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ELECTRODEPOSITION OF CuZn FROM ALKALINE SOLUTION CONTAINING MICROMETRIC SiC PARTICLES IN A FLOW-CELL FOR COMPOSITE COATINGS.

Paulo Cezar Tulio
Maria Isabel da Silva
Federal University of Technology (UTFPR) – Paraná. Av. Alberto Carazzai 1640, Centro, CEP 86300-000. Cornélio Procópio/PR – Brasil.
e-mails: pauloctulio@utfpr.edu.br, mariaisabel0808@outlook.com

Abstract. *Metal-matrix composites (MMCs) coatings can be obtained by electrodeposition. Hard particles as dispersed phase can enhance erosion-corrosion resistance by acting as obstacles for dislocations. Indirect effects of particles on the metal matrix, such as reduction in grain size and, in the case of alloys, increase of the tougher metal in the matrix also contribute for enhancing. In this work it was studied the electrodeposition of CuZn metal matrix from an alkaline solution containing SiC hard particles at* C_{SiC} *of 10 g/L. A flow-cell was employed. CuZn coatings were obtained at distinct deposition current densities (*i_g*): 15, 20, 30 and 40 mA/cm*^{2}*. Fluid velocity was 0.43 m/s. Coatings were characterized by SEM, EDS and Microindentation hardness. Formation of CuZn-SiC coating was indicated by EDS. Mass ratios (% m.Cu/% m.Zn) were influenced by the presence of SiC in the solution. They changed from 2.19 ± 0.17 (20 mA/cm*^{2} *) and 3.03 ± 0.06 (30 mA/cm*^{2}*) for* C_{SiC} *0 g/L to 3.27 ± 0.18 (20 mA/cm*^{2}*) and 2.29 ± 0.63(30 mA/cm*^{2}*) for* C_{SiC} *10 g/L. It was observed higher values of microhardness for coatings at* C_{SiC} *10 g/L than those at* C_{SiC} *of 0 g/L. There are good prospects for CuZn-SiC composite coatings to be employed against erosion-corrosion, especially in low* i_g*, where the copper content is higher.*

Keywords: *electrodeposition, copper-zinc (CuZn), composite coating, silicon carbide (SiC), alkaline solution sorbitol.*

1. INTRODUCTION

The surface is probably the main point of concern for metal parts, as well as other engineering materials. Degradation processes related to corrosion and wear begins at surfaces. Therefore, there is a continuous research for methods and materials for surface protection. Electrochemical method, as electrodeposition, is very stablished for surface modification by application of a barrier metallic coating (Winand, 2010; Paunovic and Schlesinger, 2006). It can be conducted at room temperatures, is versatile and of low-cost. Single metals and alloys can be electrodeposited.

Metal-matrix composites (MMCs) are a class of materials that combine the properties of the metal-matrix with those of the dispersed phase (Kainer, 2006; Chawla and Shen, 2001). MMC can be obtained by electrodeposition, in the sense of a controlled inclusion of the dispersed phase during the electrochemical growth of the metal matrix (Hovestad and Janssen, 1995; Musiani, 2000; Tseluikin, 2016, Walsh, 2014). In terms of protection of metal parts, composite coatings are very interesting to be applied on their surfaces.

Electrodeposited composite coatings can combine corrosion resistance of the metal matrix with improved mechanical properties given by the dispersed phase (Kainer, 2006; Chawla and Shen, 2001). In this sense, when hard particles such as SiC or Al_2O_3 are embedded in the matrix, the resulting composite coating will be very adequate for protection against erosion-corrosion. Hard particles enhance mechanical resistance of the coatings by acting as obstacles for dislocations (Chawla and Shen, 2001).

Copper-Zinc coatings can be applied for decorative purposes but also as protection against corrosion in marine environments and for adhesion of natural rubber to steel tire cords. (Winand, 2010; Yli-Pentti, 2014; Coran, 2013). By employing hard particles as SiC and Al_2O_3 as dispersed phase in the CuZn metal-matrix, improved properties could be reached, for example, against erosion-corrosion.

During electrodeposition, the hard particles are dispersed in the aqueous solution and as the coating is being electrodeposited these particles must reach its surface to be embedded in the matrix. This way, control of hydrodynamics is a key point. In this work it was studied the electrodeposition of CuZn metal matrix from an alkaline solution containing SiC hard particles. In previous studies, the electrodeposition was performed in a cell where agitation of solution was maintained with a magnetic stirrer, without rigid control of hydrodynamics (Almeida *et al.* 2015a). In this work, a flow-cell was employed for better control of hydrodynamics. Cyanide based baths are employed for CuZn electrodeposition (Winand, 2010; Yli-Pentti, 2014). In this work it was employed an alkaline free-of-cyanide electrodeposition solution with sorbitol as complexing agent.

2. EXPERIMENTAL

The CuZn electrodeposition solution was: 0.14 mol/L $CuSO_4.5H_2O$, 0.06 mol/L $ZnSO_4.7H_2O$, 0.2 mol/L D(-) sorbitol ($C_6H_{14}O_6$) and 3.0 mol/L NaOH (Almeida *et al.*, 2015b). Silicon carbide (SiC) particles (97.73% purity, D_{50} = 9.4 μm) were added as-received to this solution. The ratio: mass of SiC to volume of solution (C_{SiC}), was constant at 10 g/L. Electrodepositions were also performed for C_{SiC} = 0 g/L for comparisons.

Electrodepositions at room temperature were performed by means of a flow-cell, schematically shown in Figure 1. By means of a centrifugal pump circulation of the solution was maintained, avoiding sedimentation of SiC particles at the bottom of the cell. At the same time, the impingement of the solution with SiC particles against the surface was controlled and the fluid velocity was constant at 0.43 m/s. Impingement was maintained constant at 90° to the electrode surface.

The working electrode substrate consisted of rectangular SAE 1020 steel pieces with 5 mm thickness. These were embedded in epoxy resin but with an exposed area to be electrodeposited of 100 mm^2. Before electrodeposition the working electrode was sanded up to 600 grit-mesh emery paper, cleaned its surface with acetone and dried at room temperature. The counter-electrode was a Pt mesh of 100 mm^2.

Electrodepositions were performed at constant cathodic current densities (i_g) of: 15, 20, 30 and 40 mA/cm^2. The Biologic SP200 potentiostat was employed. Electrodepositions were performed up to a charges density of 120.4 C/cm^2, which corresponds to a theoretically thickness of 50 μm.

Scanning Electron Microscopy and semiquantitative chemical analysis by EDS employed a FEI Quanta 200 microscope coupled to an EDS-Oxford INCA microanalysis system.

Microindentation hardness tests were performed with a Panambra microhardness tester HV-1000B with the Vickers scale. 50 and 100 gf loads for 15 s were applied. At least 10 indentations were made at the top edge, center and bottom edge of the coatings. The values of Vickers microhardness were converted to MPa. Sanding of the top surface of the coatings was necessary for indentation measurements. 2000 grit-mesh emery paper was employed for this.

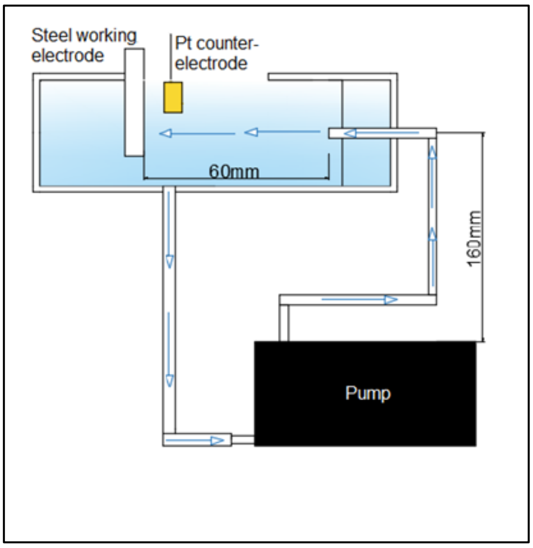


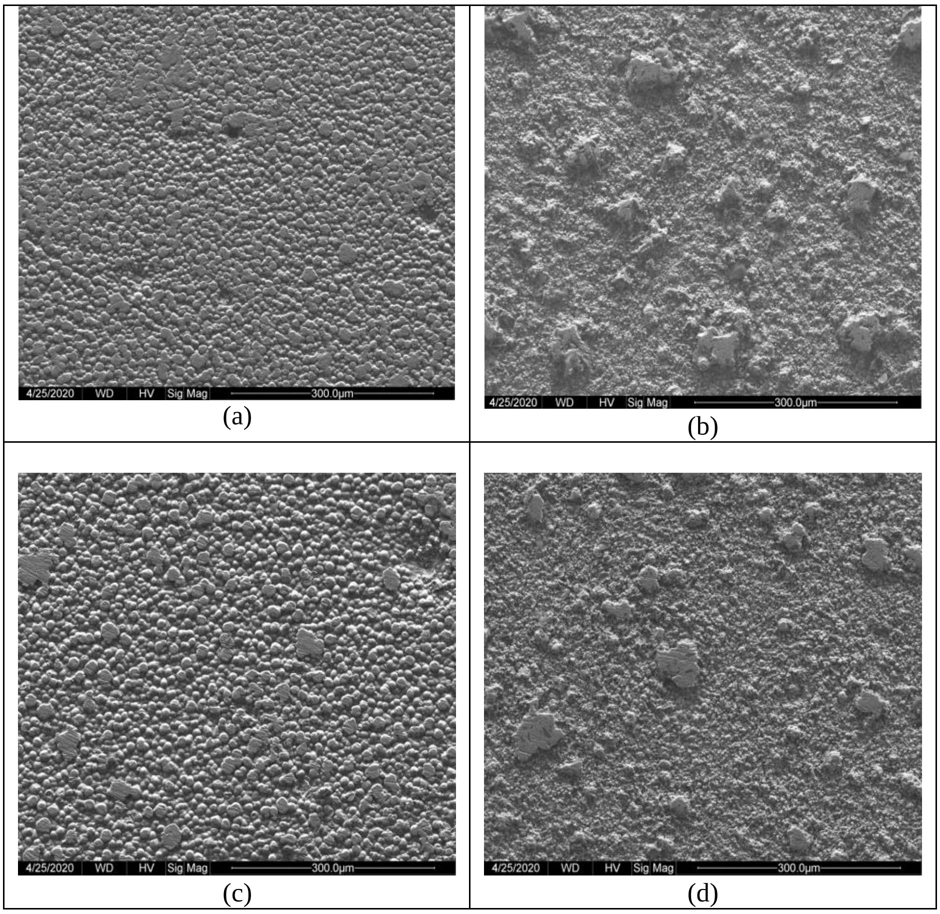
Figure 1. Schematic of the flow-cell employed.

3. RESULTS AND DISCUSSION

3.1 SEM and EDS analysis

Coatings obtained at i_g of 20 and 30 mA/cm^2 for 0 and 10 g/L of C_{SiC} were analyzed by SEM and EDS. Firstly, in Figure 2 they are shown comparative SEM images of typical coatings under these conditions. These images correspond to central areas of the coatings. Scratches seen in the images are due to previous surface sanding. This was necessary for microindentation tests. Despite this, it is clearly seen that in the presence of SiC particles in the electrodeposition solution, the surface morphology of the coatings are coarser. Cracks were not observed in all of the coatings and they are compact. The abrasive nature of SiC particles must be considered as one of the reasons to understand the development of coarser surface morphologies. The impingement of some of them to the surface of the substrate causes some erosion, leading to highly defective regions on surface. This affects the growth of the coatings. These areas do not appear in the conditions without SiC in the electrodeposition solution and the growth is more uniform. At the same time, some SiC particles are bound to the surface before embedment and also can affect the growth mode of the coatings.

In Figure 3 are shown EDS spectra of the coatings of Figure 2(c and d) at i_g 30 mA/cm^2 and for C_{SiC} 0 and 10 g/L. Peaks of Fe are related to the steel substrate and peaks of Cu and Zn characterize the CuZn matrix. It is clearly seen a peak for Silicon element in CuZn coating obtained with C_{SiC} 10 g/L. This peak is absent at C_{SiC} 0 g/L in the electrodeposition solution (Figure 3, left). As the only source of Si atoms in the studied system was SiC particles, this observation leads to infer that SiC particles are embedded in the CuZn matrix indicating the formation of CuZn-SiC composite coatings.



(a) (b)

(c) (d)

Figure 2. Typical SEM images of central areas of CuZn coatings obtained at: (a) $i_g = 20$ mA/cm^2, $C_{SiC} = 0$ g/L; (b) $i_g = 20$ mA/cm^2, $C_{SiC} = 10$ g/L; (c) $i_g = 30$ mA/cm^2, $C_{SiC} = 0$ g/L; (d) $i_g = 30$ mA/cm^2, $C_{SiC} = 10$ g/L.

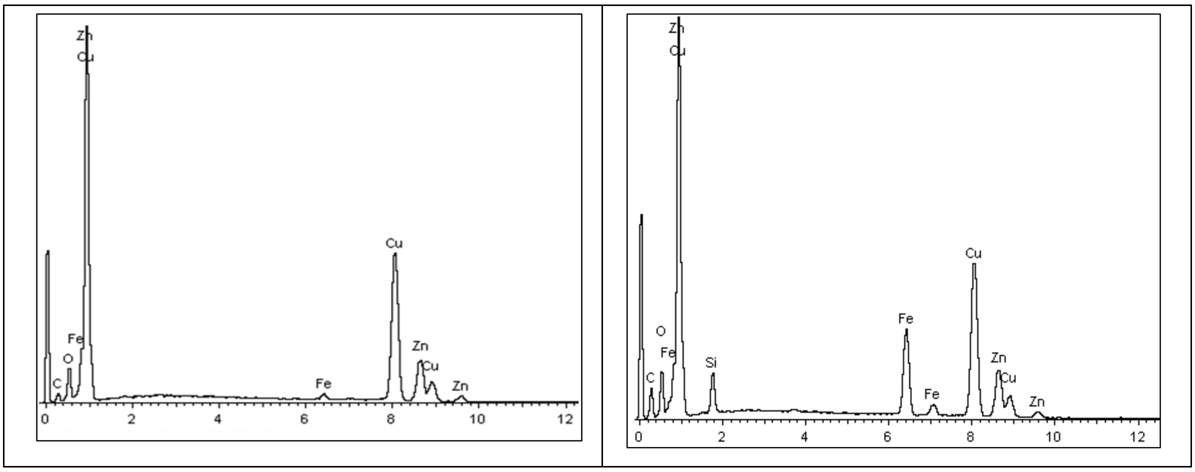


Figure 3. EDS spectra (left) of the coating in Figure 2(c) (i_g of 30 mA/cm^2, C_{SiC} 0 g/L) and (right) for that of Figure 2(d) (i_g of 30 mA/cm^2 and C_{SiC} of 10 g/L).

As CuZn is a binary alloy, possible effects of the SiC particles on the contents of Cu and Zn in the coatings were investigated by means of the mass ratio [%m.Cu / %m.Zn]. Cu is nobler than Zn and corrosion resistance properties will be affected if relative percentages of these elements change. In Figure 4, the dependence of [%m.Cu / %m.Zn] is shown as a function of C_{SiC} and i_g. For 0 g/L of SiC, increase in current density makes the coatings richer in Cu. This behavior was also observed in the same solution by Almeida *et al.* (2015b) on Pt substrates in stagnant conditions for 2 C/cm^2 of electrodeposited charge density. The authors found values of this ratio changing from 1.38 at 20 mA/cm^2 to 1.56 at 40 mA/cm^2.

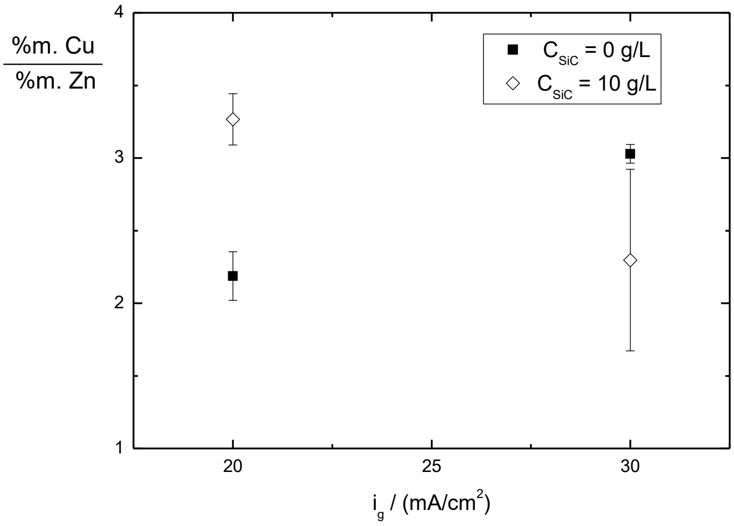


Figure 4. Variation of the mass percentage of Cu to Zn as a function of i_g and C_{SiC} indicated in the figure.

When SiC particles are present during the electrodeposition in Figure 4 there appears a tendency to the mass ratio be reduced when changing from 20 to 30 mA/cm^2. This will not be interesting for corrosion protection, since Cu is nobler than Zn.

The important feature shown in Figure 4 is the enrichment in Cu of the matrix at 20 mA/cm^2 caused by SiC in the electrodeposition solution. Figure 4 corresponds to data taken at the central area of coatings but the same was observed near the edges. This behavior for a flow-cell was also observed before for this system in a cell with magnetic stirrer (Almeida *et al.*, 2015a). One possible explanation lies in the fact that at low i_g as 20 mA/cm^2, the reduction of complexed Cu^{2+} ions is mass-transfer controlled and when micrometric particles are impinging against the electrode surface they help to increase mass-transport, by dragging with them new elements of solution, increasing the rate of copper deposition. From the point of view of corrosion resistance, coatings of CuZn richer in Cu must be more resistant than poorer ones by considering the nobler character of copper in respect to zinc. For the enrichment in Zn at 30 mA/cm^2 such action of SiC particles may also be present. However, in the potentials attained at high i_g, Zn^{2+} reduction must be under mass-transfer control, which must be verified.

Changes in composition of coatings of binary alloys promoted by hard particles dispersed in the electrodeposition solution are not uncommon. The results in Figures 2 and 4 show that SiC particles acts like an additive in electrodeposition baths since, up to this point, it affects surface morphology and chemical composition. As a consequence coating properties can be tailored.

3.2 Microindentation hardness tests

Microindentation hardness was evaluated on the top surface of the coatings. It was observed a large dispersion in microhardness values for all of the coatings. However, in spite of dispersion, it was observed that during measurements some low values of microhardness were only observed for CuZn obtained at C_{SiC} of 0 g/L. At the same time, some high values of microhardness were only observed for CuZn obtained for C_{SiC} of 10 g/L. In order to give a better representation of this tendency, the data of microhardness are presented in the form of histograms in Figure 5 for i_g of 15, 20 and 30 mA/cm^2 at the two C_{SiC}. The plots in Figure 5 express the percentage of total measurements that returned microhardnesses in a given range.

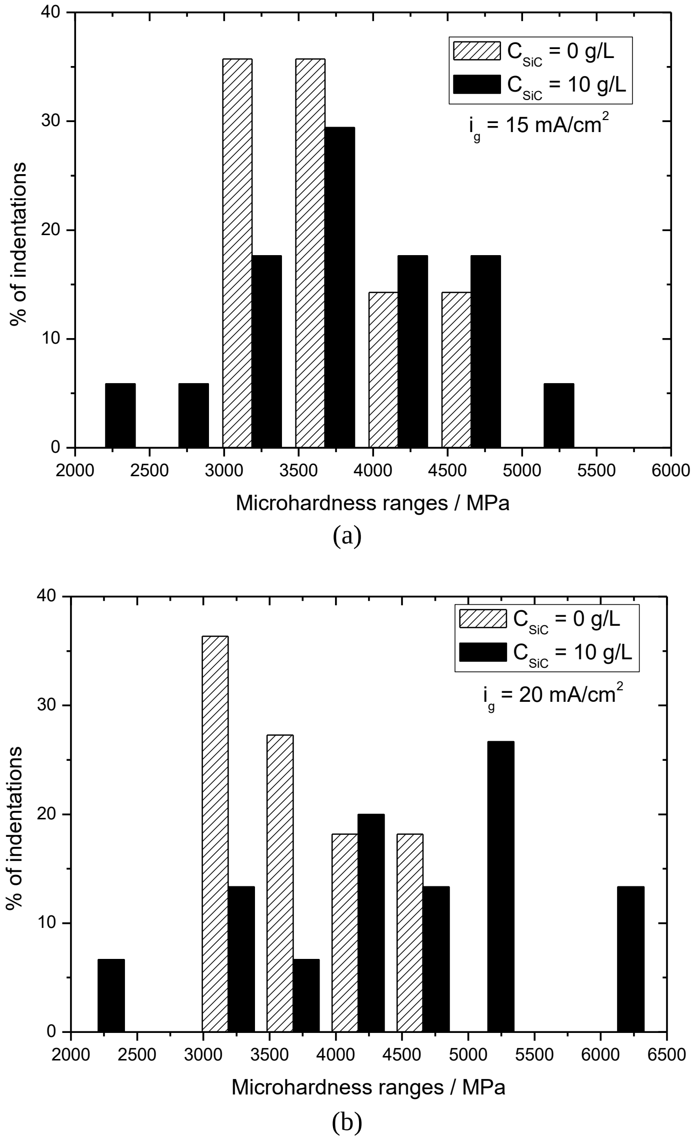
In Figure 5 it can be observed that better results in terms of microhardness are obtained by coatings at i_g of 20 and 30 mA/cm^2. In these coatings, notwithstanding the large dispersion of the data, high values of microhardness in certain points are only observed in coatings at C_{SiC} of 10 g/L and not for those at 0 g/L. For the i_g of 15 mA/cm^2 it is not so clear that microhardness was improved in comparison to coatings at C_{SiC} 0 g/L. For i_g of 40 mA/cm^2, not shown in Figure 5, the values of microhardness were not so distinct with and without SiC.

High values of microhardness for coatings obtained in the presence of SiC can reflect the hindering in dislocations motion caused by embedded SiC particles in the CuZn matrix. These high microhardness values are another indication that SiC particles were embedded in the matrix as it was inferred from EDS in Figure 3. The values in Figure 5 are similar to those obtained in this same electrodeposition solution but without the control by a flow-cell (Almeida *et al.*, 2015a).

A large number of microhardness values in Figure 5 are very high for electrodeposited CuZn (0 g/L SiC). For example, Senna *et al.* (2005) found values of around 2451 MPa (250 HV) at the cross-section of CuZn electrodeposited from pyrophosphate baths at 11.6 and 15.4 mA/cm^2. From a bath very similar to the alkaline one used here, but with glycerol instead sorbitol as complexing agent and with pulsed potential deposition, Das *et al.* (2019) found values of around 3305 MPa (337 HV). They attribute this high value to an intermetallic compound. Many factors can influence microhardness. In the case of electrodeposits the non-equilibrium condition during electrodeposition and its consequences can have great influence. In this work, the reasons for some high values of around 4500 MPa were not explored.

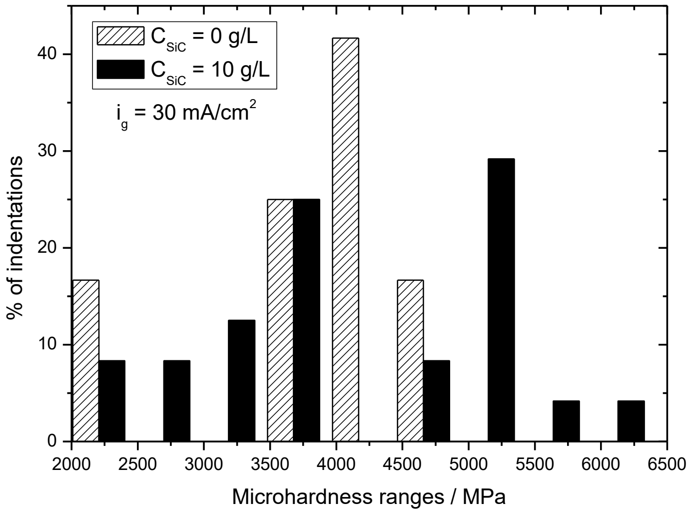
For the case of CuZn obtained from SiC solutions, there are values higher than 4500 MPa. For the sake of comparisons, the Vickers microhardness of SiC is around 26 GPa [Milman *et al.* (1999)]. The large dispersion in points could reflect the nonhomogeneous dispersion of the SiC particles in the matrix. Some indentations were taken in regions near embedded SiC and others in regions far from SiC, reflecting only CuZn behavior.

For the aim of erosion resistance of coatings, regardless of the values of microhardness, it was verified an improvement in the resistance to plastic deformation of the coatings obtained from SiC containing electrodeposition solutions, mainly for i_g 20 and 30 mA/cm^2.



(a)

(b)



(c)

Figure 5. Distribution of the microindentation hardness as a function of i_g and C_{SiC} indicated in the figures.

4. CONCLUSIONS

Coatings of CuZn were obtained from an alkaline electrodeposition solution containing sorbitol as complexing agent and micrometric SiC particles in a flow-cell configuration. Adhesion and compactness were observed for all conditions of electrodeposition.

Coatings obtained from SiC containing solutions were coarser than those from solutions without SiC.

For i_g of 20 mA/cm^2 it was verified a significant enrichment in Cu content in the CuZn matrix when obtained from SiC containing solution.

By EDS, Si peaks were detected in coatings from SiC containing solutions. Si was not observed on those obtained from free of SiC solutions. Composite coatings of CuZn-SiC are considered to be formed.

An improvement in microhardness of the coatings was verified for coatings obtained from solutions containing SiC. Better results of microhardness were observed for coatings at i_g of 20 and 30 mA/cm^2.

The presence of dispersed SiC particles in the solution during electrodeposition is beneficial for coatings properties. Enrichment in copper on CuZn matrix at low i_g and the improvement in microhardness can make the coatings more resistant to corrosion and erosion.

5. ACKNOWLEDGEMENTS

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