

ELECTROCHEMICAL DEPOSITION OF COMPOSITE COATINGS IN COPPER MATRIX WITH TiO₂ NANOPARTICLES

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Cu-nanoTiO₂ composite coatings electroplated from copper sulphate bath were obtained and characterised. The paper presents the influence of the concentration of TiO₂ nanoparticles as dispersed phase in copper matrix coatings obtained at different current densities. The concentrations of nano-TiO₂ particles (17nm) were 5, 10 and respectively 50g/L in electroplating bath. It was shown that the mechanism of electrodeposition affected the incorporation of the solid particles into copper matrix. The surface morphology and composition of layers were studied by optical and scanning electron microscopy (SEM) and EDX analysis. The results have shown that nano-TiO₂ particles presence either in solution or embedded in small amount in the copper matrix has a great influence on the structure and properties of the coatings. The microhardness of the layers with nano-TiO₂ was also determined.

INTRODUCTION

The definition of nanocomposite material has broadened significantly to encompass a large variety of systems such as one-dimensional, two-dimensional, three-dimensional and amorphous materials, made of distinctly dissimilar components and mixed at the nanometer scale.¹ The general class of nanocomposite organic/inorganic materials is a fast growing area of research. Significant effort is focused on the ability to obtain control of the nanoscale structures *via* innovative synthetic approaches. The properties of nanocomposite materials depend not only on the properties of their individual parents, but also on their morphology and interfacial characteristics.^{2,3} Nanocomposites also offer the possibility to combine diverse properties that are impossible within a single material, *e.g.* flexible mechanical properties and superconducting properties.

Experimental work it has generally shown that virtually all types and classes of nanocomposite materials lead to new and improved properties, when compared to their macrocomposite

counterparts. Therefore, nanocomposites promise new applications in many fields such as mechanically reinforced lightweight components, non-linear optics, battery cathodes and ionic, nanowires, sensors and other systems.⁴⁻⁶

The paper presents an investigation on copper coatings obtained with TiO₂ nanoparticles as dispersed phase by electrocodeposition. TiO₂ is used in many application because it has a lot of useful properties: semiconductor properties, photocatalysis activity, corrosion resistance etc. and is applicable in a lot of traditional industries, environmental treatment, self-cleaning material and anti-microbial.

The present work was undertaken to elucidate the mechanism and main factors affecting the incorporation of TiO₂ solid particles into copper deposit. Electrochemical codeposition is of widely interest as an important method to obtain nanocomposite coatings; it is a simple, inexpensive, versatile and easy controllable technique of obtaining nanocomposite coatings as compared with the conventional methods. The influence of the presence of TiO₂ nanoparticles in electrolyte

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and the properties of the coatings were studied. The results are compared with copper coatings without oxide nanoparticles to understand the effects of dispersed phase on the properties of composite coatings during electrocrystallization.

RESULTS

1. Composition of coatings. The presence of nano-TiO₂ particles in composite coatings was evidenced by energy dispersive analysis, EDX (Fig.1). The amount of nano-TiO₂ embedded in

coatings is different and depends by the current densities and the amount of nanoparticles used in bath of electrodeposition (Fig. 2).

2. Structural aspects. Optical micrographs on the cross section of the coatings revealed the presence of nano-TiO₂ particles in layers in comparison with pure copper deposits (Fig. 3, a and b).

Scanning electron microscopy (SEM) revealed the comparative surface morphology of coatings and the presence of the TiO₂ nanoparticles in the deposits, in a sinterised shape (Fig. 3 c).

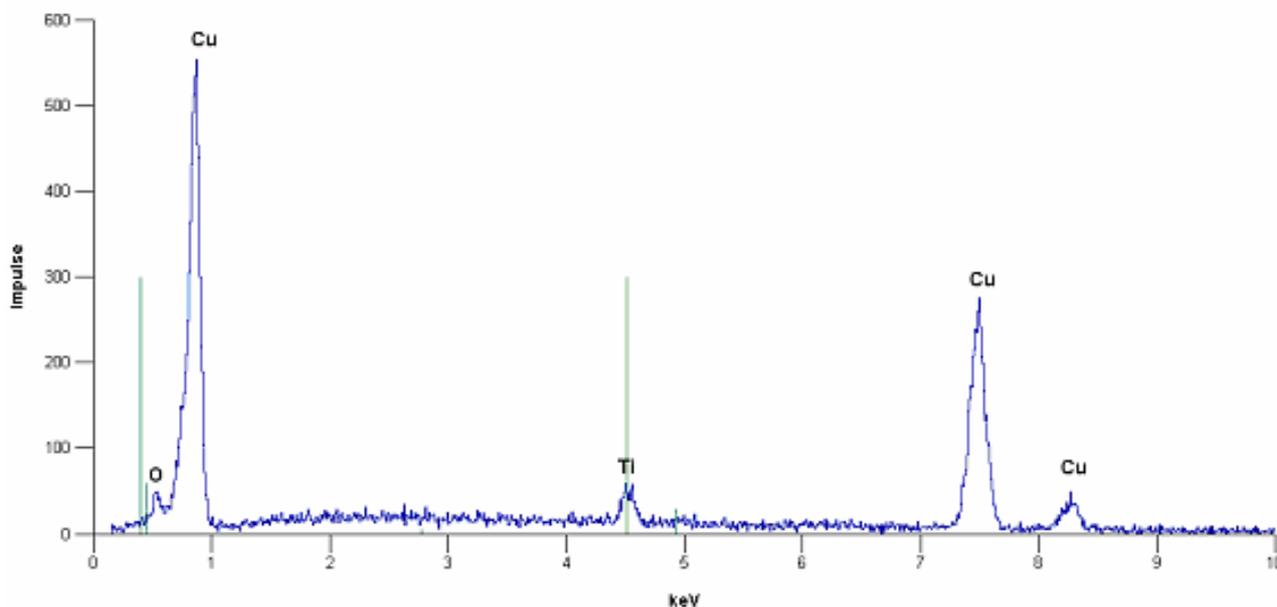


Fig. 1 – EDX spectrum of Cu/nano-TiO₂ composite coatings.

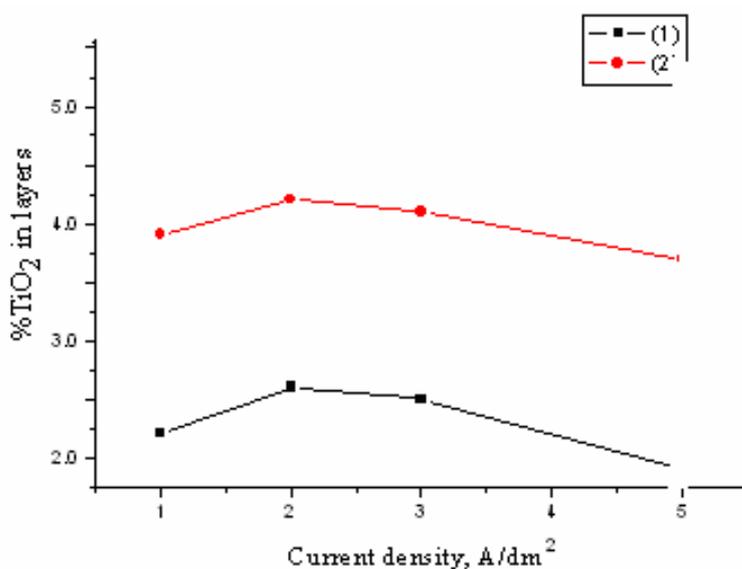


Fig. 2 – nano-TiO₂ percentages in layers versus the electrolysis current density for two TiO₂ concentration in electrolyte: 1) 10 g/L and 2) 50g/L.

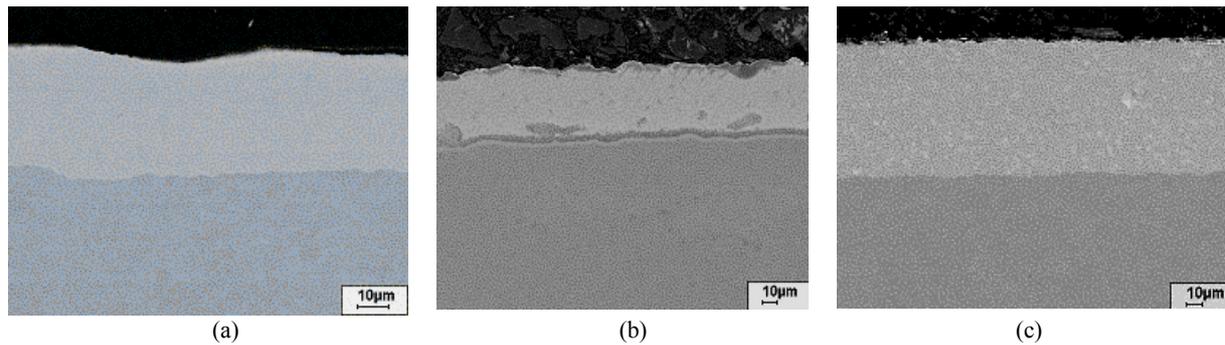


Fig. 3 – Optical micrographs of the cross section on pure copper coatings (a) and composite coatings with 10 g/L nano-TiO₂ (b) and 50 g/L nano-TiO₂ (c) in electrolyte.

a) Thickness of layers. Tests of the thickness of the deposits are most often used for metallic coatings. The layer thickness measured in the middle of the cross section ranged between 40-75 μm for 90 min of deposition time. The results obtained with Fischerscope equipment and optical microscopy Olympus PME 3 Microscope are shown in Table 1.

b) Microhardness. In Table 2 are shown the results of the Vickers microhardness (HV_{0.025}) of coatings in copper matrix.

c) Surface roughness. The values of the roughness of copper coatings obtained from electrolytes with and without particles are listed in Table 3.

Table 1

Thickness of layers in copper matrix

| nano-TiO ₂ , g/L | Minimum, [μm] | Maximum, [μm] | Thickness (medium values), [μm] | Standard deviation, [μm] |
|-----------------------------|---------------|---------------|---------------------------------|--------------------------|
| - | 31.53 | 39.35 | 35.52 | ± 2.67 |
| 5 | 37.51 | 41.00 | 39.23 | ± 1.21 |
| 10 | 41.80 | 47.53 | 44.62 | ± 1.82 |
| 50 | 42.09 | 47.64 | 45.75 | ± 1.86 |

Table 2

Microhardness of layers in copper matrix with and without nano-TiO₂ particles in electrolyte

| Dispersed phase (DP) | Concentration of DP in electrolyte, g/L | HV _{0.025} Min. value | HV _{0.025} Max. value | HV _{0.025} Average value | Standard deviation |
|----------------------|-----------------------------------------|--------------------------------|--------------------------------|-----------------------------------|--------------------|
| - | - | 98 | 115 | 108 | ± 6.3 |
| TiO ₂ | 5 | 102 | 118 | 110 | ± 5.4 |
| TiO ₂ | 10 | 104 | 121 | 113 | ± 4.6 |
| TiO ₂ | 50 | 115 | 134 | 125 | ± 5.3 |

Table 3

Roughness of copper layers with and without nano-TiO₂ in electrolyte

| Dispers phase (DP) | Concentration of DP in electrolyte, g/L | Arithmetic averaged roughness, Ra [μm] | Root-mean-squared roughness, Rz [μm] | Rz _{max} [μm] | Rz _{min} [μm] | Deviation standard, S _{Rz} |
|--------------------|-----------------------------------------|----------------------------------------|--------------------------------------|------------------------|------------------------|-------------------------------------|
| - | - | 5.69 | 37.34 | 43.36 | 32.68 | ± 3.45 |
| TiO ₂ | 5 | 1.32 | 9.41 | 10.22 | 8.08 | ± 0.74 |
| TiO ₂ | 10 | 1.14 | 7.94 | 8.92 | 7.33 | ± 0.61 |
| TiO ₂ | 50 | 1.28 | 9.26 | 9.96 | 7.89 | ± 0.69 |

DISCUSSION

1) Mechanism

According to the literature the mechanism of electrodeposition of both inert particles and metals is far from being well understood. Three mechanisms, namely, mechanical inclusion, electrophoresis and adsorption of inert particles onto the cathode were proposed.⁷⁻⁸ Guglielmi was first that proposed a mathematical model for the electrochemical codeposition of inert particles.⁷ His model is based on two successive adsorption steps:

The inert particles are loosely adsorbed on the cathode and they are in equilibrium with the particles in suspension. Adsorbed ions and solvent molecules surround the particles.

A strong electrochemical adsorption of the particles on the cathode takes place in the second step. The inert particles are now permanently bound to the cathode and are consequently embedded in the deposit.¹⁰

For this model Guglielmi derived the following equation:

$$\frac{C}{\alpha} = \frac{Wi_0}{nFdv_0} \cdot e^{(A-B)\eta} \cdot \left(\frac{1}{k} + C \right) \quad (1)$$

where W_p is the weight of one particle, the coefficient P represents the probability for a particle to become incorporated, N_p the number of particles crossing the diffusion layer at the working electrode per unit of time and surface area, M is atomic weight of the element deposited, n is number of electrons participating in the reduction reaction, F is Faraday constant and i is current density.⁹

In our experiments it was tested the validity of weight percentage of the particles embedded by performing EDX analyses (Fig 1). The results of the investigations have confirmed that titanium oxide was included into copper matrix by electrocodeposition plating.

The codeposition of nano-TiO₂ and copper from copper sulphate bath was studied at different current densities (1, 2, 3 and 5A/dm²). Fig. 2 shows the percentage of nano-TiO₂ in deposits. It can be seen that the highest amount of the particles

where C is the concentration of particles in electrolyte, α the volume fraction of particles in the deposit, W the atomic weight of the electrodeposited metal, d the metal density, n the electrons transferred and F the Faraday constant. A is a parameter related to the metal deposition process, involved in the Tafel equation:

$$i = i_0 \cdot e^{A\eta} \quad (2)$$

were i and i_0 are the current density and the exchange current density and η overpotential. The parameters v_0 and B from eq. (1) play a similar role with the parameters i_0 and A , but are related to the inert particle deposition. The parameter k is derived from the Langmuir adsorption isotherm and depends essentially on the intensity of the interaction between particles and cathode.

Guglielmi verified the validity of his model for the codeposition of either titania or silicon carbide with nickel from a nickel sulfamate bath.⁸ We suppose that this mechanism is also valid for the codeposition of titania with copper from a copper sulphate bath.

The weight percentage (w%) of embedded particles in the composite coating can generally be expressed as:

$$\% \text{ w embedded particles} = \frac{W_p \cdot N_p \cdot P}{\frac{Mi}{nF} + W_p \cdot N_p \cdot P} \cdot 100 \quad (3)$$

embedded in copper layers was obtained at 2 A/dm², a current density more favourable for the copper reduction in sulphate electrolyte.

2) Structural aspects

a) Thickness of layers. As Table 1 shows the presence of oxide nanoparticles in the electrolyte influences the process of copper reduction. For small content of nano-TiO₂ particles in electrolyte, of 5g/L oxide, there is a catalytic process and the copper reduction rate has increased. However, the presence of oxide particles in a larger amount, as 50 g/L nano-TiO₂ in electrolyte, could play as a barrier, influencing the copper reduction rate and the obtained thickness of the coatings.

b) Microhardness. The presence of dispersed particles in the electrolyte as well as in copper matrix modifies the microhardness of layers, this

fact being mainly correlated to the amount embedded in the deposit (Table 2).

c) Surface roughness. As table 3 shows, the values of the roughness of samples obtained from electrolytes with and without particles are very different. The values of the arithmetic averaged roughness (Ra) for Cu/nano-TiO₂ coatings are lower than the values of pure copper coatings. For example the value of Ra was 1.14 μm for composite obtained with 10g/L nano-TiO₂ in electrolyte in comparison with 5.69 μm for pure copper coatings. However if the electrodeposition is carried out for a larger amount of TiO₂ in the electrolyte the influence is nuclear. We notice that the layers were characterised by homogeneity of the surface, especially for samples with 10 g/L nano-TiO₂ in electrolyte.

EXPERIMENTAL

Coatings of pure copper and copper matrix having nano-TiO₂ as dispersed phase were electrodeposited using a copper sulphate bath with the following composition: 225g/L CuSO₄·5H₂O and 45 g/L H₂SO₄ (38%). Dispersed phase of nano-TiO₂ particles (17 nm) has the concentration of 5, 10 and 50 g/L in solution. The electrolyte was magnetically stirred with 500 rpm to maintain the uniformity of particles in solution. The electrochemical cell was a 500 mL glass cylinder. The pure copper electrode was used as anode. The carbon steel samples were used as cathode with an active surface of 25 cm². Before electrolysis the samples were polished using alumina powder, degreased, electrochemical cleaned and washed.

The experiments were carried out at room temperature, using a potentiostat Univat-Lab. The current densities of optimal copper reduction rate were 1, 2, 3 and 5 A/dm² in good correlation with the composition of electrolyte and the electrolysis parameters. The pH value of electroplating bath was 0.5. The thickness of deposits ranged between 40-75 μm, for 90 min of deposition time and it was measured on the cross section with Fischerscope equipment and optical microscope (Olympus PME 3 microscope). The layer thickness was measured in the middle of the cross section cut at approximately 10 mm. Furthermore, a layer thickness measurement was performed at 10 distinct points.

The uniformity of dispersed phase existing in composite layers was analysed by optical microscopy on the cross section and also by scanning electron microscopy (SEM) for a comparative study. The chemical composition was evaluated

by EDX analysis (JEOL 6400F equipment). The Vickers microhardness of layers was measured on the cross section; surface roughness was also evaluated (Buehler – micromat 1).

CONCLUSIONS

Copper composite coatings in copper matrix with nano-TiO₂ like disperse phases were obtained.

The amount of nano-TiO₂ embedded in coatings is different and depends on the current density values and the amount of nanoparticles in bath of electrochemical codeposition.

Weight percentage of the embedded particles was verified by performing EDX analysis. The results confirmed that titanium oxide was included into copper matrix by electrocodeposition plating and the Guglielmi's mechanism was verified. The presence of nano-TiO₂ was also revealed by optical and scanning electron microscopy.

The microhardness and roughness of obtained layers were modified, this fact being mainly correlated with the amount of nano-TiO₂ embedded in the deposit.

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REFERENCES

1. M. Schlesinger and M. Paunovic, "Modern Electroplating", Fourth Edition, John Wiley & Sons Inc. (Ed.), New York, 2001, p. 255-280.
2. G. Cârâc, L. Benea, C. Iticescu, Th. Lampke, S. Steinhäuser and B. Wielage, *Surf. Eng.*, **2004**, *20*, p. 353-359.
3. J. Li, Y. Sun, X. Sun and J. Qiao, *Surf. & Coat. Tech.*, **2005**, *192*, p. 331-335.
4. P. K. Jena, E. A. Brocchi, I. G. Solórzano and M. S. Motta, *Mat. Sc. and Eng.*, **2004**, *A 371*, p.72-78.
5. H.KI. Kang, *Surf. & Coat. Tech.*, **2005**, *190*, p.448-452.
6. C. S. Lin, P. C. Hsu, L. Chang and C. H. Chen, *J. Appl. Electrochem.*, **2001**, *31*, p. 925-933.
7. N. Guglielmi, *J. Electrochem. Soc.*, **1972**, *119*, p. 1009.
8. J. P. Cellis and J. R. Roos, *J. Electrochem. Soc.*, **1977**, *124*, p. 1509.
9. J. P. Cellis, J. R. Roos and C. Buelens, *J. Electrochem. Soc.*, **1987**, *134*, p. 1404.
10. O. Mitoseriu, C. Iticescu and G. Cârâc, *Rev. Chim.* (Bucharest), **2004**, *55*, 525-529.

