Effect of temperature on the electrodeposition of disperse copper deposits

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Abstract: The effect of temperature on the electrodeposition of copper at overpotentials belonging to the plateau of the limiting diffusion current density and higher was examined by the determination of the average current efficiency of hydrogen evolution and by scanning electron microscopic (SEM) analysis of the morphology of the formed copper deposits. Increasing the temperature of the solution led to a shift of both the beginning and the end of the plateau of the limiting diffusion current density towards lower electrodeposition overpotentials. Also, higher temperatures led to the formation of morphological forms of copper deposits characteristic for electrodeposition of copper at some higher overpotentials. The unexpected trend in the development of copper structures electrodeposited at an overpotential of 800 mV is discussed in terms of the effect of temperature on the viscosity and surface tension of the electroplating solution.

Keywords: electrodeposition, copper, hydrogen evolution, temperature, viscosity, surface tension.

INTRODUCTION

The open and porous structures of copper deposits with extremely high surface areas suitable for used as electrodes in electrochemical devices, such as fuel cells and chemical sensors, can be obtained by both galvanostatic[1] and potentiostatic[2] processes of electrodeposition. These copper structures obtained in the potentiostatic regime are denoted as honeycomb-like ones[3,4] and the phenomenology of their formation has been described in detail in the literature.[5] The main characteristics of this type of structure are holes or craters formed primarily due to the attachment hydrogen bubbles with agglomerates of copper grains between them.[3–6]

The critical conditions which must be fulfilled in order to obtain honeycomb-like copper structures were also determined.[2] It was shown that these stru-

ctures can be formed by electrodeposition from solutions with lower concentrations of Cu(II) ions (0.15 M CuSO$_4$ and even less in 0.50 M H$_2$SO$_4$) at overpotentials outside the plateau of the limiting diffusion current density, (potential at which hydrogen evolution was vigorous enough to change the hydrodynamic conditions in the near-electrode layer). The quantity of evolved hydrogen leading to a change of hydrodynamic conditions corresponds to an average current efficiency of hydrogen evolution of 10.0 %. The critical conditions were determined by the examination of the effect of different concentrations of copper(II) ions and overpotentials of electrodeposition on the processes of copper electrodeposition.[2,3]

The possibility of practical application of the honeycomb-like structure requires the knowledge of the effect of all parameters of electrolysis which can be of the significance for the formation of this type of structure. Except the concentration of copper(II) ions and the overpotential of the electrodeposition, electrolysis parameters of significance for the formation of honeycomb-like copper structures are primarily the temperature of electrolysis and the concentration of the supporting electrolyte (H$_2$SO$_4$). The aim of this study was to examine the effect of temperature on the electrodeposition of copper at high overpotentials.

EXPERIMENTAL

Copper was potentiostatically deposited from 0.15 M CuSO$_4$ + 0.50 M H$_2$SO$_4$ in an open cell and at temperatures of 14.0±0.5, 35.0±0.5 and 50.0±0.5 °C. Doubly distilled water and analytical grade chemicals were used for the preparation of the solutions for the electrodeposition of copper. The reference and counter electrodes were of pure copper.

Copper electrodeposition onto cylindrical copper cathodes were performed at overpotentials of 550, 650 and 800 mV. The cathodes were prepared in the following way: the 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 was later used for electrodeposition at the desired overpotential. The overpotentials at which copper was electrodeposited for 2 min were: 250, 200 and 125 mV at temperatures of 14.0±0.5, 35.0±0.5 and 50.0±0.5 °C, respectively. This manner of preparation of the copper cathodes was applied in order to obtain a uniform copper surface before electrodeposition at the desired overpotentials.

SEM Microphotographs corresponding to morphologies of copper deposits electrodeposited with a quantity of the electricity of 10.0 mA h cm^{-2} were obtained with a model JEOL T20 scanning electron microscope (SEM).

The procedure for the determination of the average current efficiency of hydrogen evolution has already been given.[2,3]

The viscosity of 0.15 M CuSO$_4$ in 0.50 M H$_2$SO$_4$ at the given temperatures was determined using an Ostwald viscometer, while the surface tension of the same electroplating solution at the examined temperatures was determined by the drop-weight method.

RESULTS AND DISCUSSION

The polarization curves for the electrodeposition of copper from 0.15 M CuSO$_4$ in 0.50 M H$_2$SO$_4$ at temperatures of 14.0±0.5, 35.0±0.5 and 50.0±0.5 °C are given in Fig. 1. The way of the determination of the length of the plateau of the limiting diffusion current density is also shown in Fig. 1. It can be seen from

Fig. 1 that increasing the temperature leads to an increase of the limiting diffusion current density, as well as to a shift of both the beginning and the end of the plateau of the limiting diffusion current density towards lower electrodeposition overpotentials. This can be explained in the following manner:

In the well-known Nernst limiting current density equation:

$$j_L = nFDc_0/\delta \qquad (1)$$

where nF is the number of Faradays per mole of consumed ions, c_0 is concentration of Cu(II) ions, D is the diffusion coefficient and δ the thickness of the diffusion layer, a change of the temperature of the solution affects both D and δ. Changes of these variables are affected by the well-known fact concerning the change of the viscosity of a solution[7] with changing temperature.
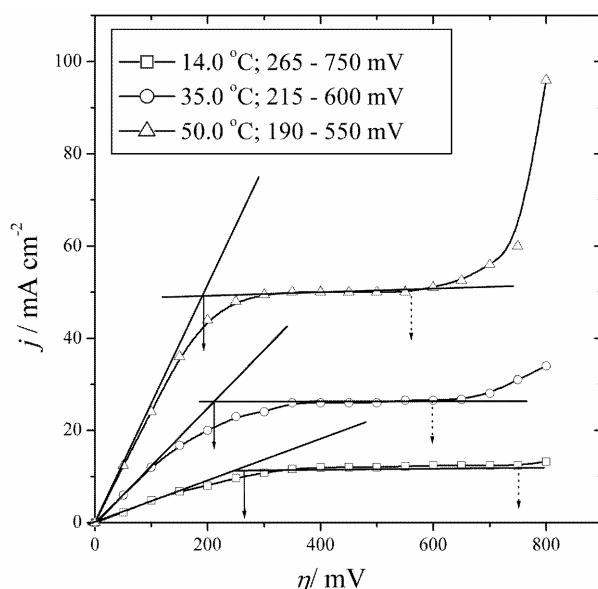

Fig. 1. Polarization curves for the electrodeposition of copper from 0.15 M CuSO$_4$ in 0.50 M H$_2$SO$_4$ at temperatures of 14.0±0.5, 35.0±0.5 and 50.0±0.5 °C.

On the other hand, it is a well known fact that the critical overpotential for the initiation of dendritic growth, η_I, is given by Eq. (2):

$$\eta_I = b_c \log \frac{4 j_L}{j_0} \qquad (2)$$

being close to the beginning of the limiting diffusion current density plateau.[8]

Furthermore, it is known that the equation of a general polarization curve for sufficiently large overpotentials is given by Eq. (3):[9]

$$j = \frac{j_0 f_c}{1 + \dfrac{j_0 f_c}{j_L}} \qquad (3)$$

and

$$f_c = 10^{(\eta / b_c)} \qquad (4)$$

In the above Equations, j, j_0 and j_L are the current density, exchange current density and limiting diffusion current density, respectively, b_c is the cathodic Tafel slope and η is the overpotential.

The cathodic current density and the overpotential are taken as positive values for the sake of simplicity. Assuming that the ohmic drop[10] can be neglected for the deposition from 0.15 M $CuSO_4$ in 0.50 M H_2SO_4, the values of j_0 can be estimated as follows. If

$$j = 0.5 j_L \qquad (5)$$

Equation (3) can be re-written in the form:

$$j_0 = \frac{j_L}{f_{c,1/2}} \qquad (6)$$

where $f_{c,1/2}$ corresponds to the overpotential $\eta_{1/2}$ measured for $j = 0.5 j_L$.

Using the data from the diagrams presented in Fig. 1 and Eqs. (2) and (4–6), the critical overpotentials for the initiation of dendritic growth, η_I, are calculated and presented in Table I. The values of the overpotentials corresponding to the beginning of the limiting diffusion current density plateau, $\eta_{b,p}$ are also presented in Table I. Although both values of overpotentials are estimated values, they illustrate well in a qualitative way the change with increasing temperature.

TABLE I. The values of the calculated critical overpotentials of dendritic growth initiation, η_I, and the estimated values of the overpotentials corresponding to the beginning of the plateau of the limiting diffusion current density, $\eta_{b,p}$, as a function of the temperature of electrodeposition

Temperature, °C	$\eta_{I,calculated}$ / mV	$\eta_{b,p,estimated}$ / mV
14.0±0.5	205	265
35.0±0.5	185	215
50.0±0.5	177	190

It is clear from Fig. 1 that an overpotential of 550 mV belongs to the plateau of the limiting diffusion current density at all analyzed temperatures. An overpotential of 650 mV belongs to the plateau of the limiting diffusion current density only at a temperature of 14.0±0.5 °C. This overpotential is about 50 mV outside the plateau at a temperature of 35.0±0.5 °C and about 100 mV outside at a temperature of 50.0±0.5 °C. Finally, an overpotential of 800 mV is outside the plateau of the limiting diffusion current density at all temperatures.

The dependences of the overall currents of electrodeposition and the volumes of evolved hydrogen on electrodeposition time are shown in Fig. 2, from which increasing electrodeposition currents with increasing temperature can be observed at all overpotentials. At an overpotential of 550 mV, hydrogen evolu-

tion was detected only at a temperature of 50.0 °C when several hydrogen bubbles were registered by visual observation. Unfortunately, this hydrogen evolution was below the sensitivity of measurement technique. On the other hand, at overpotentials of 650 and 800 mV, hydrogen evolution was detected at all temperatures. Increasing the temperature increased the quantity of evolved hydrogen and decreased the time required for the solution to become supersaturated (Figs. 2b and 2c).
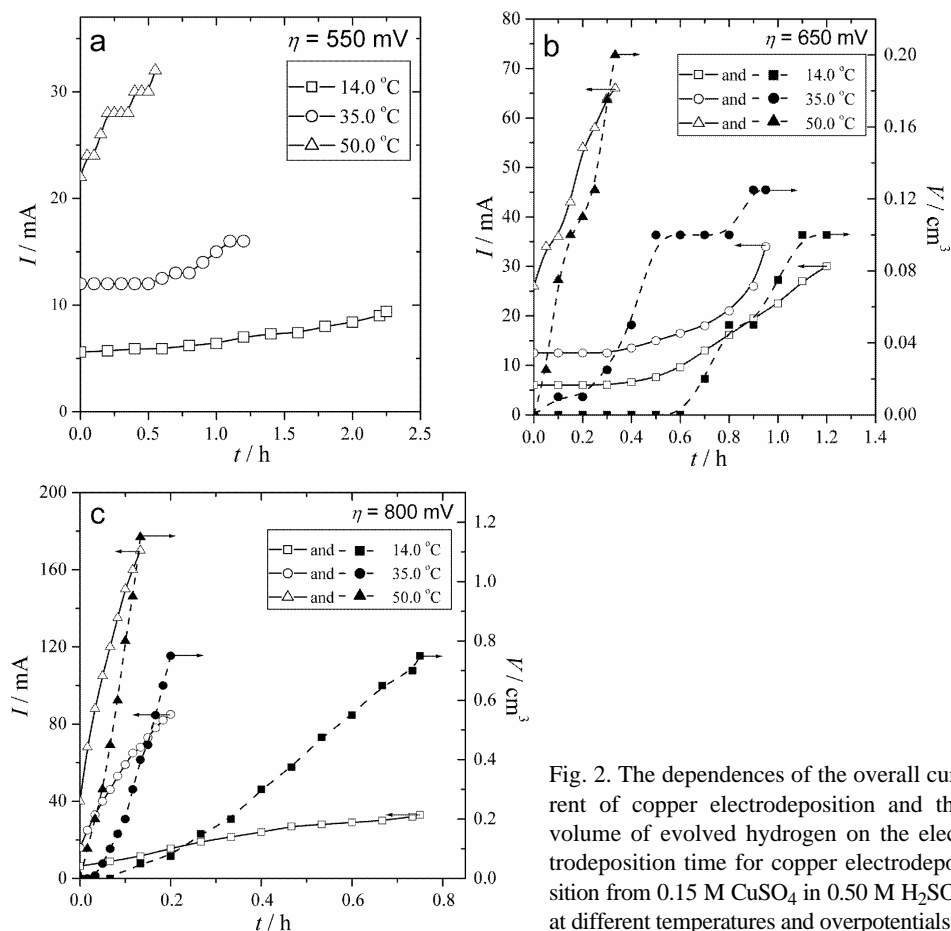

Fig. 2. The dependences of the overall current of copper electrodeposition and the volume of evolved hydrogen on the electrodeposition time for copper electrodeposition from 0.15 M $CuSO_4$ in 0.50 M H_2SO_4 at different temperatures and overpotentials.

The average current efficiencies for hydrogen evolution reaction, $\eta_{av}(H_2)$ at overpotentials of 650 and 800 mV, derived from the diagrams shown in Figs. 2b and 2c, respectively, are plotted as functions of the quantity of electricity, Q, in Fig. 3. These values are also summarized in Table II, which also includes the values of the average current efficiencies of a hydrogen evolution of 0.0 % obtained at an overpotential of 550 mV. It can be clearly seen from Fig. 3 and Table II that the electrodeposition processes at overpotentials of 650 and 800 mV are accom-

panied by increases of the average current efficiencies of hydrogen evolution with increasing temperature, causing a shift of the end of the limiting diffusion current density plateau toward lower values of the overpotential. This is due to the increased rate of hydrogen evolution with increasing temperature. In totality, three groups of the average current efficiencies of hydrogen evolution are of significance in the investigation of the effect of temperature on the electrodeposition of copper at high overpotentials.
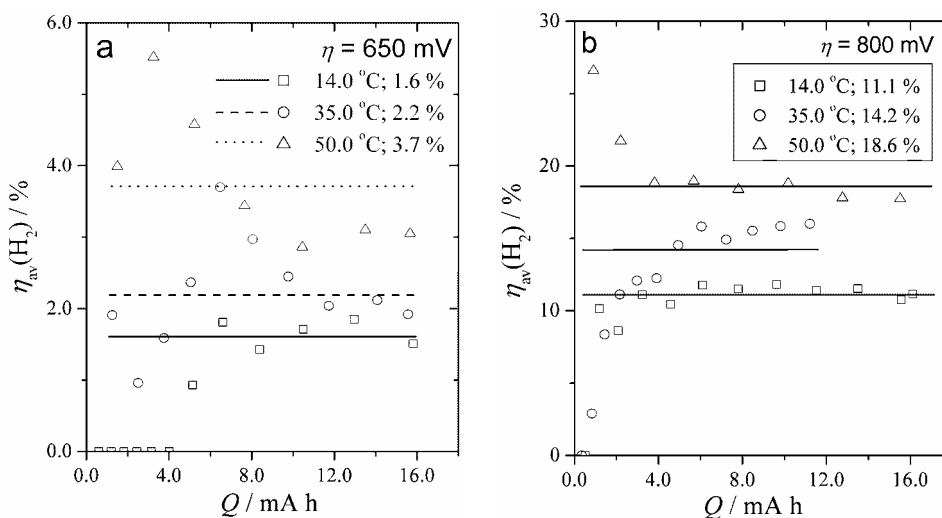

Fig. 3. The dependences of the average current efficiencies for the hydrogen evolution reaction on the quantity of used electricity, for copper electrodeposition from 0.15 M $CuSO_4$ in 0.50 M H_2SO_4 at different temperatures and overpotentials of 650 mV and 800 mV.

TABLE II. The values of the average current efficiencies of hydrogen evolution, $\eta_{av}(H_2)$, in the dependence on the temperature of electrodeposition at different overpotentials

Temperature, °C	$\eta_{av}(H_2)$ / %		
	550 mV	650 mV	800 mV
14.0±0.5	0	1.6	11.1
35.0±0.5	0	2.2	14.2
50.0±0.5	0	3.7	18.6

The first group is characterized by electrodeposition of copper at an overpotential of 550 mV, (potential at which there is no hydrogen evolution or hydrogen evolution was below the sensitivity of the measurement technique).

The second group is characterized by processes of electrodeposition at an overpotential of 650 mV (potential at which the average current efficiencies of hydrogen evolution were below the critical value of the average current efficiency of hydrogen evolution of 10.0 %, leading to a change of the hydrodynamic conditions in the near-electrode layer).

Finally, the third group includes electrodeposition processes at 800 mV, which are accompanied by an average current efficiency of hydrogen evolution above the critical value of 10.0 % required for a change of hydrodynamic conditions in the near-electrode layer. The quantities of evolved hydrogen corresponding to the average current efficiencies of hydrogen evolution above 10.0 % are only one of the ways to change the hydrodynamic conditions in the near-electrode layer. For example, a change of the hydrodynamic conditions can be realized under imposed magnetic fields (magnetohydrodynamic effects).[11-14]

The morphologies of the copper deposits electrodeposited at an overpotential of 550 mV are shown in Fig. 4. The copper deposit obtained at a temperature of 14.0 °C had a cauliflower-like structure (Fig. 4a). Spherical diffusion zones inside the linear diffusion layer of the macroelectrode were formed around the cauliflower particles (Fig. 4b). The copper deposit obtained at a temperature of 35.0 °C was a mixture of cauliflower-like (Fig. 4c) and dendritic forms (Fig. 4d). A mixture of cauliflower-like and dendritic forms was also obtained by electrodeposition at a temperature of 50.0 °C (Figs. 4e and 4f).

The size of the cauliflower-like particles did not change with increasing temperature, but the size of the sub-particles constituting the cauliflower-like forms decreased with increasing temperature of electrodeposition. The decrease of the size of sub-particles with increasing temperature can be explained by the well-known dependence of the nucleation rate on temperature,[15] which was derived by Volmer and Weber.[16]

The morphologies of the copper deposits obtained at an overpotential of 650 mV are shown in Fig. 5, from which the strong effect of temperature on the electrodeposition of copper at an overpotential of 650 mV can immediately be clearly seen. Very branched copper dendrites were formed during electrodeposition at a temperature of 14.0 °C (Fig. 5a). They were constructed of corncob-like elements (Fig. 5b). This is in accordance with the position of an overpotential of 650 mV in the limiting diffusion current density plateau. Dendritic forms were obtained during electrodeposition at a temperature of 35.0 °C (Fig. 5c) but holes, the origin of which was attached hydrogen bubbles, were also formed (the part in the circle in Fig. 5d). The increased hydrogen evolution at a temperature of 50.0 °C compared to that at 35.0 °C led to a change of the shape of the copper dendrites, which become similar to cauliflower-like forms (Fig. 5e) or, probably, degenerated dendrites were formed. Also, the holes formed due to the attachment of hydrogen bubbles can be observed in this copper deposit (Fig. 5f). These facts were unexpected because the current efficiency of the hydrogen evolution reaction was lower than 10.0 %, but it can be explained by the findings of Vogt and Balzer.[17] They showed that the bubble coverage of an electrode surface increased with temperature more than linearly. In addition, Krenz[18] observed an increase in bubble coverage of about 50 % as the temperature was raised from 25 to 50 °C.
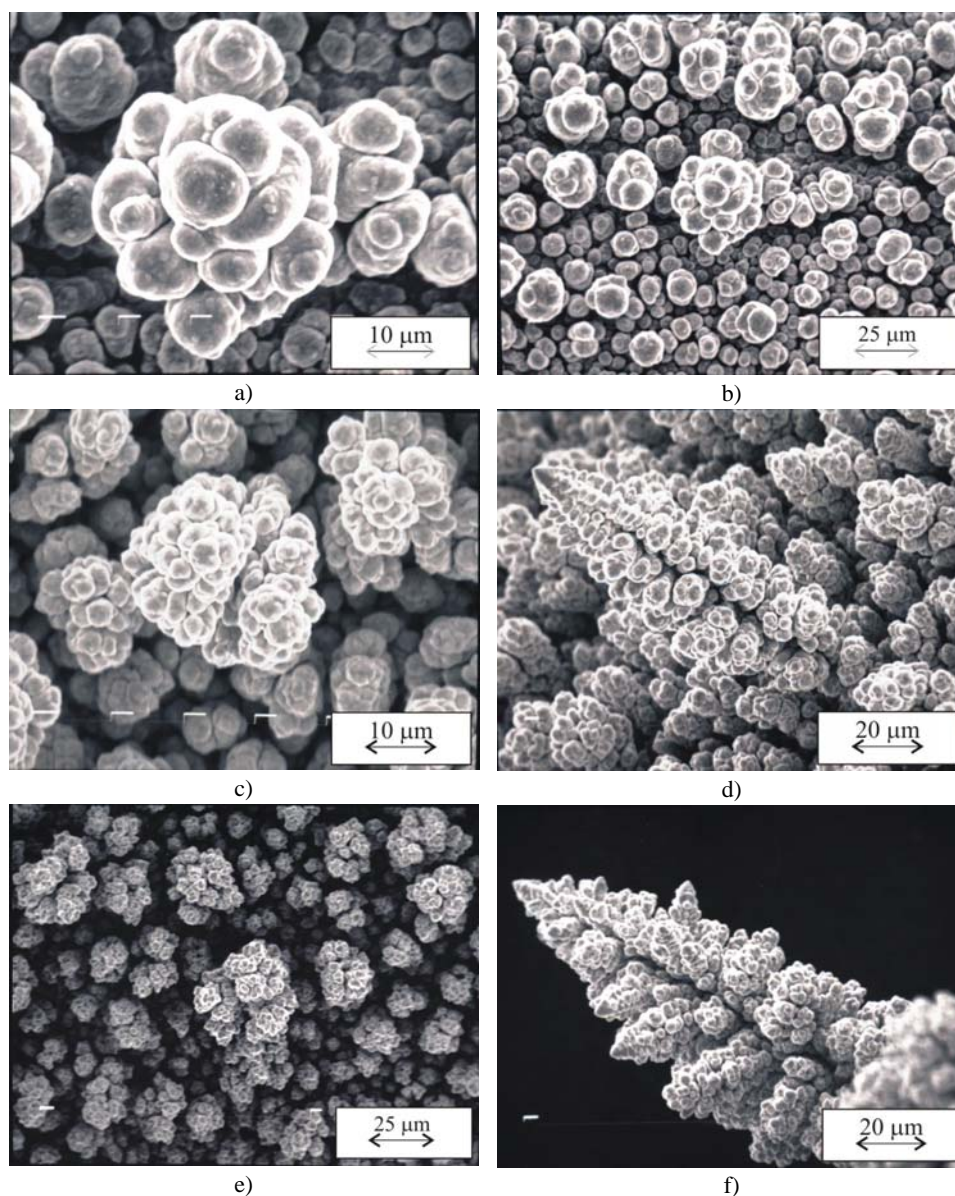
Fig. 4. Morphologies of copper deposits electrodeposited at an overpotential of 550 mV at temperatures of: a) and b) 14.0±0.5, c) and d) 35.0±0.5 and e) and f) 50.0±0.5 °C.

The morphologies of the copper deposits electrodeposited at an overpotential of 800 mV are shown in Fig. 6, from which the strong effect of evolved hydrogen on the morphologies of copper deposits is visible. Very porous structures, holes formed due to the attachment hydrogen bubbles, cauliflower-like forms and the

absence of dendritic forms were the main characteristics of copper deposits obtained at this overpotential. A decreased number of holes per mm^2 surface area of the copper electrodes and the increased diameter of the holes with increasing temperature can be observed from Fig. 6. Also, the portion of the copper structure consisting of dispersed agglomerates of copper grains, among which irregular channels were formed, increased with increasing temperature of the solution.
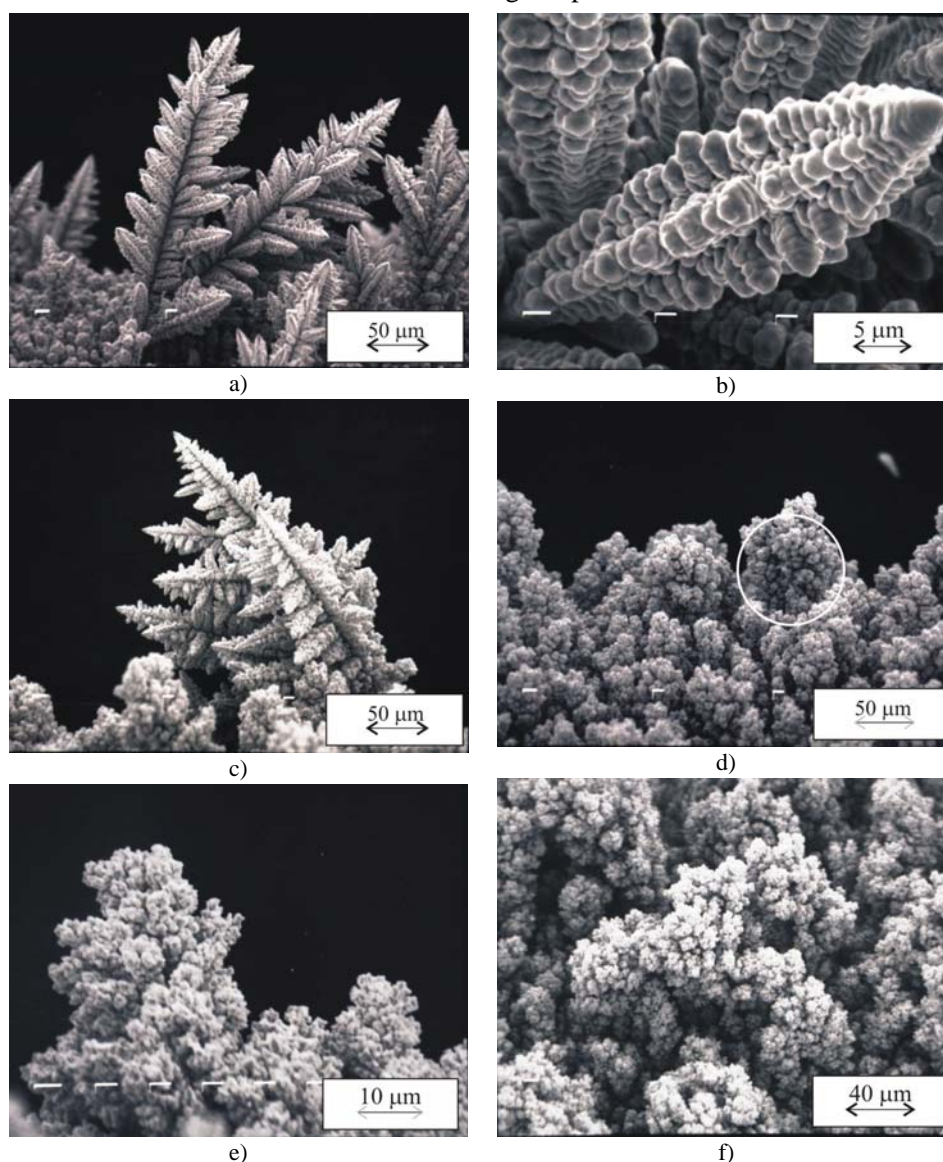

Fig. 5. Morphologies of copper deposits electrodeposited at an overpotential of 650 mV at temperatures of: a) and b) 14.0±0.5, c) and d) 35.0±0.5 and e) and f) 50.0±0.5 °C.

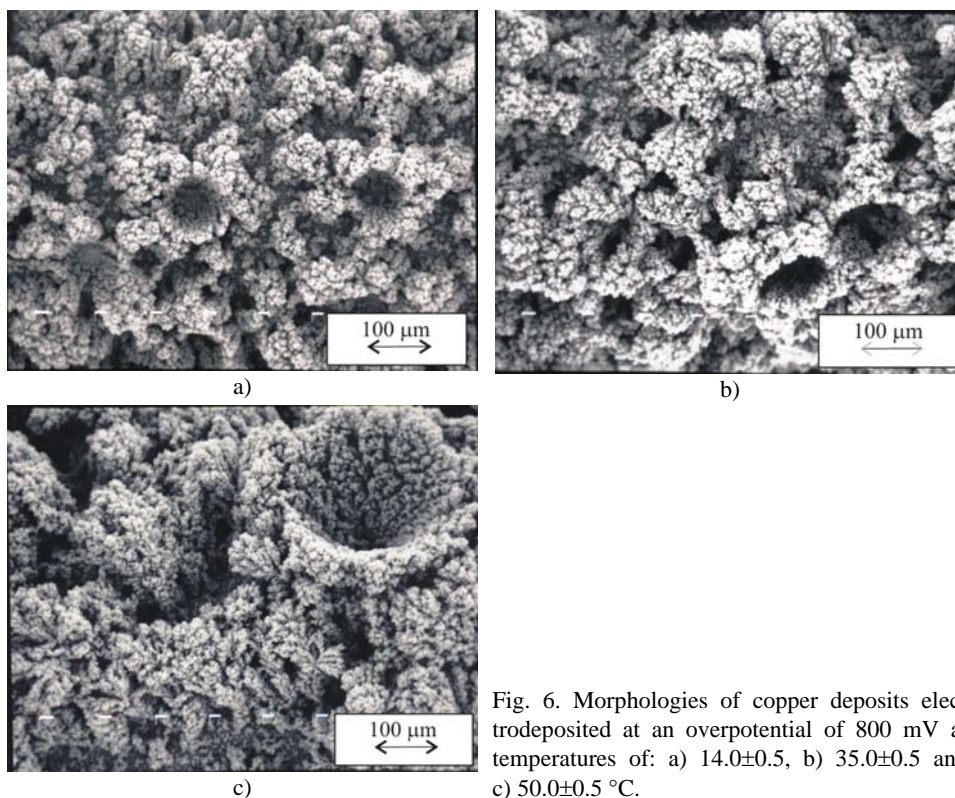a)   b)

Fig. 6. Morphologies of copper deposits electrodeposited at an overpotential of 800 mV at temperatures of: a) 14.0±0.5, b) 35.0±0.5 and c) 50.0±0.5 °C.

c)

Firstly, it is necessary to note that the decrease of the number of holes per mm^2 surface area of the copper electrode with intensification of hydrogen evolution was very surprising. It is opposed to our recently published results[2−4] when it was shown that intensification of hydrogen evolution reaction leads to an increase of the number of holes. Thus, the unexpected development of the copper structures with intensification of the hydrogen evolution reaction clearly highlights the necessity to take into consideration the effect of temperature on some properties of electroplating solution, as well as the already mentioned increased bubble coverage with the increasing temperature. The properties of an electrolyte of importance in metal electrodeposition processes which are affected by a change of temperature are the viscosity[7] and surface tension of the electrolyte.[17]

The values of the viscosity and surface tension of a copper solution containing 0.15 M CuSO$_4$ in 0.50 M H$_2$SO$_4$ at the examined temperatures are given in Table III. As expected, both the viscosity and the surface tension of this solution decrease with increasing temperature. The decrease of the surface tension of the solution lowers the break-off diameter of hydrogen bubbles from the electrode surface,[17] while the decreased viscosity of the solution probably facilitates the

transport of the detached hydrogen bubbles through the interior of the deposit, thus forming a channel structure through it. A typical channel structure formed at an overpotential of 800 mV at a temperature of 50.0 °C is shown in Fig. 7a, while the top view of this deposit shows that very disperse cauliflower-like agglomerates of copper grains were surrounded by irregular channels (Fig. 7b).

TABLE III. The values of the viscosity, ν, and surface tension, γ, of a copper solution containing 0.15 M $CuSO_4$ in 0.50 M H_2SO_4 at different temperatures

Temperature, °C	$\nu / 10^{-6}$ m^2 s^{-1}	$\gamma /$ J m^{-2}
14.0±0.5	1.17	103.2
35.0±0.5	0.832	82.0
50.0±0.5	0.637	71.8

Hence, increasing the temperature led to a redistribution of evolved hydrogen from those creating a honeycomb-like structure (holes formed due to the attachment hydrogen bubbles with cauliflower-like agglomerates of copper grains between them) to those making a copper structure with the dominant presence of cauliflower-like forms and irregular channels between them. This increase of the portion of channel structure to the overall structure of the deposit in relation to the portion of holes to the overall structure is probably due to changes of the properties of the electroplating solution, caused by the dependences of the viscosity and surface tension of solution on temperature. As result of this, the formation of holes becomes less possible and hence large holes appear only due to the edge effect, as can be clearly seen from Fig. 6c. It is obvious that the probability of the formation of the nucleus of such a structure decreases with lowering of the break-off diameter of the bubbles.

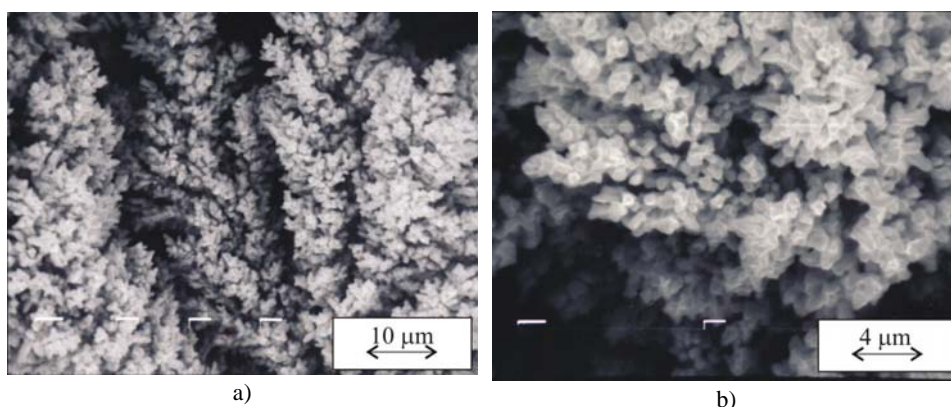a)   b)

Fig. 7. Morphologies of copper deposits electrodeposited at an overpotential of 800 mV at a temperature of 50.0±0.5 °C.

Also, it is necessary to note that increasing the temperature led to the formation of morphological forms of copper deposits characteristic for electrodeposi-

tion at higher overpotentials, probably because of the increase of bubble coverage with increasing temperature. The effect of temperature was opposite to those observed with increasing the concentration of copper(II) ions,[2] when increasing concentration of Cu(II) ions led to a formation of morphological forms of copper deposits characteristic for electrodeposition at lower overpotentials.[2]

From the point of view of the formation of copper structures suitable for electrodes in electrochemical devices, such as fuel cells and sensors, this means that increasing the temperature has a negative effect on the formation of such structures.

CONCLUSIONS

Electrodeposition of copper from 0.15 M $CuSO_4$ in 0.50 M H_2SO_4 at overpotentials belonging to the limiting diffusion current density and at higher ones was analyzed. The average current efficiencies of hydrogen evolution were determined at electrodeposition overpotentials of 550, 650 and 800 mV, and at temperatures of 14.0±0.5, 35.0±0.5 and 50.0±0.5 °C. The morphologies of the copper deposits obtained under the same electrodeposition conditions were examined by the scanning electron microscopy (SEM) technique.

Increasing the temperature led to an increase of the average current efficiencies of hydrogen evolution during electrodeposition of copper at overpotentials of 650 and 800 mV.

The morphological forms of the copper deposits obtained at overpotentials of 550 and 650 mV became similar to those obtained at some higher overpotentials. A very interesting and unexpected case was observed during copper electrodeposition at 800 mV. The intensification of the hydrogen evolution reaction caused by increasing temperature, opposite to expectation, led to a decrease of the number of holes per mm^2 surface area of the copper electrode. This decrease of the number of holes is ascribed to the effect of the temperature on both the viscosity and surface tension of the solution. The increase of a temperature led to a redistribution of evolved hydrogen from those creating holes to those favoring the formation of channel structures through the interior of the deposit.

ИЗВОД

УТИЦАЈ ТЕМПЕРАТУРЕ НА ЕЛЕКТРОХЕМИЈСКО ТАЛОЖЕЊЕ ДИСПЕРЗНИХ ТАЛОГА БАКРА

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Утицај температуре на електрохемијско таложење бакра на пренапетостима које припадају платоима граничне дифузионе густине струје, као и на вишим пренапетостима је ис-

питан одређивањем средњег искоришћења струје реакције издвајања водоника и анализом морфологија талога бакра техником скенирајуће електронске микроскопије. Повећање температуре раствора довело је до померања и почетка и краја платоа граничне дифузионе густине струје ка нижим пренапетостима. Такође, повећање температуре довело је до формирања морфолошких форми талога бакра карактеристичних за електрохемијско таложење на неким вишим пренапетостима. Неочекивани тренд у развоју структура бакра добијених на пренапетости од 800 mV је био дискутован на основу утицаја температуре на вискозност и површински напон раствора за електрохемијско таложење бакра.

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