



Comparative morphological and crystallographic analysis of copper powders obtained under different electrolysis conditions

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Abstract: Production of copper powders by the potentiostatic electrolysis under different hydrogen evolution conditions was investigated. Copper powders were characterized by the scanning electron microscope (SEM), X-ray diffraction (XRD), particle size distribution (PSD), and by the determination of the specific surface area (SSA) of the formed powders. Depending on quantity of hydrogen generated during electrolysis, the two types of particles were formed: dendrites and cauliflower-like particles. The dendrites were formed without, while cauliflower-like particles with the quantity of evolved hydrogen enough to achieve strong effect on hydrodynamic conditions in the near-electrode layer. Although macro structure of the particles was very different, they showed similar micro structure. Namely, both types of the particles consisted of small agglomerates of approximately spherical Cu grains at the micro level. The existence of the spherical morphology was just responsible for random orientation of Cu crystallites in both types of particles. The SSA of cauliflower-like particles was more than two times larger than that of the dendrites, while their size was considerably smaller than that of the dendritic particles. In this way, the useful benefit of Cu powder formation in the conditions of vigorous hydrogen evolution is shown.

Key words: electrolysis; copper; particles; specific surface area (SSA); particle size distribution (PSD)

1 Introduction

Electrolysis is widely used method for synthesis of metals or alloys of the desired characteristics suitable for application in various technologies [1–5]. Morphology of deposits, as the most important characteristic of electrodeposited metals or alloys, depends on the regime and parameters of electrolysis. Both constant and periodically changing regimes of electrolysis are used in the electrolysis processes. The parameters affecting the final morphology of electrodeposited metals are: composition and kind of electrolytes, temperature and time of electrolysis, type of working electrode, stirring of the electrolyte, the addition of additives, etc [1,6–8]. Aside from the regime and parameters of electrolysis, morphology of deposits is strongly affected by the nature

of metals, classifying them into three groups: the normal, intermediate, and inert metals [9].

Thanking to primarily good conductivity, copper has found a wide application in electrical and electronic industries for production of tubes, wires, sheets and for making copper-based alloys [8]. The compact, adherent, bright or powder copper deposits can be obtained by selection of the above-mentioned parameters and regimes of electrolysis [1,6,8,10,11]. The processes of electrolysis in both the potentiostatic [12] and galvanostatic [13,14] conditions, as well as at periodically changing rate, such as square waves pulsating overpotential (PO) [1,15] and reversing current (RC) regimes [1,16], are widely used for Cu powder production [1,11–19]. Although the sulfate electrolytes are the most often used, some other types like the nitrate ones are also used [17]. The addition of additives, such

as polyvinylpyrrolidone (PVP), sodium dodecyl sulfate (SDS), polyethylene glycol (PEG), cellulose and thiourea (Tu), significantly affects the morphology of the particles [16]. Simultaneously, the smaller particles and narrower distribution curves were obtained by electrolysis on platinum than on aluminium electrode [1].

The behaviour of powders as collection of particles is determined by so-called decisive characteristics, such as the specific surface area (SSA), the apparent density, the flowability, and the particle size distribution (PSD) [1,20]. The shape and size of particles just determine these characteristics of metal powders, irrespective of method of their synthesis.

Morphology of electrolytically produced copper powder is relatively well investigated and systematized in the literatures [1,11–19]. However, the data dealing with crystal structure of copper powders are relatively poor. It was shown recently [21,22] that there are a strong correlation between morphology and crystal structure of powdered silver obtained by chemical and electrochemical methods of synthesis, with the strong influence on some of decisive characteristics, like the specific surface area. Following this observation, we continue this type of investigation, with the aim to establish the correlation between morphology and crystal structure of copper powders obtained by the potentiostatic regime of electrolysis. Also, the specific surface area (SSA) and the particle size distribution (PSD), as the most important decisive characteristics, of the produced Cu powders, will be examined and correlated with the established dependences. The special attention will be devoted to the effect of hydrogen evolution as the parallel reaction to Cu electrolysis in the powder formation on the shape, crystal structure, SSA and PSD characteristics.

2 Experimental

2.1 Electrochemical production of Cu powders

Copper powders were produced by the potentiostatic regime of electrolysis from 0.10 mol/L CuSO_4 in 0.50 mol/L H_2SO_4 at overpotentials of 625, 925 and 1000 mV, with a quantity of the electricity of $10 \text{ mA} \cdot \text{h}/\text{cm}^2$. The processes of electrolysis were performed in an open cell of cylindrical shape at the room temperature. The working, reference and counter electrodes were made of pure copper. The working electrode was of a cylindrical shape, with a length of 2.0 cm and a diameter of 0.8 mm (the overall surface area of 0.50 cm^2). The counter electrode was in the form of foil and situated close to the wall of cell. The working electrode was situated in the middle of the cell, while the tip of Cu reference electrode was positioned at a distance of about 2 mm from the surface of working electrode.

2.2 Determination of average current efficiency for hydrogen evolution reaction ($\eta_{\text{L,av}}(\text{H}_2)$)

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 Cu electrolysis was employed. The electrodes were situated under a burette with the surface facing up so that the total amount of hydrogen evolved during the electrolysis processes went into the burette. In these measurements, the surface area of Cu electrode was 0.63 cm^2 . During the electrolysis process, the volume of evolved hydrogen $V(\text{H}_2)$ and the current of electrolysis I after a time t were recorded. Then, after graphical integration $I-t$, the current efficiency for hydrogen evolution $\eta_{\text{L}}(\text{H}_2)$ in a time t was determined according to Eq. (1):

$$\eta_{\text{L}}(\text{H}_2) = \frac{V(\text{H}_2)}{\mu(\text{H}_2) \int_0^t I dt} \quad (1)$$

where

$$\mu(\text{H}_2) = \frac{V}{nF} = 450 \text{ cm}^3/(\text{A} \cdot \text{h}) \quad (2)$$

and nF is the number of Faradays per mole of consumed ions and V is the molar volume of a gas at a temperature of 21.0°C (i.e., 24120 cm^3). The average current efficiency of hydrogen evolution, $\eta_{\text{L,av}}(\text{H}_2)$ is determined after graphical integration $\eta_{\text{L}}(\text{H}_2)-t$ as

$$\eta_{\text{L,av}}(\text{H}_2) = (1/t) \int_0^t \eta_{\text{L}}(\text{H}_2) dt$$

The specification of the experimental procedure for the determination of the average current efficiency of hydrogen evolution is given by NIKOLIĆ et al [23].

2.3 Characterization of Cu particles produced by electrolysis

Morphologies of potentiostatically produced particles were characterized by the technique of scanning electron microscopy (SEM) using TESCAN digital microscopy (Model VEGA3, Brno, Czech Republic).

The XRD (X-ray diffraction) analysis of Cu particles was performed using the Rigaku Ultima IV diffractometer (Rigaku Co. Ltd., Tokyo, Japan), with Cu K_α radiation (0.154178 nm) in 2θ range from 30° to 95° . The preferred orientation of Cu particles was estimated by the determination of the texture coefficient, $TC(hkl)$ and the relative texture coefficient, $RTC(hkl)$ in a following way [21,22,24]:

The ratio of intensity of (hkl) reflection to the sum of all intensities of the recorded reflections, $R(hkl)$, is calculated according to Eq. (3):

$$R(hkl) = \frac{I(hkl)}{\sum_i^4 I(h_i k_i l_i)} \times 100\% \quad (3)$$

where $I(hkl)$ is the intensity of the (hkl) reflection, and $\sum_i^4 I(h_i k_i l_i)$ is the sum of all intensities of the recorded reflections, for the particles under consideration.

The texture coefficient, $TC(hkl)$, for every (hkl) reflection is defined in Eq. (4):

$$TC(hkl) = \frac{R(hkl)}{R_s(hkl)} \quad (4)$$

where $R_s(hkl)$ is defined in the same way as given by Eq. (3), but is related to the Cu standard (04-0836). This coefficient gives accurate quantitative information about the absolute intensity of the reflection.

Finally, the relative texture coefficient, $RTC(hkl)$, is defined in Eq. (5):

$$RTC(hkl) = \frac{TC(hkl)}{\sum_i^4 TC(h_i k_i l_i)} \times 100\% \quad (5)$$

The $RTC(hkl)$ coefficient defines the intensity of the (hkl) reflection relative to the standard (included in the TC values).

Phase analysis was done by using the Powder Cell software (Version 2.4). The average crystallite size was calculated on the basis of the full-width at half-maximum intensity (FWHM) of the (111), (200), (220) and (311) reflection of fcc Cu by applying Scherrer's formula and the lattice strain of electrodeposited powders was estimated from Williamson–Hall plots [22,25,26].

The specific surface area of powders was determined by use of MALVERN Instruments MASTERSIZER 2000 device. The values of the specific surface area (SSA) are obtained using the Malvern Software which control the apparatus operation and processing the obtained data.

3 Results and discussion

3.1 Polarization of Cu electrodeposition system

Polarization curve for Cu electrodeposition from 0.10 mol/L CuSO_4 in 0.50 mol/L H_2SO_4 is shown in Fig. 1. The plateau of the limiting diffusion current density is defined by vertical lines in this figure, from which it can be seen that it corresponds to the range of overpotentials between 300 and 750 mV. After an overpotential of 750 mV (the inflection point), the current density increases sharply with the further increase in the overpotential.

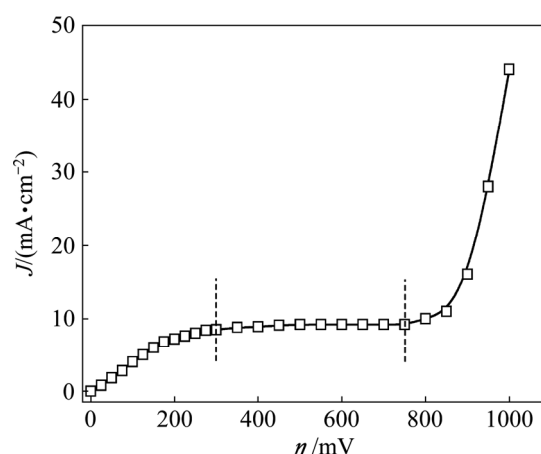


Fig. 1 Polarization curve for Cu electrodeposition from 0.10 mol/L CuSO_4 in 0.50 mol/L H_2SO_4

3.2 Morphology of electrochemically produced Cu powder particles

In the potentiostatic regime of electrolysis, Cu in the powder form is obtained at overpotentials belonging to the plateau of the limiting diffusion current density and at the higher ones. Figure 2 shows the powdered forms obtained at an overpotential of 625 mV (the plateau of the limiting diffusion current density). The 3D (three dimensional) pine-like dendrites were the dominant form obtained by electrolysis at this overpotential (Fig. 2(a)). The 3D pine-like dendrites were constructed from the corn-cob-like elements (Fig. 2(b)), while they were constructed from small agglomerates of approximately spherical Cu grains (Fig. 2(c)). The size of grains in these agglomerates was about 1 μm . The cauliflower-like particles constructed from the agglomerates of approximately spherical grains, and individual precursors of holes originating from the detached hydrogen bubbles were also formed by electrolysis at 625 mV (Fig. 2(d)). There is no any difference in the shape of dendritic particles obtained by the electrolysis process and those after their removing from electrode surface (Figs. 2(e) and (f)).

Morphologies of Cu powdered deposits obtained at overpotentials of 925 and 1000 mV in the zone of the fast increase of the current density with overpotential are shown in Figs. 3 and 4, respectively. At both overpotentials, the honeycomb-like structures were formed (Figs. 3(a) and 4(a)). These structures are formed in the conditions of vigorous hydrogen evolution [1,23], and their main elements are: holes formed from detached hydrogen bubbles (Figs. 3(b) and 4(b)) and the cauliflower-like agglomerates of Cu grains formed around them (Figs. 3(c) and 4(c)). The cauliflower-like agglomerates of Cu grains were very disperse and constructed from small agglomerates of approximately spherical grains, mutually separated by irregular

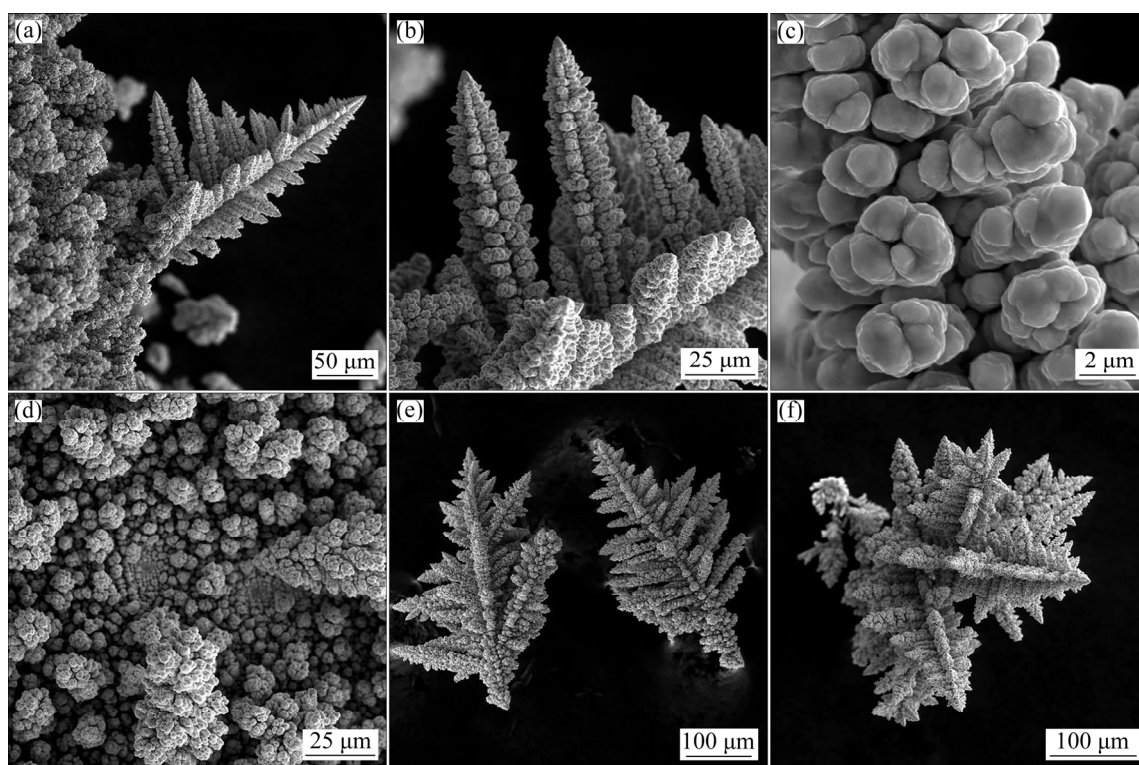


Fig. 2 Morphologies of Cu powdered deposits obtained by electrolysis at overpotential of 625 mV: (a) Dendrite; (b) Corn-cob-like forms; (c) Agglomerates of approximately spherical grains; (d) Cauliflower-like agglomerates of Cu grains and precursors of holes formed from detached hydrogen bubbles; (e, f) Dendritic particles

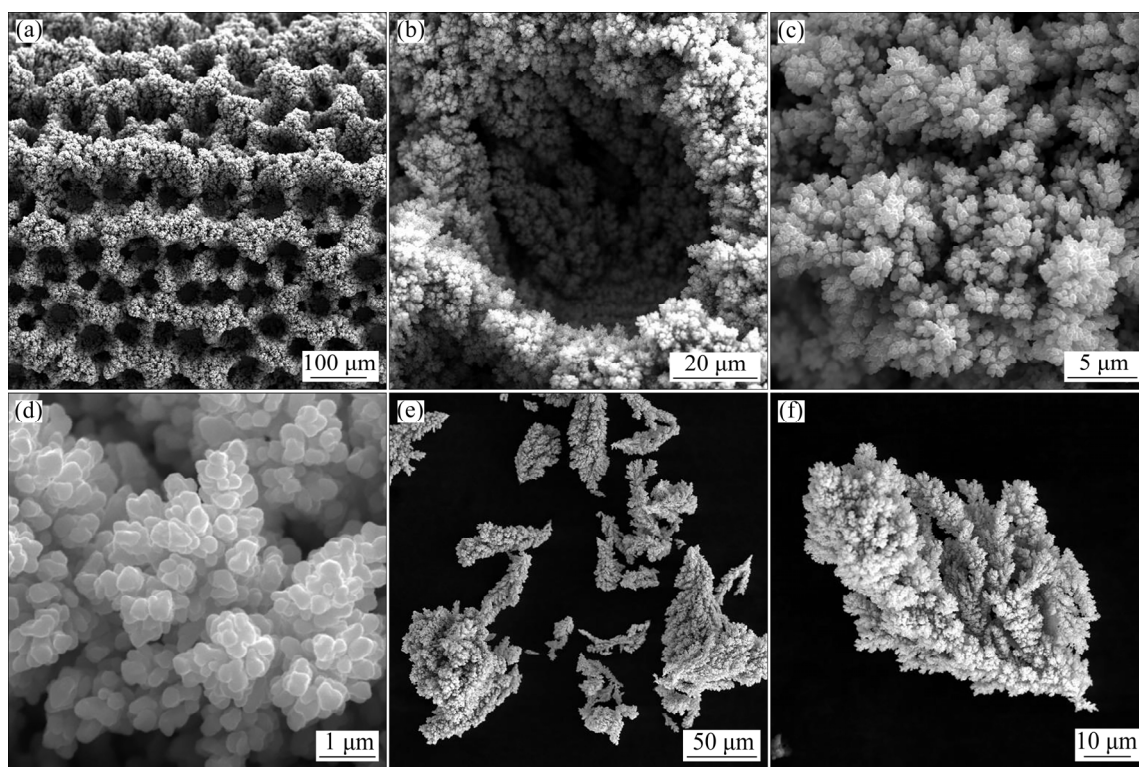


Fig. 3 Morphologies of Cu powdered deposits obtained by electrolysis at overpotential of 925 mV: (a) Honeycomb-like structure; (b) Hole formed from detached hydrogen bubble; (c) Cauliflower-like particles formed among holes; (d) Small agglomerates constructed from approximately spherical grains; (e, f) Particles obtained by removing deposits after electrolysis process

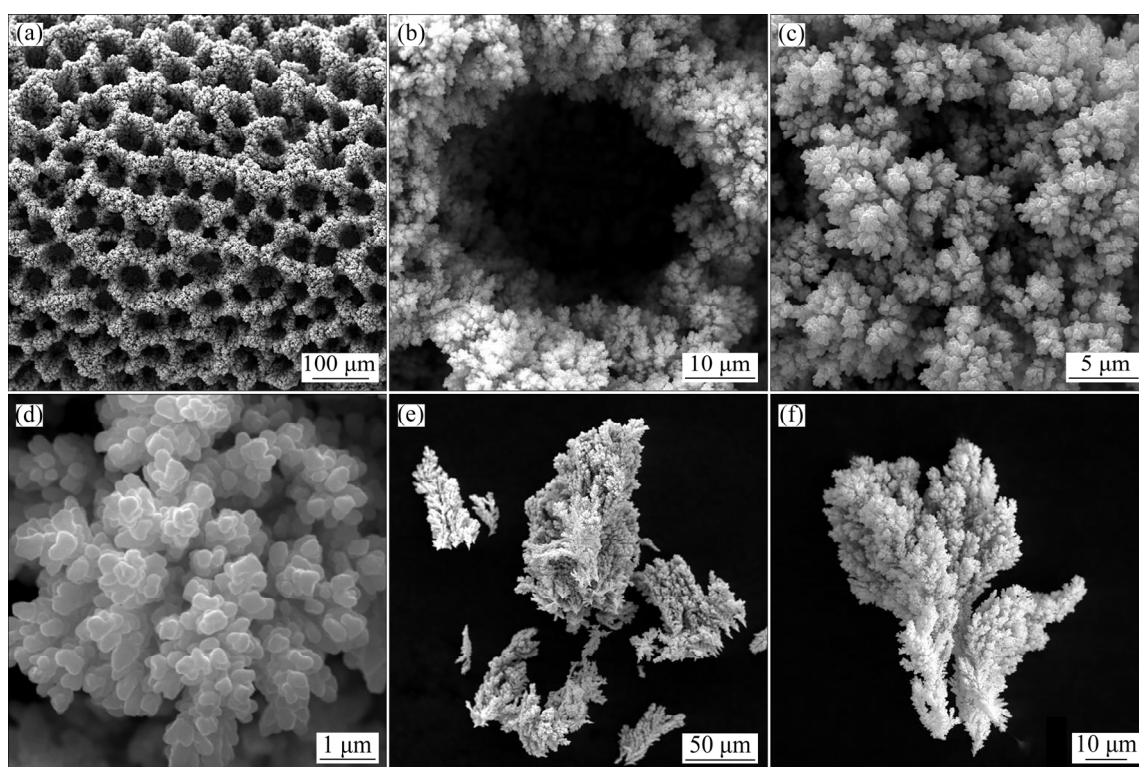


Fig. 4 Morphologies of Cu powdered deposits obtained by electrolysis at overpotential of 1000 mV: (a) Honeycomb-like structure; (b) Hole formed from detached hydrogen bubble; (c) Cauliflower-like particles formed among holes; (d) Small agglomerates constructed from approximately spherical grains; (e, f) Particles obtained by removing deposits after electrolysis process

channels (Figs. 3(c) and (d), and Figs. 4(c) and (d)). The size of grains in these agglomerates was about 200 nm. The particles obtained by removing the deposits from the honeycomb-like electrodes are shown in Figs. 3(e) and (f), for the deposit electrodeposited at 925 mV, and in Figs. 4(e) and (f), for the deposit electrodeposited at 1000 mV. Inhibition of dendritic growth and formation of the cauliflower-like particles are clearly visible from these figures.

3.3 Crystal orientation and structure of Cu powder particles

3.3.1 Preferred orientation of formed Cu particles

The XRD patterns of the powder particles obtained at overpotentials of 625, 925 and 1000 mV together with Cu standard (04-0836) are shown in Fig. 5. The peaks at 2θ of 43.3° , 50.4° , 74.1° and 89.9° correspond to (111), (200), (220) and (311) crystal planes, confirming face centered cubic (fcc) crystal lattice of Cu. In all XRD patterns, the crystallites were dominantly oriented in the (111) plane due to lower surface energy of this plane in relation to the other planes [27,28]. The preferred orientation of the produced particles was estimated by the analysis of peak intensity ratios ((111)/(200), (111)/(220) and (111)/(311)) the fast estimation, and by the determination of $TC(hkl)$ and $RTC(hkl)$ coefficients (the precise estimation).

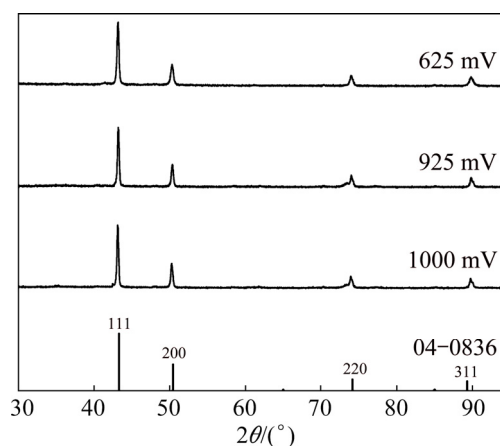


Fig. 5 XRD patterns of Cu particles obtained at overpotentials of 625, 925 and 1000 mV, and Cu standard (04-0836)

In Table 1, the values of the peak intensity ratios (111)/(200), (111)/(220) and (111)/(311) calculated for the given particles and for Cu standard are given. Analysis of the presented ratios indicates that there are no larger deviations than those for the Cu standard, suggesting the random orientation of crystallites in all powder particles.

The values of $TC(hkl)$ and $RTC(hkl)$ for the same powders are given in Table 2. The values of TC above 1 and RTC above 25% (four reflections in XRD patterns were analyzed in this study) indicate the existence of

Table 1 Ratios of intensities of diffraction peaks for analyzed powders and Cu standard

Type of powder particles	Ratio of intensities		
	(111)/(200)	(111)/(220)	(111)/(311)
Cu(625)	2.7	4.9	5.5
Cu(925)	2.5	4.3	5.2
Cu(1000)	2.5	4.6	5.4
Cu standard (04-0836)	2.2	5.0	5.9

Cu(625)—Powder produced at 625 mV; Cu(925)—Powder produced at 925 mV and Cu(1000)—Powder produced at 1000 mV

the preferred orientation in the particles [21,22,24]. Although the strict analysis of these coefficients can indicate the existence of very mild (220) and (311) preferred orientation, the obtained values are still very close to 1 and 25%, confirming the randomly oriented crystallites in the particles.

The values of the average crystallite size and lattice strain obtained for the Cu particles produced at 625, 925 and 1000 mV are given in Table 3. The obtained values for the average crystallite size clearly point out nanostructural character of the produced Cu particles.

According to expectation, the decrease of the average crystallite size was observed with an increase in electrolysis overpotential. It is necessary to note that the values obtained at 925 and 1000 mV were very close to each other.

3.3.2 Crystal structure of Cu dendrites

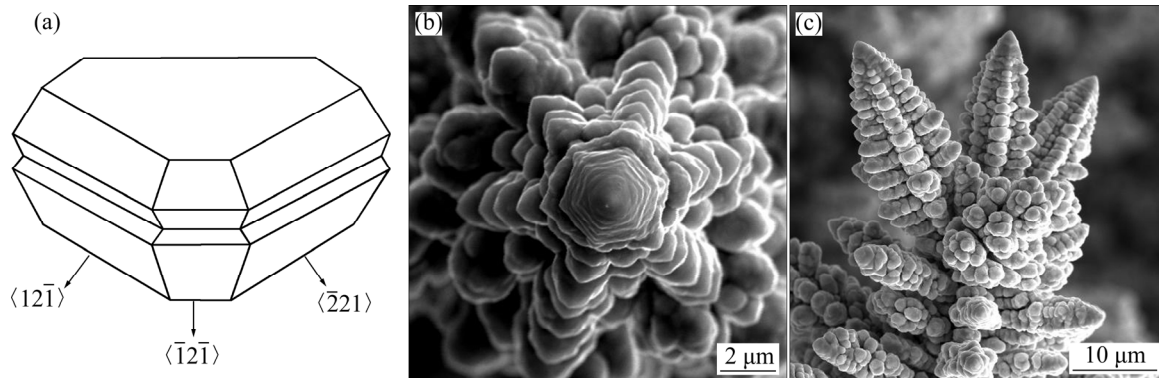
The patterns obtained at an overpotential of 625 mV, in diffusion-controlled system, are dendrites (Fig. 2). A dendrite is a crystal with a tree-like branching structure which is characterised by growth of the stalk and branches along preferred crystallographic direction. The planar dendrites are twin crystals, and a twin plane re-entrant edge (TPRE) mechanism can account qualitatively for the behaviour of all the two-dimensional dendrites [29,30]. The essence of this mechanism lies in the ability of twin boundaries to provide re-entrant grooves or two-dimensional nucleation sites, which are self-perpetuating. The twinning plane in fcc crystal is (111), and nuclei containing two or more twin planes, have six re-entrant grooves, 60° apart, located alternatively first at one twin plane and then the other. Thus, the main stem of a dendrite is formed by stacked octahedra (Fig. 6(a)) undergoing longitudinal

Table 2 Texture calculations for Cu powders obtained by electrolysis at overpotentials of 625, 925 and 1000 mV

(hkl)	R/%			R_g /%	TC			RTC/%		
	625 mV	925 mV	1000 mV		625 mV	925 mV	1000 mV	625 mV	925 mV	1000 mV
(111)	56.9	54.7	55.2	54.6	1.04	1.00	1.01	25.7	24.0	24.6
(200)	21.2	22.0	22.5	25.1	0.845	0.876	0.896	20.1	21.0	21.8
(220)	11.6	12.7	12.0	10.9	1.06	1.16	1.10	26.2	27.8	26.8
(311)	10.3	10.6	10.3	9.4	1.10	1.13	1.10	27.2	27.1	25.8

Table 3 Average crystallite size, lattice strain, average current efficiency of hydrogen evolution, η_{H_2} , and specific surface area (SSA) obtained for powders produced at overpotentials of 625, 925 and 1000 mV

η /mV	Crystallite size/nm	Lattice strain/ 10^{-3}	η_{H_2} /%	SSA/($\text{m}^2 \cdot \text{g}^{-1}$)
625	100	3.061	2.0	0.0287
925	84	2.114	36.6	0.084
1000	81	2.095	46.8	0.0952

**Fig. 6** Stacked octahedral (a), dendrites (b, c) of Cu obtained by electrolysis at overpotential of 625 mV: (b) Top view of dendrite; (c) Side view of dendrite branches

propagation in the octahedral plane (111). There are favoured re-entrant growth sites at six $\langle 211 \rangle$ directions, and rapid growth takes place in these directions. Most important, these favoured growth sites will not disappear and growth can continue indefinitely.

Dendrites also grow in thickness, by layer growth mechanism, and as a consequence, the facets appear on the main face of a dendrite [22]. The $\{111\}$ facets on the main face arise passing throughout from the stem and it is likely the dendrite branch in $\langle 111 \rangle$ direction, so that the main stem and primary branches make an angle of nearly 90° (Fig. 2(a)). In this way, dendrites grow in $\langle 211 \rangle$ and $\langle 111 \rangle$ directions, so they have 3D appearance. Furthermore, except the main stem, all the branches are formed by stacked octahedrons which have six re-entrant grooves and grow in six $\langle 211 \rangle$ directions (Fig. 6(b)). Consequently, the branches look like a corn, as seen in Fig. 6(c).

3.4 Discussion of presented results

In the dependence of conditions of electrolysis, the two types of particles were formed: dendrites and cauliflower-like particles. The different forms of the particles are caused by the appearance of hydrogen evolution reaction as parallel reaction to Cu electrolysis at the high overpotentials. Hydrogen evolution commences at some overpotential belonging to the plateau of the limiting diffusion current density and intensifies with the increase of overpotential. For this electrolyte, critical overpotential for beginning of hydrogen evolution reaction is estimated to be 590 mV [31]. Figure 7 shows the volume of evolved hydrogen, $V(\text{H}_2)$ (Fig. 7(a)) and the current of electrolysis, I (Fig. 7(b)) on the time, t , obtained at overpotentials of 625, 925 and 1000 mV. The dependencies of the current efficiency of hydrogen evolution, $\eta_{\text{H}}(\text{H}_2)$, on t derived from the data from Figs. 7(a) and (b) using Eq. (1) are presented in Fig. 7(c). The average current efficiencies of hydrogen evolution, $\eta_{\text{H,av}}(\text{H}_2)$, are obtained by the graphical integration of these dependencies and obtained values are listed in Table 3. Intensification of hydrogen evolution with the increase of overpotential is clearly visible from this table.

In this way, formation of the different forms of the particles can be explained as follows: very non-uniform electrode surface was formed by the process of electrolysis at an overpotential of 625 mV (Fig. 2). Aside from dendrites (Fig. 2(a)), as the most dominant shape of the particles, the cauliflower-like agglomerates of Cu grains and individual precursors of holes originating from the detached hydrogen bubbles (Fig. 2(d)) were also formed at this overpotential. The amount of evolved hydrogen which corresponded to $\eta_{\text{H,av}}(\text{H}_2)$ of 2.0 % was not enough to achieve any effect

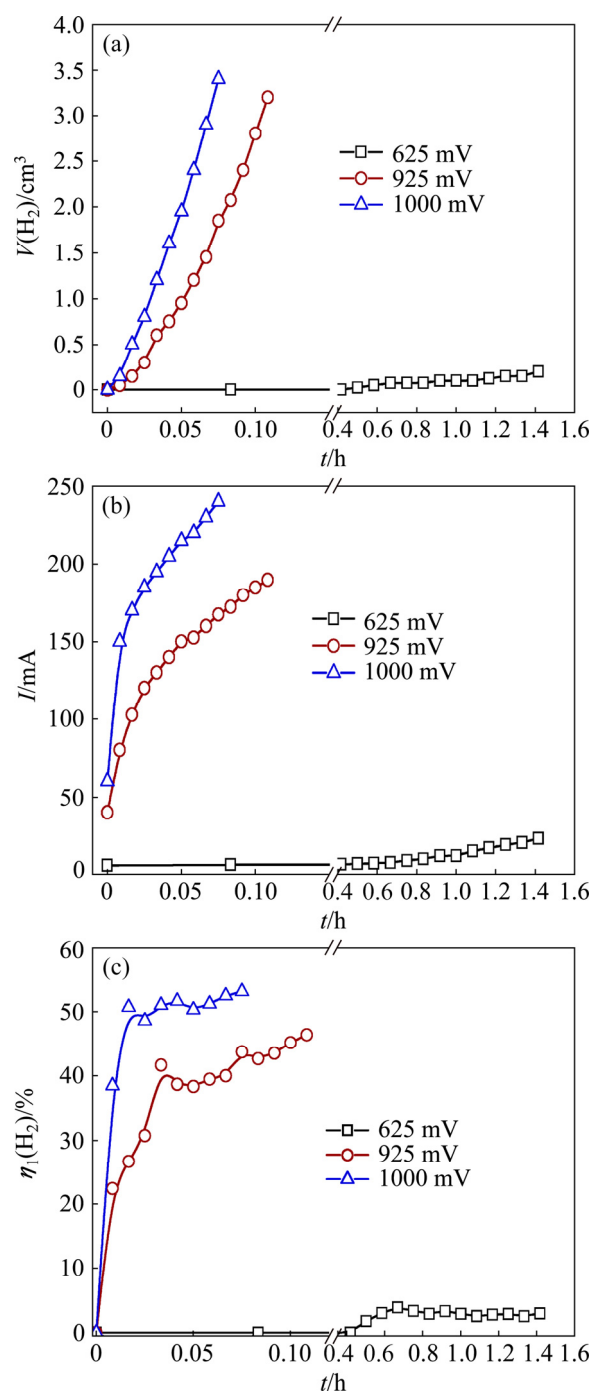


Fig. 7 Dependencies of volume of evolved hydrogen ($V(\text{H}_2)$) (a), current of electrolysis (I) (b), and current efficiency of hydrogen evolution, $\eta_{\text{H}}(\text{H}_2)$ (c), on time (t) obtained at overpotentials of 625, 925 and 1000 mV

on the hydrodynamic conditions in the near-electrode layer. The growth of these particles occurred inside the diffusion layer of the macroelectrode, and the electrolysis process was primarily controlled by the diffusion of ions to the electrode surface, rather than the kinetics of the electrodeposition [1,32].

On the other hand, hydrogen evolution at over-

potentials of 925 and 1000 mV was vigorous enough to achieve the strong effect on the hydrodynamic conditions in the near-electrode layer. The values of $\eta_{\text{lav}}(\text{H}_2)$ of 36.6% and 46.8% were considerably above the critical value of 10.0% [1], leading to the change of hydrodynamic conditions in the near-electrode layer, and an overpotential corresponding to the inflection point at the polarization curve just corresponds to this value. As a result of vigorous hydrogen evolution, deposits denoted as the honeycomb-like structures with uniform distribution of holes formed from the detached hydrogen bubbles and cauliflower-like agglomerates of Cu grains among them are formed. The main consequence of vigorous hydrogen evolution is inhibition of dendritic growth. Namely, vigorous hydrogen evolution causes stirring of the electrolyte in the near-electrode layer, leading to the decrease in the thickness of the diffusion layer and the increase in the limiting diffusion current density. As a result of these processes, the decrease in the degree of diffusion control in relation to conditions without and with insufficient hydrogen evolution to achieve any effect on the hydrodynamic conditions in the near-electrode layer is realized, and the growth of dendrites are completely inhibited.

The concept of “effective overpotential” is proposed to explain inhibition of dendritic growth and formation of the cauliflower-like particles (Figs. 3 and 4) instead of the dendrites (Fig. 2), that can be considered as follows [1,23]. In the conditions of vigorous hydrogen evolution, the electrodeposition process occurs at an overpotential which is effectively lower than that specified, and this overpotential is denoted as “effective” in a deposition process. From the morphological point of view, this means that the morphologies of metal deposits become similar to those obtained at some lower overpotentials at which hydrogen evolution does not occur or is very slow. Formation of the cauliflower-like particles instead of dendrites really confirms that there is a lower degree of the diffusion control at 925 and 1000 mV than at 625 mV.

The XRD analysis (Fig. 5) showed that crystallites of Cu were randomly orientated in the both types of the particles. This random orientation can be explained by the existence of the spherical morphology in both types of particles. Namely, in spite of completely different shapes of the particles at the macro level (dendrites and cauliflower-like particles), the micro structure of the obtained particles was very similar. Both types of the particles consisted of the small agglomerates of approximately spherical grains (Fig. 2(c), Fig. 3(d) and Fig. 4(d)). Formation of the particles with the random orientation of crystallites in them can be explained from electrochemical point of view through analysis of the rate of electrochemical processes (J_0 values, where J_0 is

the exchange current density) as follows: Cu belongs to the group of the intermediate metals with the medium J_0 values and the lower overpotentials for hydrogen discharge than the normal metals. For this electrolyte, the J_0 is 0.11 mA/cm² [31], and it is valid $J_0 < J_L$, where J_L is the limiting diffusion current density. As a result of this, the random orientation was observed in Cu particles. The strong (111) preferred orientation was observed in the particles belonging to the group of normal metals, such as Ag [21,22] and Pb [33], which are characterized by the very high J_0 values ($J_0 \gg J_L$; very fast electrochemical processes). The absence of the spherical morphology and formation of the 2D (two dimensional) needle-like and fern-like dendrites were characteristic forms of powder particles of these metals. On the other hand, the random orientation was observed for nickel particles obtained by the electrolysis process [33]. Ni belongs to the group of the inert metals, characterized by low values of both J_0 and overpotential for hydrogen evolution reaction. The spongy-like particles constructed from holes formed by the detachment of hydrogen bubbles surrounded by the cauliflower-like agglomerates of Ni grains were formed by Ni electrolysis [33]. These cauliflower-like agglomerates consisted of small agglomerates of approximately spherical Ni grains.

The further comparison of the obtained Cu powder particles was performed by the analysis of the specific surface area (SSA) and the particle size distribution (PSD) of the produced particles. The SSA values obtained at overpotentials of 625, 925 and 1000 mV are listed in Table 3. It can be seen that the SSA values increase with increasing overpotential of electrolysis. Simultaneously, the obtained values for the powders synthesized at 925 and 1000 mV were very close to each other and more than two times larger than the value obtained at 625 mV. It is understandable due to the similar morphology of the particles formed at 925 and 1000 mV in the conditions of vigorous hydrogen evolution.

The particle size distribution (PSD) curves obtained for the considered particles are shown in Fig. 8. From Fig. 8, it can be seen that the size of particles decreases with increasing the overpotential of electrolysis. The most uniform distribution of the particles is obtained for those produced at 1000 mV. For the particles produced at 625 and 925 mV, it is noticeable that the presence of particles smaller (625 mV) and larger (both 625 and 925 mV) than those occupy the maximum volume ratios on the PSD curves. At 625 mV, the presence of smaller particles can be ascribed to the formation of cauliflower-like particles (Fig. 2(d)), while the formation of the larger particles is probably the result of formation of very branchy 3D dendrites like that shown in Fig. 2(f). On the other hand, due to very vigorous hydrogen evolution, the

particles of different size can be obtained (Fig. 3(e)). Anyway, the more the intensive hydrogen evolution reaction, the more the uniform distribution of the particles is observed. In this way, hydrogen evolution reaction shows useful benefit on the shape, size and distribution of Cu particles.

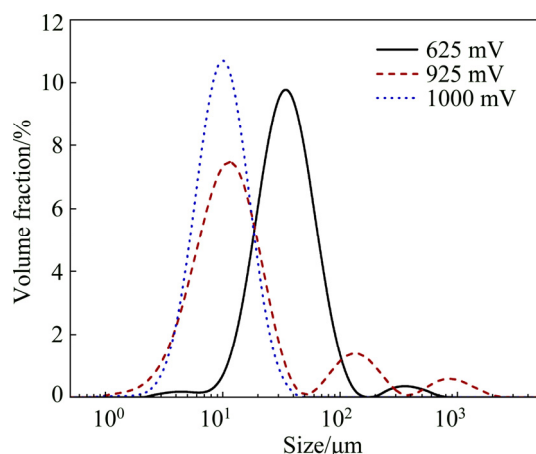


Fig. 8 Particle size distribution (PSD) curves obtained for particles produced at overpotentials of 625, 925 and 1000 mV

4 Conclusions

(1) Dendrites were formed at an overpotential of 625 mV (inside the plateau of the limiting diffusion current density), with a quantity of evolved hydrogen which corresponded to $\eta_{l,av}(H_2)$ of 2.0% insufficient to achieve any effect on the hydrodynamic conditions. Cauliflower-like particles were formed at overpotentials of 925 and 1000 mV (outside the plateau of the limiting diffusion current density), in the conditions of vigorous hydrogen evolution which corresponded to $\eta_{l,av}(H_2)$ of 36.6% and 46.8%, respectively. These quantities were enough to achieve the strong effect of evolved hydrogen on the hydrodynamic conditions in the near-electrode layer.

(2) In spite of very different macro structure, the crystallites of Cu were randomly orientated in both types of the particles. The random orientation is ascribed to their similar micro structure. Both dendrites and cauliflower-like particles were constructed from small agglomerates of approximately spherical Cu grains.

(3) The cauliflower-like particles had more than two times larger specific surface area (SSA) than the dendritic particles. The particle size distribution (PSD) analysis showed considerable decrease in the size of particles formed in conditions of vigorous hydrogen evolution. In this way, the useful benefits of hydrogen evolution reaction as parallel reaction to Cu electrolysis in powder production range on some of decisive characteristics of powders, such as SSA and PSD, are shown.

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不同电解条件下制备铜粉的形貌及结晶学比较分析

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摘 要: 研究不同析氢条件下恒电位电解法制备铜粉的过程。采用扫描电镜(SEM)、X 射线衍射(XRD)、粒度分布(PSD)和比表面积测定(SSA)对铜粉进行表征。根据电解过程析氢量的大小, 形成树枝状和菜花状两种类型的颗粒。当析氢量大到足以对近电极层中的流体动力学条件产生强烈影响时, 形成菜花状颗粒, 否则形成树枝状颗粒。虽然颗粒的宏观结构差异很大, 但他们的微观结构却相似, 也就是说, 这两种颗粒在微观层面上都是由近似球形的 Cu 颗粒小团聚体组成; 球状形貌的存在是造成两种颗粒中 Cu 晶粒随机取向的原因。菜花样颗粒的比表面积是树枝状颗粒的 3 倍以上, 其粒径则比树枝状颗粒的小很多。由此可见, 强析氢条件对于铜粉制备是有益的。

关键词: 电解; 铜; 颗粒; 比表面积; 粒度分布

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