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CHARACTERIZATION OF COPPER POWDER PARTICLES OBTAINED BY ELECTRODEPOSITION

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Abstract

Technological properties of powders depend on their granulometry and particle morphology. Very often one method is inadequate for characterization of powder particles. This paper studied different methods intended for clear definition of copper powders granulometric and morphological properties. Changes of selected structure parameters and copper powder particle morphology galvanostatically deposited as a function on current density were investigated. It was determined that selected parameters such as area, perimeter and shape factor (roundness) showed linear decreasing dependence on current density, while the morphology was changed from massive to ramified 3D dendrites.

Key words: copper powder, electrodeposition, morphology, granulometry, sieve analysis

1. Introduction

Recently, powder metallurgy has rapidly grown, both in the variety of metal powders and in the quantity produced [1]. Almost all materials can be obtained as a powder, but the method selected for production of powder depends on the specific material properties. The main categories of fabrication techniques are based on mechanical commuting, chemical reaction, electrolytic deposition and liquid metal atomization [2].

The metal powder obtained by electrodeposition represents a disperse deposit**,** removed from electrode by tapping or in a similar way [3,4], which consists of particles of various forms and sizes. The electrolytic powder production method usually yields products of high purity, which can be easily pressed and sintered. In addition, it has been also shown that by different electrolytic regimes it is possible to obtain powders not only with a wide range of properties, but also to predict the decisive characteristics of powders which are important for powder quality and appropriate application [5,6].

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].

The granulometry of powders can be determined by different methods (sieve, image and laser analysis), but the adequate description of the powder granulometry by these methods remains still uncertain. However, some investigations showed [8] that the evaluation of coarse powder granulometry (particle size above than 50 μm) by means of sieve analysis yields sufficiently good results. Evaluation of the fine powder granulometry (with particle size less than 50 μm) is more difficult. According to these facts the results of the sieve analysis do not properly describe 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 important in addition to particles size. Image analysis proved to be helpful in describing the powder particle**.** The methods used to measure the powder particle size, also enabling the analysis of the particle size distribution, could be divided into two groups, i.e. direct and indirect. The direct methods map the geometry of individual particles via optical, scanning electron and transmission microscopy. Indirect methods such as sieve and laser analysis are based on physical properties of powders.

Stereological methods could be used for precise description of powders based on their planar images. Parameters measured at individual “objects” (projection of powder particle) such as area, perimeter and roundness, a shape factor which gives a minimum value of unity for a circle, are useful for powder characterization. These parameters may be calculated from the ratio of the perimeter square to the area, i.e:

$$f_{\mathrm{R}} = \frac{L_{\mathrm{p}}^{2}}{4\pi A \cdot 1.064} \tag{1}$$

where:
f_{R} – *roundness***,** shape factor which gives a minimum value of unity for a circle; A – *area***,** total number of detected pixels within the feature; L_{p} – *perimeter*, the total length of the boundary of the feature**,** calculated from the horizontal and vertical projections, with an allowance for the number of corners**.** The adjustment factor of 1.064 corrects the perimeter for the effect of the corners produced by the digitalization of the image [9].

Pure copper powders are widely used in the electrical and the electronic industries because of its excellent electrical and thermal conductivities. Pure copper powders may be obtained for these demands by electrodeposition [4,10].

Direct and indirect measurements of copper powder particles galvanostatically deposited were the object of this paper.

2. Experimental

Copper powders were galvanostatically deposited by applying various current densities: j = 7.71, 10.28, 30.00 and 36.00 Adm^{-2}. The experiments were performed in an enlarged laboratory reactor with a cell volume of 10 dm^{3}. The electrolytic copper powders were produced from electrolyte containing 145 gdm^{3} sulphuric acid and 18 gdm^{-3} copper, at an electrolyte temperature (50±2) °C. Details about the enlarged laboratory reactor are given in our previous paper [9].

The electrolyte was prepared from chemicals of technical purity and demineralized water. The wet powders were washed at room temperature several times with a large amount of demineralized water until they were free from traces of acid. To inhibit oxidation, benzoic acid (0.1%) as a stabilizer, was added to water for washing copper powders. This substance was removed by further washing [11].

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

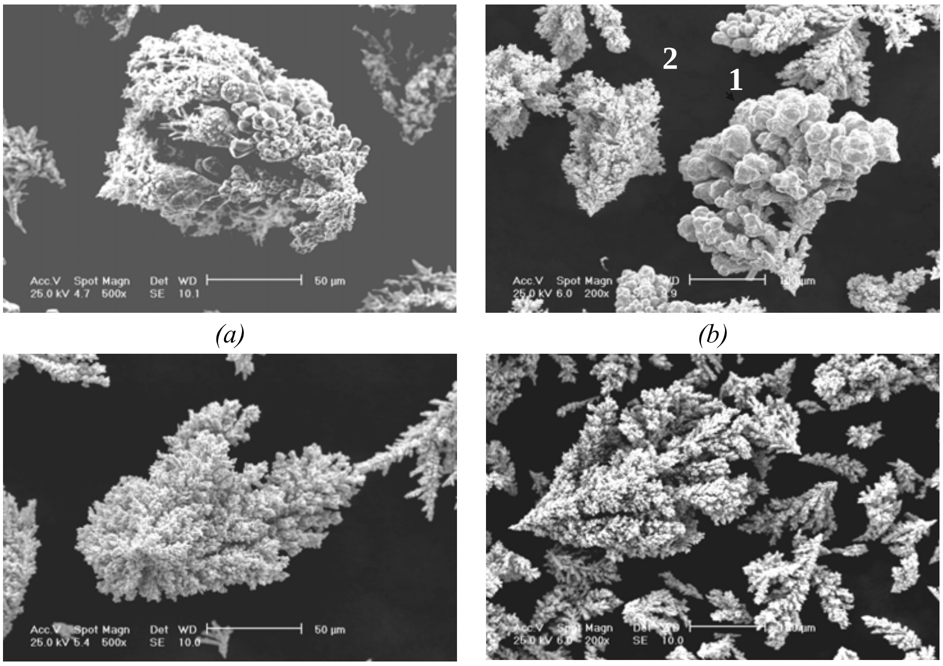
a) sieve analysis [12],
b) light microscope transmission method, to produce the projections of powder particles,
c) scanning electron microscope (SEM).

The morphology of electrodeposited copper powders was examined using SEM, PHILIPS, type XL30. Quantitative microstructural characterization of copper powders was performed using Zeiss Axiovert 25 light microscope equipped with digital camera Panasonic WV-CD50 and software Leica QWin for image analysis.

3. Results and discussion

Dendritic morphology is a characteristic of all copper powders obtained at constant current density. Typical dendritic particles of copper powder are shown in Fig.1. Careful analysis of microphotographs shows that with increased current density the morphology of copper powder particles is changed from compact, massive dendrites (Fig.1a) and massive particles (designated in Fig.1b with number 1)**,** to ramified 3D dendrites [13,14] (designated in Fig.1b with number 2) and Figs. 1c and d.

In the powder samples formed at lower current density (j = 7.71 and 10.28 Adm^{2}) both dendrite types were observed: massive dendrites with the secondary dendritic branches defined with the low-energy facets [15]**,** as well as ramified 3D dendrite. With increased current density j = 30.0 and 36.0Adm^{-2} massive dendrites disappeared.



(a) (b)

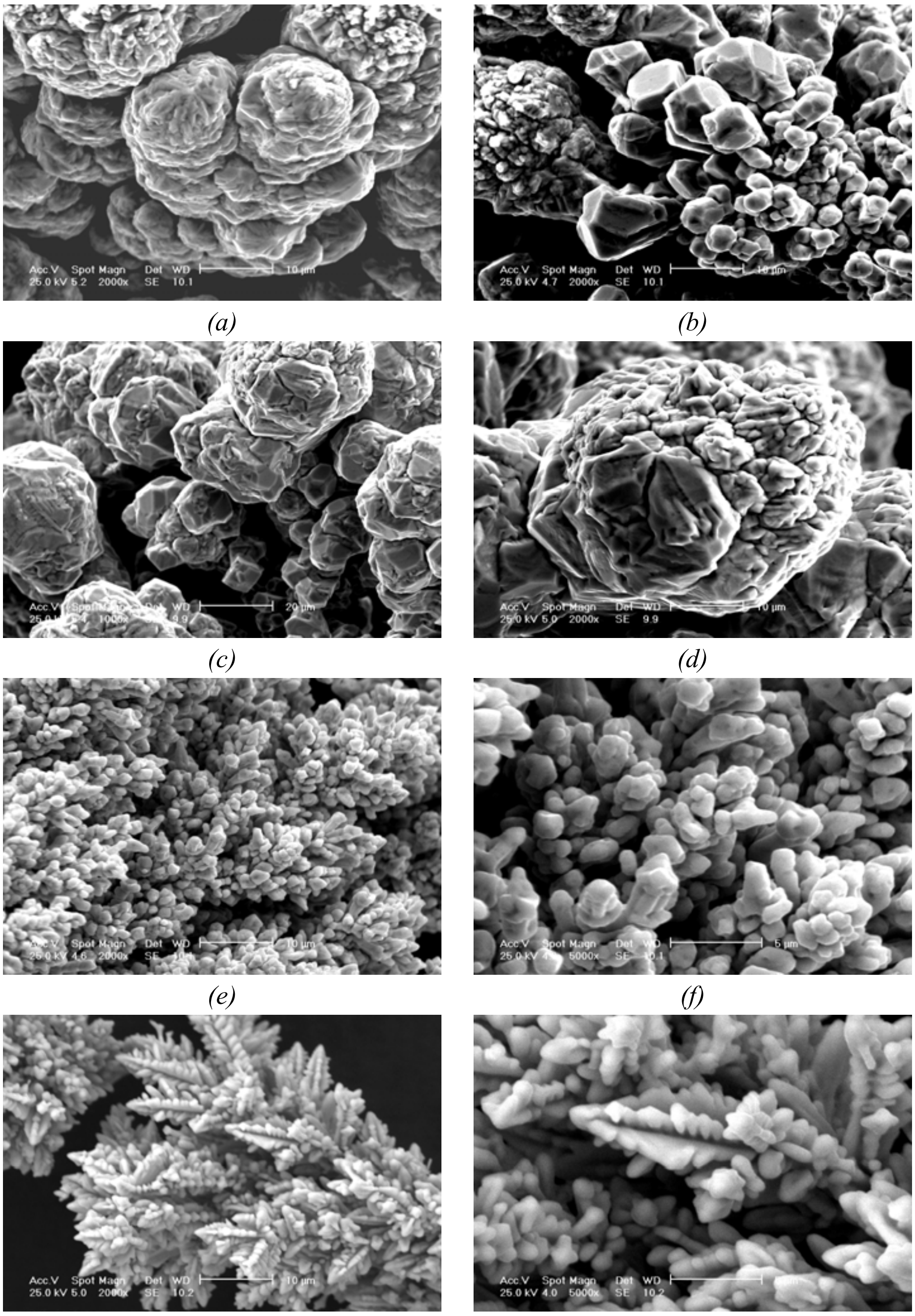
(c) (d)

Fig. 1. SEM microphotographs of copper powder particles deposited at current densities a) j = 7.71 Adm^{-2}; b) j = 10.28 Adm^{-2}; c) j = 30.0 Adm^{-2}; d) j = 36.0 Adm^{-2}

Further analysis of the surface morphologies (Fig.2a-h) indicated that with increase of the current density the surface morphology was significantly changed.

At current densities of *j* = 7.71 and *j* = 10.28 Adm^{-2} (Figs. 2a,b and 2c,d) very rough and jagged polycrystalline faces are observed which are ideal for creation of new nucleus sites 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.2b). With increased current density the possibility for diffusion control is increased and particles become more dendritic, acquiring a corn-like shape (Fig.2e,f) which belongs to a fern-like structure (Fig.2g,h). Most probably the tertiary branches ramify along the cube edges in [100] direction (Fig.2h).

Typical particle-size distribution of copper powders obtained at four different current densities is shown in Fig.3a. On the other side, from Fig.3b it may be seen that the mean particle-size decreases with increasing current density. The analysis of the presented results shows that over 50% of mean-particle values are less than 50 µm. Also, the values of mean-particle sizes based on cumulative curved distribution (at the point 50%) are within the range 52.90 and 73.63 µm (Fig.3b). Insignificant deviation with single samples containing dendrites of small granulation can be explained with unreliability of sieve analysis of smaller granulation (below 50 µm).



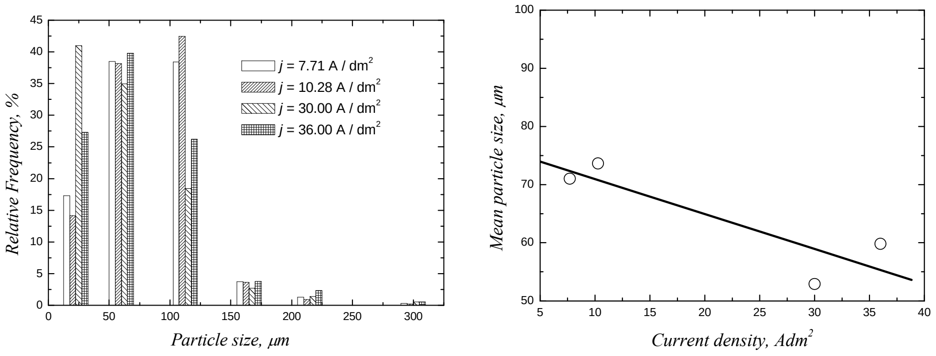
(a) *(b)*

(c) *(d)*

(e) *(f)*

(g) *(h)*

Fig. 2. Surface morphology of copper powder particles at different current densities (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}



(a) (b)

Fig. 3. (a) Particle size distribution of copper powders deposited by galvanostatic regime. Histogram obtained by sieved analysis; (b) the effect of current density change on value of mean particle size

Using quantitative microscope analysis the relevant parameters for describing copper powder particles [16-18] were selected: area, perimeter and roundness (roundness is a shape factor which unites the area and the perimeter as stereological parameters of structure).

Applying this analysis it was noticed that there were distinctly voluminous particles, especially at lower current density. It was assumed that such kind of particles was formed in conditions of deposition at the end of particle growth. At higher magnification (Fig.2) it is clear that the dendrite development with of fine dendritic branches starts at voluminous particles.

The dependence of the total length of the particle boundary (perimeter), (Fig.4) and the particle area (Fig.5a) shows the linear decreasing dependence on the current density. The analysis of change of share factor shows the same dependence (Fig.5b), with a deviation which appears with a sample of copper powder deposited at j = 10.28 Adm^{-2} (large fraction) [7]. The change of values of the area, the perimeter and roundness with current density as well as the suitable RSE (relative standard error of measurement) values are given in Table 1.

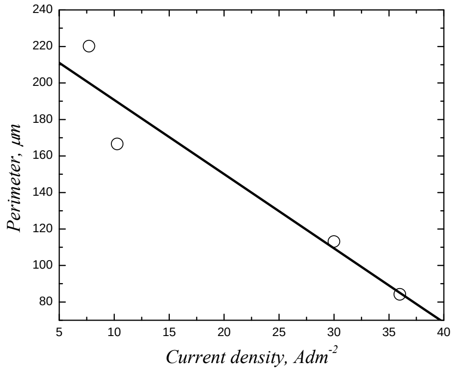
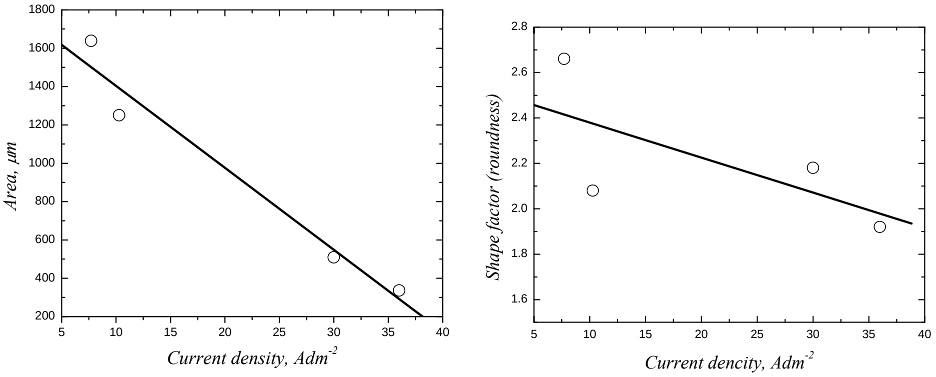


Fig. 4. The dependence of the perimeter on current density.



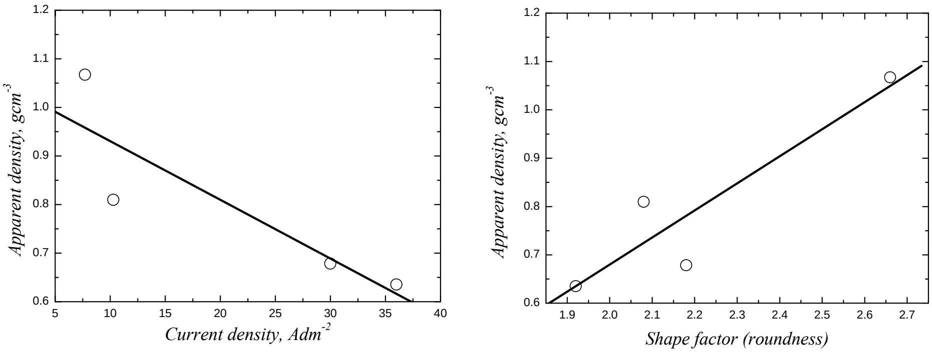
(a) *(b)*

Fig. 5. The dependence of (a) the area and (b) the roundness on current density.

Table 1. Change of values of the area, the perimeter and roundness with current density at galvanostatic regime, as well as the suitable RSE (relative standard error of measurement)

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	10.60	6.01	5.05
Area, (μm^2)	1638.55	1249.91	509.06	336.19
RSE, (%)	14.76	14.89	7.98	8.26

Dominant larger fractions with samples j =7.71A/dm^{-2} and j =10.28 Adm^{-2} determine high area values and high dissipation results. Generally, with the increase of current density the decrease of dendrites size occurs (low value of the selected shape factor) (Fig.5b). The deviation appearing in this analysis may be the result of presence of dendrites with different morphology in the same sample. The shape factor, i.e. roundness is especially useful parameter when comparing powder morphology deposited at potentiostatic and galvanostatic regimes and the reverse current regime [19]. With the powder samples obtained in the condition of reverse current, the changes of values of perimeter and area do not follow the linear dependence, as it was the case with powders obtained at constant current density [19]. The apparent density (Fig.6a) shows the linear decreasing dependence on current density, while the apparent density increases with increase of the shape factor (Fig.6b).



(a) *(b)*

Fig. 6. The dependence of the apparent density (a) on current density and (b) on the roundness.

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 overpotentional means the formation of disperse deposition. With an increase of current density the process is carried out with enlarged diffusion difficulties provoked by numerous changes in copper powder characteristics together with a large number of new crystallization centers formed. These factors influence an increase of powder particles dispersity yielding the structure closer to dendritic. The result is the reduction of both particle size and apparent density and enlargement of specific area [9].

4. Conclusion

The results of this paper showed that with increase of current density the morphology of copper powder particles was changed from compact and massive dendrites to disperse dendrites with corn-like and fern-like surface ending. At the same time the mean particle size was decreased. All selected parameters demonstrated a linear decreasing dependence on current density. The shape factor – roundness could be applied as a useful parameter for describing of powder morphology deposited at galvanostatic regime.

Acknowledgment

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