Full Paper

Determination of Critical Conditions for the Formation of Electrodeposited Copper Structures Suitable for Electrodes in Electrochemical Devices

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Abstract: Electrodeposition of copper from acid sulfate solutions at overpotentials on the plateau of the limiting diffusion current density and at higher overpotentials was examined. The average current efficiencies for hydrogen evolution reaction are determined by a measurement of the quantity of evolved hydrogen and the overall electrodeposition current as a function of electrodeposition time, while morphologies of copper deposits are examined by the use of the scanning electron microscopy (SEM) technique. It is found that the open and porous structures of copper deposits (denoted and as honeycomb – like copper structures), suitable for electrodes in electrochemical devices such as fuel cells and chemical sensors, were reached by electrodeposition processes from solutions with the lower concentrations of Cu (II) ions (0.15 M $CuSO_4$ and less in 0.50 M H_2SO_4) at overpotentials outside the plateau of the limiting diffusion current density at which the quantity of evolved hydrogen was enough to change hydrodynamic conditions in the near – electrode layer. The main characteristics of these copper structures were craters or holes formed primarily due to the attachment hydrogen bubbles with agglomerates of copper grains between them.

1. Introduction

Electrodeposition of copper at overpotentials and current densities on the plateau of the limiting diffusion current density has been the subject of much research and the results of these investigations have been summarised [1–5]. It can be seen from these investigations that dendritic forms were a main characteristic of electrodeposition processes at these overpotentials and current densities. On the other hand, electrodeposition processes at very high current densities and overpotentials outside the plateau of the limiting diffusion current density are only investigated from point of view of a formation of powders [1, 2, 4, 5]. Copper adherent deposits formed in the initial stage of electrodeposition at high current densities and overpotentials are insufficiently investigated. Investigations of such deposits formed at high current densities whereby open and very porous structures with extremely high surface areas are obtained were initiated recently [6]. The open and porous copper structures, denoted as honeycomb–like structures, are also obtained by potentiostatic electrodeposition at high overpotentials [7–9]. These structures were similar to those obtained at high current densities. The formation of these structures and the initial stage in the formation of copper powders was caused in both cases by a vigorous evolution of hydrogen.

Copper deposits obtained at high current densities and overpotentials are very important from a technological point of view. It has been stated that the open and porous structures of copper deposits obtained at high current densities were ideally suited for use as electrodes in electrochemical devices such as fuel cells, batteries and chemical sensors [6], while the extremely high surface area is relevant for evaluating some electrochemical reactions. For example, it was known that copper shows a high activity for the nitrate ion reduction [10] as well as for the reaction in which nitrate is reduced to ammonia in high yield in aqueous acidic perchlorate and sulphate media [11].

However, in spite of numerous investigations of electrodeposition processes at high overpotentials and current densities [1–5], there is no data considering the effect of hydrogen evolution on the morphology of the electrodeposited copper at high overpotentials. Having in mind a potential high technology significance of copper deposits obtained at high overpotentials, it is necessary to better recognize the effect of this process on electrodeposition of copper under these conditions. For that reason, the aim of this paper it will be to examine the effect of this process on copper electrodeposition at overpotentials on the plateau of the limiting diffusion current density or higher ones. This investigation will be done through the analysis of the effect of different concentrations of copper(II) ions on the hydrogen evolution reaction, and consequently, the morphology of copper deposits.

2. Experimental

Copper was potentiostatically deposited from the following solutions:

(a) 0.075 M $CuSO_4$ + 0.50 M H_2SO_4 (*solution (I)*),

(b)   0.30 M CuSO$_4$ + 0.50 M H$_2$SO$_4$ (*solution (II)*) and

(c)   0.60 M CuSO$_4$ + 0.50 M H$_2$SO$_4$ (*solution (III)*).

Electrodepositions were performed in an open cell and at a temperature of 18.0 ± 1.0 ^{o}C. Doubly distilled water and analytical grade chemicals were used for the preparation of solutions for electrodeposition of copper. Reference and counter electrodes were of a pure copper. Copper electrodepositions onto cylindrical copper cathodes were performed at overpotentials of 550, 650 and 800 mV. The cathodes were prepared in the following way: cylindrical copper electrodes were first covered with a thin copper film by a 2 min electrodeposition at an appropriate overpotential using the same copper plating solution which is later used for electrodeposition at the desired overpotential. The overpotentials at which copper was electrodeposited for 2 min were: 250 mV for *solution (I)*, 350 mV for *solution (II)* and 400 mV for *solution (III)*. This way of preparing of copper cathodes was used in order to obtain a uniform copper surface before electrodeposition at the desired overpotentials.

SEM microphotographs corresponding to morphologies of copper deposits electrodeposited with quantities of the electricity of 10.0 and 20.0 mAhcm^{-2} were obtained with a model JOEL T20 scanning electron microscope (SEM).

The average current efficiency of hydrogen evolution was determined in the following way: in a time *t*, the current of electrodeposition *I* and the volume of evolved hydrogen $V(H_2)$ are measured. After a graphical integration *I* – *t*, the average current efficiency for hydrogen evolution $\eta_{I, av}(H_2)$ is determined according to Eq. (1):

$$\eta_{I,av}(H_2) = \frac{V(H_2)}{\mu(H_2)\int\limits_0^t I \mathrm{d}t} \tag{1}$$

where:

$$\mu(H_2) = \frac{V}{nF} = \frac{22400 \mathrm{cm}^3}{2 \times 26.8 \mathrm{Ah}} = 418 \frac{\mathrm{cm}^3}{\mathrm{Ah}} \tag{2}$$

and *nF* is the number of Faradays per mole of consumed ions and *V* is molar volume of gas under normal conditions (i.e. 22 400 cm^3).

The experimental procedure for the determination of the average current efficiency of hydrogen evolution is given in [7].

3. Results and Discussion

3.1. Polarization measurements and the determination of the average current efficiencies of the hydrogen evolution reaction

Figure 1 shows the polarization curves for the copper electrodeposition from 0.075 M CuSO$_4$ in 0.50 M H$_2$SO$_4$ (*solution (I)*), 0.30 M CuSO$_4$ in 0.50 M H$_2$SO$_4$ (*solution (II)*) and 0.60 M CuSO$_4$ in 0.50 M H$_2$SO$_4$ (*solution (III)*). The beginning of the plateau of the limiting diffusion current density is determined as the intersect of straight lines joining currents in mixed activation – diffusion and diffusion control of electrodeposition, as shown in the figure. The end of this plateau is determined as the overpotential at

which current starts to grow with the increasing overpotential. The range of overpotentials on the plateau of the limiting diffusion current density determined in this way is given in Table 1. The open circuit potentials of copper electrodes in *solutions (I)*, *(II)* and *(III)* are also given in Table 1. From this data it can be seen that an increase of the concentration of Cu(II) ions in plating solutions leads to a corresponding decrease of the length of the plateau of the limiting diffusion current density.

Figure 1. Polarization curves for the cathodic process of copper deposition from: 0.075 M $CuSO_4$ + 0.50 M H_2SO_4 (*solution (I)*), 0.30 M $CuSO_4$ + 0.50 M H_2SO_4 (*solution (II)*) and 0.60 M $CuSO_4$ + 0.50 M H_2SO_4 (*solution (III)*).
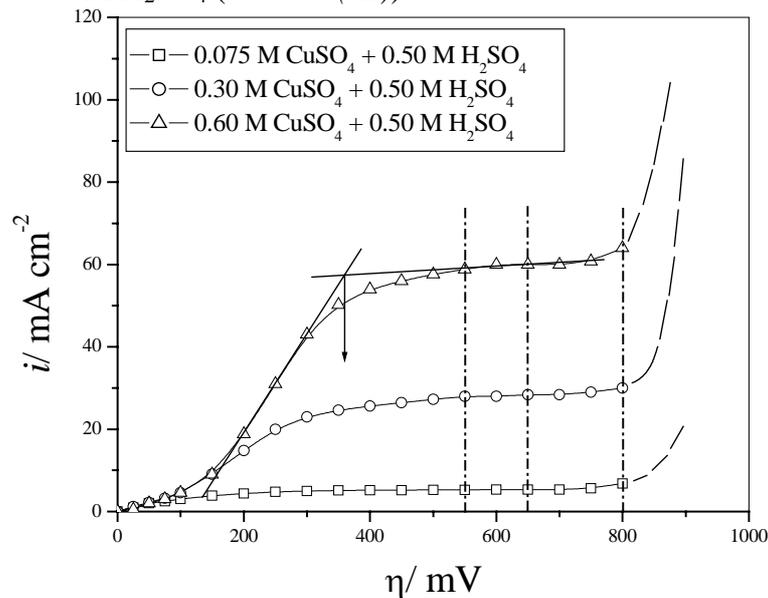

The effect of hydrogen evolution on copper electrodeposition was examined at overpotentials of 550, 650 and 800 mV. For all examined solutions, overpotentials of 550 and 650 mV corresponded to the plateau of the limiting diffusion current density, while an overpotential of 800 mV was about 50 mV outside the plateau of the limiting diffusion current density (Figure 1 and Table 1).

Figure 2 shows the dependencies between electrodeposition currents and volumes of evolved hydrogen on electrodeposition time obtained at overpotentials of 550, 650 and 800 mV from *solutions (I)*, *(II)* and *(III)*.

Table 1. The range of overpotentials belonging to the plateau of the limiting diffusion current density ($\Delta\eta$) for *solutions (I)*, *(II)* and *(III)* and the open circuit potentials of copper electrode in *solutions (I)*, *(II)* and *(III)*.

| Copper electrodeposition solution	$\Delta\eta$/ mV	Open circuit potentials/ mV
0.075 M $CuSO_4$ in 0.50 M H_2SO_4	140 – 750	296
0.30 M $CuSO_4$ in 0.50 M H_2SO_4	280 – 750	312
0.60 M $CuSO_4$ in 0.50 M H_2SO_4	360 – 750	320

Figure 2. The dependencies of the overall electrodeposition current (*open style*) and the volume of evolved hydrogen (*solid style*) on the electrodeposition time for copper electrodepositions at 550, 650 and 800 mV from *solutions (I), (II)* and *(III)*.
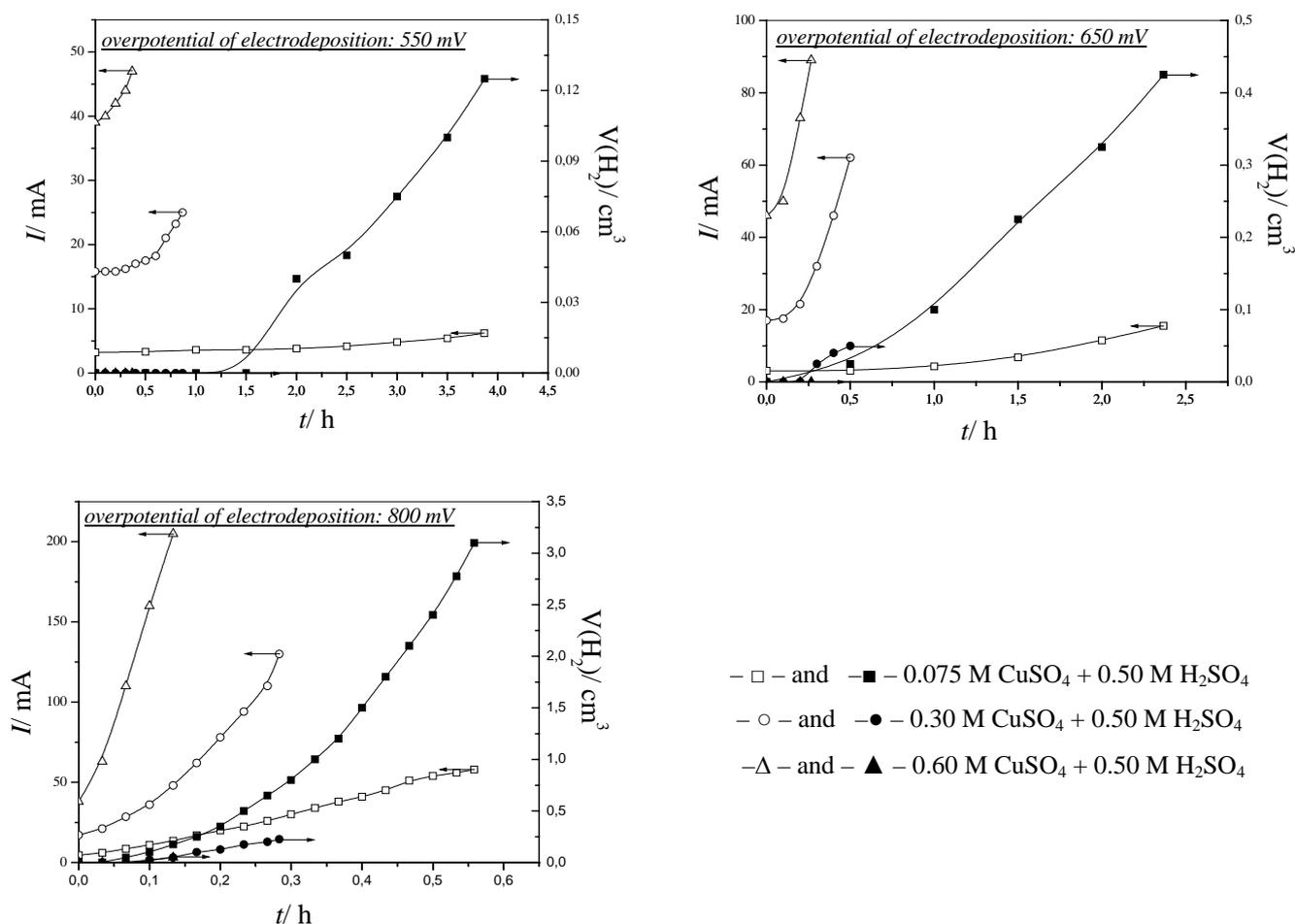
From Figure 2 can be seen that the electrodeposition currents grew with the increasing concentration of Cu(II) ions during electrodeposition processes at all overpotentials. At an overpotential of 550 mV there was hydrogen evolution only from *solution (I)*. Electrodeposition of copper at an overpotential of 650 mV led to hydrogen evolution not only from *solution (I)*, but also from *solution (II)*. The amount of evolved hydrogen was larger from *solution (I)* than from *solution (II)*. Finally, copper electrodeposition processes at an overpotential of 800 mV were accompanied by hydrogen evolution from all three solutions. A decrease of the quantity of evolved hydrogen with the increasing concentration of Cu(II) ions was observed during electrodeposition of copper at this overpotential.

The dependencies of the average current efficiencies for hydrogen evolution reactions on the quantity of passed electricity were derived from diagrams given in Figure 2 and shown in Figure 3. The summary of the obtained values of the average current efficiencies of hydrogen evolution in the dependence of concentration of Cu (II) ions and overpotential of electrodeposition are given in Table 2.

Figure 3. The dependencies of the average current efficiencies for hydrogen evolution reaction on the quantity of used electricity, for copper electrodepositions at 550, 650 and 800 mV from *solutions (I), (II)* and *(III)*.
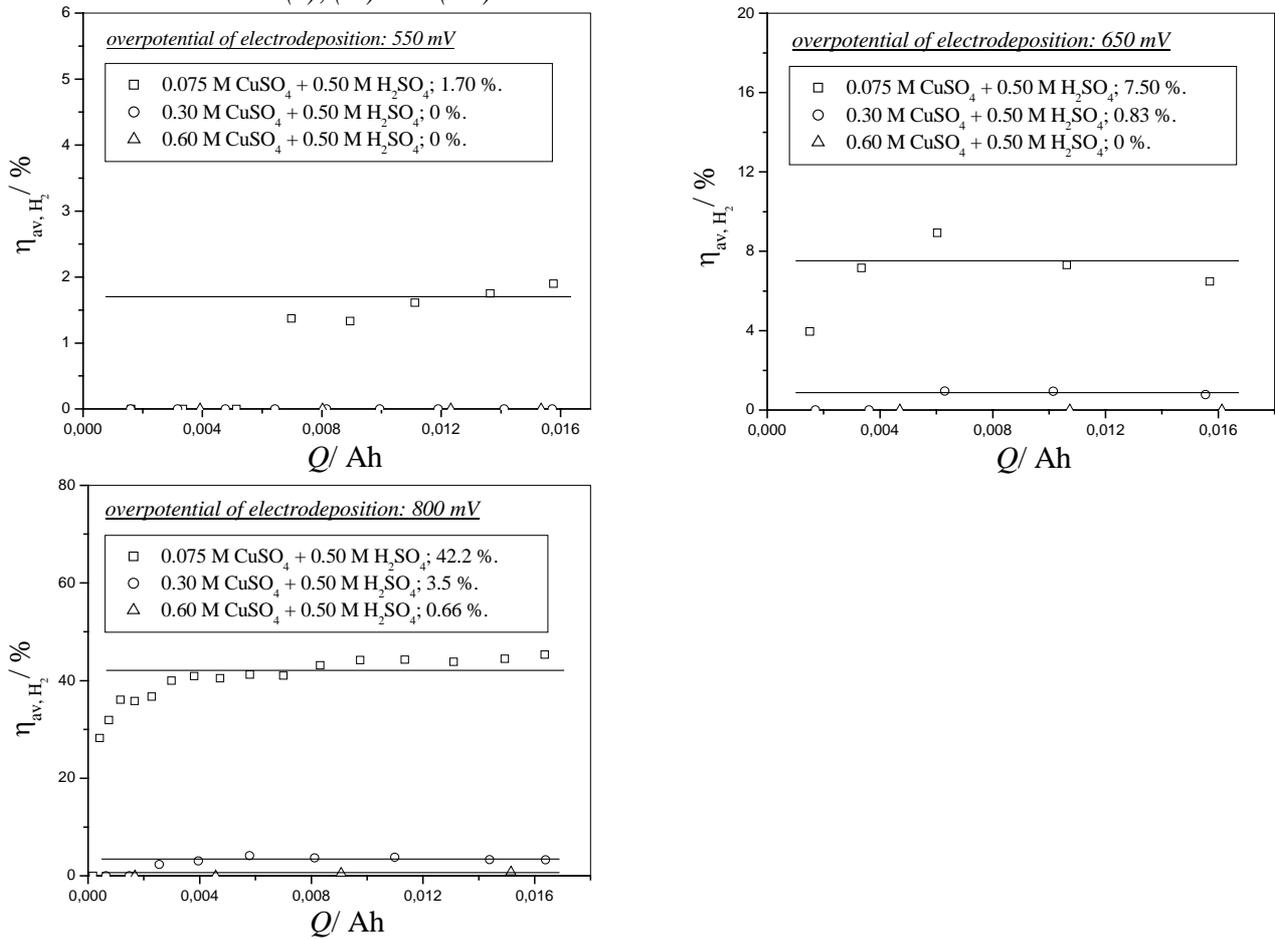
In total, the decrease of the average current efficiencies of hydrogen evolution with the increasing concentration of Cu(II) ions, as well as an increase of the average current efficiencies of hydrogen evolution with the increasing overpotential of electrodeposition were observed during these electrodeposition processes (Figure 3 and Table 2). This result can be explained by the fact that hydrogen evolution rate during copper electrodeposition from solutions containing Cu(II) ions in H_2SO_4 at some specified potential decreases with the increasing concentration of Cu(II) ions, while copper deposition rate, and consequently, the overall current strongly increase with the increasing concentration of Cu(II) ions. In this way, the current efficiency for hydrogen evolution reaction at specified potential decreases with the increasing concentration of Cu(II) ions.

Table 2.   The average current efficiencies of hydrogen evolution in the function of concentration of Cu (II) ions.

Solution for copper electrodeposition	The average current efficiencies of hydrogen evolution, η_{av} (H_2)/ %, at overpotentials of:		
	550 mV	650 mV	800 mV
0.075 M $CuSO_4$ in 0.50 M H_2SO_4	1.7	7.5	42.2
0.30 M $CuSO_4$ in 0.50 M H_2SO_4	0	0.83	3.5
0.60 M $CuSO_4$ in 0.50 M H_2SO_4	0	0	0.66

3.2. Morphologies of copper deposits obtained at overpotentials of 550, 650 and 800 mV

Figure 4 shows the morphologies of copper deposits electrodeposited at an overpotential of 550 mV from *solutions (I)*, *(II)* and *(III)* with a quantity of electricity of 10.0 mAhcm^{-2}. From Figure 4a can be seen that the copper deposit obtained from *solution (I)* had a cauliflower–like structure. Copper deposits obtained from *solution (II)* (Figure 4b) and *solution (III)* (Figure 4c) were globular structures.

Figure 4. Copper deposits obtained at overpotential of 550 mV. Quantity of electricity: 10.0 mAhcm^{-2}: (a) *solution (I)*, (b) *solution (II)*, (c) *solution (III)*. Magnification: x 750.

(a)   (b)   (c)
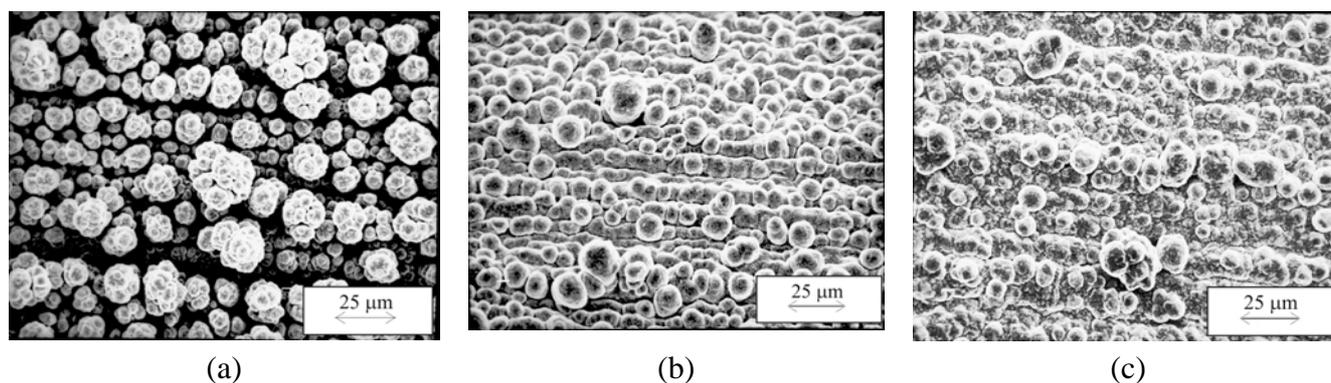
Electrodeposition of copper with twice the quantity of electricity led to a change in the morphology of copper deposits with respect to those shown in Figure 4. Figure 5 shows the morphologies of copper deposits obtained at overpotential of 550 mV with an amount of electricity of 20.0 mAhcm^{-2}. Copper dendrites instead of cauliflower–like forms were obtained during electrodeposition of copper from *solution (I)* (Figure 5a). A mixture of cauliflower–like and globular forms were obtained by electrodeposition from *solution (II)* (Figure 5b) and *solution (III)* (Figure 5c).

Copper dendrites are formed from all three solutions during electrodeposition processes at an overpotential of 650 mV with a quantity of electricity of 10.0 mAhcm^{-2}. However, from Figure 6 it can be seen that the shape of copper dendrites depends strongly on the concentration of Cu(II) ions. Very branchy copper dendrites consisting of corncob–like elements were formed from *solution (I)* (Figures 6a and b). Copper dendrites formed from *solution (II)* presented a mixture of very branchy dendritic forms (Figure

6c) and those shaped like flowers (Figure 6d). Finally, the copper deposits obtained from *solution (III)* presented a mixture of flower–like (Figure 6e) and corncob–like forms (Figure 6f).

Figure 5. Copper deposits obtained at overpotential of 550 mV. Quantity of electricity: 20.0 mAhcm^{-2}: (a) *solution (I)*, (b) *solution (II)*, (c) *solution (III)*. Magnification: x 750.
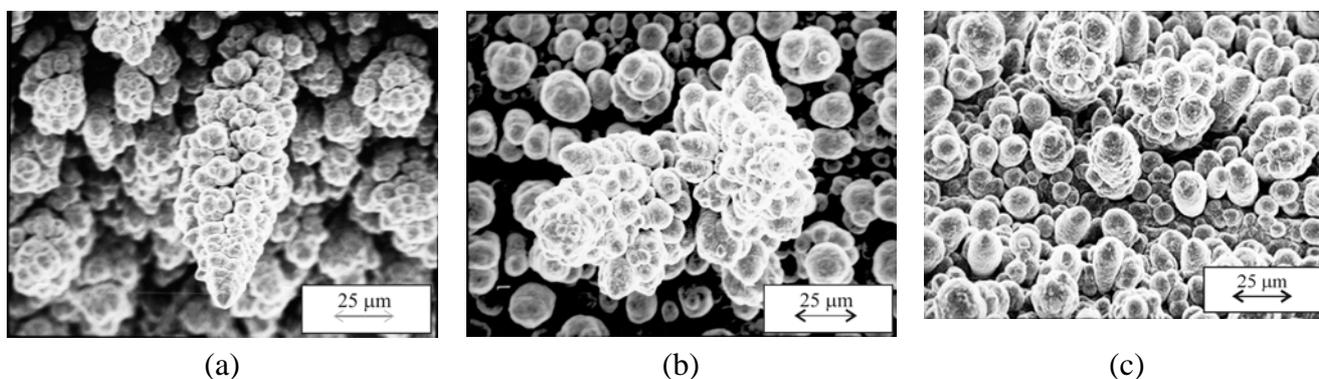

(a)   (b)   (c)

Figure 7 shows the morphologies of copper deposits obtained at an overpotential of 800 mV with a quantity of electricity of 10.0 mAhcm^{-2}, which reveals the strong effect of concentration of Cu(II) ions on copper electrodeposition at this overpotential.
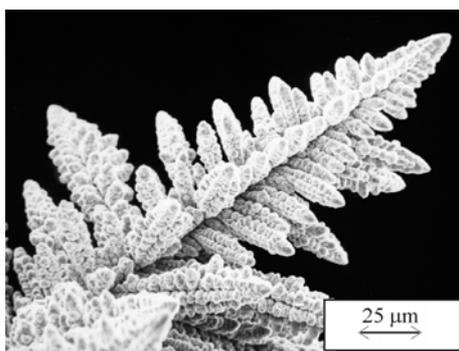
The copper deposits obtained from *solution (I)* had a very open and porous structure, and consisted of a large number of holes or craters formed due to the attachment of hydrogen bubbles (Figure 7a) with agglomerates of relatively small copper grains between them (Figure 7b).

The morphology of copper deposits obtained from *solution (II)* mainly consisted of dendritic forms but the presence of holes formed due to the attachment of hydrogen bubbles can also be seen (Figure 7c). The typical copper dendrites formed by the electrodeposition from this solution is shown in Figure 7d.

Finally, only dendritic copper forms are obtained from *solution (III)* (Figures 7e and f). These dendritic forms were more branchy structures than those formed from the same solution by the electrodeposition at the overpotential of 650 mV and with the same quantity of the electricity (cf. Figures 6e and f).

The careful analysis of the morphologies of copper deposits shown in Figures 4 – 7 indicated that an increase in the concentration of Cu(II) ions led to a shift of the formation of characteristic morphological shapes of copper deposits towards higher electrodeposition overpotentials by about 100–150 mV. For example, copper dendrites formed at 800 mV from *solution (III)* (Figures 7e and f) were very similar to those obtained at 650 mV from *solutions (I)* and *(II)* (Figures 6a – c). The globular forms obtained from *solutions (II)* and *(III)* (Figures 4b and c) were very similar to ones obtained from 0.15 M CuSO$_4$ in 0.50 M H$_2$SO$_4$ at an overpotential of 450 mV [7]. It is well known that cauliflower forms are characteristic of electrodeposition at overpotentials lower than the critical overpotential of dendritic growth initiation [1]. The different shapes of copper dendrites formed at the overpotential of 650 mV from solutions with different concentrations of Cu(II) ions (Figure 6) also pointed out the strong effect of concentration of Cu(II) ions on electrodeposition of copper at the overpotential of 650 mV.
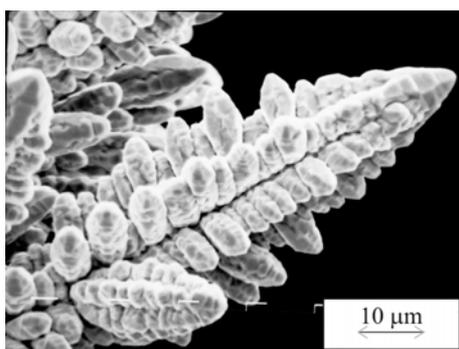
Figure 6. Copper deposits obtained at overpotential of 650 mV. Quantity of electricity: 10.0 mAhcm^{-2}. (a) and (b): *solution (I)*. Magnification: (a) x 750, (b) x 2000; (c) and (d): *solution (II)*. Magnification: (c) x 2000, (d) x 750; (e) and (f): *solution (III)*. Magnification: (e) x 750, (f) x 2000.
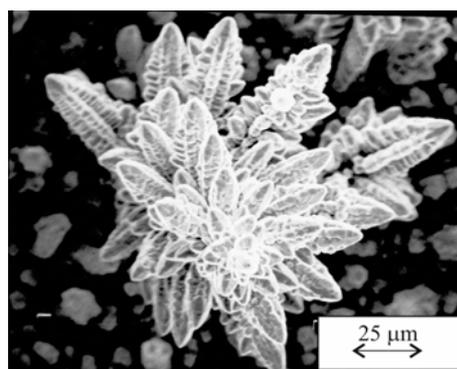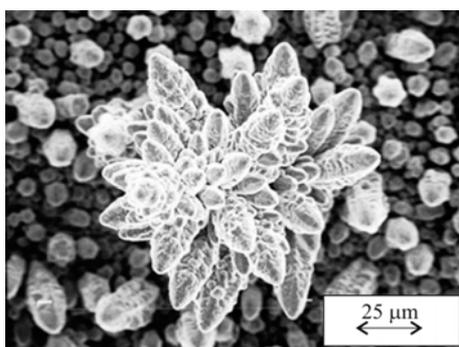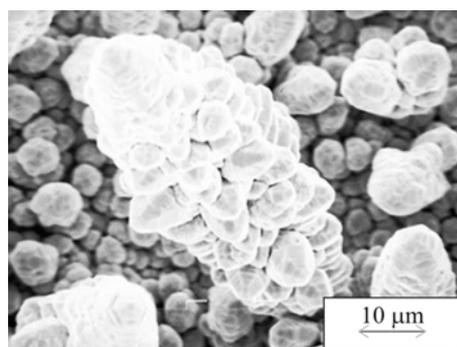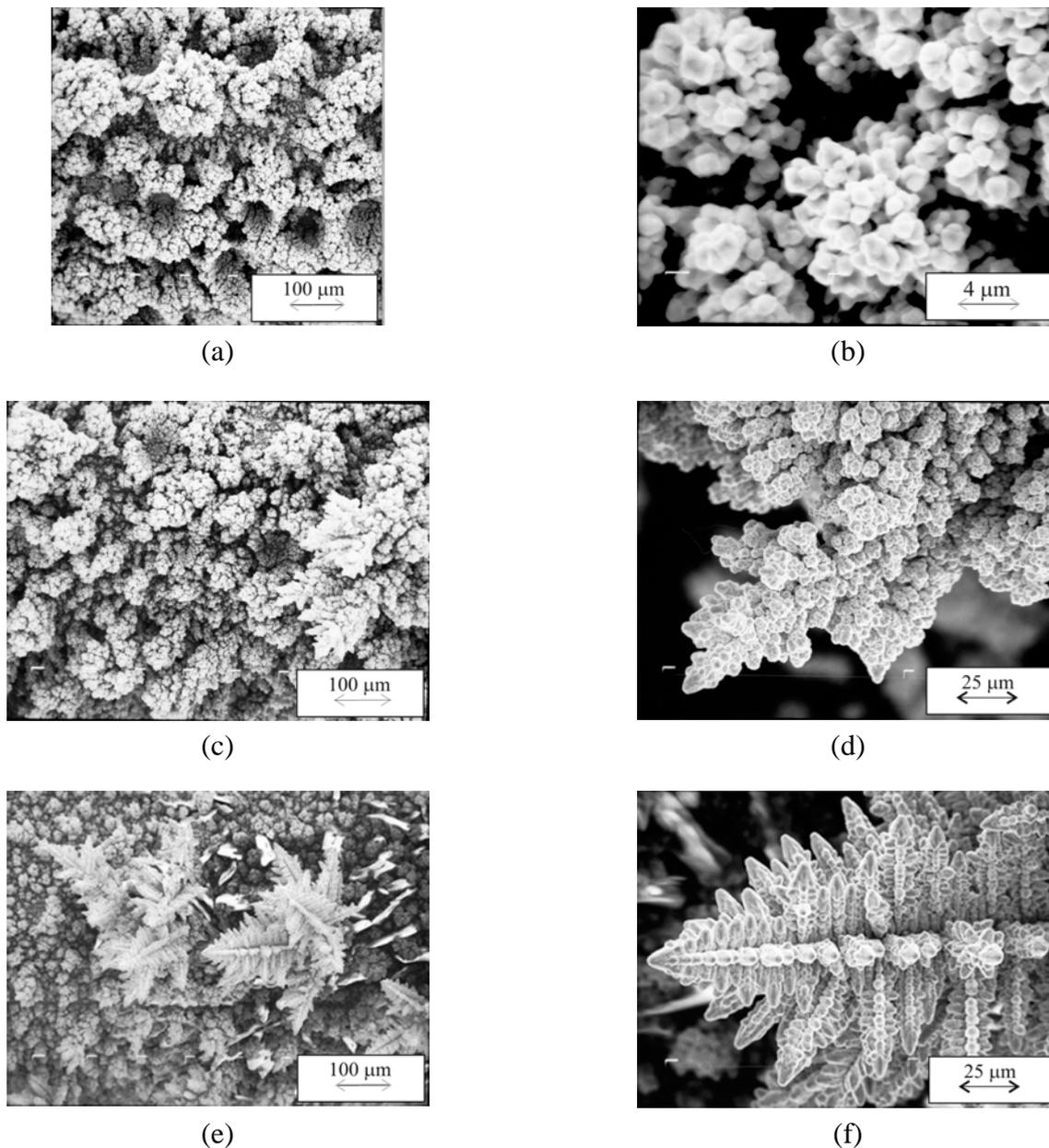

(a)
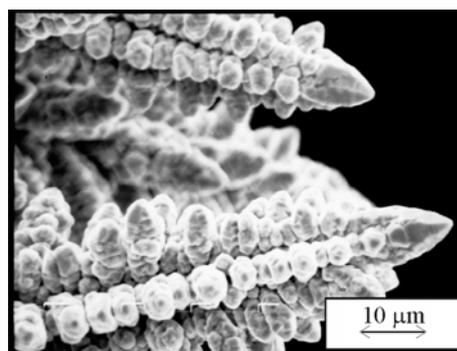
(b)

(c)

(d)

(e)

(f)

Figure 7. Copper deposits obtained at overpotential of 800 mV. Quantity of electricity: 10.0 mAhcm^{-2}. (a) and (b): *solution (I)*. Magnification: (a) x 150, (b) x 5000; (c) and (d): *solution (II)*. Magnification: (c) x 150, (d) x 750; (e) and (f): *solution (III)*. Magnification: (e) x 150, (f) x 750.

(a)

(b)

(c)

(d)

(e)

(f)

3.3. General discussion of the results obtained

The strong effect of the concentration of Cu(II) ions on the electrodeposition of copper at high overpotentials can be explained in terms of the minimum overpotential for the initiation of dendritic growth, in the following way:

The minimum overpotential at which dendritic growth is possible, η_I, is given by Equation (3) [1]:

$$\eta \geq \eta_i = \frac{b_c}{2.3} \ln \frac{i_L}{i_0}$$

(3)

where η is the overpotential, b_c the cathodic Tafel slope, i_L is the limiting diffusion current density and i_o is the exchange current density for the deposition process.

Figure 8 shows the dependence of logarithm of the limiting diffusion current density, i_L on the logarithm of the concentration of Cu(II) ions. From the obtained values of the slope and the intercept at the ordinate, it follows that the dependence of the limiting diffusion current density on the concentration of Cu(II) ions is given by $i_L = 0.32c_o^{1.18}$. On the basis of the slope value (1.18) it can be concluded that it is possible to apply Levich`s dependence of the limiting diffusion current density on the concentration of metal ions [12].

According to Levich, in metal electrodeposition under natural convection, i_L varies with concentration as

$$i_L \sim c_o^{1.25}$$

(4)

where c_o is concentration of Cu (II) ions.

This relation is valid under proper isothermal conditions [13], when the temperatures of the thermostated solutions (with a free surface) and of the surrounding air are equal.

On the other hand, for copper electrodeposition from acid sulphate solutions the following expression is valid [14]:

$$i_0 \sim c_o^{0.75}$$

(5)

and $b_c = 120$ mV/dec.

Substitution of i_0 and i_L from Eqs. (4) and (5) in Eq. (3) and further rearrangement gives that minimum overpotential for the initiation of dendritic growth depends on concentration of Cu(II) ions according to:

$$\eta_i \cong const + 60\log c_o$$

(6)

From this relation it can be easily seen how the increase of concentration of Cu(II) ions affects the formation of the copper deposit morphologies considered in this paper. According to this relation, the increase of concentration of Cu(II) ions increases the minimum overpotential for the initiation of dendritic growth. In our case, we can see that copper dendrites are formed by the electrodeposition at the overpotential of 550 mV with a quantity of the electricity of 20.0 mAhcm^{-2} only from *solution (I)*. Electrodepositions from *solutions (II)* and *(III)* with the same quantity of the electricity did not lead to the formation of dendritic forms at this overpotential. On the other hand, the difference in the shape of copper dendrites formed at 650 mV pointed out that the minimum overpotential for the initiation of dendritic growth was lower from *solution (I)* than from *solutions (II)* and *(III)*.

On the basis of the values of the average current efficiencies of hydrogen evolution reactions and the morphologies of copper deposits shown in Figures 4–7, the correlation between the quantity of evolved hydrogen and the formation of different morphological forms of copper deposits can be made.

Copper dendrites were the main morphological form during electrodeposition processes which were accompanied by average current efficiencies of hydrogen evolution up to 7.5 %. The quantities of evolved

hydrogen which corresponded to the average current efficiencies up to 7.5 % were insufficient to change the hydrodynamic conditions in the near–electrode layer, and to disarrange the diffusion layer thickness of the macroelectrode. The dominant processes are diffusion of ions from bulk solution to the electrode surface [1].

Figure 8. The dependence of logarithm of the limiting diffusion current density, i_L on logarithm of concentration of Cu (II) ions.
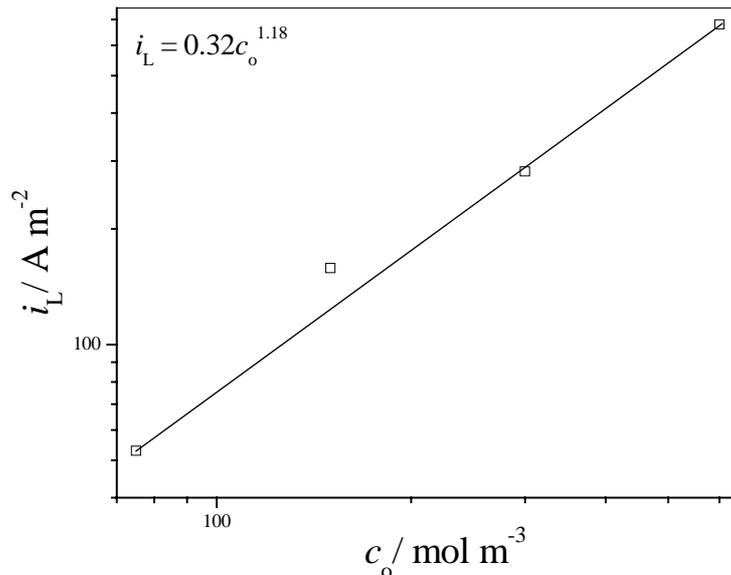

On the other hand, craters or holes formed due to the attachment of hydrogen bubbles with copper grain agglomerates between them are obtained when the copper electrodeposition process was accompanied by an average current efficiency of hydrogen evolution of 42.2 % (Figures 7a and b). The hydrogen evolution was vigorous enough to cause a stirring of the solution, thus decreasing the cathode diffusion layer thickness and increasing the limiting diffusion current density, and consequently, leading to a change of hydrodynamic conditions in the near–electrode layer. This copper structure presented the typical honeycomb–like structure. The formation of this structure was recently explained by the concept of "effective overpotential" [7]. According to this concept, when hydrogen evolution is vigorous enough to change the hydrodynamic conditions in the near–electrode layer, the electrodeposition process takes place at an overpotential which is effectively lower than the specified one. For that reason, this overpotential is denoted as the "effective overpotential" of the electrodeposition process. Because of a change of hydrodynamic conditions caused by a vigorous hydrogen evolution the morphologies of deposits become, at a macro level, similar to ones obtained at some lower overpotentials where the hydrogen evolution does not exist. In our case, the morphology of the copper deposit shown in Figure 7b (cauliflower forms) is similar to that obtained at some lower overpotentials before dendritic growth initiation (Figure 4a). The honeycomb–like structures were obtained and electrodeposition processes observed from 0.15 M CuSO₄ in 0.50 M H₂SO₄ at overpotentials of 800 and 1000 mV, with average current efficiencies of hydrogen evolution of 10.8 and 30.0 %, respectively [7]. In this case the critical value of the average current efficiency of hydrogen evolution which leads to the change of hydrodynamic

conditions in near–electrode layer and the formation of honeycomb–like structure was estimated to be about 10.0 %.

However, it is obvious that due to their very open and porous structure, the honeycomb–like copper deposits fulfilled the conditions to be considered as possible electrodes in electrochemical devices such as solid oxide fuel cells and solid–state gas sensors. Hence, the critical conditions which must be fulfilled in order to obtain copper deposits suitable for these purposes by potentiostatic electrodeposition are: electrodeposition from acid copper sulphate solutions with lower concentrations of Cu(II) ions (0.15 M $CuSO_4$ and less for a concentration of supporting electrolyte of 0.50 M H_2SO_4), at overpotentials outside the plateau of the limiting diffusion current density at which the quantity of evolved hydrogen is enough to change hydrodynamic conditions in near–electrode layer. This quantity of evolved hydrogen corresponded to the average current efficiencies of hydrogen evolution above 10.0 %. Also, we note that the number of craters or holes increased with the quantity of evolved hydrogen, as can be seen from Figure 9 which shows the dependence of the number of holes or craters formed due to the attachment hydrogen bubbles on the average current efficiencies for hydrogen evolution.

Figure 9 includes the value of the average current efficiency of hydrogen evolution of 68.7 % obtained from *solution (I)* at overpotential of 1000 mV [15]. This dependence of the number of holes per mm^2 surface area of copper electrode on the average current efficiency of hydrogen evolution clearly points out the fact that the more intense the hydrogen evolution, the more porous a copper structure is formed. Also, from Figure 9 it can be seen that more porous structures (i.e. structures with larger numbers of holes formed by evolved hydrogen) are obtained by electrodeposition of copper from solutions with the lower concentrations of Cu(II) ions (0.075 M $CuSO_4$ in 0.50 M H_2SO_4 with respect to copper electrodeposited from 0.15 M $CuSO_4$ in 0.50 M H_2SO_4).

Figure 9. The dependence of the number of craters formed due to the attachment of hydrogen bubbles per mm^2 surface area of copper electrode on the average current efficiency of hydrogen evolution.
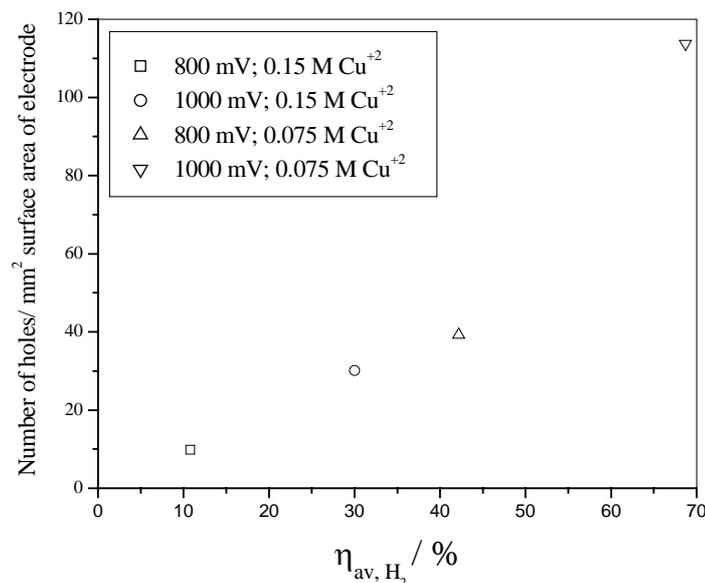
4. Conclusions

Electrodeposition of copper from 0.075 M, 0.30 M and 0.60 M $CuSO_4$ in 0.50 M H_2SO_4, at overpotentials of 550, 650 and 800 mV was examined by the determination of the average current efficiency of hydrogen evolution and the SEM technique. Dendritic forms were the main characteristic of electrodeposition processes which were accompanied by an average current efficiency of hydrogen evolution up to 7.5 %. The quantities of evolved hydrogen which corresponded to the average current efficiencies of hydrogen evolution up to 7.5 % were insufficient to change hydrodynamic conditions in the near–electrode layer.

Very open and porous honeycomb–like copper structures suitable for use as electrodes for solid–state gas sensors as well as for other electrochemical devices are obtained by electrodeposition processes which are accompanied by an average current efficiency of hydrogen evolution above 10.0 %. The main characteristics of these structures were craters or holes formed due to the attachment of hydrogen bubbles with agglomerates of copper grains between them. These structures are formed by electrodeposition at overpotentials outside the plateau of the limiting diffusion current density from solutions with lower concentrations of Cu(II) ions (0.15 M $CuSO_4$ and less in 0.50 M H_2SO_4). The quantities of evolved hydrogen which led to the formation of these structures were enough to change the hydrodynamic conditions in the near–electrode layer.

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