

CHARACTERIZATION OF COPPER-SILICON NITRIDE COMPOSITE ELECTROCOATINGS

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Abstract. *Electrolytic copper presents high electrical and thermal conductivity, good ductility and high corrosion resistance, but low mechanical strength and wear resistance. Aiming the improvement of its mechanical resistance, silicon nitride particles were incorporated to copper by co-electrodeposition (electrolysis of a copper plating bath containing suspended particles). The influence of current density, particle concentration and stirring rate on incorporated particle volume fraction was studied. The influence of incorporation of silicon nitride particles on microhardness was analysed. Smooth deposits containing well-distributed silicon nitride particles were obtained. The current density did not show significant influence on incorporated particle volume fraction, whereas the variation of particle concentration in the bath and stirring rate had a more pronounced effect. The microhardness of the composite layers was higher than that of pure copper deposits obtained under the same conditions and increased with the increase of incorporated particle volume fraction. The microhardness of composites also increased with the increase of current density due to copper matrix grain refining.*

Keywords: *electrodeposition, composites, copper, silicon nitride*

1. INTRODUCTION

Electrodeposition is widely used for the production of metallic coatings, such as copper, nickel, tin, chromium and noble metals electroplates. This is a cheap technique that does not require sophisticated equipments. In order to improve some properties of these metallic coatings (hardness, wear resistance and corrosion resistance, for example), researches were developed incorporating particles of ceramic, metallic and polymeric materials to the electrodeposits (Hovestad and Janssen, 1995; Musiani, 2000). The co-electrodeposition consists in electrolyzing a solution containing the metallic salts and the particles in suspension. The main factors that influence the amount of incorporated particles, and consequently the properties of the composite coatings, are the electrolysis parameters (composition of the bath, pH, temperature, cathodic current density, stirring rate) and the parameters related to particles (type, concentration and mean size).

The copper electroplates are widely used in engineering applications due to the high electrical and thermal conductivity of copper, good ductility and good corrosion resistance. Nevertheless, these coatings show low mechanical and wear resistance. Aiming to modify the properties of electrolytic copper, particles of ceramic materials, Al_2O_3 (Celis and Roos, 1977; Buelens *et al.*, 1983; Hayashi *et al.*, 1993; Stankovic and Gojo, 1996; Wang *et al.*, 1998; Gan *et al.*, 2007), TiO_2 (Abdullin and Saifullin, 1997; Medeliene *et al.*, 2004), ZrO_2 (Benea *et al.*, 2000), SiC (Stankovic and Gojo, 1996) and MoS_2 (Stankovic and Gojo, 1996), metallic materials or intermetallics, Cr (Medeliene *et al.*, 2006) and ZrB_2 (Jin *et al.*, 2005; Guo *et al.*, 2006), polymeric materials, polyacrylonitrile (PAN) (Tang *et al.*, 1998) and also graphite (Stankovic and Gojo, 1996), carbon nanofibers (Arai and Endo, 2005) and microcapsules containing lubricants (Zhu *et al.*, 2004a) were incorporated to copper. The effect of particle incorporation on the copper coating properties was shown to be positive or negative depending on the electrolysis parameters employed and the type and characteristics of particles.

The objective of this work was the production of copper-silicon nitride electrocomposites from acidic sulfate bath and their characterization. The influence of particle concentration in the bath, stirring rate and current density on the incorporated particle volume fraction and characteristics of the coatings (rugosity, microstructure and microhardness) was evaluated.

2. EXPERIMENTAL PROCEDURE

The Cu-Si₃N₄ composite coatings were prepared in acidic sulfate bath containing 150 gL⁻¹ CuSO₄ and 30 gL⁻¹ H₂SO₄ at room temperature. The Si₃N₄ particles were maintained suspended in the solution by magnetic stirring. Three

stirring rates were used, 240, 400 and 550 rpm. The particles employed had a 1.7 μm mean size and their concentration in the bath was 20 and 40 gL^{-1} .

Sheets of AISI 1020 carbon steel with 100mm x 6mm x 1mm dimensions were used as cathodes. These were previously ground to a 600 grit finish, degreased and dried. The cathode was placed at the center of a cylindrical electrolytic copper anode of 40 mm diameter, previously etched in dilute HNO_3 . Cathodic current densities of 10, 20, 30 and 40 mAcm^{-2} were applied for 7h40min, 3h50min, 2h33min and 1h55min, respectively, in order to obtain deposits of nearly 100 μm thickness. The effect of current density, stirring rate and particle concentration on the volume fraction of incorporated particles, roughness, texture and microhardness was investigated.

The morphology of the coatings and the distribution of particles were examined by scanning electron microscopy (SEM)(LEO VP-1450) and the crystalline orientation was analysed by X-ray diffractometry (XRD)(Siefert-Debyelex 1001, Cu-K α).

The roughness of the composite coatings was measured using a surface roughness measuring instrument Mitutoyo SJ 201.

The percentage of embedded particles in the deposits was determined from polished cross-section photomicrographs using the Image Tool 2.0 free software. The image analysis operations were performed at 2000 times magnification on at least twenty fields of view for each coating and the mean volume fraction of incorporated particles was calculated.

The microindentation hardness of the composite coatings was measured on polished cross-sections using a Vickers' microhardness tester (Micromet 2004). A 100g load was applied for 30s.

Pure copper electrocoatings were also produced and their characteristics were compared to those of the composites.

3. RESULTS AND DISCUSSION

The X-ray diffractograms of all the deposits obtained in solutions containing suspended Si_3N_4 particles presented the Si_3N_4 phase characteristic peaks, as shown in Fig. 1, proving the incorporation of Si_3N_4 to copper.

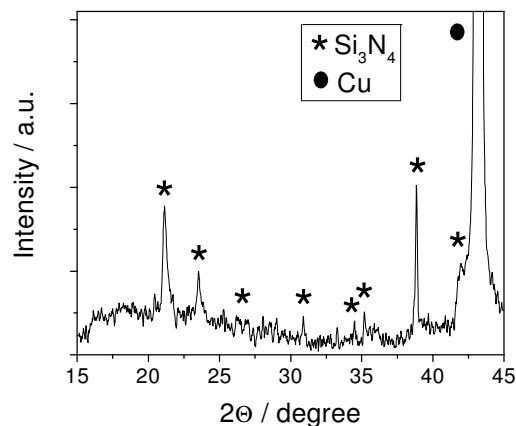


Figure 1. Typical X-ray pattern at low angles of Cu- Si_3N_4 composite coatings

The pure copper and composite coatings obtained under the experimental conditions investigated were well-crystallized but for the same current density the composites generally showed a finer surface morphology than the pure copper deposits, as seen in Fig. 2. This was also observed for other copper composites, such as Cu-ZrO $_2$ (Benea *et al.*, 2000), Cu-ZrB $_2$ (Jin *et al.*, 2005) and Cu-Al $_2$ O $_3$ (Bund and Thiemig, 2007). In the other hand, the morphology of both pure copper and composite coatings was finer when the current density increased, due to a higher nucleation rate.

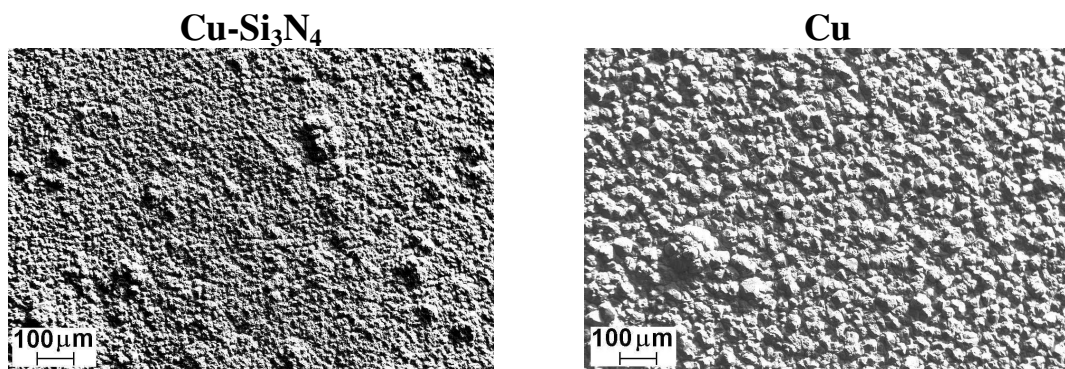


Figure 2. Surface morphology of Cu- Si_3N_4 composite and pure copper coatings obtained using 20 mA cm^{-2} current density (for the composite the Si_3N_4 concentration was 20 gL^{-1} and stirring rate 400 rpm)

Figure 3 shows the surface roughness of Cu-Si₃N₄ composite and pure copper coatings as a function of cathodic current density. For pure copper and Cu-Si₃N₄ composites obtained at 240 rpm that contained low particle amount (1.2 to 3.1%) roughnesses ranging from 1.5 to 2.7 μm were measured. The composites obtained using 400 and 550 rpm that contained 5.2 to 10.4% particle volume fraction exhibited the greatest smoothness, with roughness lower than 1.0 μm.

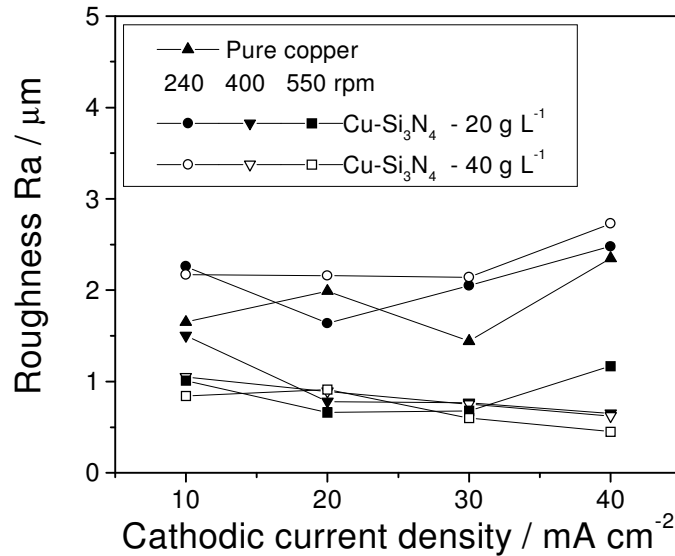


Figure 3. Surface roughness of Cu-Si₃N₄ composite and pure copper coatings

The X-ray diffratograms of the Cu-Si₃N₄ composites obtained at 400 rpm in solution containing 20 gL⁻¹ Si₃N₄ are shown in Fig. 4a. The relative intensity of the peaks associated to copper depends on the cathodic current density. The peaks relative to Si₃N₄ phase are not visible in Fig. 4a due to their low intensity. The orientation index of the (111), (200), (220), (311) and (222) planes of copper was calculated for each cathodic current density from the Eq. (1):

$$\text{Orientation index} = (I_{hkl} / \sum I_{hkl}) / (I_{ASTM\ hkl} / \sum I_{ASTM\ hkl}) \quad (1)$$

where I_{hkl} and $I_{ASTM\ hkl}$ are the intensities of (hkl) peaks related to copper phase in the composites and to copper of random orientation (Selected Powder Diffraction Data, 1978), respectively.

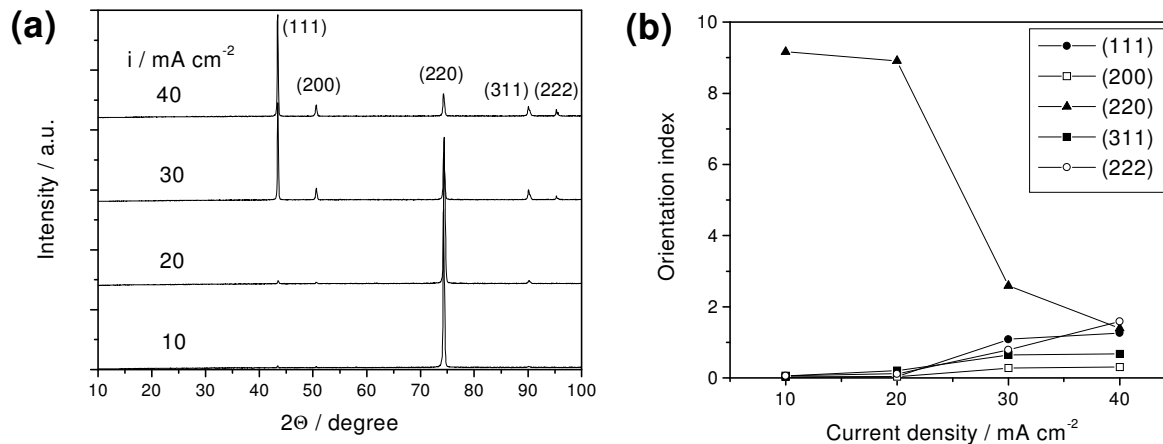


Figure 4. (a) X-ray diffratograms of the Cu-Si₃N₄ composites obtained at 400 rpm in solution containing 20 gL⁻¹ Si₃N₄ and (b) orientation index of the (111), (200), (220), (311) and (222) planes of copper in these composites, as a function of cathodic current density

Figure 4b shows that a preferential growth of copper grains in the (220) direction occurred for 10 and 20 mA cm⁻² whereas for 30 and 40 mA cm⁻² the copper grains were randomly oriented. Such results were also obtained for the other composite coatings and for the pure copper deposits. This shows that the incorporation of Si₃N₄ particles to copper did not affect the orientation of the copper grains. Indeed, it has been shown that the incorporation of particles in metallic

electrocoatings can influence the orientation of the metal matrix grains, as occurred for example for WC (Stroumbouli *et al.*, 2005) and Nb (Robin and Fratari, 2007) particles in nickel deposits.

Figure 5 shows typical SEM images of the cross-sections of composite coatings. The Si_3N_4 particles appear as dark spots in the lighter copper matrix. The distribution of the Si_3N_4 particles was homogeneous for all composite coatings but the incorporated particle volume fraction was dependent on experimental conditions.

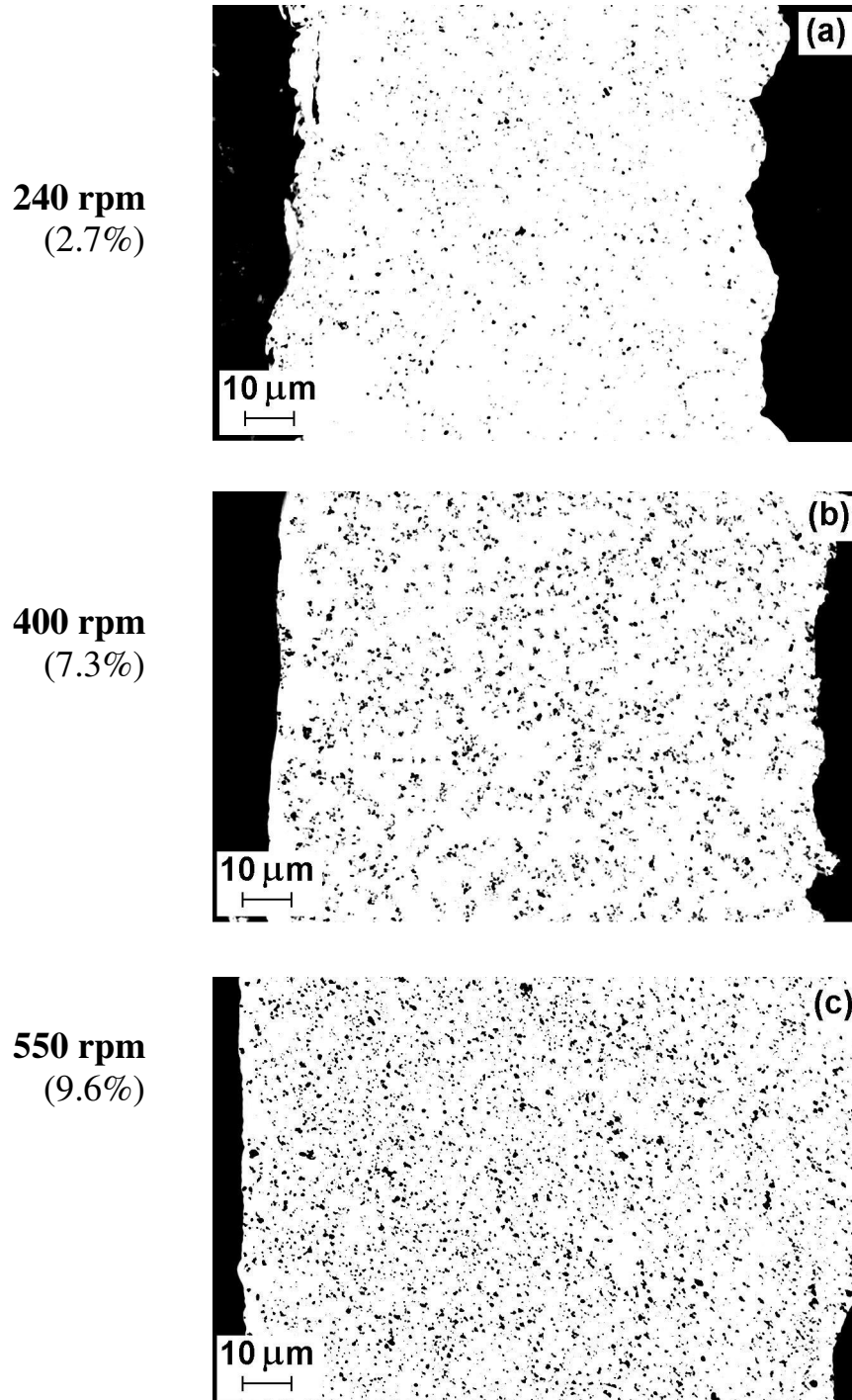


Figure 5. SEM photographs (backscattered mode) of cross-sections of Cu- Si_3N_4 composite coatings obtained in bath containing 20 g L^{-1} Si_3N_4 particles using (a) 240 rpm, (b) 400 rpm and (c) 550 rpm stirring rate (the number in parentheses corresponds to the incorporated particle volume fraction measured by image analysis)

The influence of cathodic current density, Si_3N_4 particle concentration in the bath and stirring rate on the incorporated particle volume fraction in composite coatings was summarized in Fig. 6. The incorporated particle fraction was not influenced by the current density. In the other hand, for the same particle concentration, an increase in

stirring rate increases the incorporated fraction. The increase of particle concentration in the bath from 20 to 40 g L⁻¹ decreased the incorporated particle volume fraction.

It was verified in literature that the evolution of the amount of particles incorporated to copper is highly dependent on the electrolysis conditions, and type, size and concentration of particles. For example, Zhu *et al.* (2004b) observed an increase in SiC particles content when the current density increased from 20 to 50 mA cm⁻² but a decrease for densities higher than 50 mA cm⁻². In the other hand, Hayashi *et al.* (1993) showed that the incorporated Al₂O₃ particle fraction diminished when the current density increased from 10 to 70 mA cm⁻². The relative independence of the current density on the incorporated particle fraction under our experimental conditions could be related to the diffusion control of the metallic ions. In relation to particle concentration effect, Zhu *et al.* (2004b) measured an increase of SiC particle fraction when the particle concentration increased from 15 to 35 g L⁻¹ but a decrease between 35 and 45 g L⁻¹. Differently, Stankovic and Gojo (1996) evidenced an increase of both Al₂O₃ and SiC particle contents when their concentration in the bath increased from 20 to 125 g L⁻¹. In our case the decrease of the incorporated particle volume fraction with increasing concentration of particles from 20 to 40 gL⁻¹ could be due to collision factor. The chance of collisions increases with increasing concentration, which could lead to the decrease of the incorporated particle volume fraction. The increase of the incorporated particle volume fraction with increasing stirring rate might be due to the increase of particles reaching the cathode. Such trend was observed by Wang (1998) for the incorporation of Al₂O₃ to copper but he also showed that high stirring rate can reduce the amount of incorporated particles due to collision factor.

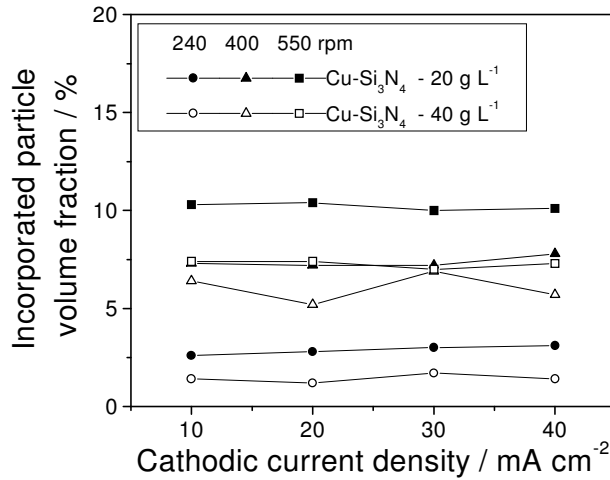


Figure 6. Incorporated particle volume fraction in Cu-Si₃N₄ composite coatings as a function of cathodic current density, particle concentration in the bath and stirring rate

The evolutions of microhardness of both Cu-Si₃N₄ composite and pure copper coatings as a function of cathodic current density shown in Fig. 7 are very similar but the microhardness of the composites was higher than that of pure copper. Since the increase in microhardness of pure copper electrodeposits with increasing current density has been attributed to copper grain refining and the incorporated particle fraction was shown in Fig. 6 not to depend on current density, a grain refinement of copper matrix probably also occurred for the composites as the current density increased.

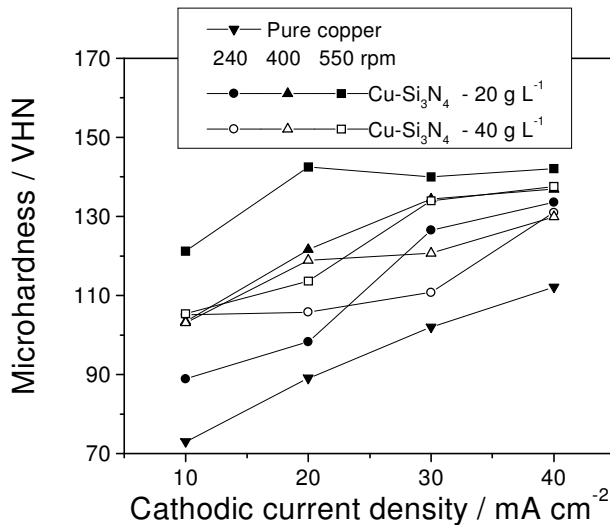


Figure 7. Microhardness of the Cu-Si₃N₄ composite and pure copper electrocoatings as a function of cathodic current density, particle concentration in the bath and stirring rate

The microhardness versus incorporated particle volume fraction for the composites obtained under the investigated experimental conditions is presented in Fig. 8. For a given current density a clear tendency of increasing in microhardness with increase of incorporated Si_3N_4 particle content is observed. For the highest current density used in this work (40 mA cm^{-2}), the matrix was already harder due to the finest copper grain and the Si_3N_4 particle incorporation could not significantly harden the composite. Thus, very close microhardness values were measured for the composites obtained using 40 mA cm^{-2} .

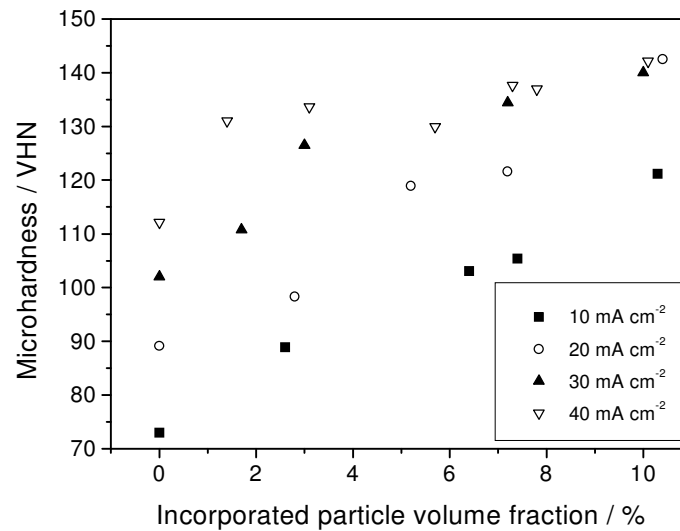


Figure 8. Microhardness of the Cu- Si_3N_4 composite as a function of incorporated particle volume fraction and cathodic current density

The higher microhardness of Cu-particles coatings when compared to that of pure copper was also observed for the incorporation of other types of particles to copper, such as SiC (Stankovic and Gojo, 1996; Zhu *et al.*, 2004b), Al_2O_3 (Stankovic and Gojo, 1996; Wang *et al.*, 1998) and ZrB_2 (Guo *et al.*, 2006). Three reasons could explain this increase in microhardness (Garcia *et al.*, 2001): (i) particle-strengthening, (ii) dispersion-strengthening and (iii) grain refining. Particle-strengthening is generally related to the incorporation of hard particles with volume fraction above 20%. In this case, the load is carried by both the matrix and the particles and strengthening is achieved because the particles restrain the matrix deformation. Dispersion-strengthening is associated to the incorporation of fine particles and volume fraction lower than 15%. In this case, the matrix carries the load and the small particles hinder dislocation motion. As the Si_3N_4 particles used in this work are fine ($< 2 \mu\text{m}$) and the highest incorporated particle volume fraction was 10.4%, it seems that the composite hardening may be due to dispersion-strengthening. Since a refining of the copper matrix grain was also observed due to particle incorporation, the third reason can also explain the higher hardness of the composites.

4. CONCLUSIONS

Smooth Cu- Si_3N_4 composite electrocoatings with uniform particle distribution were obtained on carbon steel by electrolysis of acid sulfate bath containing suspended Si_3N_4 particles.

Both pure copper and Cu- Si_3N_4 composite electrocoatings showed a preferential growth of copper grains in the (220) direction for 10 and 20 mA cm^{-2} . For 30 and 40 mA cm^{-2} the copper grains were randomly oriented for both types of deposits.

The incorporated particle volume fraction was not influenced by the current density. In the other hand, an increase in stirring rate and a decrease in particle concentration in the bath from 40 to 20 g L^{-1} increased the incorporated particle volume fraction.

The microhardness of the composite coatings was higher than that of pure copper due to dispersion-strengthening and matrix grain refining and increased with the increase of incorporated Si_3N_4 particle content.

The microhardness of both pure copper and composite coatings increased with an increase in cathodic current density due to copper matrix refinement.

5. ACKNOWLEDGMENTS

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