

# Self-lubricating metal-matrix composite CuZn-graphite coatings obtained by electrodeposition from near neutral solutions. Surface morphological analyses and chemical composition.

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## ABSTRACT

CuZn coatings were obtained from cyanide-free electrodeposition solutions, pH 6.6, containing graphite particles (2  $\mu\text{m}$ ) dispersed on them. The aim is to obtain CuZn metal-matrix composites with lubricating graphite particles as the dispersed phase. These composites, obtained by electrodeposition are called electrocomposites. They can be considered self-lubricating. Surface morphological analysis of these deposits reveal a compact fine-grained layer and above this a

poorly adherent coarse-grained one. The last is due to the presence of graphite particles in the solution, since this poorly adherent layer is not present in deposits obtained from free-of-graphite conditions. Only in few cases it was observed occlusion of graphite particles in the CuZn matrix. However, this occlusion occurs in the poorly adherent layer. Under the analyzed conditions of electrodeposition it was difficult to obtain CuZn-graphite electrocomposites. Regardless of graphite occlusion, chemical composition of CuZn matrix was affected by graphite dispersed in the electrodeposition solution. When comparing with CuZn matrix obtained from free-of-graphite conditions, graphite caused enrichment in Cu content of the matrix for all current densities.

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## INTRODUCTION

Metallic materials, due to their availability and properties, can be considered the structural base of industrial parks and infrastructure of any country. However, with the impossible large scale use of expensive noble metals such as gold and platinum, metals like copper, iron, steel, zinc, etc. suffer from corrosion. Corrosion is a natural process of chemical degradation of a metal and, as a consequence, of its mechanical properties [1]. Costs of corrosion [1-<sup>2,3</sup>], for a developed country, are of the order of 3.1% of GDP. In order to minimize corrosion, prevention methods must be developed and applied.

Another way of metallic degradation is related with wear by erosion or abrasion. Erosion is the progressive loss of original surface material due to the interaction of that surface with a fluid, a multicomponent fluid or by impingement of liquid or solid particles [4]. Abrasion is the wear of a surface due to the movement of hard particles over it or the presence of hard protuberances forced against and moving along a solid surface [4]. Corrosion and erosion or abrasion can coexist, accentuating degradation of metal properties. This joint action is known as erosion-corrosion or abrasion-corrosion and they are found, for example, in pipelines, propellers, impellers and pump impellers [5].

One way to minimize abrasion and abrasion-corrosion is to reduce the friction coefficient of the contacting surfaces with the use of a lubricating. Examples of lubricating are greases and solid lubricating as graphite and  $\text{MoS}_2$ . Interest in lubricating has increased, since friction problems demands higher energy consumption and resources, with higher emissions [6]. Lubricating can be directly applied between surfaces, requiring inspection and control of lubricating levels. On the other hand, self-lubricating materials are characterized by the ability of the system to transfer microscopic amounts of the lubricating between the sliding surfaces throughout of its operational lifes [7]. This transfer process creates a film that provides lubrication and reduces friction.

Electrocomposite coatings [8,9,10] are metal-matrix composites with an insoluble dispersed phase of, for example, hard particles:  $\text{SiC}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{B}_4\text{C}$  or lubricating particles: PTFE,  $\text{MoS}_2$ , obtained by electrodeposition. Electrocomposite coatings have received increased attention in the last years. The aim is to combine the properties of the metal (ductility, corrosion resistance) with the properties of the dispersed phase (hardness, lubricity).

Copper and its alloys, such as brass, have good thermal and electrical conductivity and good corrosion resistance [11,12]. However, they do not have good mechanical strength. In the context of erosion-corrosion or abrasion-corrosion or only abrasion or erosion, electrocomposites of Cu or Cu alloys with hard particles (for erosion or erosion-corrosion) or lubricating particles (abrasion or abrasion-corrosion) could be a possibility to have a material in which better corrosion resistance and mechanical properties are met. In the cases of abrasion and abrasion-corrosion, it will be of interest to have a self-lubricating electrocomposite of Cu based metal-matrix and a solid lubricating as the dispersed phase. As the metal surface is degraded by abrasion, solid particles of the lubricating in the dispersed phase of the electrocomposite will be placed in between the contacting surfaces, reducing friction.

There are few works with electrocomposite coatings of Cu based alloys metal matrix with graphite [11,13,14]. Mechanical strength can be reduced with graphite occlusion [8]. In the present work, it will be described the features of the processes for obtaining CuZn-graphite electrocomposite coatings from a cyanide-free

electrodeposition solution in near neutral pH. Cyanide-based electrodeposition baths give rise to very good coatings [15]. However, cyanide ion is toxic [16] and research for alternative less aggressive complexing agents are in progress. In this work, the citrate anion is the complexing for  $\text{Cu}^{2+}$ .

## EXPERIMENTAL

The electrodeposition solution was:  $0.02 \text{ M CuSO}_4 \cdot 5\text{H}_2\text{O} + 0.2 \text{ M ZnSO}_4 \cdot 7\text{H}_2\text{O} + 1 \text{ M Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$  (sodium citrate dihydrated). The pH of this solution was 6.6. This solution was based on Silva *et al.*[17]. This solution was chemically stable, in agreement with Chassaing *et al.*[18] due to the high ratio  $[\text{citrate}]/[\text{Cu}^{2+}]$ . Graphite (C) particles (kindly furnished by TIMCAL), mean diameter  $2 \mu\text{m}$ , were added as-received to this solution and a previous 12 hours of magnetic stirring was performed in the particle-loaded solution for good dispersion and disaggregation of the graphite particles. Distinct ratios (mass of graphite/volume of solution) ( $C_c$ ) were employed. No change in pH was verified after graphite addition.

The working electrode (WE) was a rotating disk electrode (RDE) consisting of an interchangeable mild steel cylinder embedded in an epoxy resin, with an electroactive flat disk surface area of  $0.38 \text{ cm}^2$ . Before each experiment, WE was polished with 600-emery paper, rinsed with distilled deionized water and dried. After this, the electrode was immersed in the electrodeposition solution and a constant cathodic current density ( $j_{\text{dep}}$ ) was immediately applied between WE and the counter-electrode. The counter-electrode was a Cu wire with  $6.3 \text{ cm}^2$ . All electrochemical measurements were conducted at room temperature ( $25^\circ\text{C}$ ) and under forced convection conditions produced by the RDE at a constant frequency ( $\omega$ ) of 500 rpm. The electrodeposition charge density ( $q_{\text{dep}}$ ) was set in  $72,1 \text{ C cm}^{-2}$ , which corresponds to a thickness of a  $30 \mu\text{m}$  according to Faraday's law assuming 100 % of efficiency in current density.

Surface morphological analyses were performed by scanning electron microscopy (SEM) with a FEI Quanta 200 microscope coupled with an EDS-Oxford software INCA, for semiquantitative chemical analysis.

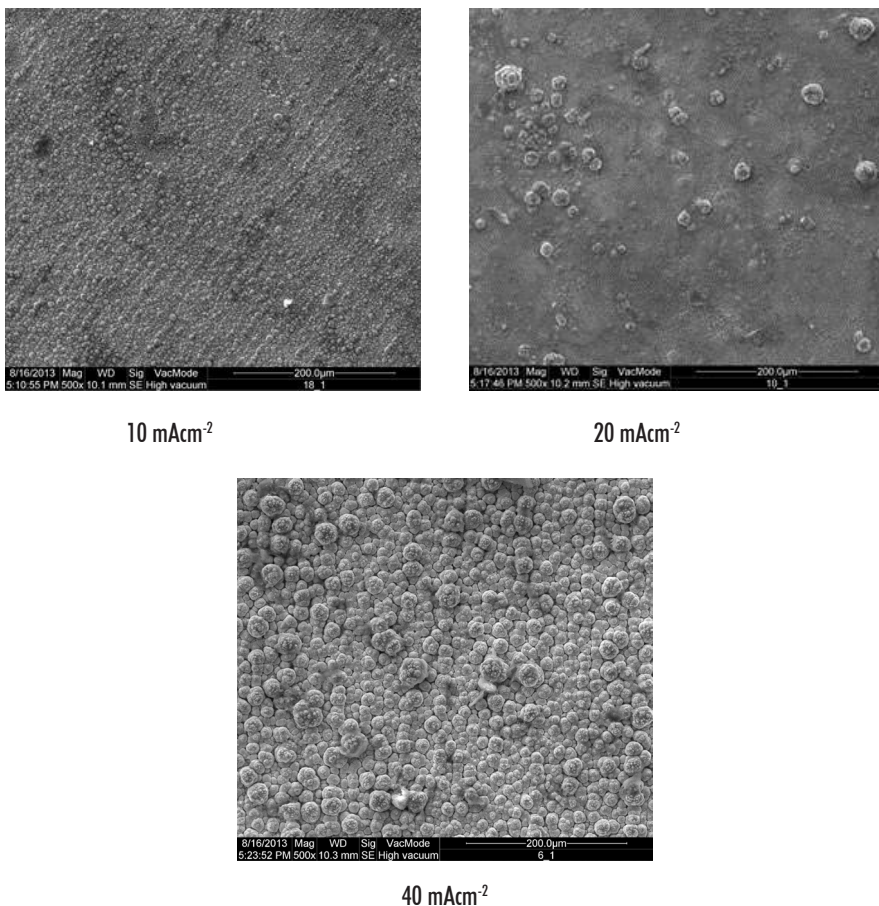
## RESULTS AND DISCUSSION

### Surface morphological analysis

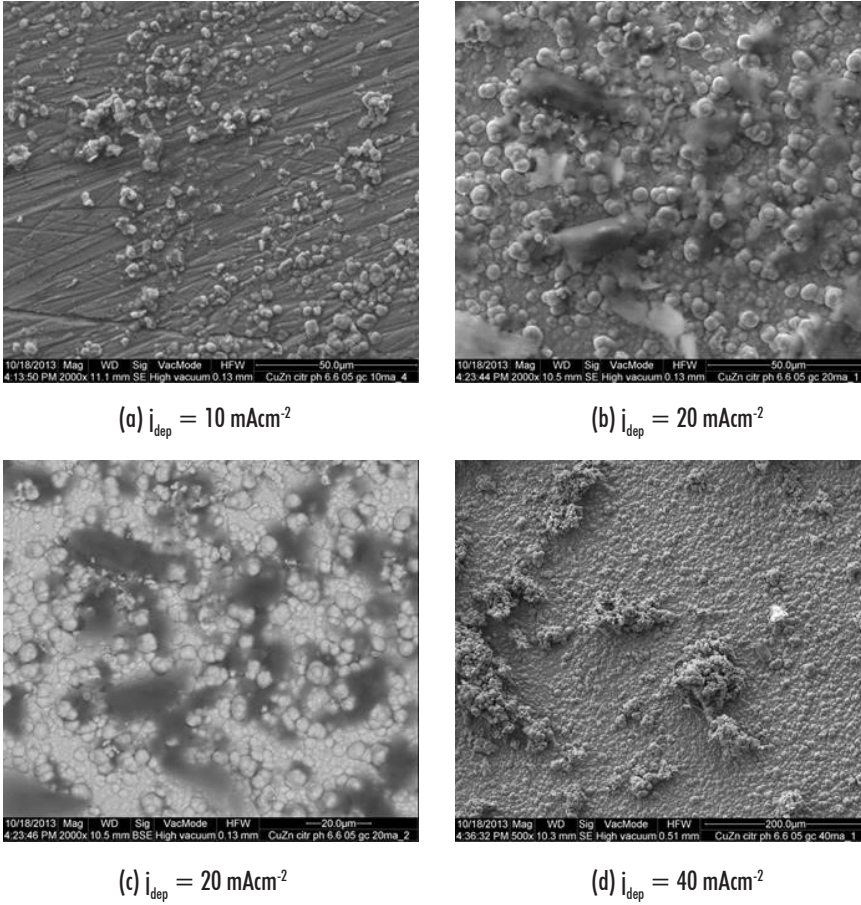
In Figure 1 they are shown some typical SEM micrographs of CuZn deposits obtained from free-of-graphite electrodeposition solutions. The deposits are continuous and exhibit only one layer with a coarse-grained structure at high  $j_{\text{dep}}$ . When CuZn deposits are obtained from graphite loaded electrodeposition solu-

tions, the surface morphology changes. This can be visualized in Figures 2 and 3. Two layers appear: a bottom fine-grained compact and adherent layer and an upper coarse-grained discontinuous layer. This upper layer is poorly adherent and its formation is due to the graphite particles, since as high is the mass of graphite to solution volume ( $C_c$ ), more evident is this layer as it can be seen in Figure 3 for 10 g/L of graphite.

Graphite particles have a detrimental effect on the growth of electrodeposits and this is one of the reasons for the difficulties in obtaining these electrocomposite coatings, at least for the high  $q_{dep}$  analyzed. Similar effects of graphite on surface morphology were already observed by Ghorbani *et al.* [13] in cyanide baths for CuZn electrodeposition. In strongly alkaline solutions, employing sorbitol as complexing agent, also the same features were observed [19]. Graphite is a conductive material and one possible explanation for the development of the upper poorly adherent layer is that graphite particles adsorbed on the surface can act as a center for a disordered growth.



**Figure 1:** Typical SEM micrographs of CuZn deposits obtained from citrate electrodeposition solution free-of-graphite particles at distinct  $j_{dep}$  indicated.  $\omega = 500$  rpm.  $q_{dep} = 72,1$  Ccm<sup>2</sup>.

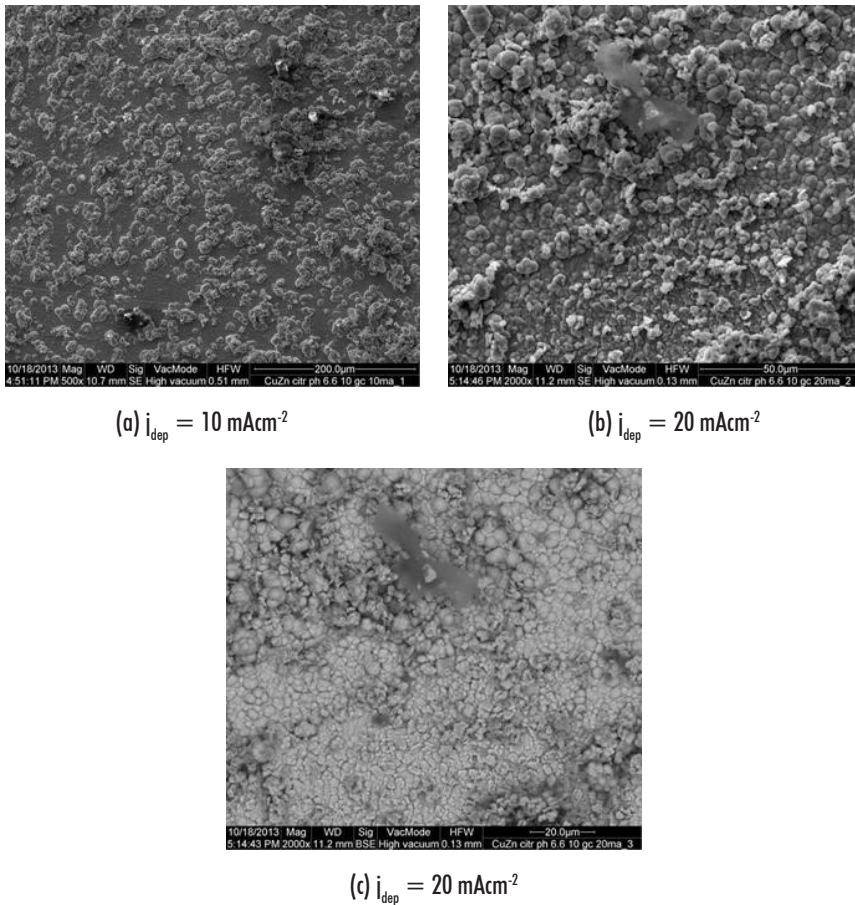


**Figure 2:** CuZn deposits obtained from citrate electrodeposition solutions with 0,5 g/L of graphite. Distinct  $i_{\text{dep}}$  indicated. Figure 2.c, image with backscattered electrons.  $\omega = 500 \text{ rpm}$ .

## CuZn-graphite electrocomposites

Graphite particles in these deposits could be detected only in some few cases within the conditions of this work. In Figures 2.b and 2.c and in Figure 3.b and 3.c, some graphite particles dispersed in the upper layers can be observed. From this, it can be concluded that electrocomposites CuZn-graphite are difficult to obtain, since the particles are partially occluded and in a discontinuous matrix. Increase in  $C_c$  does not bring benefit to graphite occlusion. The reasons for these difficulties need to be understood with additional experiments.



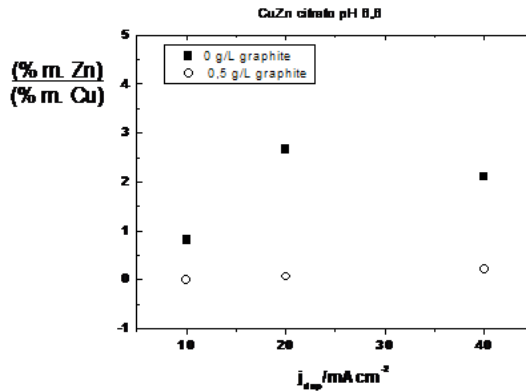


**Figure 3:** The same as Figure 2 for 10 g/L of graphite. Figure 3.c image with backscattered electrons.

## Chemical composition

EDS analyses of the metal matrix of CuZn were performed for the deposits of Figures 1 (free-of-graphite solution) and of Figure 2 ( $C_C = 0,5 \text{ g/L}$ ). It was observed a compositional variation affected by the graphite particles, even without occlusion of then into the metal-matrix. These results are shown in Figure 4 as the ratio of mass percentage of Zn (% m. Zn) to the mass percentage of Cu (% m. Cu).

For all  $j_{\text{dep}}$ , graphite dispersed in the electrodeposition solution makes the metal matrix to be enriched in copper, the nobler metal. The kinetics of the  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$  reductions is being affected by the graphite. It is not possible to infer if graphite particles are favoring  $\text{Cu}^{2+}$  reduction or hindering  $\text{Zn}^{2+}$  reduction and their complexes. Apart from that, this enrichment in Cu could improve corrosion resistance of the coating. Compositional variation of the metal-matrix in electro-composite coatings literature is a normal finding [20,21,22,23] and is also now observed for CuZn-graphite form citrate solutions.



**Figure 4:** Compositional variation of the CuZn matrix obtained from citrate electrodeposition solution, at  $\omega = 500$  rpm, as a function of  $j_{dep}$ , for distinct graphite contents in solution.

## CONCLUSIONS

CuZn deposits obtained at constant current densities from citrate based electrodeposition solutions exhibit a dual layer. It consists of a compact and adherent fine-grained bottom layer and over this, a coarse-grained poorly adherent upper one. The upper layer is due to the presence of graphite particles in the electrodeposition solution. Graphite particles have a detrimental effect in the surface morphology of CuZn for the high employed  $q_{dep}$ .

Occlusion of graphite particles in the CuZn matrix could be observed in some few cases. CuZn-graphite electrocomposites were obtained. However, the occlusion was partial and observed in the upper, poorly adherent layer.

Graphite particles in the electrodeposition solution make the CuZn deposits to be enriched in copper, with a good prospect for improved corrosion resistance of the CuZn matrix.

## FUTURE PROSPECTS

Changing in the electrodeposition parameters such as:  $j_{dep}$ ,  $q_{dep}$ , solution pH, solution composition and  $\omega$ , could improve the surface morphology and the occlusion of graphite particles.

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