemical composition of the obtained coatings were presented and the coating characteristics were tested.*

KEYWORD: electrochemical deposition, structure, coating

## 1. Introduction

The present study refers to the obtaining of composite coatings in the copper matrix by electrochemical co-deposition of molybdenum. The particles used were of 3µm and 7µm in size.

There is no data in the literature on composite coatings of copper and molybdenum in disperse phase.

The composite coatings obtained by including the dispersed-phase particles in the matrix material have a wide technological interest for many fields of applications. These materials have a wide range of new properties, in particular improved mechanical properties [1].

## 2. Results and experimental researches

An ELLY BUDAPESTA type electrolyser, a magnetic stirring machine and an electrolyte tank (receiver) were used in order to obtain the copper coatings.

It was used a solution volume of 250 ml, and the experiments took place at 20ºC.

Like in Cu electrodeposition with a view to determining the optimal electrodeposition parameters use was made of copper samples - base metal, substances for the preparation of electrolytic solutions, molybdenum powder (size 3µm and 7 µm) solutions and substances for preparation of surfaces.

By electrodeposition composite materials were obtained with molybdenum disperse phase. Concentrations of molybdenum powder of 7µm and 3µm respectively were 20%, 40%, 60% in the electrolyte solution [2].

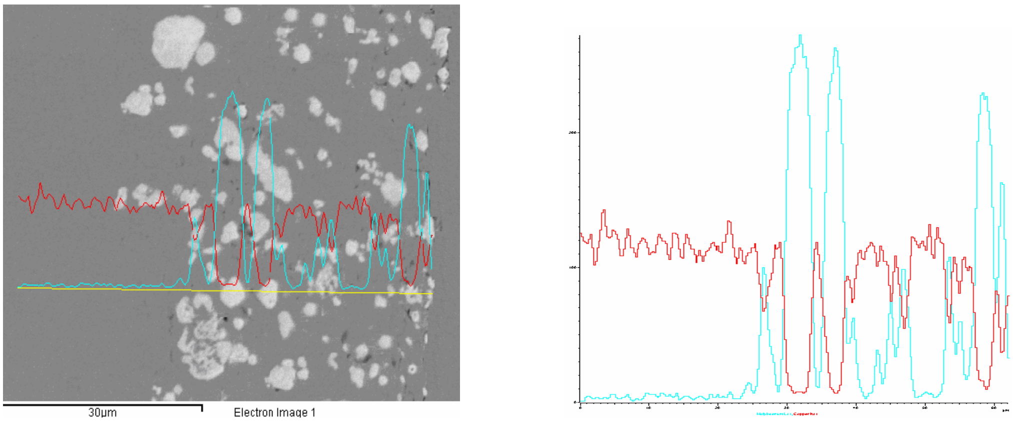
The coppering electrolyte used had the following chemical composition:

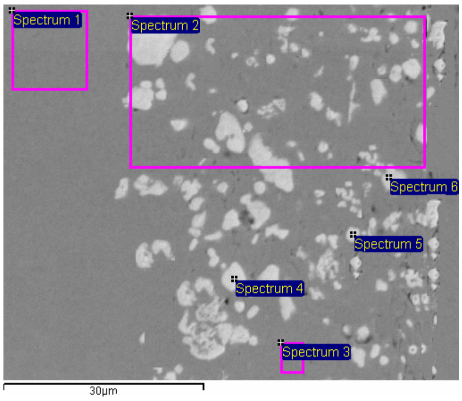
$CuSO_4 \cdot 5H_2O$: 200g/L; $H_2SO_4$:80 g/L.

Since the composite materials Cu-Mo are entirely new, the electrochemical deposition technology was established. In copper electrodeposition, certain parameters were kept: orientation of electrodes, distance between electrodes 2cm. A high purity cooper anode and cathode of cooper tape having an active area of 16 were used.

The cathode face that did not come in direct contact with the anode was insulated.

The presence of particles was highlighted by EDX tests. By electron microscopy in cross section and EDX spot analysis it was observed a homogeneous distribution of the additional phase (Mo 3 micrometres and 7 µm) in the copper matrix (Figures 1, 2).

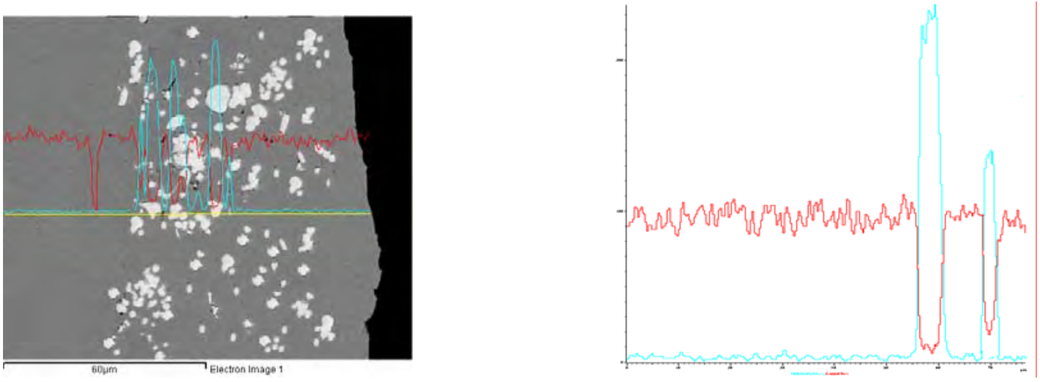


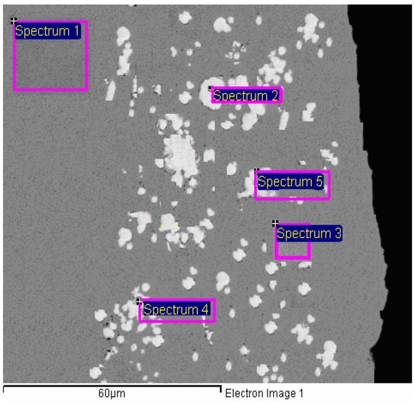


Processing option : All elements analysed (Normalised)
All results in weight%

| Spectrum | O | Cu | Mo | Total |
|---|---|---|---|---|
| Spectrum 1 | | 100 | | 100 |
| Spectrum 2 | | 76.4 | 23.6 | 100 |
| Spectrum 3 | | 100 | | 100 |
| Spectrum 4 | 2.11 | 4.24 | 93.65 | 100 |
| Spectrum 5 | 2.01 | 14.36 | 83.64 | 100 |
| Spectrum 6 | 3.41 | 6.18 | 90.4 | 100 |

***Fig. 1.*** *EDX analysis in cross- section and spot for Cu-Mo composite coatings obtained at $1.5\ A/dm^2$, 60min, 500rpm, 40g/L particles in electrolyte solution, particle size 3µm.*





Processing option : All elements analysed (Normalised)
All results in weight%

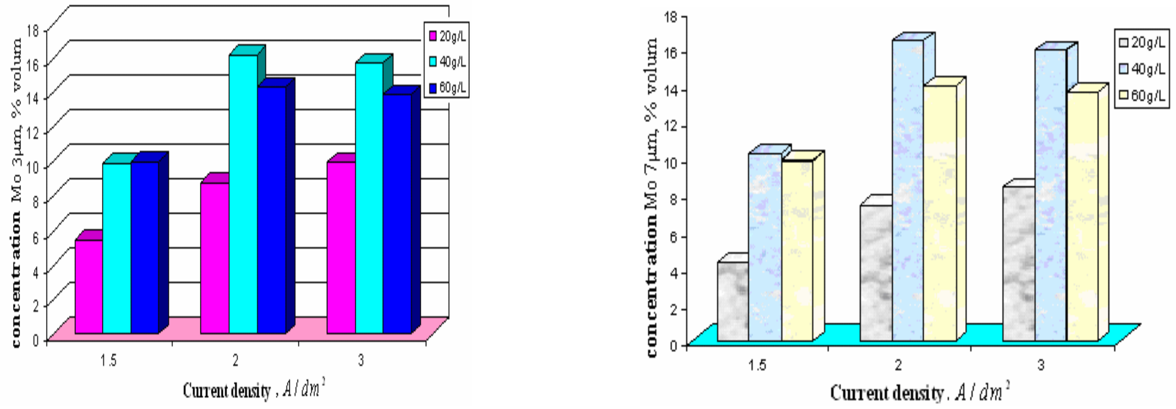
| Spectrum | O | Cu | Mo | Total |
|---|---|---|---|---|
| Spectrum 1 | | 100 | | 100 |
| Spectrum 2 | | 93.45 | 6.55 | 100 |
| Spectrum 3 | | 100 | | 100 |
| Spectrum 4 | 2.35 | 11.76 | 85.89 | 100 |
| Spectrum 5 | 2.1 | 31.19 | 66.7 | 100 |

***Fig. 2.*** *EDX analysis in cross section and spot for Cu-Mo composite coatings obtained at $2\ A/dm^2$, 60min, 500rpm, 40g/L particles in electrolyte solution, particle size 7 m.*

The concentration of particles in the composite layer increases with increasing current density up to a certain value (Imax) and then decreases [3]. Figure 3 illustrates the relationship of interdependence between the concentration of Mo 3µm, 7 µm particles in the composite layer and current density for different amounts of particles contained in the electrolyte.

It is noted that the percentage of inclusion increases with increasing current density to a concentration of 20g/L, and the concentrations of 40, 60g/L particles in the electrolyte solution increases with increasing inclusion rate of current density and reaches a maximum at $i_{max}$ = 2 $A/dm^2$ then decreases [4]. The highest degree of inclusion has been determined for Cu-Mo composite coating obtained at 2 $A/dm^2$, 180 min, 500rpm, 40g/L, and the minimum degree of inclusion of molybdenum particle, size of 3µm (size 7µm) in copper matrix was obtained at 1.5 $A/dm^2$, 30 min, 500rpm, 20g/L.

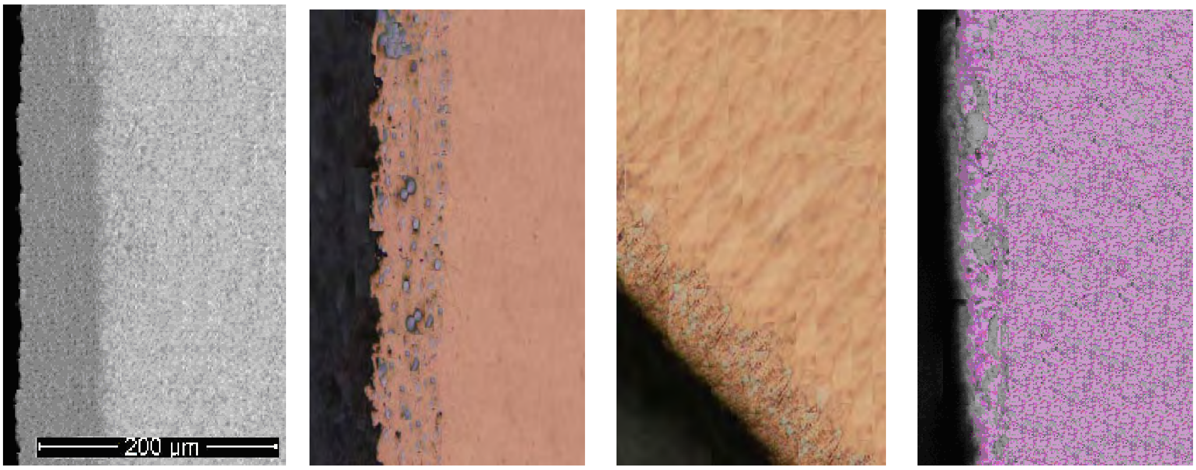
Analyzing the cross-section microstructures it is observed the uniform distribution of the molybdenum layer. For concentrations of 40g/L and 60g/L Mo agglomerations of particles of molybdenum can be observed [5].



a) b)

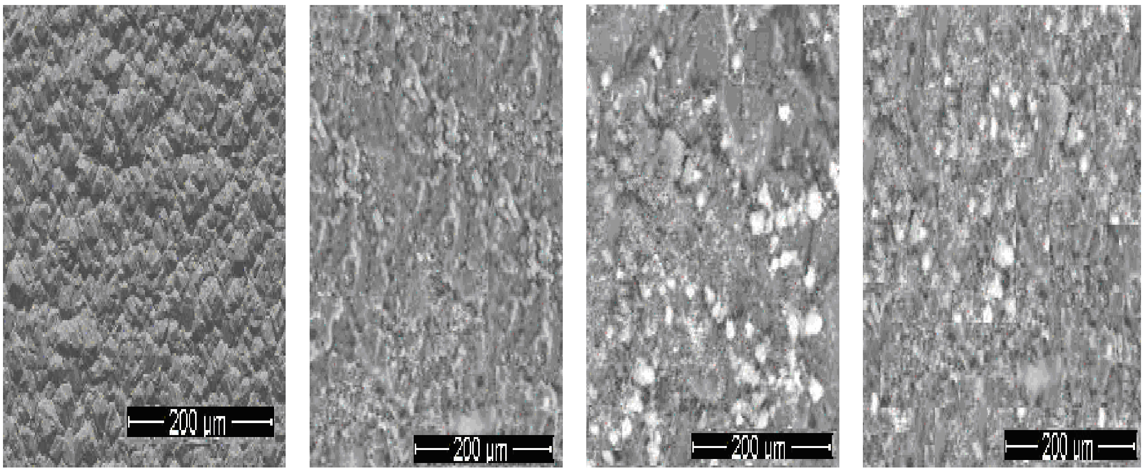
***Fig. 3.*** *Variariation of the percentage content of Mo particles in the composite deposit as a function of current at a concentration of 20g/L, 40g / L, 60g/L Mo in the electrolyte solution, 180min: a) Mo size 3µm, b) Mo size 7µm.*

The Cu-Mo composite coatings with a size of 3 µm and 7 µm appear very well distributed, they are compact, continuous with a finishing tendency of crystals as compared with pure copper, leading to the formation of fine, compact and continuous deposits (Figures 4,5,6,7).



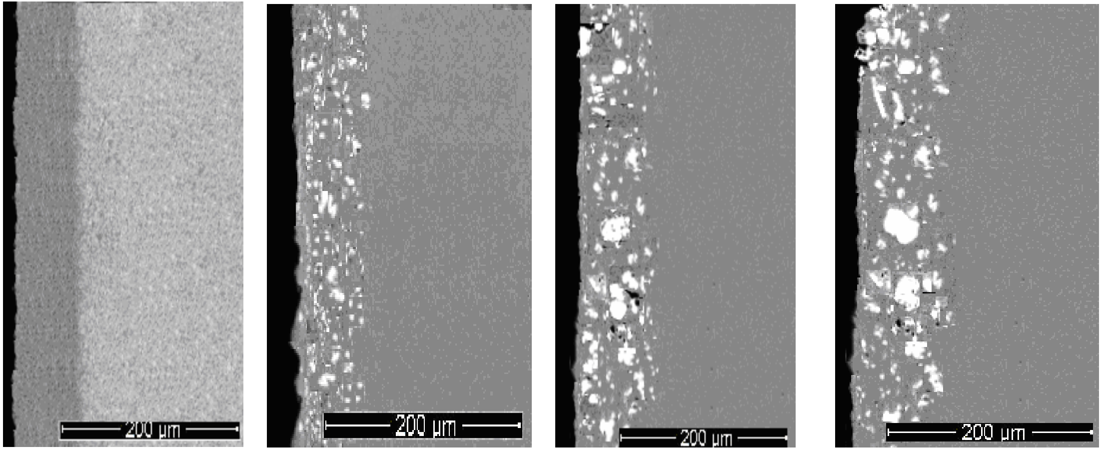
a) b) c) d)

***Fig. 4.*** *Cross-section microstructures for the Cu- Mo coatings with particle size 3µm , 180min, 500rpm, i= 2 $A/dm^2$ : a) pure Cu, b)Cu- Mo, 20g/L; c)Cu-Mo 40g/L; d)Cu-Mo, 60g/L, magnifying x 500.*



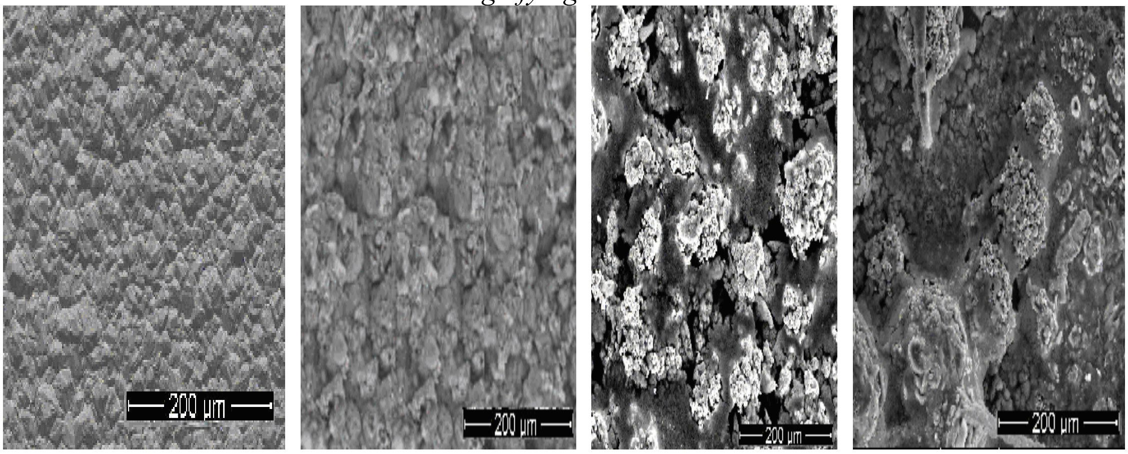
a) b) c) d)

***Fig. 5.** SEM surface microstructures for Cu- Mo coatings , particle size 3µm , 180min, 500rpm, $i = 2\ A/dm^2$ : a) pure Cu , b)Cu- Mo, 20g/L; c)Cu-Mo 40g/L; d)Cu-Mo, 60g/L, magnifying x 500.*



a) b) c) d)

***Fig. 6.** Figure 6. SEM surface microstructures for Cu- Mo coatings, particle size 7µm, 180min, 500rpm, $i = 2\ A/dm^2$ : a) pure Cu , b)Cu- Mo, 20g/L; c)Cu-Mo 40g/L; d)Cu-Mo, 60g/L, magnifying x 500.*



a) b) c) d)

***Fig. 7.** Cross-section microstructures for the Cu- Mo coatings with particle size 7µm, 180min, 500rpm, $i = 2\ A/dm^2$ : a) pure Cu, b)Cu- Mo, 20g/L; c)Cu-Mo 40g/L; d)Cu-Mo, 60g/L, magnifying x 500.*

It is noted an increase in the inclusion of molybdenum, particle size of 3 micrometres and 7 µm, in the copper matrix with increased concentration in the electrolyte up to 40g/L and for a concentration of 60g/L, a decrease of particle inclusion. The presence of particles in the deposited layers will change both their structure and properties. Layer thickness values are given in Table 1. For the layer thickness metallographic examinations were made in the middle of the sample on portions of 10 mm. The sample was divided into 10 equal parts and each time three measurements were made [6].

As regards roughness of the coatings obtained by adding molybdenum particles in the electrolyte solution there are quite large variations in the level of roughness for composite coatings obtained under different conditions.

***Table 1.*** *Thickness of Cu – Mo layer*

| Current density, I $A/dm^2$ | Conc. Fd. in electrolyte [%] | Thickness [µm] | | | |
|---|---|---|---|---|---|
| | | 30 [min] | 60[min] | 90[min] | 180[min] |
| I=2 $A/dm^2$ (Cu-Mo 3µm) | M | 9 | 25 | 36 | 50 |
| | 20g/L | 9 | 13 | 19.5 | 37 |
| | 40g/L | 9.5 | 14 | 34 | 45 |
| | 60g/L | 11.5 | 15 | 20 | 30 |
| I=2 $A/dm^2$ (Cu-Mo 7µm) | M | 9 | 25 | 36 | 50 |
| | 20g/L | 7 | 13 | 17 | 28 |
| | 40g/L | 10 | 16 | 30 | 42 |
| | 60g/L | 12 | 19 | 29 | 40 |

These values are lower compared to the roughness values determined for pure copper. The presence of molybdenum particles has catalytic role in the copper reduction reaction. The immediate effect of this phenomenon is the modification of the structure deposited by decreasing the size of crystals which implicitly leads to lower surface roughness.

It is noted that the average absolute roughness ranges from 2.9 to 1.6 µm for Cu-Mo 3 µm and 2.7 to 2µm for Cu-Mo 7 µm.

## 3. Conclusion

By electron microscopy in cross section and the EDX spot analysis it was observed the inclusion of the dispersed phase and homogeneous distribution of the additional phase (Mo 3 µm and 7 µm, respectively) in the copper matrix, when the electrochemical method is applied.

The degree of inclusion of molybdenum particle size of 3 µm and 7 µm in the copper matrix increases with increasing their concentration in the electrolyte up to 40g/L.

The presence of molybdenum particles has catalytic role in the copper reduction reaction.

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