

Application of pulsating overpotential regime on the formation of copper deposits in the range of hydrogen co-deposition

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Abstract Electrodeposition of copper by pulsating overpotential (PO) regime in the range of hydrogen co-deposition was examined by scanning electron microscopy. It was found that the increase of the pause-to-pulse ratio produced a strong effect on the morphology of electrodeposited copper. Honeycomb-like copper structures were formed with the pause-to-pulse ratios up to 5. Up to this value of the pause-to-pulse ratio, the diameter of the holes formed by attached hydrogen bubbles was decreasing, while their number was increasing by the application of PO regime. The compactness of the formed honeycomb-like structures was also increasing with the increasing pause duration. The increase of the pause-to-pulse ratio suppressed a coalescence of neighboring hydrogen bubbles. Copper dendrites in the interior of the holes and at their shoulders were formed with the higher pause-to-pulse ratios. The size of the formed dendrites, as well as their number, increased with the increasing pause duration. Depth of holes was decreasing with the increasing pause duration. The increased compactness of the obtained structures was explained by the use of a

set of equations describing the effect of square-wave PO on electrodeposition process.

Keywords Electrodeposition · Copper · Hole · Dendrites · Pulsating overpotential · Scanning electron microscope (SEM)

Introduction

Formation of open porous structures with an extremely high surface area is of great technological significance because they are very suitable to be used as electrodes in many electrochemical devices, such as fuel cells, batteries, and chemical sensors [1]. The open porous structure enables rapid transport of gas and liquid, while the extremely high surface area is desirable for the evolution of electrochemical reactions.

The open porous structures of copper with an extremely high surface area can be obtained by electrodeposition at very high current densities [1, 2] and overpotentials outside the plateau of the limiting diffusion current density [3–9], where parallel to copper electrodeposition hydrogen evolution reaction occurs. These copper electrodes, denoted as both 3D foam [1, 2] and honeycomb-like ones [3–9], are constructed of holes or pores formed due to the attached hydrogen bubbles and agglomerates of copper grains among them. The walls of holes are very porous, and they are composed of disperse copper grains agglomerates [6] or of dendritic particles [2]. From the technological point of view, electrodeposition of copper in the range of hydrogen co-deposition is very useful for the construction of both nanocomposite anodes (consisting of Cu and CeO₂) for solid oxide fuel cells [1] and copper–tin alloy deposits suitable for the negative electrode in a rechargeable lithium battery [10]. In addition,

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copper shows a high activity for the nitrate ion reduction [11] as well as for the reaction in which nitrate is reduced to ammonia in high yield in aqueous acidic perchlorate and sulphate media [12].

The number, distribution, and the hole size in copper deposits can be easily controlled by the choice of appropriate electrolysis parameters [6]. The increasing overpotential, the decreasing concentration of Cu(II) ions, as well as the increasing concentration of H₂SO₄ as the supporting electrolyte intensifies hydrogen evolution reaction, and consequently, the number of holes formed per square millimeter surface area of electrode is increased [4, 6, 9]. The average diameter of holes increases with electrolysis time due to the growth of hydrogen bubbles with time as well as due to a coalescence of closely formed hydrogen bubbles.

The decrease of diameter of holes as well as the increase of their number in 3D foam copper structures can be realized by the addition of acetic acid to the copper sulfate solution [2]. Furthermore, the addition of chloride ions dramatically reduces the size of the copper branches in the walls of holes. The reduction in pore size is a result of lowering hydrophobic force of the generated hydrogen gas by adding bubble stabilizer (e.g., acetic acid) that suppresses the coalescence of bubbles, while the decrease in branch size in the foam wall is a consequence of the catalytic effect of chloride ions on the copper deposition reaction. Mechanical strength of the foam structure can be improved by the addition of (NH₄)⁺, Cl⁻, polyethylene glycol, and 3-mercapto-1-propane sulfonic acid to the deposition bath [13]. The foam structure obtained by a combination of these additives was highly porous with better mechanical strength than the one obtained without additives, owing to higher compactness of crystallites.

The use of additives in electroplating practice leads to their consumption during electrodeposition processes, and the requirement for their permanent control is necessary. The consumption of additives occurs due to the removal with the plated objects, by their incorporation in the deposit (co-deposition) and by reaction on the plated object [14, 15]. It has been known for a long time [16–18] that the use of a periodically changing regimes of electrolysis, such as pulsating overpotential (PO), pulsating and reversing current, as well as alternating current superimposed on direct current, can produce a similar effect on the quality of deposits as the use of additives. However, in spite of numerous investigations of the effect of pulse regimes on electrodeposition of metals [19–22], their effect on formation of metal deposits in the range of hydrogen co-deposition is insufficiently explored. The first report that has considered the effect of PO regime on the creation of copper deposits with extremely high surface area has been presented recently [23]. The aim of this paper is to continue this investigation.

Experimental

Copper was electrodeposited from 0.15 M CuSO₄ in 0.50 M H₂SO₄, in an open cell and at a temperature of 20±0.5 °C. Potentiostatic and square-wave PO techniques were used for electrodeposition of copper. In constant overpotential electrolysis, the overpotential of deposition used was 1,000 mV. In PO deposition, the overpotential amplitude of 1,000 mV and pulse duration of 10 ms were applied in all experiments. A pause duration was selected to be 5, 20, 50, and 100 ms (the pause-to-pulse ratios were 0.5, 2, 5, and 10, respectively). Electrodeposition of copper was performed at cylindrical copper electrodes. In all experiments, the geometric surface area of copper electrodes was 0.50 cm². The counter electrode was copper foil of 0.80 dm² surface area placed close to the walls of the cell, while the reference electrode was copper wire, which the tip was positioned at a distance of 0.2 cm from the surface of the working electrode. Copper was electrodeposited with quantities of electricity of 10 mA h cm⁻².

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

Cross-section analysis of the copper electrodes was performed using Zeiss Axiovert 25 optical microscope equipped with digital camera Panasonic WV-CD50. To observe the cross-section of the obtained structure, an immovable electrode with deposit with mounting epoxy resin mix was used. On that way, the cross-section was represented by the plain parallel to the line of deposit growth. Samples were polished several times, and cross-section structure was observed in non-etching state.

The obtained copper deposits were examined using a scanning electron microscope – Tescan digital microscopy.

Results and discussion

It is known [3, 4] that the honeycomb-like copper structures are formed by electrodeposition on overpotentials outside the plateau of the limiting diffusion current density, where hydrogen evolution is vigorous enough to change hydrodynamic conditions in the near-electrode layer. The typical honeycomb-like structure electrodeposited from 0.15 M CuSO₄ in 0.50 M H₂SO₄ at an overpotential of 1,000 mV (that was for 250 mV outside the plateau of the limiting diffusion current density [3, 4]) with a quantity of the electricity of 10 mA h cm⁻² is shown in Fig. 1.

Figure 2 shows copper deposits obtained in PO regime with used amplitude overpotential of 1,000 mV, pulse duration of 10 ms, and different pause durations. The selected pause durations were 5 ms (Fig. 2a), 20 ms (Fig. 2b), 50 ms (Fig. 2c), and 100 ms (Fig. 2d). It can be seen in Fig. 2 that honeycomb-like structures were formed by this regime of electrolysis if the applied pause durations were 5, 20, and 50 ms (Fig. 2a–c,

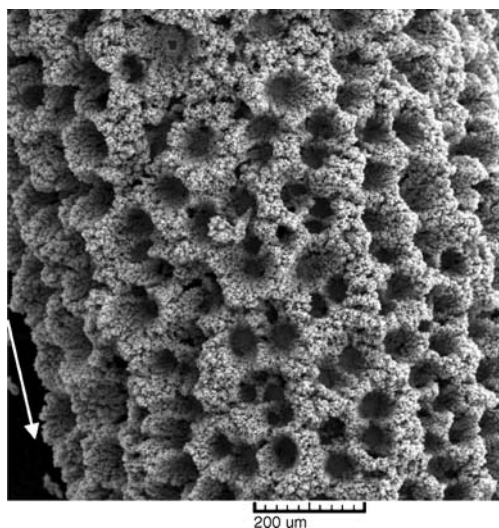
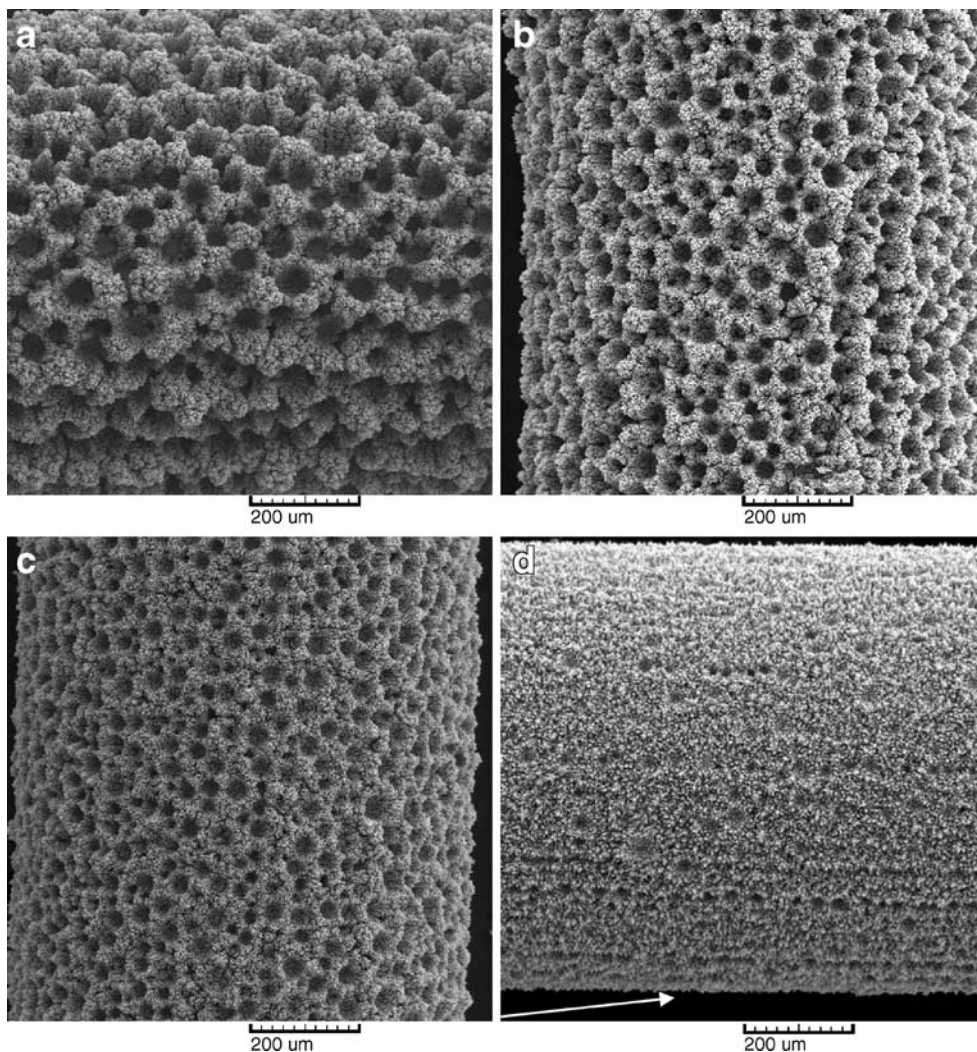


Fig. 1 Copper deposit obtained at an overpotential of 1,000 mV

respectively). Although holes formed of the attached hydrogen bubbles can also be detected on copper deposit formed by PO regime with pause duration of 100 ms (Fig. 2d), their number, size, and distribution were completely different from those formed with the shorter pause durations (Fig. 2a–c).

The detailed analysis of copper structures shown in Fig. 2 revealed a strong effect of pause durations on the size and shape of holes, as well as on the structure of deposits between holes. The decrease of a diameter of holes formed of the attached hydrogen bubbles and the increase of their number can be detected with the increasing pause durations from 5 to 50 ms (Fig. 2a–c). The honeycomb-like structures obtained with pause duration shorter than 5 ms approached to the one obtained by electrodeposition in a constant regime [23]. The prolonged pause duration led to a suppression of a coalescence of closely formed hydrogen bubbles. The coalesced holes can be observed in the honeycomb-like copper structures obtained with pause duration up to 20 ms. The typical coalesced hole obtained with pause duration of 5 ms is shown in Fig. 3. Figure 4 shows non-coalesced holes

Fig. 2 Influence of the pause duration between overpotential impulses on copper electrodeposition. Pause duration: **a** 5 ms, **b** 20 ms, **c** 50 ms, **d** 100 ms



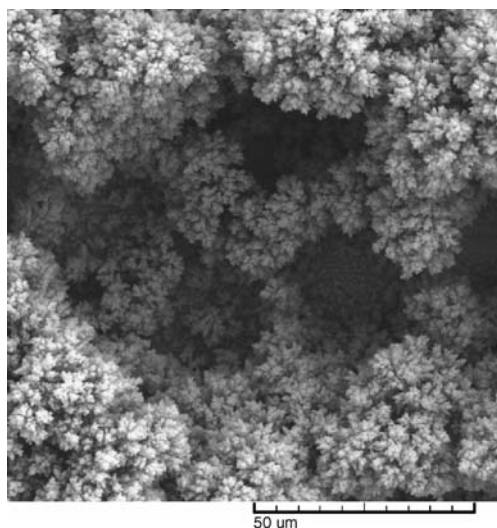
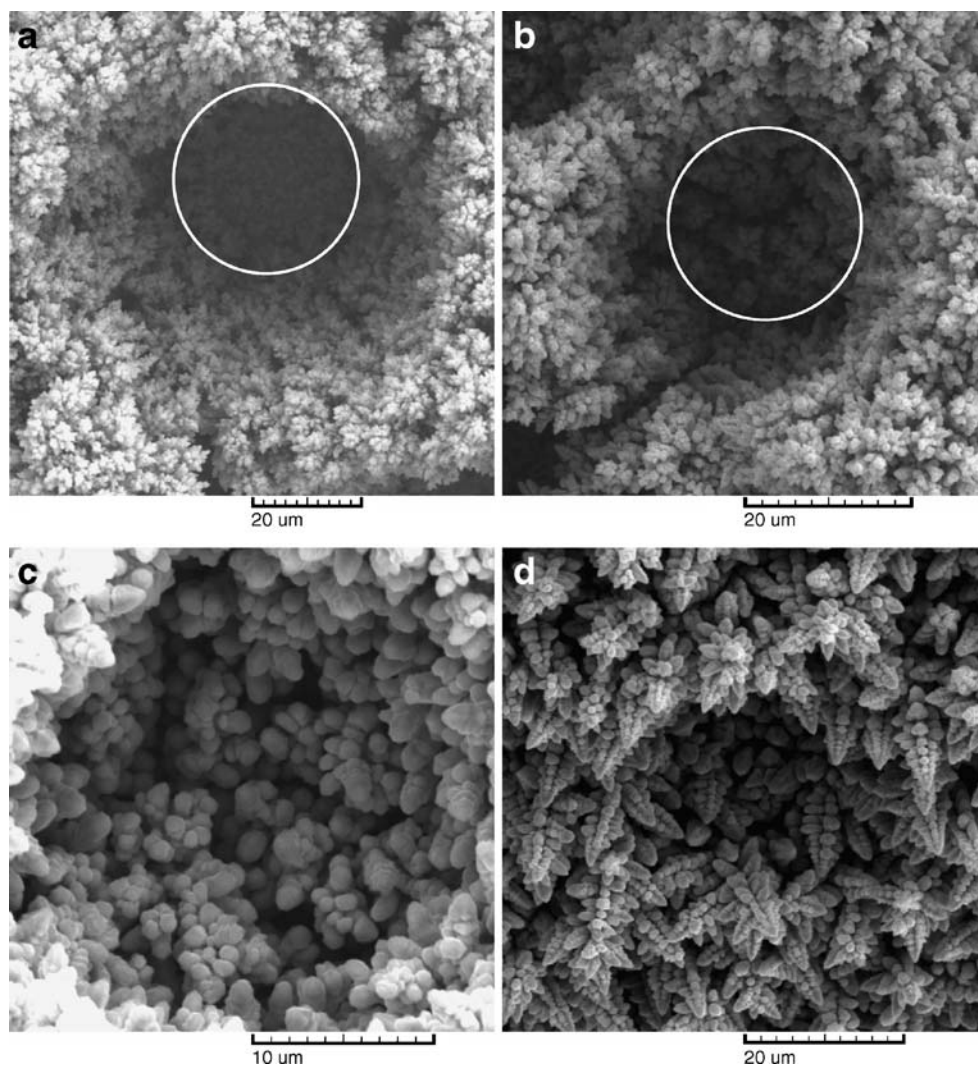


Fig. 3 The coalesced hole obtained by PO regime of electrolysis with a pause duration of 5 ms

obtained with pause durations of 5 (Fig. 4a) and 20 ms (Fig. 4b), as well as those obtained with pause durations of 50 (Fig. 4c) and 100 ms (Fig. 4d). The clear difference in shape and size of holes can be observed in Fig. 4. Aside from the decrease of a diameter of holes, the prolonging of pause duration led to a change of a shape of bottom of holes (parts in cycle in Fig. 4a and b) from compact (Fig. 4a) to one constructed of very disperse agglomerates of copper grains (Fig. 4b).

From Fig. 4, it can be also seen that the prolonging of pause duration leads to the appearance of dendritic forms in the interior of holes and at their shoulders. The interior of the hole obtained with pause duration of 5 ms was constructed of a very disperse agglomerates of copper grains. Copper dendrites can be noticed at shoulders of holes electrodeposited with pause duration of 20 ms and their number and size increased with the prolonging pause durations. Finally, the walls of holes obtained with pause duration of 100 ms were only composed of dendrites (Fig. 4d). The appearance of dendritic forms clearly

Fig. 4 Non-coalesced holes obtained by PO regimes of electrolysis. Pause duration: **a** 5 ms, **b** 20 ms, **c** 50 ms, **d** 100 ms



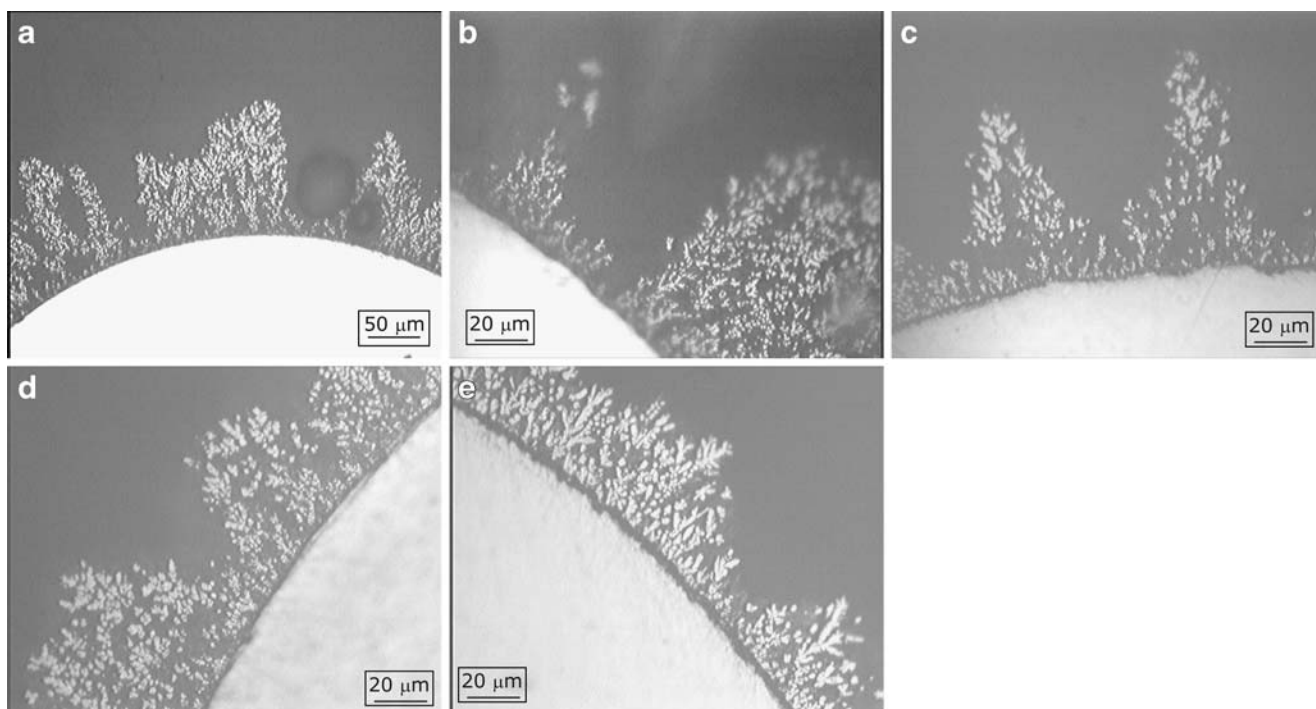


Fig. 5 Cross-section of copper deposits electrodeposited: **a** at an overpotential of 1,000 mV, and by PO regime with a pause duration of **b** 5 ms, **c** 20 ms, **d** 50 ms, **e** 100 ms

indicates a decrease of effectiveness of stirring of copper solution by evolved hydrogen with the increase of pause duration. Analysis of the interior of holes obtained with pause durations up to 50 ms shows that the prolongation of pause duration leads to a reduction of the size of agglomerates of copper grains of which the walls of holes are constructed. The compactness of the formed agglomerates was increased, as well. In this way, pores in the walls of holes were increased, and then, a transport of electroactive species through the interior of structures is facilitated, which is very desirable for the evaluation of electrochemical reactions. With the prolonging pause duration up to 50 ms, holes became closer to each other, while compactness of the formed agglomerates between them was also increased [23].

The increased uniformity of copper structures, determined by hole size distribution and by compactness of agglomerates of copper grains formed between the holes, with the increase of duration of pause, can be easily seen in Figs. 1 and 2d (parts denoted by arrow). The increase of compactness of deposits is accompanied by the decrease of a depth of holes formed by attached hydrogen bubbles. This can be easily seen from Fig. 5 showing cross-section of holes electrodeposited at the constant overpotential (Fig. 5a) and those obtained by PO regime with different pause durations (Fig. 5b–e). The dependence of the depth of holes on pause-to-pulse ratio is shown in Fig. 6. It can be seen in Fig. 6 that the increasing pause duration leads to a sharp decrease of hole depth.

Figure 7a shows the dependences of the average current densities on electrodeposition times obtained at an overpotential

of 1,000 mV and in PO regimes with pause durations of 5, 20, 50, and 100 ms. The prolonging duration of the pause led to the decrease of the average current densities, and the values obtained by PO regimes were smaller than the ones obtained in the constant regime of electrolysis. A better understanding of the effect of the pause duration on copper electrodeposition processes can be obtained from Fig. 7b, which shows the dependence of the average current densities calculated as $j_{av}' = \int_0^t j_{av} dt / t$ on pause-to-pulse ratio. The sharp decrease of the average current density is observed with the prolonging pause duration.

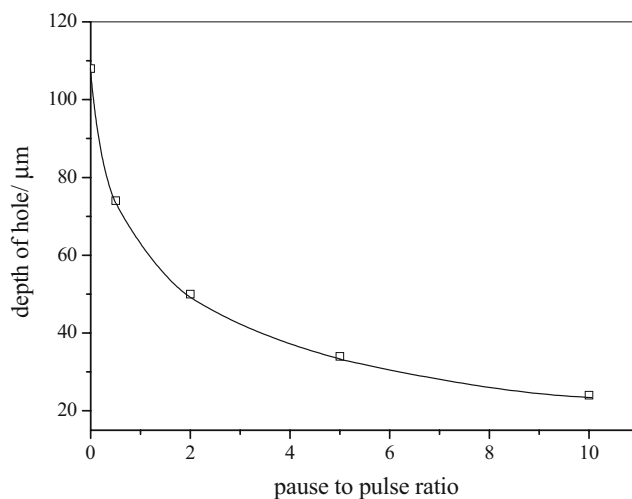


Fig. 6 The dependence of a depth of holes on the pause-to-pulse ratio

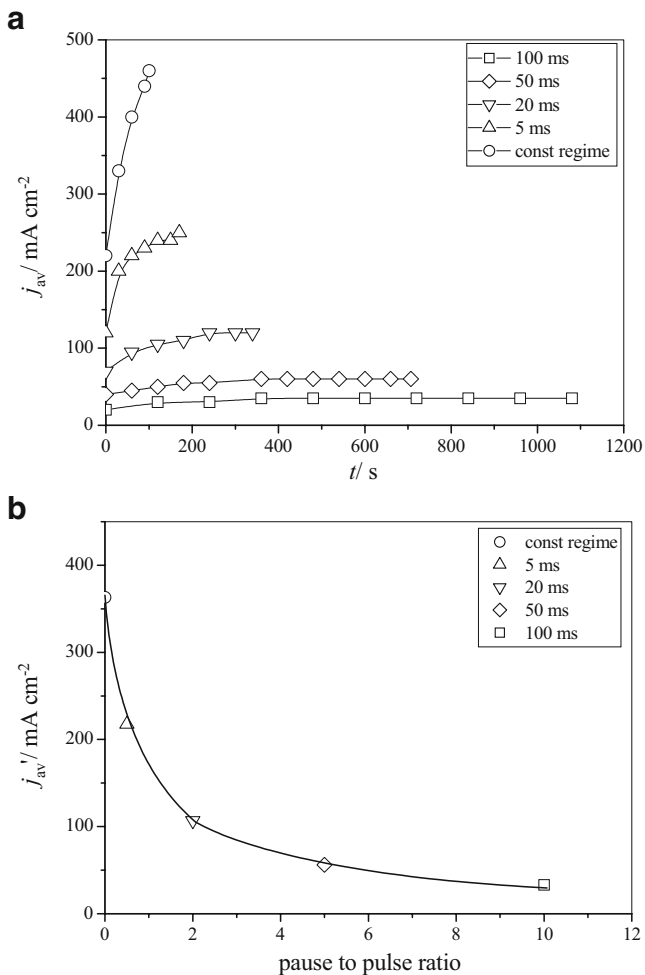


Fig. 7 The dependences of: **a** the average current densities on electrodeposition times, obtained at an overpotential of 1,000 mV, and by PO regimes with pause durations of 5, 20, 50, and 100 ms, **b** the average current density on pause-to-pulse ratio

The effect of pause duration in PO regime on electrodeposition of copper in the range of hydrogen co-deposition can be explained by the following consideration.

The square-wave PO is described by [24]:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (1)$$

$$C(\infty, 0) = C_0 \quad (2)$$

$$C(\delta, t) = C_0 \quad (3)$$

$$\frac{\partial C(0, t)}{\partial x} = \frac{j_0}{zFD} \left[\frac{C(0, t)}{C_0} \exp\left(\frac{2.3\eta}{b_c}\right) - \exp\left(-\frac{2.3\eta}{b_a}\right) \right] \quad (4)$$

where j_0 is the exchange current density, z is the number of transferred electrons, F is the Faraday constant, D is the

diffusion coefficient, b_c and b_a are the cathodic and anodic Tafel slopes, and η is the overpotential. C is concentration, C_0 is the bulk concentration, t is time, δ is the diffusion layer thickness, and x is the coordinate in horizontal direction.

The surface concentration in PO electrodeposition does not vary with time at sufficiently high frequencies and Eq. 5 is valid [24], where j_{av} is the average current density and j_L is the limiting diffusion current density.

$$\frac{C(0, t)}{C_0} = 1 - \frac{j_{av}}{j_L} \quad (5)$$

Substitution of $C(0, t)/C_0$ from Eq. 5 in Eq. 4 gives

$$\frac{\partial C(0, t)}{\partial x} = \frac{j_0}{zFD} \left[\left(1 - \frac{j_{av}}{j_L}\right) \exp\left(\frac{2.3\eta}{b_c}\right) - \exp\left(-\frac{2.3\eta}{b_a}\right) \right] \quad (6)$$

The input square-wave PO is defined by [24]:

$$\eta = \begin{cases} \eta_A & \text{for } mT_p < t \leq \left(m + \frac{1}{p+1}\right)T_p \\ 0 & \text{for } \left(m + \frac{1}{p+1}\right)T_p < t \leq (m+1)T_p \end{cases} \quad (7)$$

$m=0,1,2,\dots$ where η_A is the overpotential amplitude, T_p is the period of pulsation, and p pause-to-pulse ratio. Substitution of η_A and 0 from Eq. 7 in Eq. 6 produces the current responses during “on” and “off” periods:

$$j = zFD \frac{\partial C(0, t)}{\partial x} = \begin{cases} j_0 \left(1 - \frac{j_{av}}{j_L}\right) \exp\left(\frac{2.3\eta_A}{b_c}\right) - j_0 \exp\left(-\frac{2.3\eta_A}{b_a}\right) & \text{for } mT_p < t \leq \left(m + \frac{1}{p+1}\right)T_p \text{ (a)} \\ -j_{av} \frac{j_0}{j_L} & \text{for } \left(m + \frac{1}{p+1}\right)T_p < t \leq (m+1)T_p \text{ (b)} \end{cases} \quad (8)$$

The above equations are valid for the formation of both homogenous flat surface and powdered deposits, and hence, they can be, to the first approximation, considered as valid for the formation of honeycomb-like electrodes, as well.

Although the anodic current density during “off” periods (Eq. 8b) can be neglected in comparison with the cathodic one during “on” periods (Eq. 8a), it is clear from Figs. 1–6 that it is of a high significance for the formation of the presented deposits.

First of all, the anodic current density during the “off” period is concentrated at the higher points of the surfaces due to the edge effect [18]. In this way, a growth of deposits around growing hydrogen bubbles will be prevented, which will lead to the increase of compactness of deposits and the

decrease of depth of holes. As result of this, a coalescence of neighboring hydrogen bubbles will be suppressed, and larger number of holes with smaller diameters will be formed with the prolonging pause durations. Hence, the larger is the pause-to-pulse ratio, the larger is the leveling effect of PO. This should be the macro-effect of the PO deposition on the morphology of the honeycomb-like structured surfaces. There is also an effect on the micromorphology of deposit obtained in PO deposition. This effect can be explained by the fact that particles with lower tip radii are dissolved faster than those with larger ones [25]. Thus, particles obtained in PO deposition at one and the same η_A value are more compact with increasing p . This can be explained as follows. Eqs. (1)–(8) are valid for flat electrode surfaces or protrusions with sufficiently large tip radii, where the surface energy term [25] can be neglected. If it cannot be neglected, the effect of the surface energy term on the reaction rate [26] for two electron reaction steps is described by:

$$\frac{\partial C(0,t)}{\partial x} = \frac{j_0}{zFD} \left[\left(1 - \frac{j_{av}}{j_L} \right) \exp\left(\frac{2.3\eta}{b_c}\right) - \exp\left(\frac{2\sigma V}{RT r}\right) \exp\left(-\frac{2.3\eta}{b_a}\right) \right] \quad (9)$$

where σ is the metal surface energy, V is the metal molar volume, T is the temperature, R is the gas constant, and r is the radius of the spherical grain.

The right-hand side of Eq. 6 should be transformed by taking Eq. 9 into account. The output current density, j , during pauses ($\eta=0$) at the grain with radius r is

$$j = j_0 \left(1 - \frac{j_{av}}{j_L} \right) - j_0 \exp\left(\frac{2\sigma V}{RT r}\right) \quad (10)$$

The corresponding output current density on the flat surface is given by Eq. 8b. The difference between the current density at the spherical grain and on the flat surface during the “off” period is given by

$$\Delta j = j_0 - j_0 \exp\left(\frac{2\sigma V}{RT r}\right) \quad (11)$$

in case $j_{av} \approx j_L$, which is satisfied in honeycomb-like copper electrodeposition.

It is obvious from Eq. 11 that the lower is the grain radius, the larger is the anodic current density during “off” period. The effect of anodic polarization increased with the pause duration.

Finally, the specific surface area of copper electrodes (determined by the sizes of the holes and agglomerates of copper grains in the walls of holes) increased up to the pause-to-pulse ratio 5. The compactness of the agglomerates of copper grains formed among the holes was also increased. The effects of the application of the PO regime on the microstructural characteristics of the honeycomb-like

structures were comparable with those obtained by electro-deposition in the constant potential regime in the presence of additives. In this way, electrodeposition in the presence of additives can be successfully replaced by electrodeposition from a basic solution by the use of periodically changing regimes of electrolysis, such as PO.

Conclusions

Copper deposits formed in the hydrogen co-deposition range by the regime of PO were analyzed by the SEM technique. The applied parameters of a square-wave PO were amplitude overpotential of 1,000 mV, a deposition pulse of 10 ms, and pause durations of 5, 20, 50, and 100 ms (pause-to-pulse ratios were 0.5, 2, 5, and 10, respectively).

Honeycomb-like structures were formed with pause-to-pulse ratios up to 5. The diameter of holes formed by attached hydrogen bubbles decreased, while the number of holes formed at surface area of copper electrodes increased with the increasing pause-to-pulse ratio.

The prolongation of pause duration led to an inhibition of coalescence of neighboring hydrogen bubbles. The increase of the pause duration reduced effectiveness of stirring of solution by evolved hydrogen that was manifested by the appearance of dendrites in the hole walls and at their shoulders.

The increased compactness of deposits formed around hydrogen bubbles was successfully explained by the use of set of equations considering the effect of the square-wave PO shape on morphology of electrodeposited copper.

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