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Original Scientific paper

The effect of the particle shape and structure on the flowability of electrolytic copper powder. IV. The internal structure of the powder particles

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Abstract: The structure of powder particles was analysed by considering their cross sections. It was shown that the structure of powder particles of nonsieved flowing powders is sufficiently dense to produce a continuous surface, which does not allow the particles to jam and hence permits the free flow of nonsieved powder. It was also shown that the representative powder particle, the elementary cell of which can be presented by a 3D-cross, describes the properties of the powder relative to its flowability well.

Keywords: copper powder flowability, nonsieved flowing powder, cross section of powder particles.

INTRODUCTION

It was pointed out in previous papers[1–4] that the free flow of a copper powder is possible if the surface structure of powder particles prevents them from jamming. The surfaces were analyzed using SEM microphotographs of the powder particles, but little attention was paid to their internal structure. The aim of this work was to analyse the internal and surface structures of powder particles by considering their cross sections and to correlate them with each other.

EXPERIMENTAL

The experiments were performed as described earlier.[3,5] The cross sections of the copper powder particles were determined as follows. Specimens of copper powder were connected by a cold mounting resin. Preparation of the metallographic specimen was performed using silicon carbide abrasive paper 320, 600 and 800. Nap cloths with 2 – 5 µm-diamond paste were used for the final polishing. Microstructural characterization of the copper powders was performed using a "Zeiss Axiovert 25" optical microscope.

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RESULTS AND DISCUSSION

The cross sections of powder particles of nonsieved copper powder obtained at 1600 A/m^2 are shown in Fig. 1. As expected, the particles are of very different sizes, but the internal structure is the same. In all cases the subparticles of the powder particles practically touch each other. This does not allow jamming of the different particles, regardless of their size, because the surface of the particles is rough and coarse, but continuous. The cross section of particles of fraction 149–177 μm of copper powder deposited at 1800 A/m^2 are presented in Fig. 2. By considering them, it can be concluded, that this fraction will flow, because jamming of the particles is not possible. On the other hand, the particles are porous and it is to be expected that nonsieved powder obtained under the same conditions would not flow, because the larger particles can be abridged by the smaller ones, as shown earlier.[3]

The same fraction of a powder obtained at 3600 A/m^2, as well as the nonsieved powder, will not flow due to the structure of the particles shown in Fig. 3, which permits jamming of the particles. It was shown in a previous paper[4] that a less dense surface structure, which does not allow jamming of the particles, is characterized by

$$b = 2a \tag{1}$$

where a is the size of a full segment and b of an empty one, as illustrated in Fig. 4. The corresponding apparent density can be taken as the critical density at which a powder becomes non-flowing. The determination of the critical apparent density at which a powder cannot flow is presented here in a simpler form than in a previous work.[4] Assuming that the elementary cell of the structure of the particles is as shown in Fig. 4, it is obvious that

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

where ρ and ρ'' are the densities of the bulk metal and the powder particles, respectively.

Bearing in mind that for a representative particle of spherical shape

$$\rho'' = 2\rho' \tag{3}$$

as shown previously,[1] where ρ' is the apparent density of the powder, it follows

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

It follows from Eqs. (1) and (4) that the critical apparent density for free flow of a copper powder is given by

$$\rho' \approx \frac{\rho}{8} \tag{5}$$

being about two-times lower than the critical value determined experimentally.[6] Regardless, the same fractions of powders can flow at apparent densities close to that from Eq. (5), as well as the same powders obtained by reversing current deposition. It is obvious that the critical value of the apparent density for the free flow of nonsieved powder, obtained by direct current deposition, is

$$\rho' = \frac{\rho}{4} \tag{6}$$

as obtained earlier,[1] being in accordance with literature data.[6]

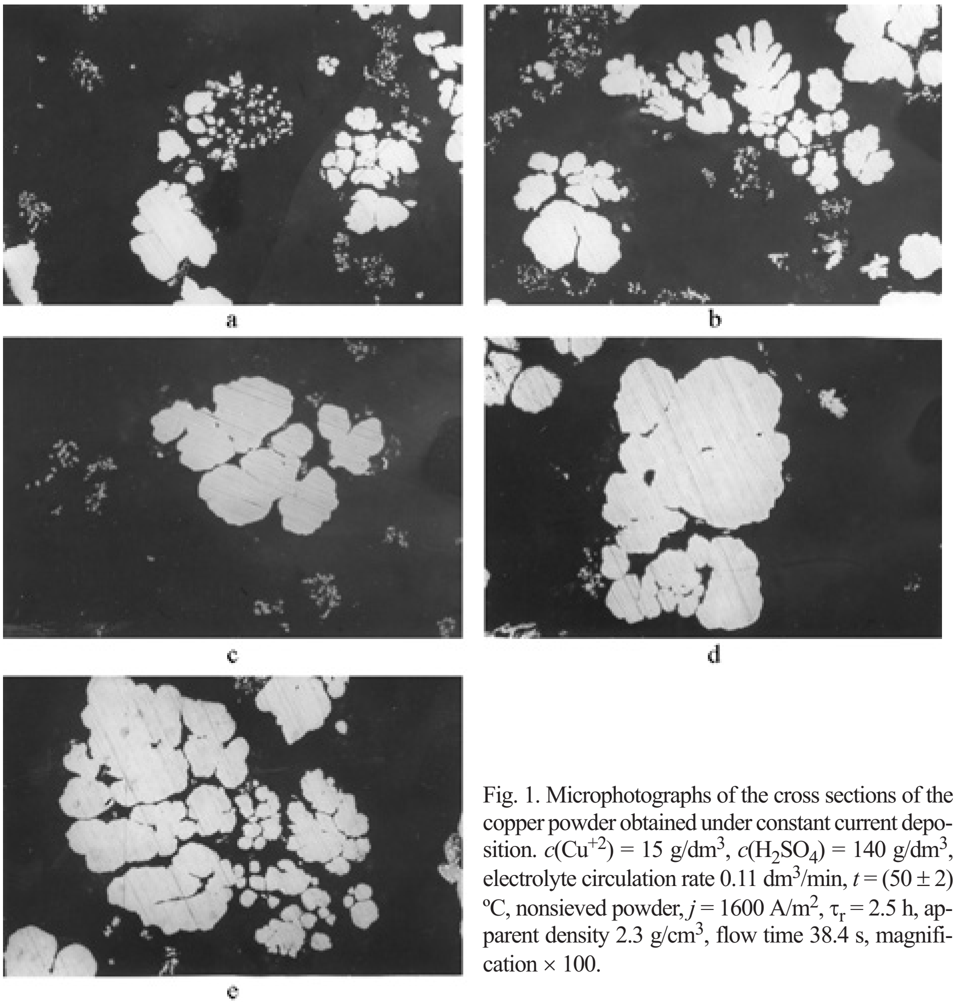

Fig. 1. Microphotographs of the cross sections of the copper powder obtained under constant current deposition. $c(Cu^{+2})$ = 15 g/dm^3, $c(H_2SO_4)$ = 140 g/dm^3, electrolyte circulation rate 0.11 dm^3/min, $t = (50 \pm 2)$ ºC, nonsieved powder, j = 1600 A/m^2, τ_r = 2.5 h, apparent density 2.3 g/cm^3, flow time 38.4 s, magnification × 100.

The surface structure of powder particles derived from the elementary cell from Fig. 4 does not allow jamming of the particles, but the corresponding critical apparent density is given by Eq. (5), meaning that the elementary cell from Fig. 4 does not represent the internal structure of the particles well. This is because it does not take into account the branching of the dendrites which form the copper powder particles. The structure of the surface of powder particles which does not allow jamming between them is schematically presented in Fig. 5.

It is obvious that the same particle surface can be formed by repeating the elementary cells from Fig. 4, as well as elemnentary cells like 3D-cross from Fig. 6, as described earlier.[7]

The density of each elementary cell like 3D-cross si given by

$$\rho" = \frac{G}{V} = \frac{\rho(6a^2h + a^3)}{b^3} \tag{7}$$

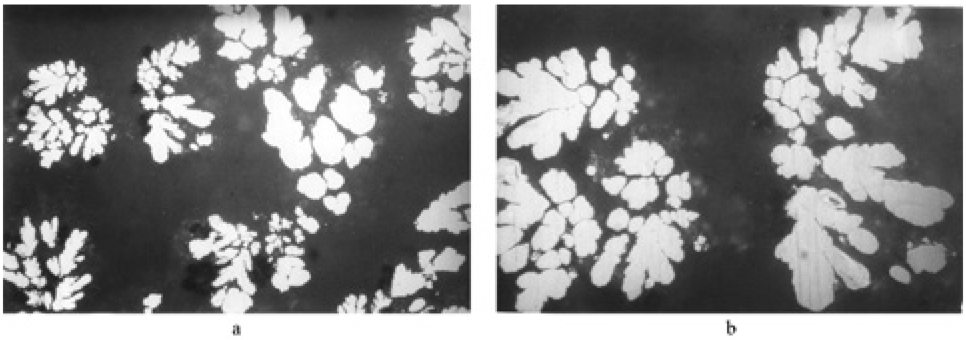

Fig. 2. Microphotographs of the cross sections of the copper powder obtained under constant current deposition. $c(Cu^{+2})$ = 15 g/dm^3, $c(H_2SO_4)$ = 140 g/dm^3, Q = 0.11 dm^3/min, t = (50 ± 2) ºC, fraction (149 – 177) μm, j = 1800 A/m^2, τ_r = 1.5 h, apparent density 1.122 g/cm^3. Apparent density of nonsieved powder 1.838 g/cm^3 a) ×100, b) × 270.

or, taking into account that

$$h = \frac{b-a}{2} \tag{8}$$

$$\rho'' = \rho\left(3\frac{a^2}{b^2} - 2\frac{a^3}{b^3}\right) \tag{9}$$

where G is the mass and V the volume of the elementary cell, assuming that the density of the powder particle is equal to the density of the elementary cell. It follows from Eqs. (1), (3) and (9) that the critical apparent density for the free flow of powders is given by Eq. (6), which is in a perfect agreement with experiments.

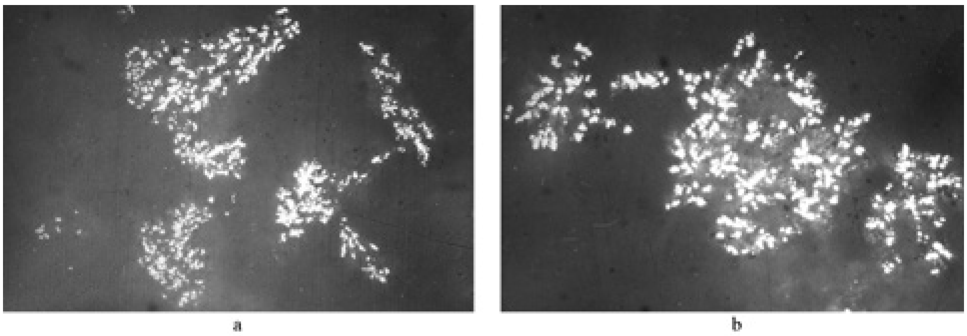

Fig. 3. Microphotographs of the cross sections of the copper powder obtained under constant current deposition. $c(Cu^{+2})$ = 15 g/dm^3, $c(H_2SO_4)$ = 140 g/dm^3, Q = 0.11 dm^3/min, t = (50 ± 2) ºC, fraction (149 – 177) μm, j = 3600 A/m^2, τ_r = 15 min, apparent density 0.524 g/cm^3. Apparent density of nonsieved powder 0.528 g/cm^3 a) × 100, b) × 270.

Hence, the representative powder particle which models the branching of the formed dendrites by a 3D-cross as the elementary cell, describes well the properties of copper

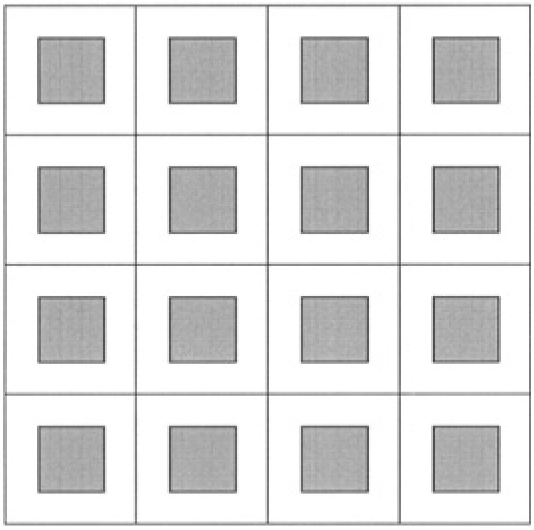

Fig. 4. Schematic presentations of the elementary cell of a powder particle a) cross section in the horizontal plane, b) cross section in the vertical plane.

powder relative to its flowability. Besides, taking into account that the secondary and tertiary dendrite arms are preferentially dissolved during the anodic pulses in the deposition of dendrites and powders by reversing current[8] changes the elementary cell of the repre-

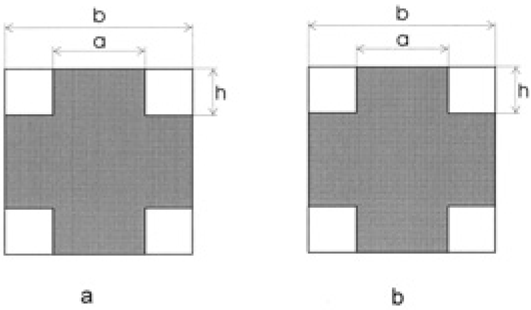

Fig. 5. Schematic presentation of the surface structure which does not allow the particles to jam.

sentative particle from that in Fig. 6 to that from Fig. 4, which explains why nonsieved copper powder obtained by reversing current deposition can flow at apparent densities close to those given by Eq. (5)

The structure of powder particles can be semiquantitatively estimated in the following way. The specific surface, S_{Sp}, of a 3D-cross is obviously

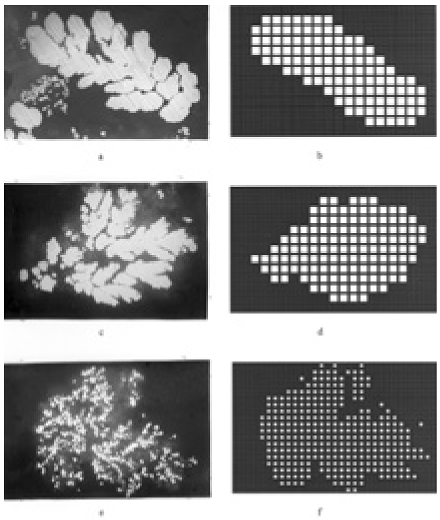

Fig. 6. Schematic presentations of the 3D-cross like elementary cell a) cross section in the horizontal plane, b) cross section in the vertical plane.

$$S_{Sp} = \frac{S}{G} \tag{10}$$

where S is the surface and G the mass of 3D-cross shaped particle. Obviously

$$S_{Sp} = \frac{24ah + 6a^2}{\rho(6a^2h + a^3)} \tag{11}$$

for single 3D-crosses, but

$$S_{Sp} = \frac{24ah}{\rho(6a^2h + a^3)} \tag{12}$$

for 3D-crosses inside the lattice of a powder particle. Substitution of h from Eq. (8) in to Eq. (12) and further rearranging results in

$$S_{Sp} = \frac{12b - 12a}{\rho(3ab - 2a^2)} \tag{13}$$

or

$$S_{Sp} = \frac{12b - 12kb}{\rho(3kb - 2k^2b^2)} = \frac{12(1-k)}{3k - 2k^2} \cdot \frac{1}{\rho b} \tag{14}$$

if

$$a = kb \tag{15}$$

The values of k for any ρ” (2ρ’) can be calculated from Eqs. (9) and (15) and further substitution into Eq. (14) permits the calculation of S_{Sp} as a function of ρ and b. For $k = 0.5$,

Fig. 7. Microphotographs of the cross-sections of powder particles obtained as described in the captions of the Figures (a, c, e) and the calculated cross sections (b, d, f). Magnification × 270. a) and b) Fig. 1; c) and d) Fig. 2; e) and f) Fig. 3.

for example, it can be written

$$S_{\mathrm{Sp}} = \frac{6}{\rho b} \tag{16}$$

Taking into account that

$$S_{Sp} = \frac{K}{\rho'} \tag{17}$$

is valid to a first approximation,[9] elimination of S_{Sp} from Eqs. (16) and (17) gives

$$b = \frac{6\rho'}{K\rho} \tag{18}$$

where $K \approx 1000\ cm^{-1}$. This is obviously the value for the representative powder particle, as well as $a = 0.5b$, from Eq. (15) for $k = 0.5$.

Assuming that all the particles of a powder are composed of the same elementary cells, the cross section of any particle can be simulated by repeating the elementary cells obtained by multiplying the values *a* and *b* with magnification of the photomicrographs. On the other hand, very different cross sections of powder particles can be obtained, depending on the position and angle, so some equivalent cross section should be defined. If it is assumed that inside an empty cube with edge *b* there is a cube of equivalent bulk metal with edge a_r, the mass of which is equal to the mass of the 3D-cross under metal with edge a_r, the mass of which is equal to the mass of the 3D-cross under consideration, a_r can be calculated from

$$a_r^3 \rho = b^3 \rho'' = 2b^3 \rho' \tag{19}$$

$$a_r = b\left(\frac{2\rho'}{\rho}\right)^{\frac{1}{3}} \tag{20}$$

where *b* is given by Eq. (18) and the equivalent cross section can be defined as one parallel to the basal plane. Using Eqs. (9), (15), (18) and (20) and appropriate values for ρ and ρ', it is possible to obtain the values of *a*, *b* and a_r. These values for powders for which ρ is 8.9 g/cm^3 and ρ' are 2.3, 1.838 and 0.528 g/cm^3 respectively, are calculated and given in Table I. These values under a magnification of 270 and also given in Table I.

TABLE I. Values of *a*, *b* and a_r for different apparent densities

$\rho'/(kg/cm^3)$	k	$\frac{12(1-k)}{3k-2k^2}$	b/cm	a/cm	a_r/cm	$b \times 270$/cm	$a_r \times 270$/cm
2.25	0.5	6.0	1.55×10^{-3}	0.78×10^{-3}	1.25×10^{-3}	0.42	0.34
1.838	0.442	7.16	1.48×10^{-3}	0.65×10^{-3}	1.10×10^{-3}	0.40	0.30
0.528	0.215	17.05	1.01×10^{-3}	0.22×10^{-3}	0.50×10^{-3}	0.27	0.13

It can be seen from Fig. 7 that the cross sections of experimentally obtained particles from Fig. 7a, 7c and 7e can be successfully simulated by Fig. 7b, 7d and 7f using the elementary cells calculated by the above procedure. This means that modeling of the representative particle allows a fair estimation of the internal, as well as the surface structure of the particles.

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ИЗВОД

УТИЦАЈ ОБЛИКА И СТРУКТУРЕ ЧЕСТИЦА НА ТЕЧЉИВОСТ ЕЛЕКТРОЛИТИЧКОГ БАКАРНОГ ПРАХА.IV. УНУТРАШЊА СТРУКТУРА ЧЕСТИЦА ПРАХА

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Анализирана је структура честица праха разматрањем њиховог попречног пресека. Показано је да је структура честица несејаног праха који тече довољно густа да образује континуалну површину, која не дозвољава заглављивање честица и самим тим омогућава слободно течење несејаних прахова. Такође је показано да репрезентативна честица праха, чија се елементарна ћелија може представити 3D-крстом, добро описује особине праха које се односе на течљивост.

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REFERENCES

1. K. I. Popov, S. B. Krstić, M. G. Pavlović, *J. Serb. Chem. Soc.* **68** (2003) 511
2. K. I. Popov, S. B. Krstić, M. Č. Obradović, M. G. Pavlović, Lj. J. Pavlović, E. R. Ivanović, *J. Serb. Chem. Soc.* **68** (2003) 771
3. K. I. Popov, M. G. Pavlović, Lj. J. Pavlović, E. R. Ivanović, S. B. Krstić, M. Č, Obradović, *J. Serb. Chem. Soc.* **68** (2003) 779
4. K. I. Popov, S. B. Krstić, M. Č. Obradović, M. G. Pavlović, Lj. J. Pavlović, E. R. Ivanović, *J. Serb. Chem. Soc.* **69** (2004) No 1
5. M. G. Pavlović, Lj. J. Pavlović, E. R. Ivanović, V. Radmilović, K. I. Popov, *J. Serb. Chem. Soc.* **66** (2001) 923
6. E. Peisseker, *Intern. J. Powder Metallurgy and Powder Technology* **20** (1984) 27
7. K. I. Popov, N. D. Nikolić, Z. Rakočević, *J. Serb. Chem. Soc.* **67** (2002) 861
8. K. I. Popov, E. R. Stoiljković, V. Radmilović, M. G. Pavlović, *Powder Technology* **93** (1997) 55
9. K. I. Popov, P. Živković, S. B. Krstić, *J. Serb. Chem. Soc.* **68** (2003) 903.