Effect of parameters of square-wave pulsating current on copper electrodeposition in the hydrogen co-deposition range

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ARTICLE INFO

ABSTRACT

Copper electrodeposition processes in the hydrogen co-deposition range by the pulsating current (PC) regime were examined by the determination of the average current efficiency of hydrogen evolution and by the scanning electron microscopic (SEM) analysis of the morphology of the formed deposits. The two sets of the square-wave PC of the same pause to pulse ratios, but with different duration of deposition pulses and pauses were analyzed. The one set of square-wave PC was with the constant pause duration and different deposition pulses. In the other set, the deposition pulse was constant while the pause duration was varied. The obtained results were compared with those obtained by electrodeposition at the constant overpotential from solutions of different $CuSO_4$ and H_2SO_4 concentrations. It was found that the effect of the increasing deposition pulse was equivalent to the decreasing $CuSO_4$ concentration, while the effect of the decreasing pause duration was equivalent to the increasing H_2SO_4 concentration. It is shown that it is possible to achieve a substitution of more solutions of different $CuSO_4$ and H_2SO_4 concentartions by the use of the only one solution if the appropriate PC parameters were applied, what can be of high technological significance.

1. Introduction

The most often employed electrolytes for the electrodeposition of copper are those based on aqueous solutions of sulfuric acid (H_2SO_4) and cupric sulfate ($CuSO_4$) [1]. There is an ionic equilibrium of a lot of species in the $CuSO_4$–H_2SO_4–H_2O system [2], and Pitzer's model [3] was used to calculate the ionic equilibrium of these species over a wide range of concentrations and temperatures. Using this model, the dependence of the relative concentration of hydrogen ions (H^+) on H_2SO_4 concentration for different copper concentration is done and it was shown that increasing the copper concentration produces a sharp decrease in the hydrogen ion concentration, while increasing the concentration of sulfuric acid produces an increase in the hydrogen ion concentration (Fig. 9 in Ref. [2]).

Electrodeposition processes at high current densities and over-potentials are very suitable for experimental verification of the proposed dependence. This is due to parallel evaluating of both copper electrodeposition and hydrogen evolution reaction at high current densities and overpotentials [4,5]. Good agreement between the prediction of the ionic equilibrium in the $CuSO_4$–H_2SO_4–H_2O system and morphologies of copper deposits obtained by electrodeposition at the constant overpotential in the hydrogen co-deposition range from six solutions of different concentrations of $CuSO_4$ and H_2SO_4 was observed [6].

Application of periodically changing regimes of electrolysis, such as pulsating overpotential, pulsating and reversing current, in metal electrodeposition processes is of great both academic and practical significance [7,8]. Deposits with desired composition, structure, porosity and hydrogen content, the enhanced throwing power especially in the holes, reduction of the use of additives are some of advantages of the use of pulse regimes of electrolysis. Furthermore, the improvement of microstructural characteristics of open and porous structures, denoted as 3D foam or honeycomb-like, can be realized by the application of regime of pulsating overpotential (PO) [9,10]. The effect of the PO regime on microstructural characteristics of these structures was similar to those attained by the application of additives [11–13].

Anyway, the effect of periodically changing regimes of electrolysis on electrochemical processes in the hydrogen co-deposition range is insufficiently explored. In this study, it will be considered the possibility of substitution of more electroplating solutions by the use of only one solution by the choice of the appropriate square-waves pulsating current (PC).

2. Experimental

Copper was electrodeposited from 0.15 M $CuSO_4$ in 0.50 M H_2SO_4, in an open cell at a temperature of 18.0 ± 0.50 °C. Doubly distilled

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water and analytical grade chemicals were used for the preparation of the solution for electrodeposition of copper.

Copper electrodeposition was performed by the use of square-wave pulsating current (PC) technique. In all experiments, the current density amplitude of 0.20 A/cm² was used. The two sets of experiments with the same pause to pulse ratios, but with different duration of deposition pulses and pauses were done.

In the first set of experiments, deposition pulses of 1, 2 and 50 ms, and constant pause duration of 10 ms were analyzed (pause to pulse ratios: 10, 5 and 0.2, respectively).

In the second set of experiments, the constant deposition pulse of 10 ms and pause durations of 100, 50 and 2 ms were analyzed (pause to pulse ratios: 10, 5 and 0.2, respectively).

The working electrodes used for electrodeposition of copper were cylindrical copper wires. The counter electrode was of pure copper.

Copper was electrodeposited with quantities of electricity of 10 mA h cm^{-2}.

The obtained copper deposits were examined using a scanning electron microscope—TESCAN Digital Microscopy.

For the determination of the average current efficiency of hydrogen evolution, an electrochemical cell with the same arrangement of copper electrodes as that used for the preparation of the copper deposits for SEM analysis was employed. The electrodes were situated under a burette with the surface facing up so that the total amount of hydrogen evolved during the electrodeposition processes went into the burette. The working electrode was cylindrical platinum

wire previously covered by the copper thin film by electrodeposition from the same solution at a current density of 10 mA/cm² during 5 min in order to eliminate the effect of platinum on hydrogen evolution reaction.

The current efficiency of hydrogen evolution in a time t, $\eta_l(H_2)$ is given by Eq. (1):

$$\eta_l(H_2) = \frac{V(H_2)}{\mu(H_2)S_0 i_{av} t} \tag{1}$$

where

$$\mu(H_2) = \frac{V}{nF} = \frac{23900\,\text{cm}^3}{2 \times 26.8\,\text{Ah}} = 446\,\frac{\text{cm}^3}{\text{Ah}} \tag{2}$$

and nF is the number of Faradays per mole of consumed ions, V is the molar volume of a gas at a temperature of 18.0 °C (i.e. 23,900 cm³) and S_0 is surface area of working electrode ($S_0 = 0.63$ cm²). Hydrogen generated at the cathode during electrodeposition process was collected in the burette up to moment when the quantity of the electricity, $i_{av}t$ of 10 mA h cm^{-2} was attained.

The average current density in the pulsating current regime, i_{av} is given by Eq. (3):

$$i_{av} = \frac{i_A}{1 + p} \tag{3}$$

where i_A is the current density amplitude of 0.20 A/cm² and p is the pause to pulse ratio defined as $p = t_p/t_c$, where t_c is deposition pulse and t_p is pause duration.

The average current efficiency of hydrogen evolution, $\eta_{l,av}(H_2)$ is determined after graphical integration $\eta_l(H_2) - t$ as $\eta_{l,av}(H_2) = (1/t)\int_0^t \eta_l(H_2)dt$.

3. Results and discussion

Fig. 1 shows the dependences of the volumes of evolved hydrogen and the average current efficiencies of hydrogen evolution on electrodeposition times obtained by the pulsating current (PC) regimes with deposition pulses of 1, 2 and 50 ms and a pause duration of 10 ms (Fig. 1a) and with a deposition pulse of 10 ms and pause durations of 100, 50 and 2 ms (Fig. 1b). Increasing quantities of evolved hydrogen, and hence, the increase of the average current efficiencies of hydrogen evolution were observed with the increasing deposition pulses and the decreasing pause durations.

Morphologies of copper deposits obtained with deposition pulses of 1, 2 and 50 ms and a pause duration of 10 ms are shown in Fig. 2. Holes formed by attached hydrogen bubbles, very branchy dendrites and small agglomerates of copper grains are formed when the applied deposition pulse was 1 ms (Fig. 2a and b). The mixture of holes and degenerate dendrites was formed with a deposition pulse of 2 ms (Fig. 2c and d). Honeycomb-like copper structure constructed of holes and cauliflower-like agglomerates of copper grains formed around them was obtained with a deposition pulse of 50 ms (Fig. 2e and f).

It is clear that there is a strong effect of the applied regimes of PC on both quantity of evolved hydrogen and morphology of the formed copper deposits. Hydrogen evolution by which the honeycomb-like structure is formed was enough vigorous to cause such stirring of the copper solution in the near-electrode layer which led to the decrease of the cathode diffusion layer thickness and to the increase of the limiting diffusion current density [5]. The uniform distribution of morphological forms, i.e. copper grains agglomerates means the existence of the same hydrodynamic conditions over the whole electrode surface [14]. Formation of degenerate dendrites instead of agglomerates of copper grains is consequent to the decreased effectiveness of stirring of solution by evolved hydrogen when a
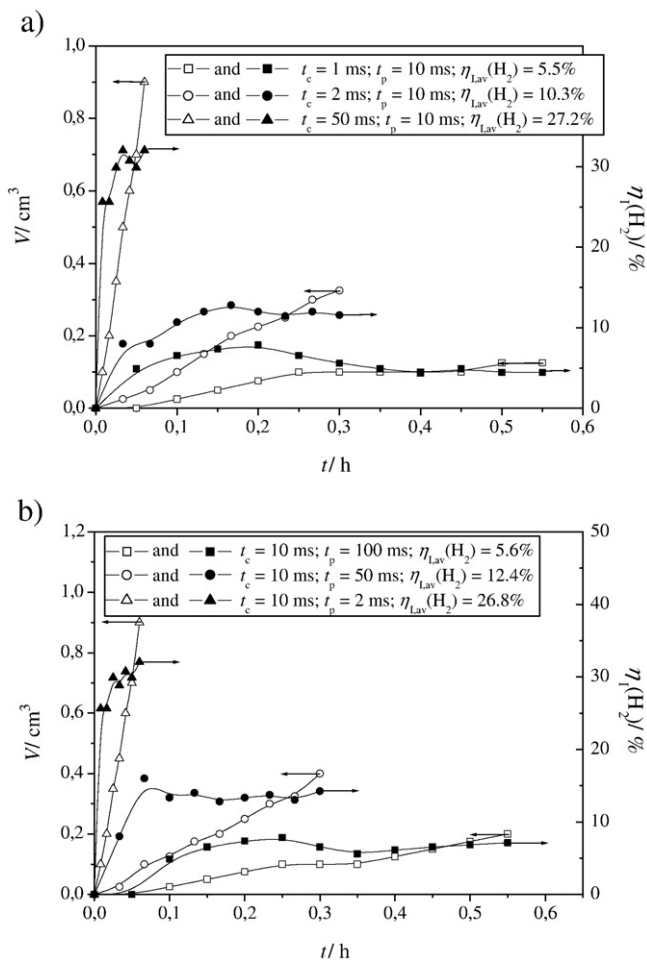

Fig. 1. The dependences of the volume of evolved hydrogen and the average current efficiency of hydrogen evolution on time of electrolysis for copper electrodeposition by the PC regimes with: a) deposition pulses of 1, 2 and 50 ms, and a pause duration of 10 ms, and b) a deposition pulse of 10 ms, and pause durations of 100, 50 and 2 ms.
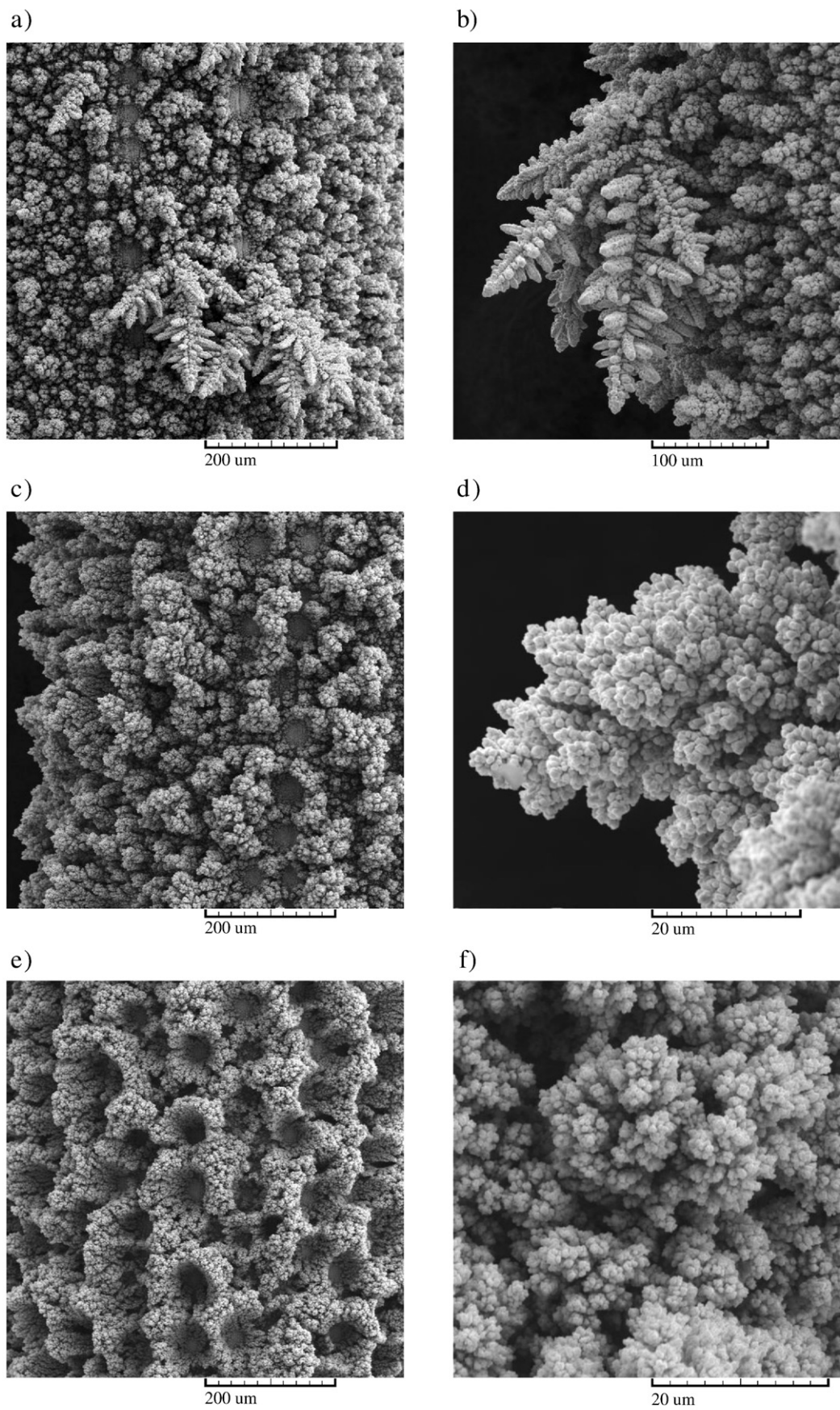
a)

b)

c)

d)

e)

f)

Fig. 2. Copper deposits obtained by the PC regimes with a pause duration of 10 ms, and deposition pulses of: a) and b) 1 ms; c) and d) 2 ms; and e) and f) 50 ms.
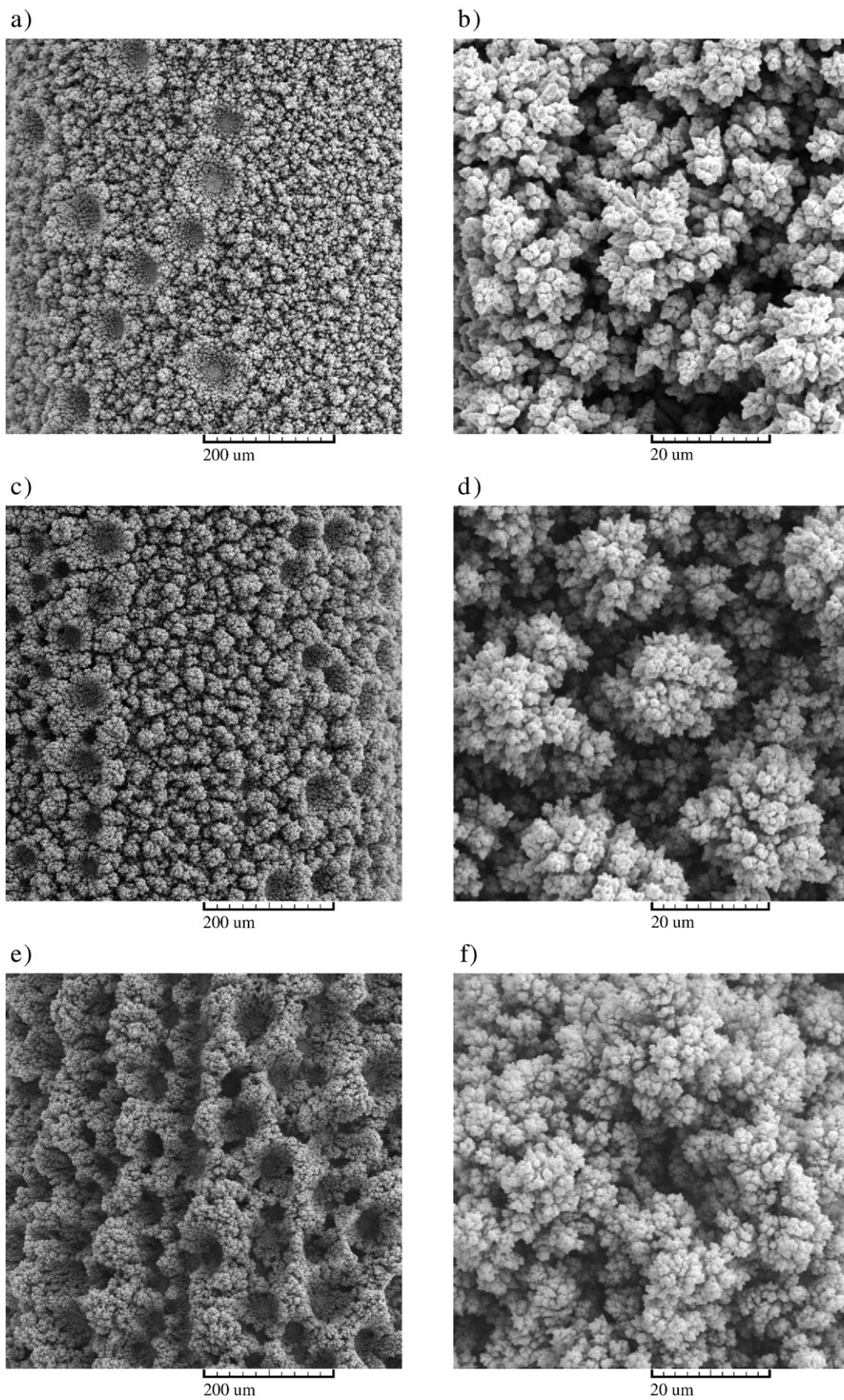
Fig. 3. Copper deposits obtained by the PC regimes with a deposition pulse of 10 ms, and pause durations of: a) and b) 100 ms; c) and d) 50 ms; and e) and f) 2 ms.

deposition pulse of 2 ms was applied. Finally, the formation of very branchy dendrites and very small agglomerates of copper grains around rare holes clearly indicate the insufficiency of evolved hydrogen to disturb the diffusion layer of the macroelectrode with a deposition pulse of 1 ms.

Morphologies of copper deposits obtained with a deposition pulse of 10 ms and pause durations of 100, 50 and 2 ms are shown in Fig. 3. Holes which the walls were constructed of dendrites and dendritic particles formed between holes were primarily formed by square-wave PC with a pause of 100 ms (Fig. 3a and b). These copper dendrites were considerably smaller and formed over the whole electrode surface in relation to those formed by the PC regime of the same pause to pulse ratio ($p = 10$) but with a deposition pulse of 1 ms and a pause of 10 ms (Fig. 2b). The shortening of pause duration from 100 to 50 ms led to the increase of number of holes formed by attached hydrogen bubbles (Fig. 3c) and the change of morphology of electrodeposited copper from dendritic particles to agglomerates consisted of copper grains and rare small dendrites on them (Fig. 3d). Finally, the typical honeycomb-like structure is formed with a pause of 2 ms (Fig. 3e and f). The increase of the number of holes, as well as the change of morphology of electrodeposited copper from dendrites to agglomerates of copper grains is a result of the increasing quantity of evolved hydrogen and the increased effectiveness of solution stirring by evolved hydrogen with the shortening of pause duration.

The parameters of square-wave PC were selected to enable a comparison of the obtained results with those obtained by electro-depositions in the hydrogen co-deposition range at the constant overpotential from six solutions of different concentrations of $CuSO_4$ and H_2SO_4 [6]. It was shown [6] that the increasing concentration of $Cu(II)$ ions led to the decrease of the quantity of evolved hydrogen and the change of morphology of electrodeposited copper from the honeycomb-like structure to dendritic one. It is clear that the effect of increasing concentration of $Cu(II)$ ions was equivalent to the effect of the decreasing deposition pulses, while the constant pause duration was equivalent to H_2SO_4 concentration used. In the similar way, the effect of different H_2SO_4 concentrations (for the constant $CuSO_4$ concentration) can be correlated with the effect of different pause durations. It was shown [6] that the increasing H_2SO_4 concentration led to the increase of the quantity of evolved hydrogen and the change of morphology of electrodeposited copper from degenerate dendrites to the honeycomb-like structure with the dominant presence of holes and cauliflower-like agglomerates of copper grains formed between them. Hence, the effect of increasing H_2SO_4 concentartion was equivalent to the effect of the decreasing pause duration, while the constant $CuSO_4$ concentration is equivalent to the constant deposition pulse used. Of course, the constant overpotential used [6] corresponds to the amplitude current density used.

Hence, effects attained by the choice of appropriate parameters of square-wave PC were equivalent to those obtained by electrodeposition at the constant overpotential in the hydrogen co-deposition range from solutions of different concentrations of $CuSO_4$ and H_2SO_4. In this way, the ionic equilibrium in the $CuSO_4$–H_2SO_4–H_2O system, determined by the dependence of the relative concentration of H^+ ions on H_2SO_4 concentration for different copper concentration was successfully simulated. Also, the substitution of more different electrodeposition solutions by the one solution was achieved. This is of potential high technological significance because it enables saving of chemicals for the preparation of electrodeposition baths, as well as saving of place in the plating plants due to the reduced number of needed electrochemical cells.

4. Conclusion

Electrodeposition of copper in the hydrogen co-deposition range by the PC regime was analyzed. Hydrogen evolution and morphology of electrodeposited copper strongly depended on the applied parameters of square-wave PC. The equivalence between morphologies of electrodeposited copper obtained at the constant overpotential from solutions of different concentrations of $CuSO_4$ and H_2SO_4 and those formed by the PC regime was observed. It is shown that more different electroplating solutions can be replaced by only one solution by the application of the appropriate square-waves PC.

Acknowledgement

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