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## Comparison of morphology of powder particles obtained by the constant and periodically changing regimes of electrolysis

*Morphologies of copper powder particles obtained by both potentiostatic and pulsating overpotential (PO) regimes of electrolysis were analyzed using the technique of scanning electron microscopy (SEM). The parameters of square waves PO were selected to enable a comparison of the obtained particles with those obtained in the potentiostatic regime from solutions of different CuSO<sub>4</sub> and H<sub>2</sub>SO<sub>4</sub> concentrations. It is shown that more solutions of different CuSO<sub>4</sub> and H<sub>2</sub>SO<sub>4</sub> concentrations can be replaced by the one solution if the appropriate PC parameters are applied, what can be of high technological significance.*

**Key words:** morphologies of copper powder particles, electrolysis, electron microscopy

### INTRODUCTION

Pure copper powder is widely used in the electrical and the electronics industries due to its excellent electrical and thermal conductivities. Alloyed with tin, zinc, nickel and other elements, copper in powder form is used in structural parts and friction materials. Copper and copper alloy powders are also used in such nonstructural applications as brazing, cold soldering, and mechanical plating, as well as for medals and medallions, metal-plastic decorative products and a variety of chemical and medical purposes [1].

The four main categories of fabrication techniques are based on mechanical comminuting, chemical reaction, electrolytic deposition and liquid metal atomization. The main advantages of powder production by electrolysis are high purity of the produced powder which can be easily pressed and sintered and low oxygen content [2, 3]. It is environmentally friendly way of powder production which enables working in a closed-circuit [4].

Metal powders can be obtained by the constant (in both potentiostatic and galvanostatic modes) and by periodically changing regimes of electrolysis (the regime of pulsating overpotential (PO), the regime of pulsating current (PC) and the reversing current (RC) [5-8]. The aim of this paper is comparative analysis of copper powder particles obtained by the regime of pulsating overpotential (PO) and by the potentiostatic regime of electrolysis.

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### EXPERIMENTAL

Copper was potentiostatically deposited at an overpotential of 1000 mV from the following solutions: a) 0.075 M CuSO<sub>4</sub> in 0.50 M H<sub>2</sub>SO<sub>4</sub>, and b) 0.30 M CuSO<sub>4</sub> in 0.50 M H<sub>2</sub>SO<sub>4</sub>.

Also, electrodeposition of copper was performed from 0.15 M CuSO<sub>4</sub> in 0.50 M H<sub>2</sub>SO<sub>4</sub> by the regime of pulsating overpotential (PO). In pulsating overpotential deposition the overpotential amplitude of 1000 mV and a pause duration of 10 ms were applied in all experiments. Deposition pulses of 3 and 20 ms were selected.

Electrodeposition of copper was performed at cylindrical copper electrodes at the room temperature. In all experiments, the geometric surface area of copper electrodes was 0.50 cm<sup>2</sup>. The counter electrode was copper foil of 0.80 dm<sup>2</sup> 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<sup>-2</sup>. The corresponding powder particles were obtained by the tapping of the copper deposits.

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

Morphologies of obtained copper deposits and powder particles were examined using a scanning electron microscope – TESCAN Digital Microscopy.

### RESULTS AND DISCUSSIONS

Figure 1 shows powdered deposits obtained by the regime of pulsating overpotential (PO) with a deposition pulse of 3 ms (Fig. 1a) and 20 ms (Fig.

1b). In both cases, copper solution containing 0.15 M  $\text{CuSO}_4$  in 0.50 M  $\text{H}_2\text{SO}_4$ , the overpotential amplitude of 1000 mV and a pause duration of 10 ms were applied. Analysis of these deposits at higher magnifications showed that very branchy dendrites were formed around holes with the applied deposition pulse of 3 ms (Fig. 1c), while cauliflower-like

agglomerates of copper grains were obtained with a deposition pulse of 20 ms (Fig. 1d). The quantities of hydrogen spent for the formation of these deposits corresponded to the average current efficiencies of hydrogen evolution,  $\eta_{\text{H}_2, \text{av}}$  in % of: 16.4% (for a deposition pulse of 3 ms) [9] and 28.1% (for a deposition pulse of 20 ms) [9].

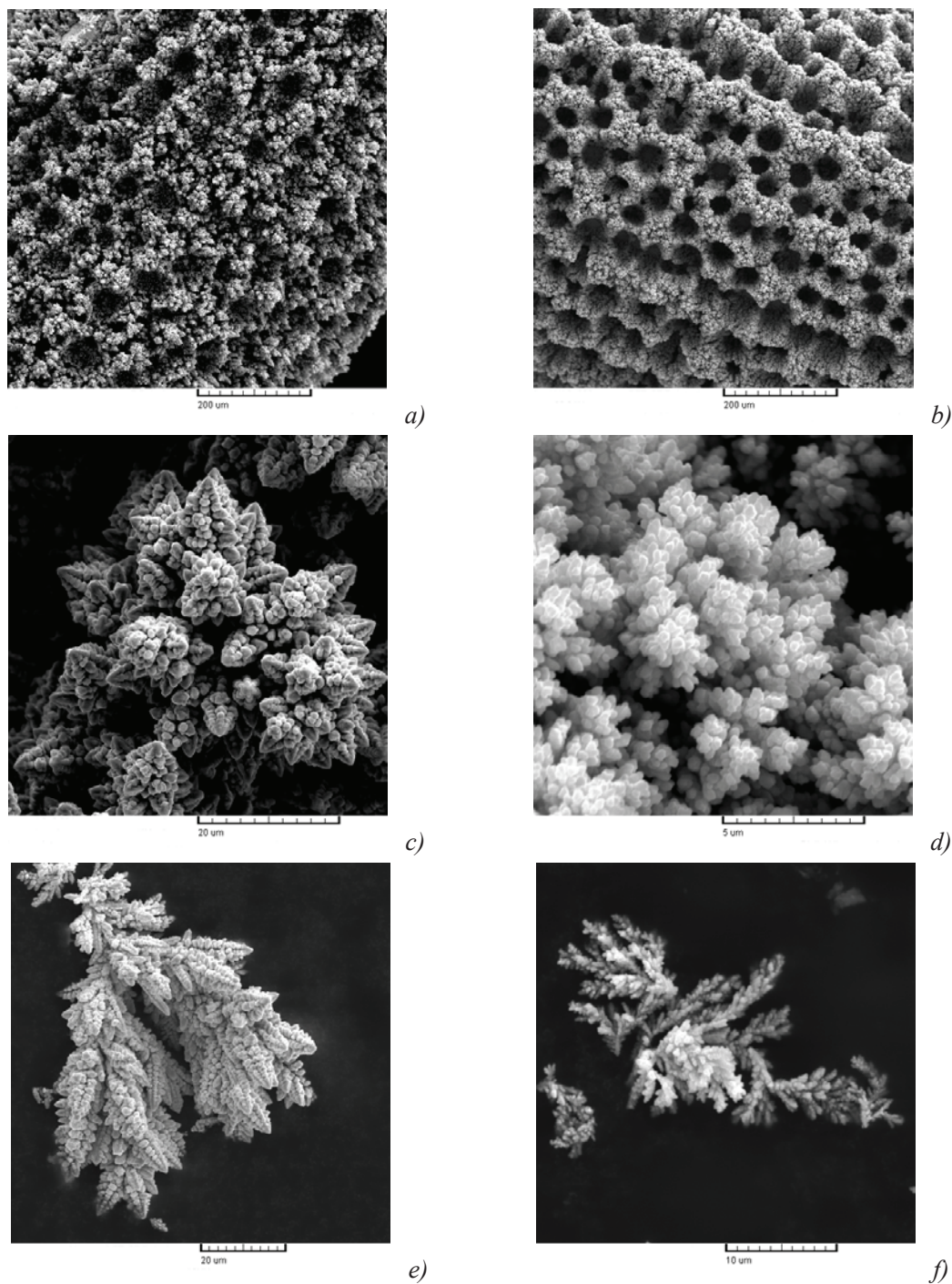


Figure 1. Powdered deposits and powder particles obtained by the pulsating overpotential (PO) regime with a deposition pulse of: a), c) and e) 3 ms; b), d) and f) 20 ms. The overpotential amplitude: 1000 mV. Pause duration: 10 ms.

The typical powder particles obtained by tapping of the powdered deposits shown in Fig. 1a and b are presented in Fig. 1e and f. Dendritic character of a powder particle obtained with a deposition pulse of 3 ms is clearly seen from Fig. 1e. Dendrites are constructed from corn-cob-like elements. Analysis of corn-cob-like elements at the micro level showed that they are composed of small agglomerates of copper grains. A channel structure formed by *in situ* by the simultaneous processes of copper nucleation and strong hydrogen evolution can be noticed by the analysis of powder particle obtained with a deposition pulse of 20 ms (Fig. 1f). Analysis of this particle at the micro level showed that the particle is constructed from aggregates of small agglomerates of copper grains. Hence, macro structure of the obtained particles was very different (dendrites or cauliflower-like particles), while micro structures of these particles were similar to each other (small agglomerates of copper grains).

The obtained particles were compared with those obtained in the potentiostatic regime from solutions of different  $\text{CuSO}_4$  and  $\text{H}_2\text{SO}_4$  concentrations. Figure 2 shows powder particles obtained at an overpotential of 1000 mV from 0.075 M  $\text{CuSO}_4$  (Fig. 2a), as well as from 0.30 M  $\text{CuSO}_4$  in 0.50 M  $\text{H}_2\text{SO}_4$  (Fig. 2b). These powder particles were obtained with the quantities of evolved hydrogen which corresponded to  $\eta_{l,av}(\text{H}_2)$  of: 68.7% (for copper solution containing 0.075 M  $\text{CuSO}_4$  in 0.50 M  $\text{H}_2\text{SO}_4$ ) [10] and 16.0% (for copper solution containing 0.30 M  $\text{CuSO}_4$  in 0.50 M  $\text{H}_2\text{SO}_4$ ) [10]. Macro structure of the powder particles obtained from 0.075 M  $\text{CuSO}_4$  in 0.50 M  $\text{H}_2\text{SO}_4$  at the constant overpotential was very similar to the one obtained by the square wave PO with a deposition pulse of 20 ms. In both cases, cauliflower-like particles composed of small copper grains agglomerates were formed. On the other hand, dendrites constructed from corn-cob-like elements were obtained by electrodeposition from 0.30 M  $\text{CuSO}_4$  in 0.50 M  $\text{H}_2\text{SO}_4$  at 1000 mV. The formed dendrites were similar to those obtained by the PO regime with a deposition pulse of 3 ms. It is necessary to note that regardless of the type of used regime of electrolysis, dendrites are formed with the approximately same quantity of evolved hydrogen. On the other hand, cauliflower-like agglomerates of copper grains are always formed when copper electrochemical deposition process was accompanied by the average current efficiency of hydrogen evolution larger than 20.0% [11]. With the  $\eta_{l,av}(\text{H}_2)$  above 20.0%, macro structures of powdered deposits consisted of holes formed of detached hydrogen bubbles surrounded by cauliflower-like copper grains agglomerates (the honeycomb-like structures). In the hydrogen co-depo-

sition range corresponding to  $\eta_{l,av}(\text{H}_2)$  between 10.0 and 20.0%, macro structure of powdered deposits consisted of holes formed of detached hydrogen bubbles and dendrites around them [11].

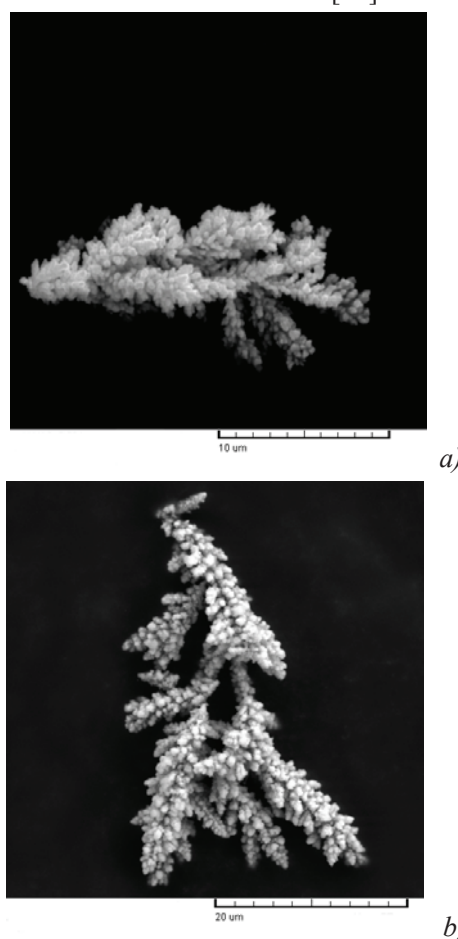


Figure 2. Powder particles electrodeposited at an overpotential of 1000 mV from: a) 0.075 M and b) 0.30 M  $\text{CuSO}_4$  in 0.50 M  $\text{H}_2\text{SO}_4$ .

From the above consideration, it is clear that the effect of the increase of deposition pulse duration on both hydrogen evolution reaction and copper electrodeposition rate was equivalent to the one observed by the decrease of  $\text{CuSO}_4$  concentration (for the constant  $\text{H}_2\text{SO}_4$  concentration). The effect of the constant pause duration ( $t_p = 10$  ms) was equivalent to the constant  $\text{H}_2\text{SO}_4$  concentration. Of course, the overpotential amplitude in the PO regimes corresponded to overpotential of electrodeposition in the constant regimes of electrolysis. In this investigation, it is shown that more different electroplating solutions can be replaced by the one solution if the appropriate parameters of the PO regimes are selected. It is necessary to note that similar effects on the formation of disperse copper deposits were observed by the application of the regime of pulsating current (PC) [12]. This is of potential high technological signi-

ficance 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.

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#### IZVOD

##### POREĐENJE MORFOLOGIJE ČESTICA PRAHA DOBIJENIH KONSTANTNIM I PERIODIČNO PROMENLJIVIM REŽIMIMA ELEKTROLIZE

*Tehnikom skenirajuće elektronske mikroskopije su analizirane morfologije bakarnih čestica praha dobijenih režimom pulsirajuće prenapetosti i potenciostatskim elektrohemijjskim taloženjem. Parametri režima pulsirajuće prenapetosti su bili tako odabrani da su omogućili poređenje dobijenih čestica sa onima dobijenim potenciostatskim režimom elektrolize iz rastvora različitih koncentracija  $\text{CuSO}_4$  i  $\text{H}_2\text{SO}_4$ . Pokazano je da se više rastvora različitih koncentracija  $\text{CuSO}_4$  i  $\text{H}_2\text{SO}_4$  mogu zameniti jednim rastvorom ako se primene pogodni parametri režima pulsirajuće prenapetosti, što može biti od visokog tehnološkog značaja.*

**Ključne reči:** morfologija čestica praha, elektroliza, elektronska mikroskopija