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Morphology of copper deposits obtained by metallic electrodeposition

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Abstract

Electrochemical deposition of copper from copper nitrate aqueous electrolyte on graphite substrate was investigated at current densities between 0.03 mA/cm² - 1.36 mA/cm² and in the voltage range of 3 V to 15 V. The surface morphology and elemental composition of the resultant deposit were characterized by electron microprobe analysis (EMPA). These images illustrate the influence of current density on the shape of copper electrodeposited on the electrode surface. Rods, polyhedral bodies, pentagonal pyramids, dendritics, spiked spheres or cauliflower-like shapes are observed depending on the electrodeposition conditions.

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1. Introduction

Electrodeposition of copper is an economical processing method that allows obtaining copper of high purity in an environmentally friendly way. The morphology of copper electrodeposits obtained from synthetic solutions was widely investigated by Nikolic et al. (2008, 2012) and Panda et al. (2009). Controlled shape metallic particles have received tremendous attention due to unique electronic, magnetic, optical and catalytic properties; further they have a wide range of application, such as chemical biosensing, catalysis, photonic, optoelectronics (Ko et al. (2009)). The fabrication of metallic nanostructures with controllable shapes is important for utilizing the shape-tunable properties of nanomaterials. The shape and size of deposited particles strongly depends on the operational parameters of the electrodeposition process such as temperature, agitation, electrical potential (overpotential), electrolyte, pH, copper concentration, nature of the substrate, additives, hydrogen evolution on the electrode surface, electrolysis time and particularly current density (Hu et al. (2003) and Orhan & Hapçı (2010)). Hence, different electrochemical conditions produce different growing forms. The particle shapes obtained have been named as spiked spheres by Jayakumar et al. (2011), cauliflowers-like by Nikolic et al. (2006), pyramids by Alamanova et al. (2008), nanorods by Au et al. (2011), and nanowires by Inguanta et al. (2009). In this study the morphology of copper electrodeposited on graphite substrate was analyzed by EMPA-EDS and the system conditions were correlated.

2. Experimental

The electrodeposition measurements were carried out at 25°C in a 1 L beaker as an open cell with graphite as working electrode and also as a counter electrode. The working electrodes were graphite cylinders of 2.2 mm in diameter from pencil leads that were arranged by three and by two of them placed vertically together in a parallel array leaving an exposed area in the range of 5 to 12 cm². The distance between the working and the counter electrodes was 15 mm. High-purity chemicals and Milli-Q (from Millipore) water were used to prepare aqueous 8.33-8.82 mM Cu(NO₃)₂ (Merck) (corresponding to the initial concentration of Cu²⁺) and 1.48 mM KNO₃ (Cicarelli) solutions. A direct current (DC) energy source with a range of 0 to 30 V and 1.5 A at maximum current was used. A magnetic device to maintain the homogeneity thereof constantly stirred the electrolytic solution. The studies of surface morphology of copper deposition on electrodes and the corresponding elemental analysis were carried out by using a microprobe Jeol JXA 8230 with an energy dispersive spectrometer (EMPA-EDS).

3. Results and Discussion

The effect of different experimental conditions on the morphology of electrodeposited copper was studied. The microprobe image obtained after copper electrodeposition onto graphite is shown in Figure 1a). Copper particles were electrodeposited at 3 V during 120 min (current density 1.36 mA/cm², pH 4.36). An area predominantly of agglomerates of copper grains and some crystalline structures can be observed. One of them is amplified in the Figure 1b) that clearly shows a pentagonal pyramid. It is noticeable that these shapes are in the border of void regions. It can be also seen from Figure 1b) the different zones where the elemental compositions were obtained by EDS. Figures 1c) and 1d) are the EDS patterns of zone 001 and 003, respectively. In 001 zone, grains with well-defined crystal planes of pentagonal pyramid are present and in 003 zone, the agglomerated one. Despite the different shapes found, the elemental composition is the same, corresponding only to elemental copper.

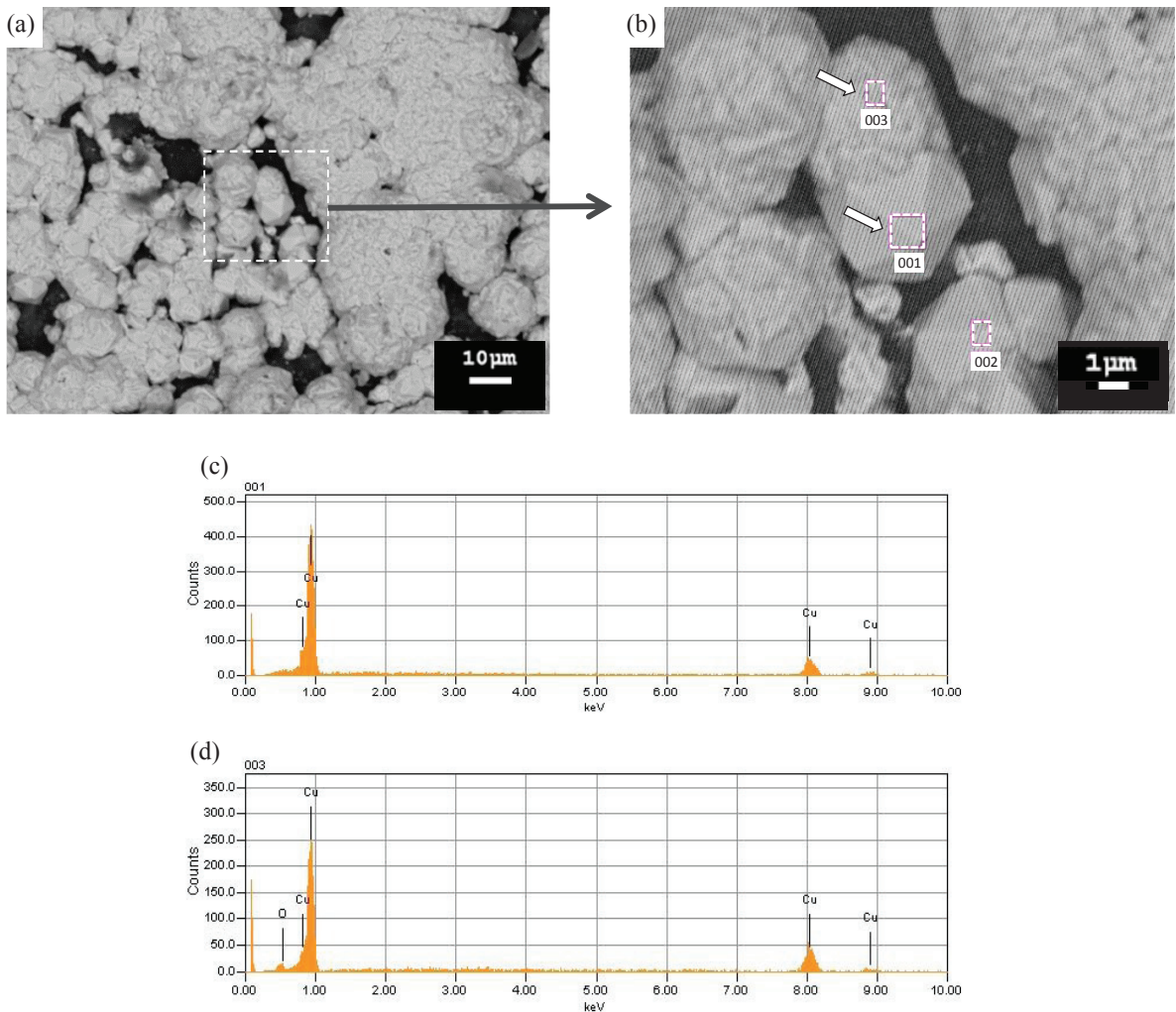


Figure 1. Surface micrographs of copper particles electrodeposited at a 3V during 120 min (current density 1.36 mA/cm², pH 4.36) onto graphite electrode. a) X3,500. b) x6,000. c) and d) EDS patterns of the 001 and 003 zones showed in b).

Figure 2 a) shows copper particles electrodeposited at 10 V during 120 min (current density 0.03mA/cm², pH 3.11) from a solution of initial concentration of 8.82 mM of Cu²⁺. As it can be seen, the shapes are clearly distinct from the previous figures. At these experimental conditions, it is possible to observe parallel planes, rhomboidal and some truncated forms and rods with rectangular section. Figure 2 a) also shows the different zones where the elemental compositions were analysed by EDS. Figures 2 b) and 2 c) are the EDS patterns of zone 002 and 003, respectively. A similar composition was observed in both zones in spite of seeing the area as a rod or as a grain with a rectangular shape.

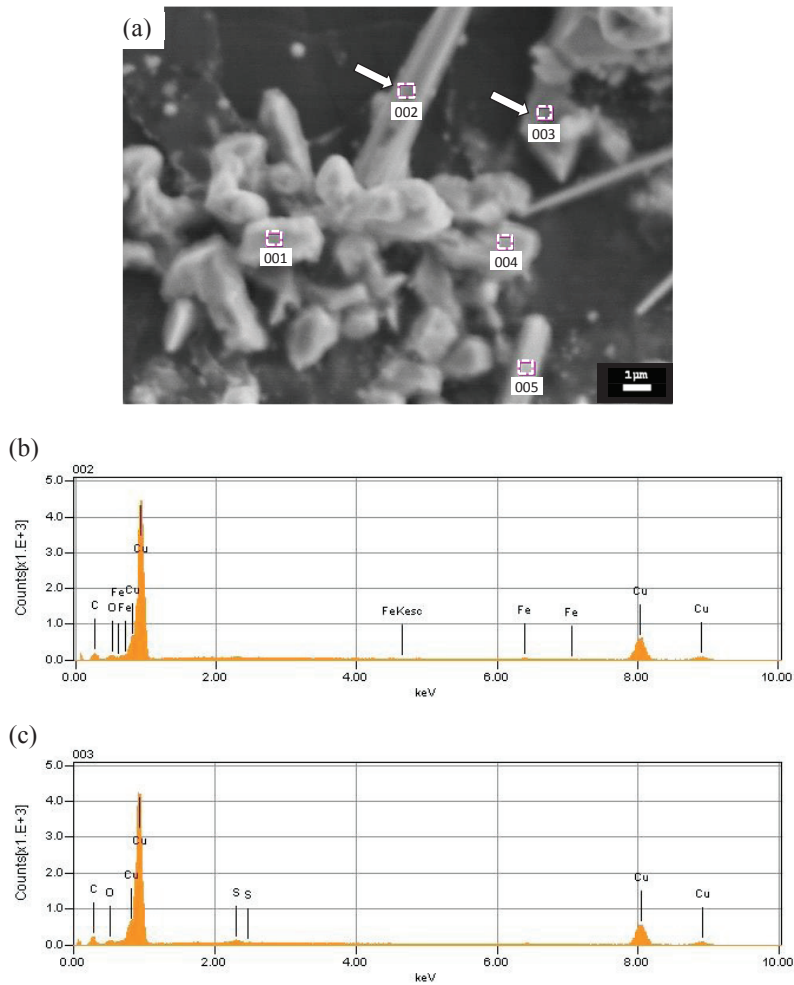


Figure 2. Surface micrograph of copper electrodeposited. a) x6,000. b) and c) EDS patterns of the 002 and 003 zones showed in a).

On the other hand, Figure 3 a) shows copper particles with cauliflower-like form obtained by electrodeposition at 15 V during 120 min (current density 0.03 mA/cm², pH 3,00) from a solution of initial concentration of 8.76 mM of Cu²⁺. Furthermore, dendritic forms, spiked spheres and small rods can also be seen. The formation of the cauliflower-like structure could be attributed to the gradual increase of the quantity of the electrodeposited metal by an increase in the voltage applied [6]. Thus, these forms could represent different stages of the metal growth process. Figures 3 b) and 3 c) show the elemental composition obtained by EDS of zones 001 and 002 in Figure 3 a), respectively. The 003 zone have a similar EDS pattern. As in the previous samples, the elemental analysis reveals the same compositions in all of the deposits obtained. A micrograph of another area of the same electrode shown in Figure 3 a) is presented in Figure 3 d). Copper particles exhibiting spiked spheres, dendritic or rod forms are also shown. It is noticeable the presence of holes between the agglomerates which are a consequence of the evolution of the hydrogen bubbles formed during the electrodeposition process (Bozzini et al. (2006)). The white dashed circles marked in the figure evidence these voids. Figure 3 e) and 3 f) show the compositions referred to a spiked sphere and the crossing of rods, respectively. EDS patterns also exhibit the same elemental composition.

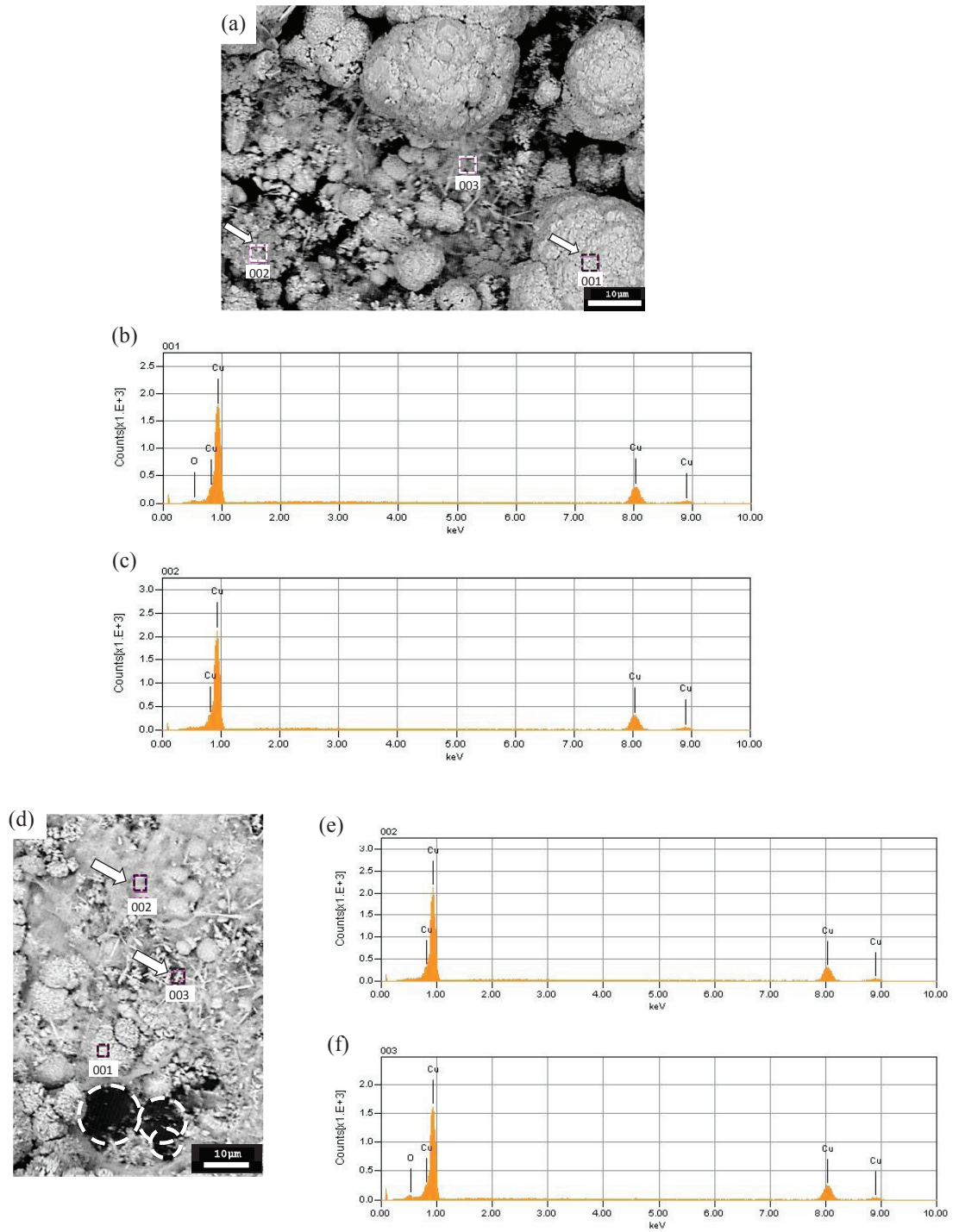


Figure 3. a) Surface micrograph of copper electrodeposited. x1,500. b) and c) EDS patterns of the 001 and 002 zones showed in figure a). d) Another area of the same electrode. x1,300. e) and f) EDS patterns of the 002 and 003 zones showed in figure d).

4. Conclusions

Electrochemical deposition was investigated at current densities between 0.03 mA/cm² and 1.36 mA/cm² and in the voltage range of 3 to 15V. Electrodeposition of copper on graphite substrate produced deposits with different shapes. The morphology and the elemental analysis of such obtained deposits were characterized by EMPA-EDS.

The images illustrate that at lower current densities the predominant shapes are spiked spheres, pentagonal pyramid, parallel planes polyhedrons, rhomboidal, some truncated forms, small rods with rectangular section, dendritic and cauliflower-like agglomerates. On the other hand, at higher current densities is noticeable the absence of previously described forms and instead of them are apparent a crystalline ones, for instance a pentagonal pyramid structure embedded in bigger agglomerates

As it have been mentioned along all of this work, although different deposit shapes were observed, the elemental composition was the same, corresponding only to copper in high grade of purity.

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