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Original scientific paper

The effect of the particle shape and structure on the flowability of electrolytic copper powder. III. A model of the surface of a representative particle of flowing copper powder electrodeposited by reversing current

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Abstract: The structure of the surface of copper powder particles is discussed and correlated with the lowest apparent density at which copper powder can still flow. It is shown that such structures can be easily obtained in the electrodeposition of powders in reversing current regimes.

Keywords: copper powder flowability, surface structure of particles of flowing copper powder.

INTRODUCTION

A model of the shape and surface structure of powder particles which permit the free flow of copper powder was developed in previous papers.[1–3] From this model, an apparent density of 2.2–2.3 g/cm^3 was determined as the lower limit for the free flow of copper powder, being in fair agreement with literature data.[4] On the other hand, powders obtained by reversing current electrodeposition can flow at considerably lower apparent densities. The aim of this work was to discuss this phenomenon.

EXPERIMENTAL

Experiments were performed as described in previous papers.[3,5,6]

RESULTS AND DISCUSSION

It was shown previously[2,3] that the flowability of copper powder is mainly determined by the structure of the surface of the powder particles. The effect of the particle shape is also important, but is probably not the decisive factor. If the surface structure of

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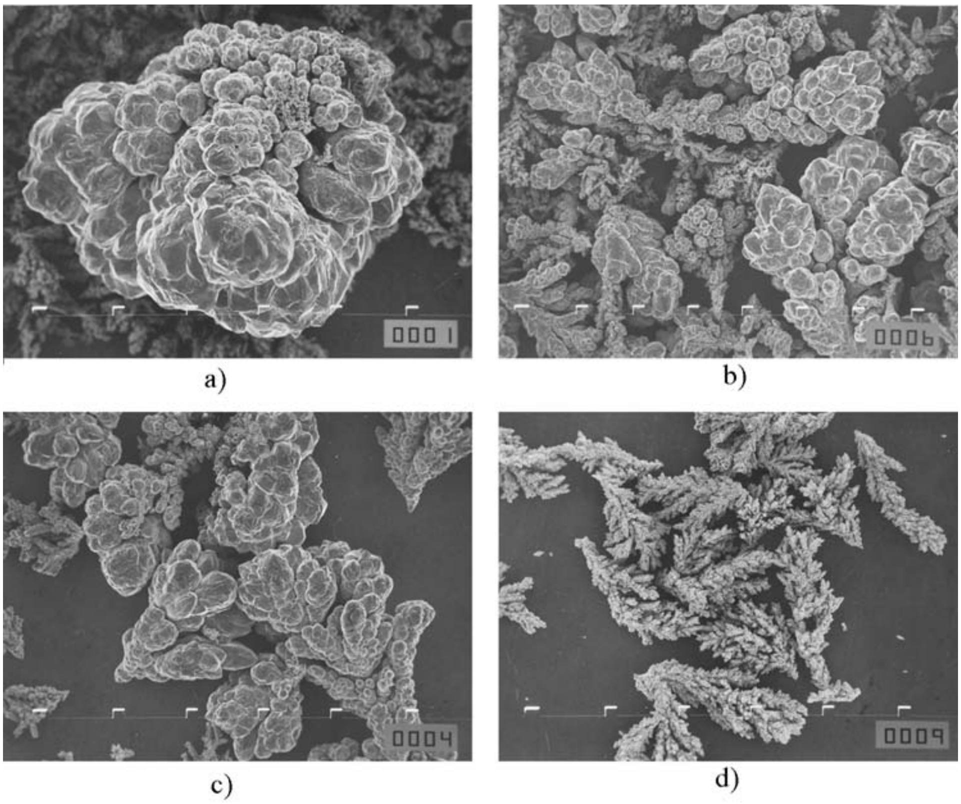
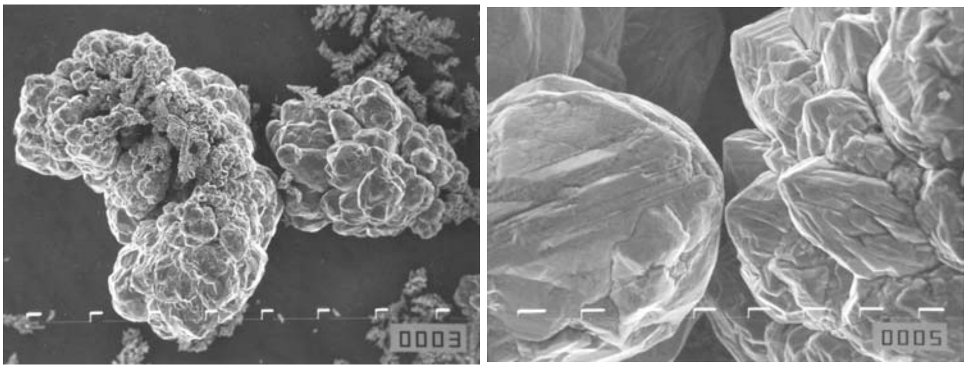


Fig. 1. SEM Photomicrographs of copper powder particles obtained by constant current deposition. $c(Cu^{2+})$ = 15 g/dm^3, $c(H_2SO_4)$ = 140 g/dm^3, electrolyte circulation rate 0.11 dm^3/min, t = 50±2 ºC, non-sieved powder, j = 1600 A/m^2, τ_r = 2.5 h, apparent density 2.3 g/cm^3, flow time 38.4 s a) × 200; b) × 150; c) × 200; d) × 200.

powders approaches the structure of the surface of bulk copper and if the shape of the particles approaches a sphere, the friction in the powder mass is low and the flow of the powder is efficient. Besides, in these cases, the particle size distribution will not have an effect on the flowability of the copper powder, so non-sieved powders exhibit free flow. The model of the representative powder particle developed in previous papers[2,3] requires contact between the subparticles of the copper powder particle and in that way the behavior of powders with large apparent densities characterized by free flow of non-sieved powder is explained, as is illustrated in Fig. 1 and Fig. 2. It can be seen from Fig. 1 that very different particles are obtained, which is in accordance with the fact that the powder under consideration was not sieved. Regardless of this, it consists mainly of particles like those shown in Fig. 1.a–c and Fig. 2, which are close to the model.[2,3] It can also be seen from Fig. 1 and Fig. 2 that jamming of the particles is not possible and that a non-sieved powder obtained at 1600 A/m^2 can flow because of the structure of the particles. This is in accordance with the fact that dendrites deposited at low overpotentials (current densities)[7–10] are less branched and more dense than ones obtained at higher overpotentials (current densities).



a) b)

Fig. 2. The same as in Fig. 1 but a) × 150; b) × 1500.

On the other hand, as powders with considerably lower apparent densities, obtained by electrodeposition with reversing current flow can flow freely, a new model of the surface structure of these particles which permits this flow should be developed. This can be done as follows. It is known that dendrites,[7–10] and hence powder particles, obtained at large current densities or overpotentials are very disperse, as can be seen from Fig. 3. Naturally, such a structure is characterized by low apparent density and permits jamming of the particles, as is illustrated in Fig. 4.

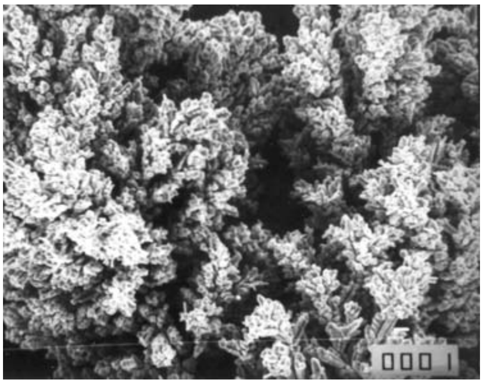


Fig. 3. SEM Photomicrographs of copper powder particles obtained by constant current deposition. $c(Cu^{2+})$ = 15 g/dm^3, $c(H_2SO_4)$ = 140 g/dm^3, electrolyte circulation rate 0.11 dm^3/min, t = 50 ± 2 ºC, fraction (149–177) µm, j = 3600 A/m^2, τ_r = 15 min, apparent density 0.524 g/cm^3, does not flow, × 1000.

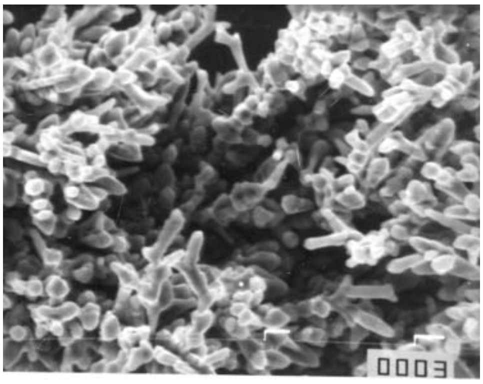


Fig. 4. The same as in Fig. 3, but × 3500.

This structure is presented schematically in Fig. 5 by the full line.

It is also known that in pulsating overpotential and reversing current electrodeposition of metals,[9–11] the parts of the metal surface characterized by a lower radius of curvature dissolve faster during the anodic period than the parts with a larger radius of curvature. In

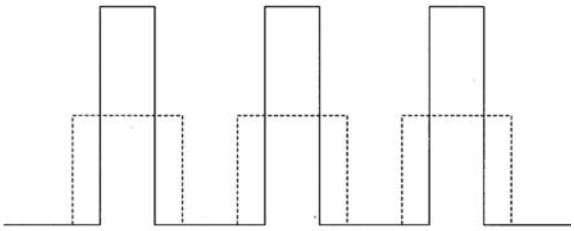
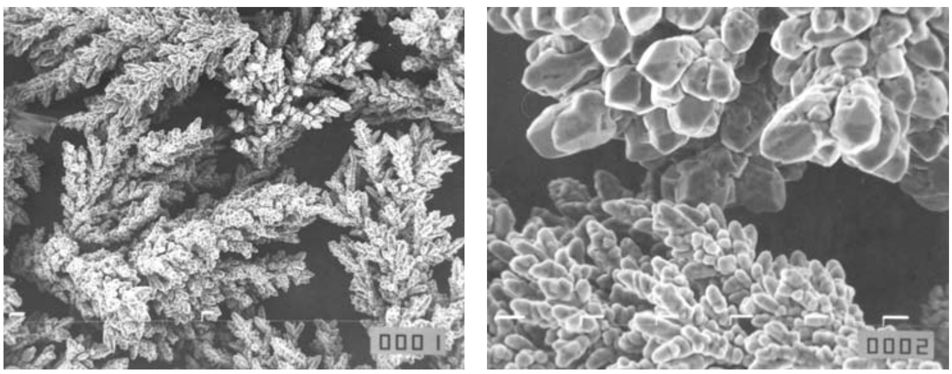


Fig. 5. Schematic presentation of the surface profile of powder particles. Full line obtained at constant current, dashed line obtained by reversing the current.

that way more compact structures are obtained, as is illustrated by the dashed line in Fig. 5, as well as in Fig. 6.

The powder obtained by reversing current, the particles of which are presented in Fig. 6a, flows regardless of the dendritic microstructure of the particles as can be seen in Fig. 6a. As a result of this structure, the appaent density of this powder is low. On the other hand, the surface structure, or microstructure, of the particles, shown in Fig. 6b, does not allow the jamming of the particles and, hence, powders with considerably lower apparent densities than the critical for powders formed by direct current electrodeposition, can flow. The micrstructure of the particles shown in Fig. 6b is similar to those shown in Fig. 1a-c. The critical apparent density for free flow of powder obtained in reversing current regimes can be estimated as follows. The top view of the surface, the cross section of which is snown in Fig. 5, is presented in Fig. 7. It is obvious from Fig. 7 that the surface characterized with full segments denoted by dashed lines cannot jam, while the one denoted by the full lines can jam together. Assuming uniform distribution and the square shape of the full segments, the elementary cell of such a surface is shown in Fig. 8a. The elementary cell consists of a square full segment with edge *a*, placed in the middle of a square empty segments with edge *b*. The distance between the edges of two full segments is *l*. The smallest value of *l* for which jamming of two surfaces both represented by the same elementary cell is not possible is obviously



a) b)

Fig. 6. The same as in the Fig. 1 but for reversing current deposition. Amplitude current density 3600 A/m^2, cathodic time 1 s, anodic time 0.2 s, τ_r = 15 min, apparent density 0.772 g/cm^3, flow time 100.2 s
a) × 1000; b) × 2000.

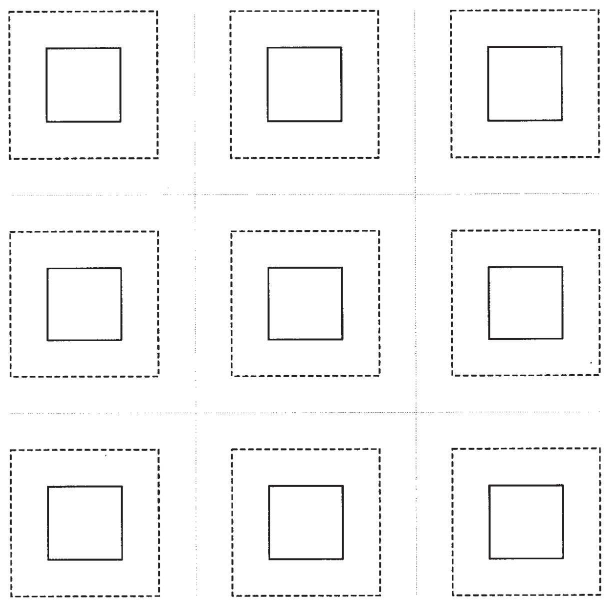


Fig. 7. The top view of the surface the cross section of which is presented in Fig. 5; full line – full segments in constant current regime, dashed line – full segments in reversing current regime, dotted line – empty segments.

$$l \leq a \tag{1}$$

and hence

$$b \leq 2a \tag{2}$$

as can be seen from Fig. 8b.

Assuming a spherical shape for the representative particle and $a \ll R$ and $b \ll R$, where R is the radius of the representative spherical particle, then the structure of the surface can be approximately presented by squares, as shown in Fig. 9. The full and empty segment can then be assumed to be the basis of pyramids with height R and edges a and b, respectively. Bearing in mind that the volume of each segment depends on the product of the base area of the segment and its height,[2] R it can be concluded that the ratio of the surfaces of segments with edge a and the surfaces of ones with edge b is equal to the ratio of the volume of full segments to the total volume of the representative particle.

Using the procedure described in a previous paper[1] one obtains

$$\rho'' = \frac{a^2}{b^2} \rho \tag{3}$$

and

$$\rho' = \frac{\pi}{6} \frac{a^2}{b^2} \rho \tag{4}$$

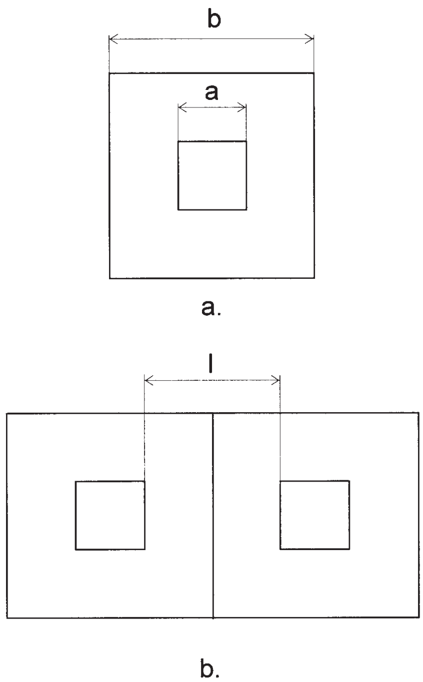


Fig. 8. a) The schematic presentation of an elementary cell of the surface from Fig. 7. *a* is the length of the empty segments. b) The mutual position of two elementary cells, *l* is the distance between the edges of the full segments.

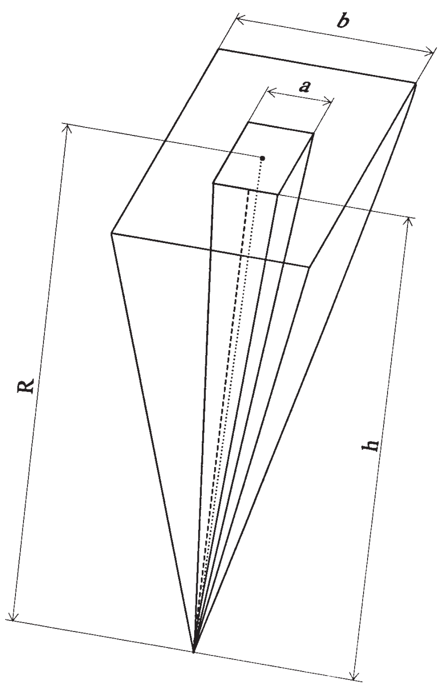


Fig. 9. The elementary cell of a powder particle the surface of which is shown in Fig. 8a. *R* is the radius of the particle and *h* is the height of a lateral side of a segment

Taking into account Eq. (2) the critical value for free flow can then be obtained as

$$\rho' \geq \frac{\pi}{24}\rho \tag{5}$$

where ρ is the density of bulk metal (8.9 g/cm^3), ρ' is the apparent density of the powder and ρ'' is the density of the representative spherical particle. Hence, free flow of copper powder can be expected at apparent densities larger than 1.16 g/cm^3. This model can also be valid for powders obtained by direct current and can be considered as being more general than the earlier one. Regardless of this, the structure of the surface cannot be determined by the ratio *a*/*b* only, the absolute values of *a* and *b* are also required for this purpose. They can be calculated in the following way.

It was shown recently[12] that

$$\frac{S}{V} = K \tag{6}$$

where *S* is the surface of a powder placed in a volume *V* and *K* can be considered as being

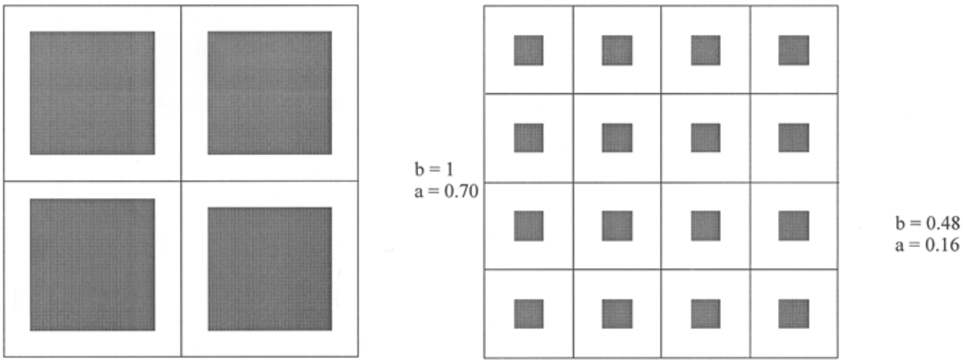


Fig. 10. The top view of the surfaces of powder particles. Apparent density a) 2.3 g/cm^3; b) 0.524 g/cm^3.

approxmately constant for electrolytic copper powders. Assuming that the ratio *S*/*V* calculated for one elementary cell is equal to the same ratio for the whole particle and taking the pyramidal shape of the elementary cell as illustrated by Fig. 9, one can write

$$S=\frac{4aR}{2}+a^2\approx 2aR \tag{8}$$

and

$$V=\frac{b^2R}{3} \tag{9}$$

if the surface of the base can be neglected and if

$$h\approx R \tag{10}$$

It follows from Eq. (6), Eq. (8) and Eq. (9) that

$$a=\frac{K}{6}b^2 \tag{11}$$

Substitution of *a* from Eq. (11) in Eq. (4) and further rearranging gives

$$\rho'=\frac{\pi}{216}\rho K^2b^2 \tag{12}$$

and

$$b=\left(\frac{216}{\pi}\right)^{1/2}\frac{1}{K}\left(\frac{\rho'}{\rho}\right)^{1/2} \tag{13}$$

Substitution of *b* from Eq. (13) in Eq. (11) gives

$$a=\frac{36}{\pi}\frac{1}{K}\frac{\rho'}{\rho} \tag{14}$$

and

$$\frac{a}{b}=\frac{2.45}{\pi^{1/2}}\left(\frac{\rho'}{\rho}\right)^{1/2}\approx 1.38\left(\frac{\rho'}{\rho}\right)^{1/2} \tag{15}$$

Using Eq. (13) – Eq. (15) and the apparent density of the powder, the structure of the particles can be calculated.

The surface structure of two powders with different apparent densities can be compared as follows.

Powder 1 obtained at 1600 A/m^2 is characterized by an apparent density $\rho_1' = 2.3$ g/cm^3. If $b = 1$ arbitrary units, a can be calculated using Eq. (15) and the density of bulk copper $\rho = 8.9$ g/cm^3, as $a = 0.70$. The fraction of (144 – 177) μm of powder 2, obtained at 3600 A/m^2 is characterized by an apparent density $\rho_2' = 0.524$ g/cm^3. If follows from Eq. (13) and Eq. (14) that

$$\frac{b_2}{b_1}=\left(\frac{\rho_{-2}'}{\rho_1'}\right)^{1/2} \tag{16}$$

and

$$\frac{a_2}{a_1}=\frac{\rho_2'}{\rho_1'} \tag{17}$$

and using the values of the corresponding apparent densities, it can be calculated that $b_2 = 0.48$ and $a_2 = 0.16$.

The strucures of both surfaces can be represented as shown in Fig. 10. It follows from the above calculations and condition 2 that powder 1 can and powder 2 cannot flow.

Assuming a homogeneous distribution of full and empty segments inside the powder particles, it can be concluded that the structure of the surface of a powder particle will be determined by the apparent density regardless of the shape of the particles. It is to be noted that this model, in some manner, takes into account the macrostructure as well as the microstructure of the particles and permits an estimation of flowability if the apparent density of a copper powder is known.

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ИЗВОД

УТИЦАЈ ОБЛИКА И СТРУКТУРЕ ЧЕСТИЦА НА ТЕЧЉИВОСТ ЕЛЕКТРОЛИТИЧКОГ БАКАРНОГ ПРАХА. III. МОДЕЛ ПОВРШИНЕ РЕПРЕЗЕНТАТИВНЕ ЧЕСТИЦЕ ТЕЧЉИВОГ БАКАРНОГ ПРАХА ДОБИЈЕНОГ ЕЛЕКТОХЕМИЈСКИМ ТАЛОЖЕЊЕМ РЕВЕРСНОМ СТРУЈОМ

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Разматрана је структура површине честица бакарног праха и корелисана с најмањом насипном масом при којој бакарни прах још увек може да тече. Показано је да се таква структура може лако добити електрохемијским таложењем праха у режиму реверсне струје.

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