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CUZN-SIC METAL-MATRIX COMPOSITES OBTAINED BY ELECTRODEPOSITION FROM ALKALINE NON-CYANIDE SOLUTIONS. MECHANICAL, PHYSICAL AND CHEMICAL CHARACTERIZATIONS.

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Abstract. *Metal-matrix composite coatings consisting of CuZn and silicon carbide (SiC) hard particles, CuZn-SiC composites, could be obtained by employing galvanostatic electrodeposition. The electrodeposition solution was an alkaline free-of-cyanide one, with sorbitol as the complexing agent. It was observed that surface morphology of CuZn-SiC was, in a small degree, coarser than that of CuZn. The CuZn metal-matrix of the composites was richer in copper than CuZn at low electrodeposition current densities (i_g). The microhardness of the CuZn-SiC coatings was significantly increased when comparing with CuZn. Composite coatings of CuZn-SiC have prospects for application in pieces subject to erosion-corrosion or cavitation.*

Keywords: *metal-matrix composite coatings, CuZn-SiC, electrodeposition, alkaline sorbitol solution, mechanical properties.*

1. INTRODUCTION

Degradation of metals properties by corrosion or by some form of corrosion in environmentally assisted cracking has safety and economic impacts. They are estimated that 3.5% of Gross National Product of countries is related to direct costs with corrosion (Verinck, 2000; Davis, 2000; Schweitzer, 2010). In this sense, the search for methods to minimize and control the corrosion is always an active area in research and development.

The erosion-corrosion is a form of corrosion which involves synergism between the chemical action (anodic dissolution of the metal) and a mechanical force (erosion). This synergism accelerates the rate of corrosion (Davis, 2000; Schweitzer, 2010; Postlethwaite and Nesic, 2000). Erosion can be caused by, for example, impingement of solid particles in a liquid fluid, impingement of liquid droplets in high-speed gas or vapor flows and cavitation. This impingement can destroy protective passive layers or induce deformations in the surface which can increase the corrosion rate of the metal (Postlethwaite and Nesic, 2000). High corrosion resistance stainless steel could be employed to minimize corrosion. However, it is an expensive method (Postlethwaite and Nesic, 2000). Hard materials could be employed to eliminate the erosion problem. These materials, however, can have poor corrosion resistance and are hard to weld and often brittle (Postlethwaite and Nesic, 2000; Fontana and Greene, 1967).

Metal-matrix-composites are a class of materials which can combine highly corrosion resistant metal-matrixes with hard particles as the dispersed phase (Kainer, 2006). Metal-matrix composites can be obtained as coatings by the electrodeposition technique (Hovestad and Janseen, 1995; Musiani, 2000; Tulio *et al.* 2007). In this sense, they could be adequate coatings to minimize erosion-corrosion problems. An example of corrosion resistant metal-matrix is CuZn alloys. If in the CuZn matrix were dispersed hard particles of, for example, abrasive SiC particles, the hardness of the composite could be increased. CuZn can be commercially obtained by electrodeposition, but from cyanide containing solutions, since the ion cyanide is an excellent complexig agent, furnishing commercially accepted electrodeposited films (Geissman and Bennett, 1974; Parthasaradhy, 2009). Cyanide, however, has environmental and health concerns. Extensive research for less aggressive complexing agents is in course (Johannsen, *et al.*, 2001; Ballesteros, *et al,*. 2014; Survila, *et al.*, 2013; de Almeida, *et al.*, 2015). One example is sorbitol (de Almeida, *et al.*, 2015), which the baths can give fine-grained, uniform, smooth and with distinct colorations CuZn films. There is no study related to obtain CuZn composites coatings from sorbitol solutions.

The aim of the present work was to obtain metal-matrix composite coatings of CuZn-SiC from sorbitol alkaline non-cyanide electrodeposition solutions and evaluate their mechanical, physical and chemical properties.

2. EXPERIMENTAL

The electrodeposition solution consisted of: $CuSO_4.5H_2O$ 0.14 M + $ZnSO_4.7H_2O$ 0.06 M + NaOH 3 M + D (–) Sorbitol ($C_6H_{14}O_6$) 0.2 M. This alkaline solution has sorbitol as the complexing agent for substituting cyanide. It was developed by de Almeida, *et al.*, 2015. For obtaining composite coatings, micrometric silicon carbide (SiC, 97.73 %, mean diameter of 9.5 µm) particles (Treibacher-Schleifmittel Brazil Ltd.) were added, as-received, to the electrodeposition solution. Particles were added up to a mass of SiC to volume of solution ratios of 10 and 20 g L^{-1}. Before the electrodeposition, the solution containing SiC particles was mechanically stirred for 12 h. The substrate consisted of rectangular 1020 steel plates, embedded in epoxy resin, with only one face exposed to the solution, with an area for electrodeposition of 4.8 cm^2. The substrates (electrodes) were sanded up to 600 emery papers, washed in distilled water, immersed in acetone and dried before electrodeposition. The anode was a large rod of electrolytic copper placed in front of the substrate. Electrodeposition was performed under constant cathodic current density (i_g) for a time of deposition which corresponded to a charge density of 72.5 C cm^{-2}. This charge density corresponds to a theoretical coating thickness of 30 µm. During electrodeposition it was maintained the magnetic stirring of the solution.

Scanning electron microscopy (SEM) and semiquantitative energy-dispesive X-ray spectroscopy (EDS) chemical analysis were performed with a FEI Quanta 200 microscope coupled with an EDS-Oxford INCA. For EDS, a large central area of 2.4 x 2.1 mm^2 was analyzed.

The Vickers microhardness of the electrodeposited coatings was performed on three distinct samples of the same coating and it was a result of a minimum of 10 measures in a large central area of each sample coating. Microhardness measurements were performed by a microhardness tester model HV-1000B.

3. RESULTS AND DISCUSSION

3.1 Electrodeposition of CuZn-SiC composite coatings

In the SEM micrograph of Fig. 1 they are shown particles of SiC employed in this work. It can be seen that there is a size distribution of the same and with distinct forms.

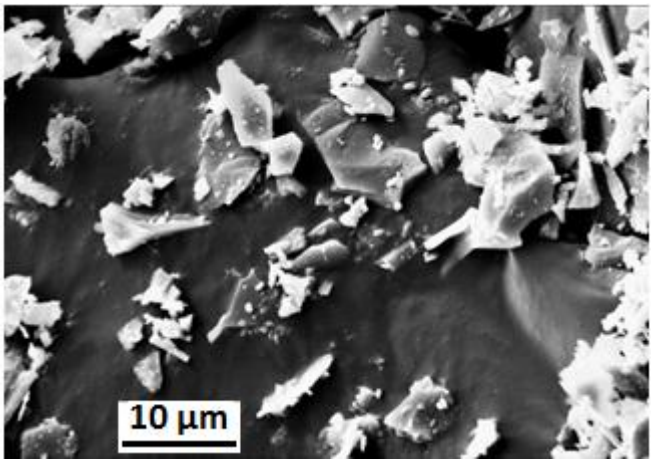


Figure 1. SEM micrograph of SiC particles employed in this work. Dark background corresponds to carbon conductive adhesive tape.

After the electrodeposition from solutions containing SiC particles, the coatings were analyzed by SEM and EDS to evaluate if there were SiC particles occluded in the CuZn metal-matrix. This first analysis will prove the obtaining of CuZn-SiC composite coatings. In the micrograph of Fig. 2 it is shown the surface morphology of a CuZn coating obtained from electrodeposition solution with C_{SiC} of 10 g L^{-1} at i_g of 20 mA cm^{-2}. For this same coating, an amplified region is seen in Fig. 3. In this last micrograph they can be seen some SiC particles partially occluded in the CuZn metal-matrix. As a surface analysis, only partially occluded SiC particles could be seen. However, there must be considered that are totally occluded SiC particles in the matrix. EDS analysis detected Si in the local region of the particles. As will be seen ahead, increase in microhardness also indicates SiC occlusion. Similar results were observed for i_g of 10 mA cm^{-2} and C_{SiC} of 10 g L^{-1}. These observations prove that CuZn-SiC composite coatings can be obtained from this free-of-cyanide alkaline electrodeposition solution.

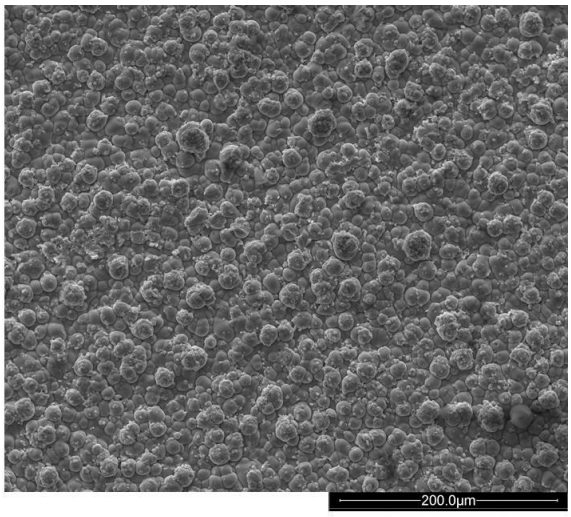


Figure 2. Typical SEM micrograph of a CuZn coating obtained from sorbitol electrodeposition solution containing 10 g L^{-1} of SiC. i_g = 20 mA cm^{-2}.

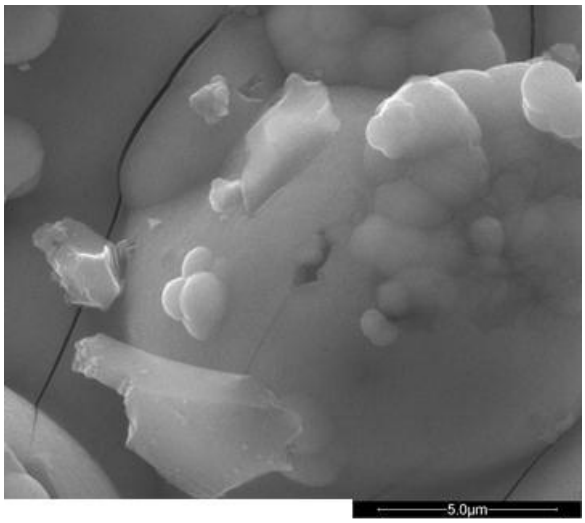
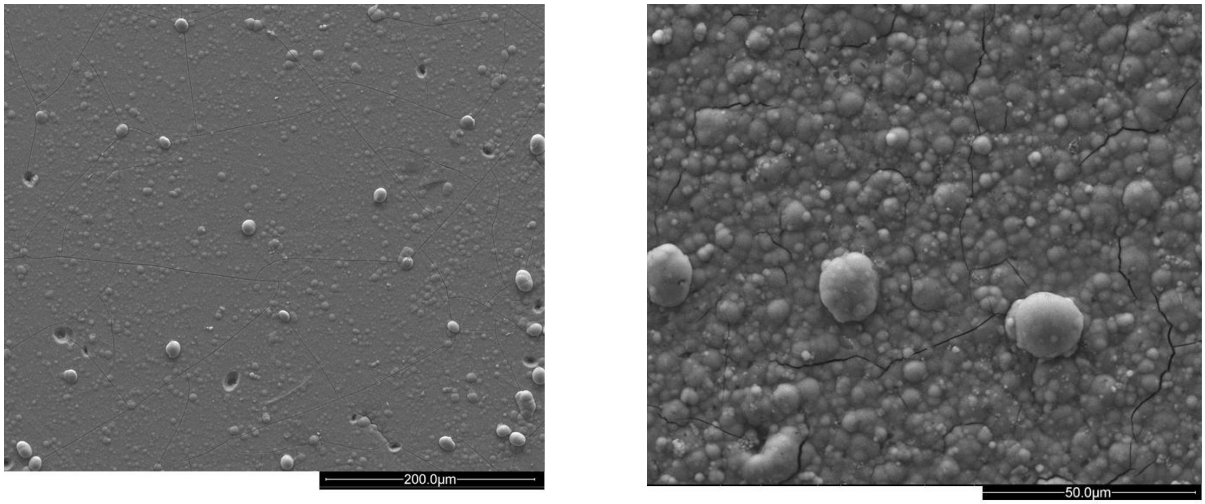


Figure 3. Amplified region of the micrograph in Fig. 2. They can be seen partially occluded SiC particles.

Comparisons can be made with CuZn coatings from electrodeposition solution without SiC in terms of surface morphology. In Fig. 4 they are shown SEM micrographs of a CuZn and CuZn-SiC coatings at i_g of 10 mA cm^{-2} and C_{SiC} of 10 g L^{-1} for CuZn-SiC. The surface morphology of CuZn-SiC is, in some degree, coarser than CuZn. This effect is clearly related with the presence of SiC in the electrodeposition solution and in the CuZn matrix. Before SiC particles occlusion, these particles are in contact with the growing metal-matrix. The SiC particles can be considered insulating in the electrodeposition. In this sense, SiC particles will not act as sites for Cu^{2+} and Zn^{2+} reduction. If they were conductive, deposition will occur over SiC particles and surface morphology of CuZn-SiC would have a higher degree of coarseness. Higher degree of coarseness was observed for Cu-graphite and CuZn-graphite coatings, since graphite is

a conductor (Schiavinato, *et al.*, 2014). This is not the case for SiC, as could be evidenced in Fig. 3. The change in coarseness could be related to the changes in the metal-matrix/solution interface characteristics due to the presence of the micrometric SiC particles in this region.



(a) (b)

Figure 4. Typical SEM surface micrographs of: (a) CuZn and (b) CuZn-SiC coatings from electrodeposition solution with C_{SiC} of 10 g L^{-1}. For both, i_g = 10 mA cm^{-2}.

3.2 Chemical composition of the coatings

The composition of the coatings was determined by employing EDS semiquantitative chemical analysis. A large central area of 2.4 x 2.1 mm^2 was analyzed. The aim was the content of Cu and Zn in the CuZn matrix. The results, in terms of the mass percentage (% m.) ratio of Cu to Zn are shown in Fig. 5.

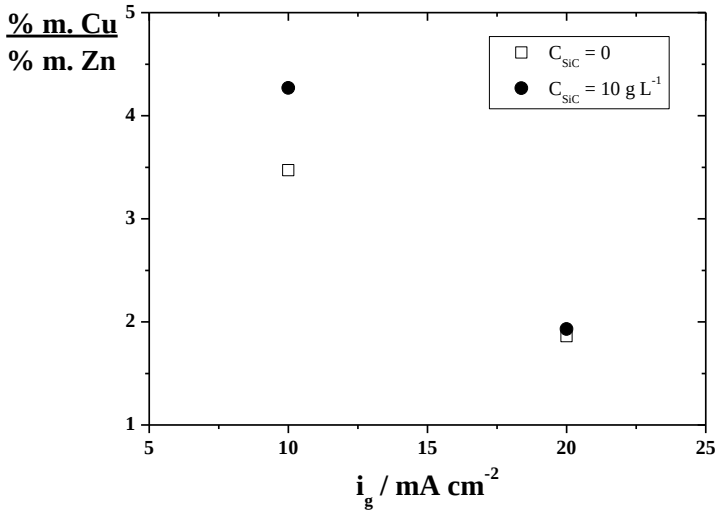


Figure 5. Mass percentages ratio of copper to zinc for CuZn coatings as a function of i_g obtained from electrodeposition solutions free-of SiC and with C_{SiC} of 10 g L^{-1}, indicated in the figure.

As it can be seen, this ratio decreases with i_g, as normally found for electrodeposited films with metals with large differences in standard reduction potentials. At low current densities, in normal alloy electrodeposition, the reduction rate of the nobler metal cation is very high. For CuZn, Cu is the nobler metal. However, when the electrodeposition occurs in the presence of SiC particles, there is a markedly increase in the mass percentage ratio, but only in the lowest current density (10 mA cm^{-2}). The SiC particles, despite their inert chemical character, are affecting the reduction kinetics of the Cu^{2+} and Zn^{2+} ions at low current densities. For CuZn-SiC in this work, it is not clear if, in the lower

current densities, SiC are hindering Zn^{2+} reduction or increasing Cu^{2+} reduction. In terms of coating properties, however, a high content of Cu in CuZn-SiC coatings could lead to improved corrosion resistance.

3.3 Microhardness of the coatings

In Fig. 5, they are shown the Vickers microhardness of the coatings as a function of i_g and C_{SiC}.

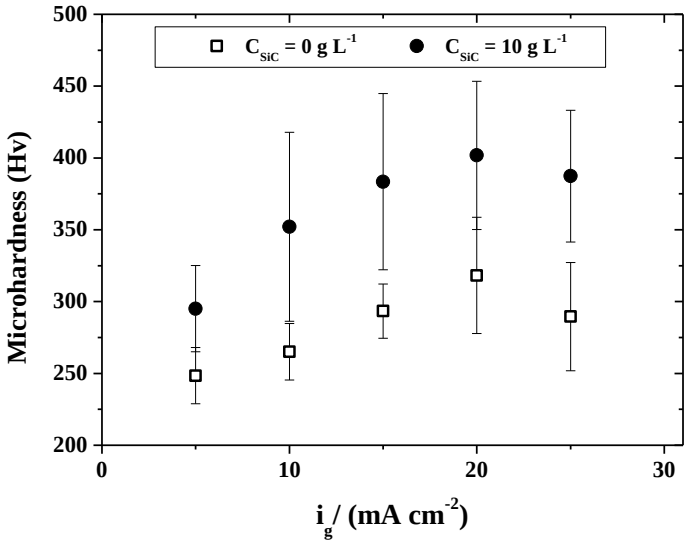


Figure 6. Vickers microhardness as a function of i_g for CuZn coatings obtained from free-of-SiC electrodeposition solutions (C_{SiC} = 0) and CuZn-SiC composite coatings obtained from 10 g L^{-1} of SiC electrodeposition solutions, indicated in the figure.

For CuZn (C_{SiC} = 0 g L^{-1}), there is a tendency of increasing microhardness with i_g. This increase could be related with the reduction in grain size with higher reduction rates, related to the Hall-Petch mechanism. The values of microhardnesses for CuZn in Fig. 6 are higher than those for cast alloys. Electrodeposited films can exhibit higher microhardness when comparing with cast alloys (Brenner, 1963; de Senna, *et al.*, 2005).

For CuZn-SiC, mean microhardnesses are higher than those for CuZn as expected, for all i_g. This is an indirect prove that hard SiC particles are occluded in the CuZn matrix. Despite the high microhardnesses of electrodeposited CuZn, the occlusion of SiC particles contributed to the increase in this property. The pattern of variation with i_g follows the one for CuZn. In this sense, for CuZn-SiC, reduction in grain size with i_g together with hindering of dislocations by the occluded SiC particles are acting to increase microhardness.

This increase in microhardness for CuZn-SiC is of interesting for purposes of applications against erosion-corrosion and cavitation.

4. CONCLUSIONS

CuZn-SiC composite coatings can be obtained from free-of-cyanide alkaline electrodeposition solutions containing sorbitol as complexing agent under constant current electrodeposition (galvanostatic electrodeposition).

Surface morphology of composite coatings was slightly coarser than those for CuZn.

The CuZn metal-matrix of composite coatings CuZn-SiC obtained at low i_g were richer in copper than those for CuZn. Corrosion resistance can be improved in composites due to this high copper content.

Microhardness of both, CuZn and CuZn-SiC coatings, increased with i_g. The microhardnesses of electrodeposited CuZn coatings were higher than cast CuZn alloys.

Microhardnesses of CuZn-SiC were significantly increased in terms of mean values as compared with those of CuZn.

The CuZn-composites obtained from the free-of-cyanide electrodeposition solution have good prospects for protection of metallic pieces against, for example, erosion-corrosion and cavitation.

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