Characterization and Morphology of Copper Powder Particles as a Function of Different Electrolytic Regimes

M. G. Pavlović[1,*], Lj. J. Pavlović[1], V. M. Maksimović[2], N. D. Nikolić[1] and K.I. Popov[3]

[1] University of Belgrade, Institute of Electrochemistry ICTM, 11000 Belgrade, Njegoševa 12, Serbia
[2] Institute of Nuclear Sciences, ¨Vinča¨, 11001 Belgrade, P.O.Box 522, 11001 Belgrade, Serbia
[3] University of Belgrade, Faculty of Technology and Metallurgy, Belgrade, Karnegijeva 4, Serbia
[*]E-mail: duki@tmf.bg.ac.rs

The effect different deposition regimes (constant and reversing currents), on the powdered copper electrodeposits morphology were investigated. The results obtained in constant regimes were compared with those obtained in reversing regimes. The morphology of electrodeposited copper powder were investigated using a scanning electron microscope (SEM). The effect of the current amplitude, cathodic-to-anodic time ratio and period of the current wave are discussed. It is shown that the parameters determining the reversing current wave determine the micromorphology of the copper powder particles deposited. On the other side, technological properties of powders depend on their granulometry and particle morphology. Very often one method is inadequate for characterization of the morphology of powder particles. This paper also studied different methods for clear describing of the copper powder granulometry and morphology.

1. INTRODUCTION

Morphology is probably the most important property of electrodeposited metals. It depends mainly on the kinetic parameters of the deposition process and the deposition overpotential or current density. For the application of metal powders, many of their properties are of interest. The size and shape of the particles, bulk weight, flow rate, corrosion resistance, specific surface area, apparent density and quality of sintered product. In general, they depend on the shape and the size, which can be influenced by appropriate electrolysis regime [1,2]. Thanks to a rapid increase in significance of powder metallurgy, metal powders are being produced in large quantities nowadays and big part is being produced by electrolysis. Almost all materials can be obtained in powder, but the method

selected for production of powder depends on the specific material properties. The four main categories of fabrication techniques are based on mechanical commuting, chemical reaction, electrolytic deposition and liquid metal atomization [3,4].

The electrolytic metal powder represents a disperse electrodeposit removed from electrode by tapping or in a similar way [5,6], which consists of particles of various forms and sizes. The electrolytic powder production method usually yields products of high purity, which can be well pressed and sintered. Besides, in recent years, it has been shown that by different electrolysis regimes it is possible, not only to obtain powders with a wide range of properties, but also to predict the decisive characteristics of powders, which are very important for powder quality and for appropriate application [2,4].

Main characteristics of powders are particle size (granulometry) and particle shape (morphology). Technological properties of powders (bulk density, flowability, surface area, apparent density, etc.) as well as the potential areas of their application depend on these characteristics [7].

Copper deposits obtained at high current densities and overpotentials are very important from a technological point of viev. It has been stated that the open and porous structures of copper deposits obtained at high current densities were ideally sited for use as electrodes in electrochemical devices such as fuel cells, batteries and chemical sensors [8,9], while the extremely high surface area is relevant for evaluating some electrochemical reactions. For example, it was known that copper shows a high activity for the nitrate ion reduction [10] as well as for the reaction in which nitrate is reduced to ammonia in high yield in aqueous acidic perchlorate and sulphate media [11]. Having in maind a potential high technology significance of copper deposits obtained at high overpotentials, it is necessary to better recognize the effect of this process on electrodeposition of copper under these conditions. For that reason, one of the aims of this paper it is to examine the effect of this process on copper electrodeposition at overpotentials on the plateau of the limiting diffusion current densitiey or higher ones.

It is well known that copper powders with different properties can be obtained by electrodeposition from different electrolyte solutions under different operating conditions. The same effects can be also obtained by changing overpotential wave shape during pulsating overpotential deposition a keeping all other conditions unchanged [1,2,12,13].

The electrodeposition of metal powders by pulsating overpotential produces particles of changed morphology relative to those obtained in classic potentiostatic deposition [1,2]. It is also known that it is easy use pulsating overpotential deposition in the laboratory-scale cell but difficulties arise on a practical scale because of the demands for higher power and a high-speed potentiostat. The output current for input pulsating overpotential is a reversing current [14], and similar effects on the morphology and grain size of powder particles can be expected in deposition by pulsating overpotential and by reversing current. However, it is easier to obtain reversing currents on a practical scale and the deposition of copper powder by reversing current is of greater practical importance than pulsating overpotential deposition.

The granulometry of powders can be determined by different methods (sieve analysis, image analysis, laser analysis, etc.), but the question is how adequately they describe the powder granulometry. Some investigation showed [15] that the evaluation of course powder granulometry

(particle size more than 50 μm) by means of sieve analysis guarantees sufficiently good results. Evaluation of the fine powder granulometry (with particle size less than 50 μm) is more difficult. The results of the sieve analysis do not describe adequately the powder granulometry. The morphology of powder particles is characterized by description (spherical, angular, dendritic, dish-shaped, acicular) or quasi-quantitatively, for example, by means of geometrical parameters. For characterization of real particles the particle shape becomes more and more important in addition to particles size. Image analysis can give valuable service. The method used to measure the powder particle size, enabling the analysis of the particle size distribution, could be divided into two groups: direct and indirect. The direct methods map the geometry of individual particles via optical, electron scanning and transmission microscopy. Indirect methods are based on physical effects, such as sieve and laser analysis [7,15].

Stereological methods could be used for precise description of powder based on their planar images. Useful for powder characterization are parameters measured for individual "objects" such as: area, perimeter and roundness, a shape factor which gives a minimum value of unity for a circle. This is calculated from the ratio of the perimeter square to the area [16,17]:

$$f_R = \frac{L_p^2}{4\pi A \cdot 1.064}$$

where is:

A – *area* total number of detected pixels within the feature

L_p – *perimeter*, the total length of the boundary of the feature. This is calculated from the horizontal and vertical projections, with an allowance for the number of corners.

f_R - *roundness* shape factor which gives a minimum value of unity for a circle. This is calculated from the ratio of perimeter squared to area. The adjustment factor of 1.064 corrects the perimeter for the effect of the corners produced by the digitalization of the image.

Electrocrystallisation of copper powder has two stages, nucleation and growth, for smooth cathodes growth is enhanced through nucleation but the converse is true for powder production where each nucleus is a powder particle. Therefore, the key for changing of the particle size of the copper powder is the changing of the relative rates of nucleating and crystal growth [6,18].

The goal of this work was to investigate the effect of the parameters different deposition regimes on the morphology of electrodeposited copper powder particles as well as to study different methods for clear describing of the copper powder granulometry and morphology.

2. EXPERIMENTAL PART

The experiments were performed in an enlarged laboratory reactor with cell volume of 10 dm³. The electrolytic copper powders were produced from electrolyte containing 145 gdm⁻³ sulphuric acid and 18 gdm⁻³ copper, using an electrolyte temperature (50±2) °C. Details about the enlarged laboratory reactor are given in the reference [16].

Copper powders were deposited by galvanostatic regime; values of current densities (j = 7.71, 10.28, 30 and 36 Adm^{-2}) and reversing current (the amplitude current densities values were, j_A, from 18, 24, 30 to 36 Adm^{-2}). The cathodic time was 1s, and the anodic time was 0.4s, in all cases.

The deposition time (brush-down interval) in all experiments was 30 min keeping all other conditions unchanged as in the case of constant current density regime.

The electrolytes were prepared from technical chemicals and demineralized water.

The wet powders were washed several times with a large amount of demineralized water until the powders were free from traces of acid, at room temperature. To inhibit oxidation, benzoic acid, as stabilizer, was added as additive (0.1%) to water for washing copper powders, to protect the powders against subsequent oxidation. This substance was removed by further washing [19].

Granulometry and morphology studies of powders were carried using three methods:

a) sieve analysis [20];

b) optical microscope transmission method, to produce the projections of powder particles;

c) scanning electron microscope.

The morphology of electrodeposited copper powders was examined using scanning electron microscope (SEM), PHILIPS, type XL30. Quantitative microstructural characterization of copper powders was performed by using of Zeiss Axiovert 25 optical microscope equipped with digital camera Panasonic WV-CD50 and software Leica QWin for automatic analysis of a picture.

3. RESULTS AND DISCUSSION

The photomicrographs of copper powder particles obtained in the constant current regime are given in Fig.1. It is obvious that increase in current density leads to a more disperse structure of the powder particles, as expected [12].

It has been shown that metal powder deposits can be obtained at current densities higher than limiting diffusion value [2,4,21,22]. In such cases deposition overpotential is determined by hydrogen co-deposition. Hence, the larger the difference between actual apparent density and the limiting diffusion current for copper deposition, the larger is the deposition overpotential. On the other hand, increasing overpotential leads to increased nucleation rate [23], as well as the number of sites suitable for instantaneous dendritic growth initiation [2]. The number of nucleation sites on the initial surface is obviously limited, while the nucleation on the growing grains can take place continuously. Assuming that powder grains and grain subparticles are the product of further dendritic growth on nuclei formed on the initial surface and the grains themselves, respectively, it is easy to explain the well known fact that powder particle grain size decreases with increasing current density [12,24] as well as the size of subparticles.

Dendritic morphology is a characteristic of all copper powders got at constant current density. Typical dendritic particles of copper powder are shown in Fig.2. Careful analysis of microphotographs shows that with increased current density the morphology of copper powder particles is changed from compact, massive dendrites (Fig.2a) and massive particles (designated in Fig.2b with number 1) to ramified 3D dendrites [25,26] (designated in Fig.2b with number 2) as well as in Figs. 2c and 2d.
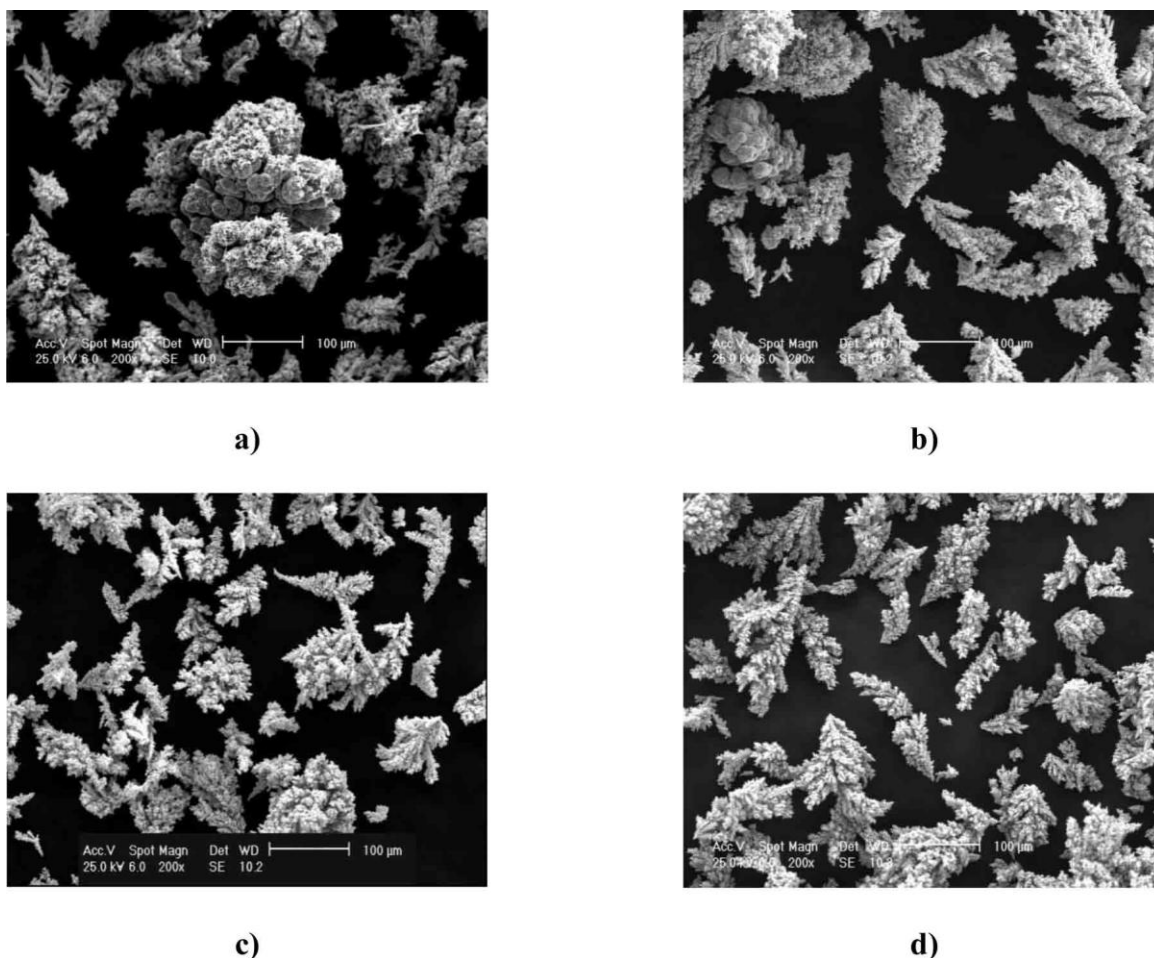
Figure 1. SEM photomicrographs of copper powder particles obtained in constant current deposition. Current density: j=7.71 Adm^{-2}; b) j=10.28 Adm^{-2}; c) j=30 Adm^{-2}; d) j=36 Adm^{-2}

In the powder samples which have been got at lower current density (j = 7.71 and 10.28 Adm^{-2}) were observed both dendrite types: massive dendrites with which the secondary dendritic branches are defined with the low-energy facets [27] as well as ramify 3D dendrite. With increased current density j=30 Adm^{-2} and j=36 Adm^{-2} massive dendrites despaired.

Further careful analysis of the surface morphologies of copper powder particles shown in Fig.3a-h indicated that with the increase of the current density the surface morphology is significantly changed.

At current density of j = 7.71 and j = 10.28 Adm^{-2} (Figs. 3a,b and 3c,d) are observed polycrystalline faces which are very rough, with a lot of unevennesses so there are ideal conditions for creation of new nucleuses and the crystal growth (mixed activation-diffusion control).

Some dendritic branches of massive dendrites are defined by the flat cubic {100} and octahedral {111} faces (Fig.3b). With increased current density the diffusion control share is also increased, at which particles become more dendritic, with a corn-like (Fig.3e,f) that is a fern-like structure (Fig.3g,h).

Most probably the tertiary branches ramify a long the cube edges respectively in [100] direction (Fig.3h).
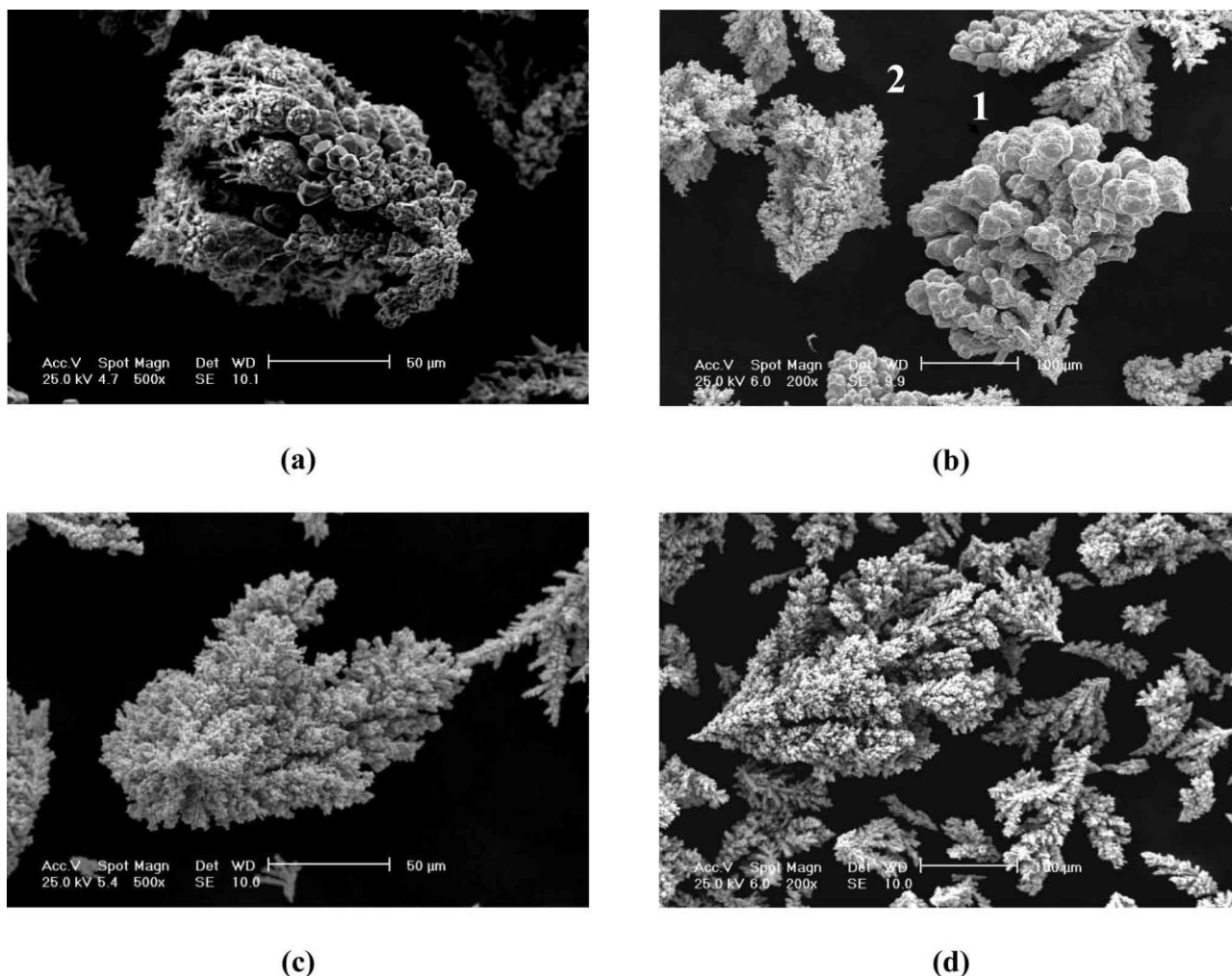
Figure 2. SEM photomicrographs of copper powder particles deposited at constant current density; a) j=7.71 Adm^{-2}; b) j=10.28 Adm^{-2}; c) j=30 Adm^{-2}; d) j=36 Adm^{-2}
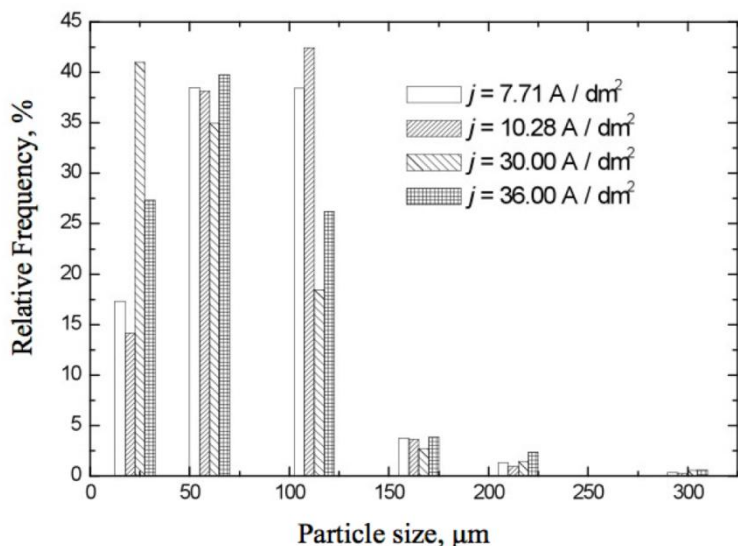
Typical particle-size distributions of copper powders obtained at four different current densities are shown in Fig.4a. It is observed from Fig.4b that the mean particle-size decreases with increasing of current density. The analysis of in this way obtained results shows that over 50% values are less than 50 µm and that the obtained mean values particle sizes based on cumulative curved distribution (at the point 50%) are within range 52.90 µm and 73.63 µm (Fig.4b). With increased current density the mean particle size decreases. Insignificant deviation with single samples can be explained with unreliability of sieve analysis at powder analysis of smaller granulation (below 50 µm) which is the case with the examined samples containing dendrites of small granulation.

As relevant parameters for describing copper powder particles using quantitative microscope analysis [30,31] were selected: area, perimeter and roundness (roundness is shape factor which unites the area and the perimeter as stereological parameters of structure).

During this analysis it was noticed that there were distinctly voluminous particles, especially at lower current density. It was assumed that such kinds of particles arose in conditions of deposition at the end of particle growth. At higher magnification (Fig.3) it is clear that at voluminous particles starts the development dendrite with of fine dendritic branches.
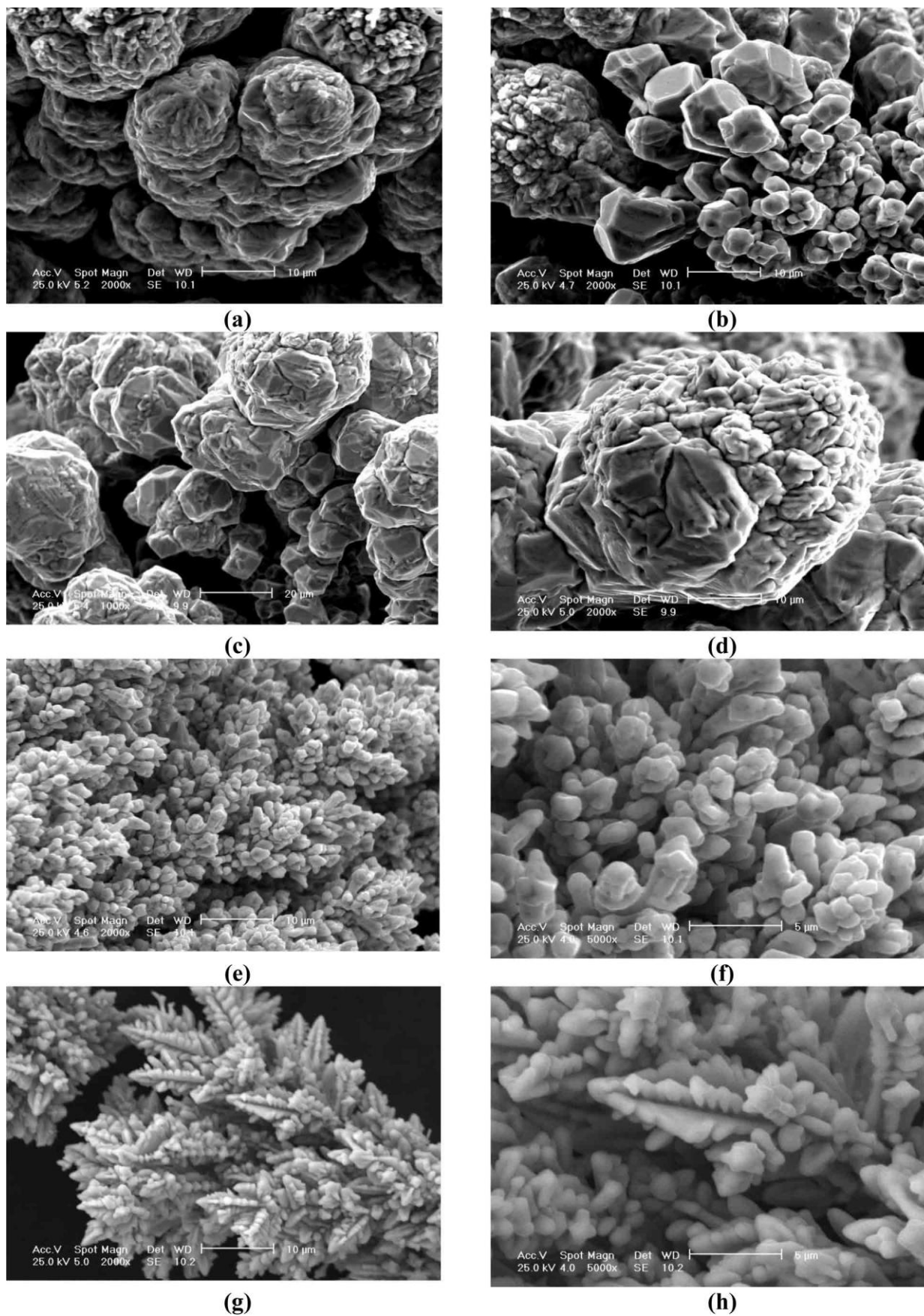
Figure 3. Surface morphology of copper powder particles; (a,b) j=7.71 Adm^{-2}; (c,d) j=10.28 Adm^{-2}; (e,f) j=30 Adm^{-2}; (g,h) j=36 Adm^{-2}
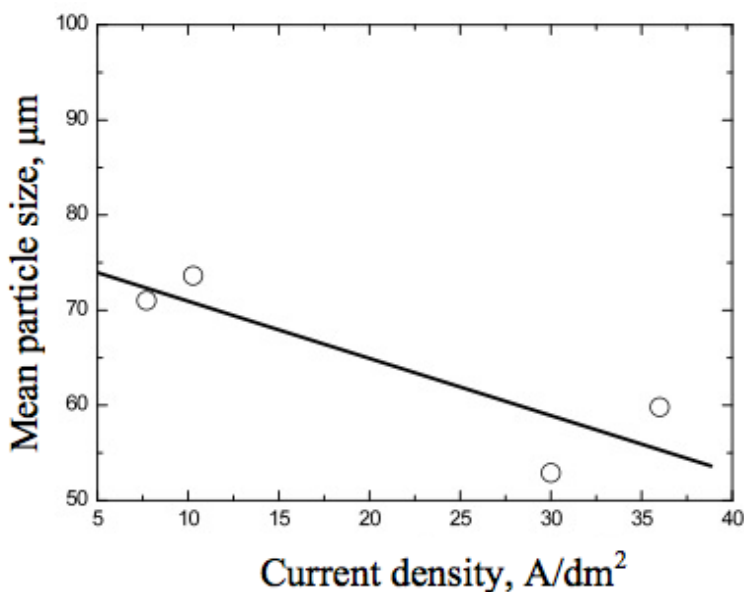
Figure 4. (a) Particle size distribution of copper powders deposited by galvanostatic regime. Histogram obtained by sieved analysis; (b) The effect of change current density on the value of mean particle size

The dependence of the total length of the particle boundary (perimeter), (Fig.5) and the particle area (Fig.6) shows the linear decreasing dependence of current density. The analysis of change of share factor shows the same dependence (Fig.7), with a deviation which appears with a sample of copper powder deposited at $j = 10.28$ Adm^{-2} (large fraction) [7]. In Table 1 are given the changes of values of the area, the perimeter and roundness with current density as well as the suitable RSE values.

Table 1. The change of stereological parameters and RSE (relative standard error of measurement) values as dependence of current density at galvanostatic regime

Current density [Adm^{-2}]	7.71	10.28	30	36
Roundness	2.66	2.08	2.18	1.92
RSE (%)	6.70	4.94	3.41	2.29
Perimeter, [µm]	220.13	166.55	113.13	84.19
RSE (%)	10.23	10.6	6.01	5.05
Area, [µm^2]	1638.55	1249.91	509.06	336.19
RSE (%)	14.76	14.89	7.98	8.26
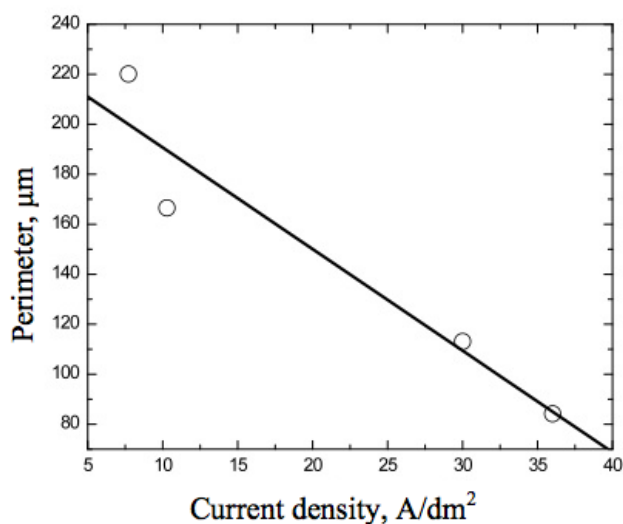
Figure 5. The effect of current density on the value of perimeter (galvanostatic regime)
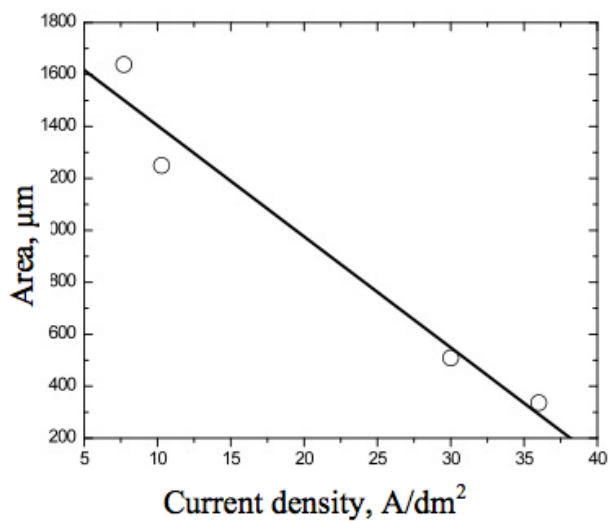
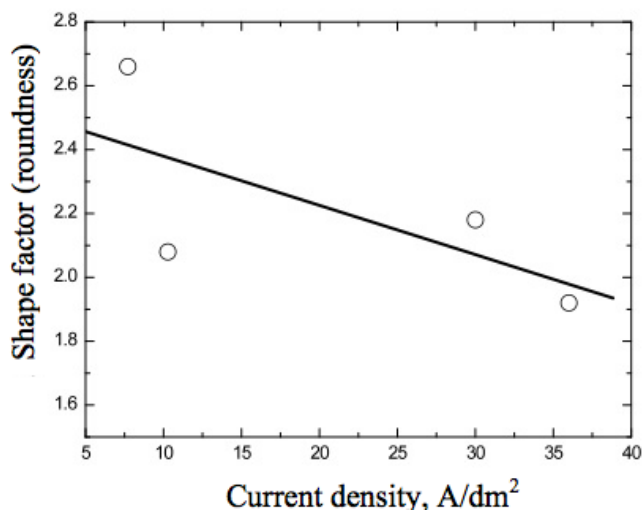**Figure 6.** The effect of current density on the value of area (galvanostatic regime)

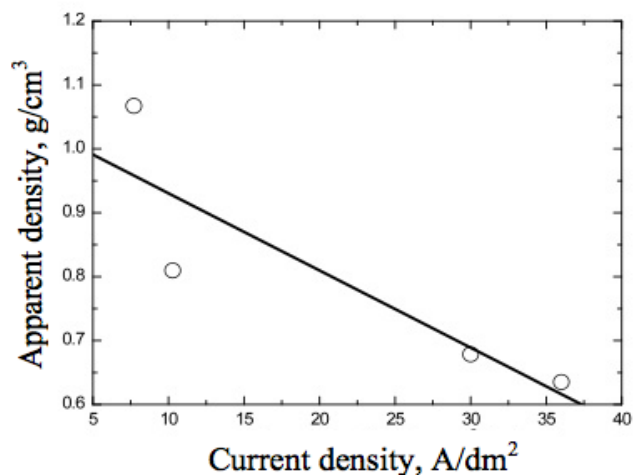**Figure 7.** The roundness as a function of current density (galvanostatic regime)

Figure 8. The apparent density as a function of current density (galvanostatic regime)
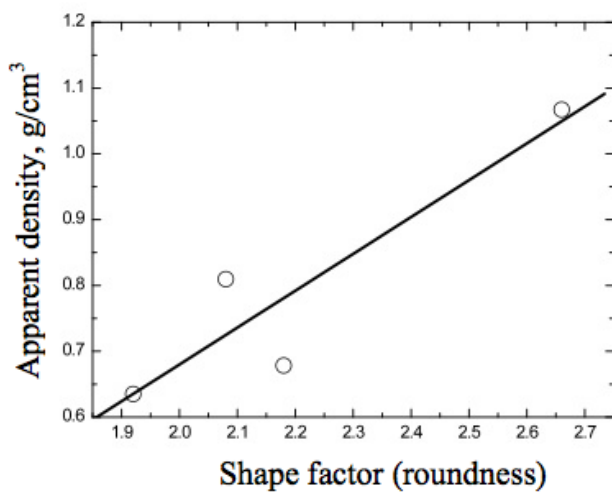

Figure 9. The roundness as a function of apparent density (galvanostatic regime)

Dominant lager fractions with samples $j = 7.71 \text{A/dm}^{-2}$ and $j = 10.28 \text{ Adm}^{-2}$ stipulate of high area values and high dissipation results. With the increase of current density, generally comes to the decrease of dendrites (low value of the selected shape factor) Fig.6. The deviation that appeared in the shown analysis can be the result of presence of dendrites of different morphology in the same sample. The shape factor – roundness is an especially useful parameter when comparing of powder morphology deposited at potentiostatical and galvanostatical regime is done [17], as well as in the reverse current regime. With the powder samples obtained in the conditions of reverse current, the values of the changes of values of perimeter and area do not follow the linear dependence, as it is case with powders obtained at constant current density [32]. The dependence of the apparent density, (Fig.8.) shows the linear decreasing dependence of current density while the apparent density increases with increase of the shape factor – roundness (Fig.9).

In the case of deposition of powder at constant current, the apparent current density remains constant, but the real current density decreases due to an increased surface of the electrode. This results in a decrease of overpotential of the deposition. A higher decrease of deposition overpotential means the formation of disperses deposition. With an increase of current density the process is carried out with enlarge diffusion difficulties: a large number of changes in copper powder characteristics appear and a large number of new crystallization centers is formed.

These factors influence an increase of powder particles dispersity and their more dendritic structure. It leads to reduction of particle size and apparent density and to enlargement of specific area [16].

It is known that the proportion of powder metal deposit in the total amount of deposit, as well as the size of the particles in the powder deposit can affect, on one hand, change in the composition of electrolyte, its temperature, viscosity and hydrodynamic regime, and on the other hand selection of deposition regimes (galvanostatic or potentiostatic). If the metal, instead of constant regime, is deposited at a periodically changing rate, new possibilities open up for adjustment of the size and morphology of particles, by varying the wave of periodically changing current or overpotential [1]. From a theoretical point of view of particular importance is pulsating overpotential regime, but for wider application in practice it is more convenient to use a reverse current of square-wave shape.

Induction time for dendritic growth initiation is equal to the transition time in galvanostatic deposition at current densities larger than limiting diffusuion current [21,22,28]. Doubtless, at very beginning of the deposition the dendrites are formed, leading to a strong increase in the real electrode surface area [25], and the real deposition current density and overpotential decrease rapidly [29]. At overpotentials lower than some critical value only compact metal is deposited onto the initial dendritic structure. Due to this the powder particles are not dendritic but corn-like.

The morphology of the copper powders formed with the increase in current density in the reversing current regime while keeping all other conditions unchanged, are shown in Fig. 10. It is seen from Figs. 3 and 10 that the microstructure of grains deposited by the reversing current (RC) and constant current (DC) are quite different. Even subparticles deposited by the almost same cathodic current density are different in the size and structure. Subparticles in the DC case are smaller and polycrystalline while in the RC case they are larger and characterized by defined crystal planes.
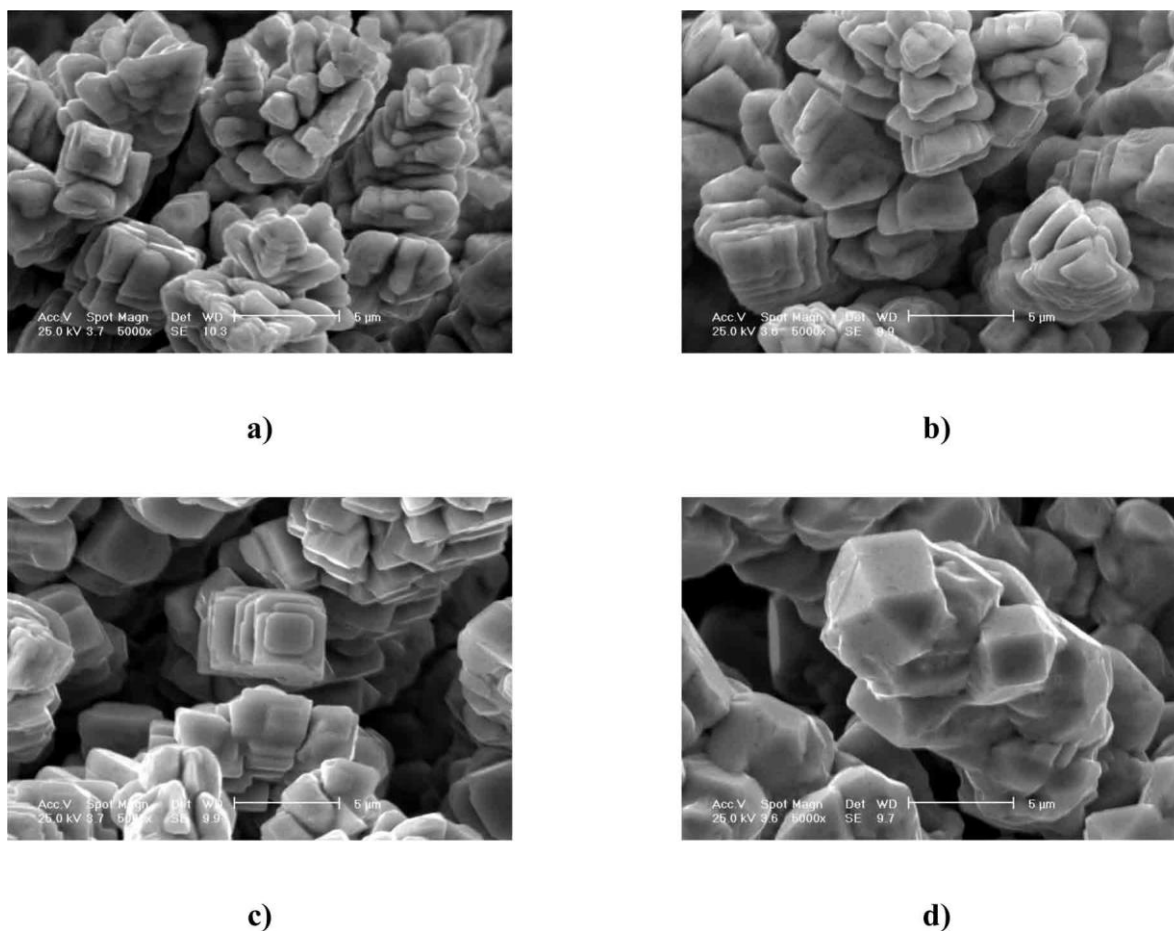
Figure 10. SEM photomicrographs of copper powder particles obtained by reversing currents. Cathodic-to-anodic time ratio 2.5. Cathodic pulse duration 1s. Anodic pulse duration 0.4s. Cathodic (anodic) amplitude current densities and average current densities: a) $j_c=j_a=18$ A/dm^2, $j_{av}=7.71$A/dm^2, b)) $j_c=j_a=24$ A/dm^2, $j_{av}=10.28$ A/dm^2, c) $j_c=j_a=30$ A/dm^2, $j_{av}=12.85$ A/dm^2 and d) $j_c=j_a=36$ A/dm^2, $j_{av}=15.42$ A/dm^2

It was shown [33] that the protrusions characterized by lower tip radii are dissolved faster during anodic pulses than those with larger ones because of the effect of tip radii on the reversible electrode potential [34]. During the DC deposition all the stable nuclei formed in the beginning grow during further deposition; under RC conditions many nuclei are dissolved during the anodic pulses making further growth possible at considerably lower growth sites. In this way an increase in the subparticle size in RC deposition can be expected compared to the DC case. Polycrystalline copper deposits are obtained at overpotentials lower than that critical for dendritic growth initiation but still in diffusion-controlled deposition [24,35]. Hence, this kind of deposit can be expected in prolonged deposition of powder particles because of the decrease in the overpotential, due to the increasing real surface area. In the RC case the anodic current density is activation controlled. It is known that the value of j_0 (exchange current density) strongly depends on the crystal orientation [36]. Being different from point to point on the electrode surface, and a selective dissolution takes place during the anodic pulses, producing deposits with defined crystal planes. A similar effect was observed in the deposition of copper by pulsating overpotential [37].
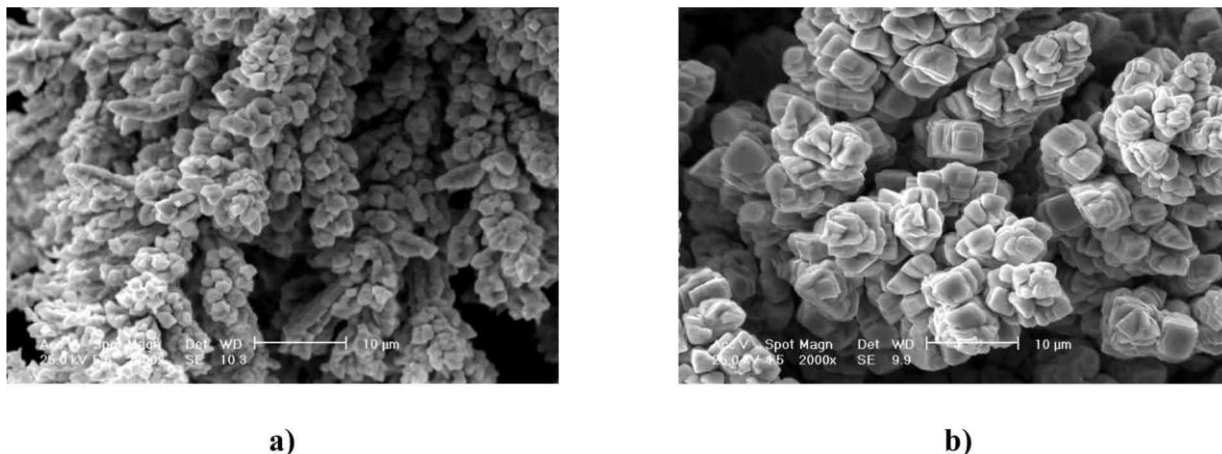
Figure 11. SEM photomicrographs of copper powder particles obtained by reversing currents. Cathodic-to-anodic time ratio 5. Cathodic (anodic) amplitude current density and average current density: a) $j_c=j_a=18$ A/dm^2, $j_{av}=12$ A/dm^2. Cathodic pulse duration: a) 10s and b) 0.5s

The effect of reversing current time period is illustrated by Fig.11. The net time of dendritic growth increases with the increase in the period of reversing current wave, leading to the more disperse deposit.

The decreased anodic current amplitude exhibits a strong effect on the structure of subgrains, i.e. decreasing anodic amplitude current permits formation of a more disperse structure of subgrains, as colud be expected from earlier discussion (from well defined crystal planes to polycrystalline ones, Figs. 10,11).

Typical particle-size distributions of copper powders particles obtained by reversing current are shown in Fig. 12. It was shown many times that the particles of electrodeposited powder are more compact and less branched if powder is obtained by pulsating overpotential or reversing current than in constant current electrolysis. This is explained by the selective dissolution of metal in different points of electrode surface during the anodic period. This means that the dissolution of a protrusion with tip radii is faster relative to the flat surface or a protrusion with a sufficiently large *r* which results in formation of more compact powder particles. On the other hand, increasing current density leads to the decrease of the mean powder particle size in constant current electrolysis (Fig. 4b). It can be seen from Fig. 13 that in the case of powder production with reversing current, the size of particles increases with increasing average current density. This can be explained in the following way. Nucleation does not occur simultaneously over the entire cathode surface but is a process extended in time, so that crystals generated earlier may be considerably larger in size than ones generated later. During anodic time, due to the faster dissolution of lower grains, the smaller nuclei formed during the cathodic pulse will be completely or partially dissolved during the anodic pulse and the current density on the smaller grains during the next cathodic pulse because of their more negative reverzible potentials and the growth of larger grains will be favorized [38]. Mean particle sizes obtained from cummulative distribution curves are in the range from 93.38 μm to 107.79 μm.
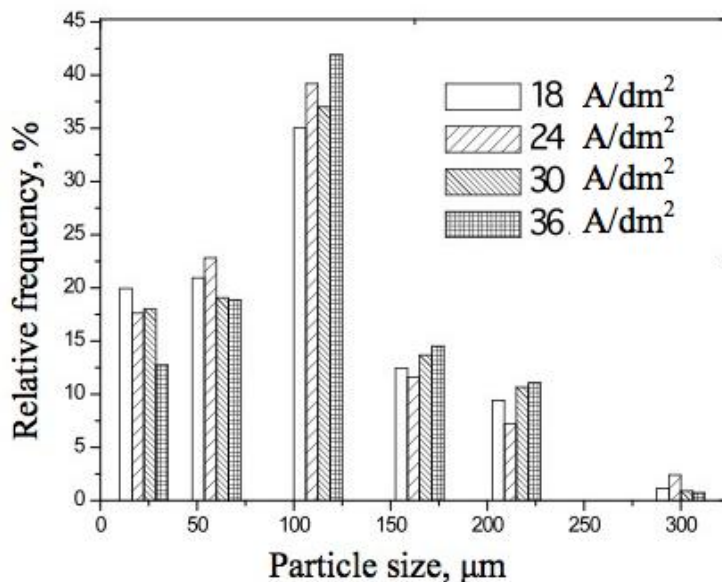
Figure 12. Particle size distribution of copper powder particles obtained by reversing currents (sieve analysis)
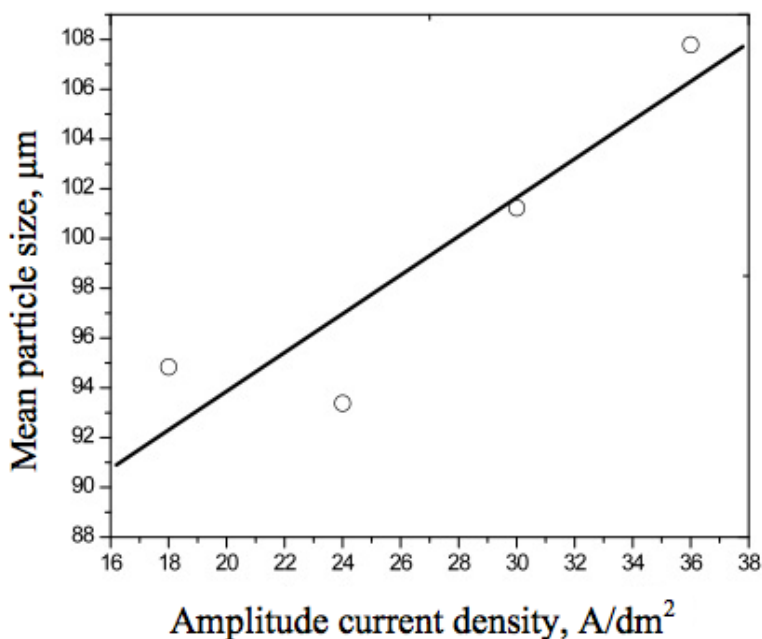
Figure 13. The effect of amplitude current density on the value of mean particle size (reversing current-sieve analysis)

Perimeter change and area do not follow linear pattern with powder samples obtained in reversing current regime, as it was the case in constant current density regime.

Based on the shape factor (roundness), morphology of the obtained dendrites can be described under reversing current regime, and compared to the copper powder particles obtained under constant current density regime (Figures 7 and 14).
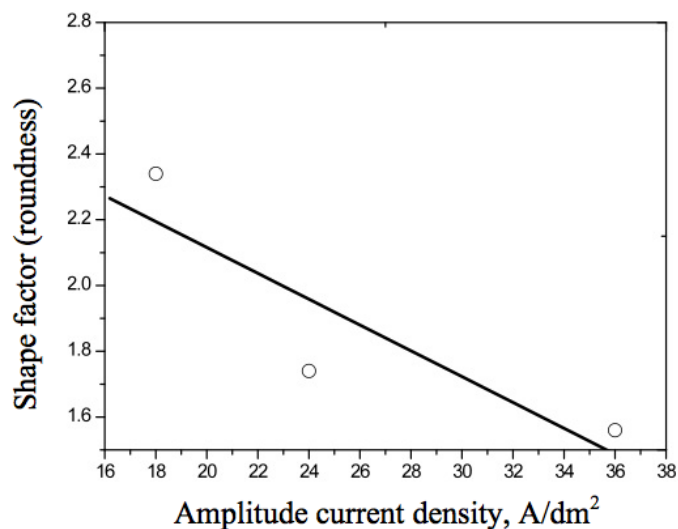
Figure 14. The roundness (a shape factor of area) of copper powder particles as a function of amplitude current density (reversing current)

Increase in current density leads to decrease in shape factor of copper powder particles obtained with constant current density and under reversing current regime. Lower values of shape factor that are characteristic for copper powders obtained by reversing electrolyse regime show that dendrites are less elongated.
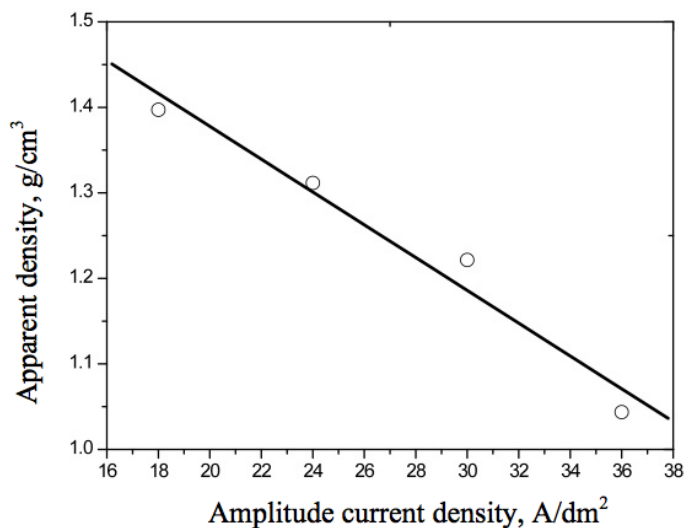
Figure 15. The apparent density of copper powder particles as a function of amplitude current density (reversing current)

Figure 15 shows dependance of apparent density from amplitude current density. As in the case of powder deposition by reversing current wave, there is significant effect of deposition regime on

particle structure in the direction of increase of particle density (compactness). This leads to increase of apparent density of copper powder, compared to galvanostatic regime (Figures 8 and 15).

4. CONCLUSIONS

The effect of various parameters in DC and RC conditions were investigated. The quantitative microstructural analysis of copper powder as well as the scanning electron microscopy analysis of the copper powders particles were performed. During the DC deposition, with the increase of current density the morphology of copper powder particles is changed from compact, massive dendrites to disperse dendrites with corn-like and fern-like surface ending. At the same time the mean particle size is decreased. All selected parameters are shown linear decreasing dependence of current density. In the RC case, the effects of the current amplitude, cathodic-to-anodic time ratio and period of the current wave are discussed. It is shown that the parameters determining the reversing current wave determine the micromorphology of the copper powder particles deposited. The shape factor – roundness could be useful parameter for describing of powder morphology.

References

1. K.I. Popov and M. D. Maksimović: in *Modern Aspects of Electrochemistry*, Theory of the Effects of Electrodeposition at a Periodically Changing Rate on the Morphology of Metal Deposits, B. E. Conway, J. O'M. Bockris and R. E. White, Eds., Plenum Press, New York, Vol. XIX, 1989, p.193
2. K.I. Popov and M.G. Pavlović in: *Modern Aspects of Electrochemistry*, Electrodeposition of Metal Powders with Controlled Particle Grain Size and Morphology, Vol. XXIV, R.W. White, J.O'M. Bockris, B.E. Conway (Eds.), Plenum Press, New York, 1973. p.299
3. R.M.German, *Powder Metallurgy Science*, 2nd ed., Metal Powder Industries Federation, Princeton, New Jersey, 1994, pp. 15-429
4. M.G. Pavlović and K.I. Popov,*Electrochem. Encyclopedia*, http://electrochem.cwru.edu/ed/encycl/, 2005
5. A.Despić and K.I.Popov: in *Modern Aspects of Electrochemistry*, Transport Controlled Deposition and Dissolution of Metals, in: B.E.Conway, J.O'M. Bockris (Eds.), Vol. VII, Plenum Press, New York, 1972. pp.199-313
6. N.D. Nikolić, Lj.J. Pavlović, M.G. Pavlović and K.I. Popov, *Powder Technol.*, 185 (2008) 195
7. V. Mikli, H. Käerdi, P. Kulu and M.Besterci, *Proc. Estonian Acad. Sci. Eng.,* 7 (2001) 22
8. Heon-Cheol Shin, Jian Dong and M. Liu, *Adv. Mat.* 15 (2003) 1610
9. N.D. Nikolić, K.I. Popov, Lj.J. Pavlović and M.G.Pavlović, *Sensors*, 7 (2007) 1
10. G.E. Dima, A.C.A. de Vooys and M.T.M. Koper, *J. Electroanal.Chem*. 554-555 (2003) 15
11. D. Pletcher and Z. Poorbedi, *Electrochim Acta,* 24 (1979) 1253

12. N. Ibl: in *Advances in Electrochemistry and Electrochemical Engineering*, The Formation of Powdered Metal Deposits, Vol. II, New York, 1962, p.50

13. A. Calusaru, Electrodeposition of Metal Powders, Elsevier, New York, 1979

14. K.I.Popov, M.G.Pavlović, J.N.Jovićević: Hydrometallurgy, 23 (1989) 127

15. P. Kulu, A. Tümanok, V. Mikli, H. Käerdi, I. Kohutek and M.Besterci, *Proc. Estonian Acad. Sci. Eng.* 4 (1998) 3

16. M.G. Pavlović, Lj.J. Pavlović, E.R. Ivanović, V. Radmilović and K.I. Popov, *J. Serb. Chem. Soc.* 66 (2001) 923

17. V.M. Maksimović, Lj.J. Pavlović, M.G. Pavlović, M.V. Tomić, *Journal of Metallurgy,* 15 (2009) 1

18. J. Xue, Q. Wu, Z. Wang, and S. Yi, *Hydrometallurgy* 82 (2006) 154

19. M.G. Pavlović, Lj.J. Pavlović, I.D. Doroslovački, N.D. Nikolić, *Hydrometallurgy*, 73 (2004) 155

20. ASTM B214-ISO 4497

21. O. Kudra, M.E. Lerner, *Ukrain. Khim. Zh.* 17 (1951) 890

22. K.I. Popov, M.G. Pavlović and M.D.Maksimović, *J.Appl.Electrochem*. 12 (1982) 525

23. I. Gucov, *Izv. Inst. Fizickochim. Bulg. Akad. Nauk*, 4 (1964) 69

24. M.G. Pavlović, K.I. Popov, G.Ž. Remović, V.P. Komnenić and Ž.V. Štrbački, *Hydrometallurgy*, 35 (1994) 267

25. G. Wranglen, *Electrochim. Acta,* 2 (1960) 130

26. V.M. Maksimović, M.G. Pavlović, Lj.J. Pavlović, M.V. Tomić and V.D. Jović, *Hydrometallurgy*, 86 (2007) 22

27. Y. Sun, Y. Xia, *Science*, 298 (2002) 2176

28. O. Kudra and E. Gitman, Elektroliticheskoe Poluchenie Metallicheskiekh Poroshkov, Iz. Akad. Nauk Ukr. SSR Kiev (1952), p.43

29. M.D. Maksimović, K.I. Popov, Lj.J. Jović and M.G. Pavlović, *Bull. Soc. Chim. Beograd*, 44 (1979) 547

30. R.T. De Hoff and F.N. Rhines, Quantitative Microscopy, Mac Graw Hill Bool Comp., New York, 1968

31. H. Modin and S. Modin, Metallurgical Microscopy, Butterworths, London, 1973

32. M.V. Tomić, V.M. Maksimović, Lj.J. Pavlović, M.G. Pavlović, K.I. Popov, M.J. Gligorićand V.D. Jović, *Zaštita materijala*, 47 (2006) 25, (in serbian language)

33. K.I. Popov, M.G. Pavlović and G.Ž. Remović, *J. Appl. Electrochem*. 21 (1991) 743

34. J.L. Barton and J.O'M. Bockris, *Proc. R. Soc. London Ser*. A268 (1972) 485

35. K.I. Popov, Lj.J. Pavlović, M.G. Pavlović and M.I. Čekerevac, *Surf. Coat. Technol.* 35 (1988) 39

36. A. Damjanović, *Plating,* 52 (1965) 1017

37. K.I. Popov, M.G. Pavlović, M.I. Čekerevac and G.Ž. Remović, *Surf. Coat. Technol.* 34 (1988) 355

38. K.I. Popov, S.S. Đokić, B.N. Grgur, Fundamental Aspects of Electrometallurgy, Kluwer Academic/plenum Publisher, N. York, 2002, p.158.