J.Serb.Chem.Soc. 67(12)861–866(2002) JSCS–3010 UDC 63–49.2–034.3:548.5 Original scientific paper

The respresentative particle of copper powder and branching of copper dendrites

K. I. POPOV^{1,*,#}, N. D. NIKOLIĆ² and Z. RAKOČEVIĆ³

¹Faculty of Technology and Metallurgy, Karnegijeva 4, P. O. Box 3503, YU-11001 Belgrade,
²ICTM - Institute of Electrochemistry, Njegoševa 12, P. O. Box 473, YU-11001 Belgrade and
³Vinča Institute of Nuclear Sciences, P. O. Box 522, YU-11001 Belgrade, Yugoslavia

(Received 22 July 2002)

Abstract: Electrochemically deposited copper powders, which are formed of particles of different size and morphology, are characterized by some properties like specific surface and apparent density. A procedure of the determination of a representative powder particle, exhibiting the same values of specific surface and apparent density as the powder is proposed. The proposed procedure also permints an explanation of the branching of copper dendrites.

Keywords: copper powder, copper particle, representative powder particle, dendritic branching.

INTRODUCTION

A copper powder represents a dendritic deposit which can spontaneously fall or can be removed from the electrode by tapping or in another similar way.¹

A copper powder is not formed of particles of identical size and morphology; the individual particles may assume various forms and have very different surface areas for the same average size of the granule.² As a result of this, it is not possible to relate the powder properties with the deposition process parameters and the deposition conditions, and, hence, a representative particle of the metal powder, having at least one property the same as the powder should be determined. Obviously, a powder can then be considered as a group of identical particles.

DISCUSSION

The representative powder particle can be defined as follows: The specific surface and the apparent density can be common properties of a metal powder and an individual powder particle. The specific surface of powder, S_{sp} , measured in cm² g⁻¹,² can be determined by the method available in the literature.³ On the other hand, the specific surface of an individual powder particle can be calculated from its known regular geometric form.

^{*} Corresponding author. Fax: +381 11 337 03 87. E-mail address: kosta@elab.tmf.bg.ac.yu.

[#] Serbian Chemical Society active member.

Hence, a representative powder particle is that one which is characterized by the same specific surface as a powder consisting of a mixture of different particles. The specific surface of a powder particle, $S_{sp,p}$, is given by:

$$S_{\rm sp,p} = \frac{S}{G} \tag{1}$$

where *S* and *G* are the surface and the mass of particle, respectively. For a cubic particle, the specific surface $S_{sp,cub}$ is then:

$$S_{\rm sp,cub} = \frac{6}{\rho a} \tag{2}$$

where ρ is the density of the metal and *a* is the height of the edge of the particle. The size, *a*_r of a representative metal powder particle can be determined by substitution of *S*_{sp} instead of *S*_{sp,cub} into Eq. (2), which after further rearrangement gives:

$$a_{\rm r} = \frac{6}{\rho S_{\rm sp}} \tag{3}$$

In this way the size of a cubic representative powder particle is related to the property of the powder which can be determined experimentally and even calculated, as was shown recently.^{4,5} The above discussion is valid if the representative particle is made of compact metal.

The apparent density or volumetric mass⁶ is also one of the most important properties of a metal powder.^{2,6} It is defined as the mass per unit volume of powder and can also be experimentally determined.⁷ Powder particles from the same size fraction of different powders occupy approximatelly the same volume, but the structure of the metallic copper can be considerably different with different apparent densities. Obviously, the more dendritic the powder particles are, the smaller is the apparent density of the copper powder.⁷

A representative particle of copper powder more realistic than a regular cube is shown in Fig. 1, and the cross section of it is shown in Fig. 2. The structure of this particle is like a 3D cross and the volume it occupies is the same as that of a cube with side 3a, as can be seen from Fig. 2.

Assuming complete symmetry, the surface areas, *S*, of such a particle is:

$$S = 30 a^2$$
 (4)

and the mass G is:

$$G = 7 a^3 \rho \tag{5}$$

The specific surface $S_{\text{sp,p}}$ is then given by:

$$S_{\rm sp,p} = \frac{30}{7\,\rho a} \tag{6}$$

COPPER POWDER





Fig. 1. A representative 3D cross - like particle of copper powder.

Fig. 2. The cross section of the particle from Fig. 1 and the cross section of the cube occupied by it.

and

$$a_{\rm r} = \frac{30}{7\,\rho S_{\rm sp}} \tag{7}$$

if

$$S_{\rm sp} = S_{\rm sp,p} \tag{8}$$

Hence, the larger the specific surface is, the lower is the size of the representative powder particle. This is in accordance with literature data.² Increased current density leads to the formation of a copper powder of smaller particle size and increased specific surface.



Fig. 3. An improved model of a representative powder particle.

The apparent density of such a particle is obviously:

$$\rho' = \rho \frac{7a^3}{27a^3} = \frac{7}{27}\rho$$

being independent of *a*. This is not in agreement with experimental data, because increasing the overpotential or current density of deposition leads to a decrease of the apparent density of the copper powder.² Hence, the proposed model of a representative particle is not operative and an improved version of it is shown in Figs. 3 and 4, or in Fig. 5 for the general case, where b = a/m and d = 2a/(m + 1) and *m* is the number of "branches" into which the initial one from Fig. 1 is divided, obviously b m + d(m + 1) = 3a.



Fig. 5. The cross section of a representative particle with branches into which the first one is divided. The surface of such particle is:

$$S = 30a^2 + 8(m-1)a^2 \tag{9}$$

whereby the mass of it is still given by Eq. (5). Hence, the specific surface $S_{sp,p}$ is:

$$S_{\rm sp,p} = \frac{[30 + 8(m-1)a^2]}{7\rho a^3}$$
(10)

COPPER POWDER

or after rearanging:

$$S_{\rm sp,p} = \frac{22 + 8m}{7\rho a} \tag{11}$$

On the other hand, the whole volume, V, of one particle, given by:

$$V = 27 a^3$$
 (12)

can be treated as being made of some homogenous material the density, ρ' , of which is equal to the apparent density of the powder. The specific surface of such a particle, $S'_{sp,p}$ is

$$S'_{\rm sp,p} = \frac{6(3a)^2}{\rho'(3a)^3} = \frac{2}{\rho'a}$$
(13)

If

$$S_{\rm sp,p} = S'_{\rm sp,p} \tag{14}$$

it follows from Eqs. (11) and (13) that

$$m = \frac{1}{8} (14 \frac{\rho}{\rho'} - 22) \tag{15}$$

which is valid for $\rho' < 0.6 \rho$, and is hence valid for dendritic copper powders. The size and structure of the representative powder particle can then be determined by using Eqs. (11) and (15) and the experimental values of S_{sp} and ρ' . Assumming that

$$A = 3a \tag{16}$$

Eq. (13) can be rewritten in the form

$$A_{\rm r} = \frac{6}{S'\rho'} \tag{17}$$

where A_r is the dimension of a representative particle, and the above discussion can be verified in the following way. According to Peissker,⁵ a copper powder characterized by $\rho' = 2.40 \text{ g/cm}^3$ and $S_{sp,p} = 300 \text{ cm}^2/\text{g}$ consist of 94 % particles + 0.080 mm.

Hence, the representative particle of such powder, calculated using Eq. (13) and the above data, is $A_r = 0.083$ mm which is in accordance with the sieve analysis. On the other hand,⁵ a copper powder characterized by $\rho' = 1.00$ g/cm³ and $S_{sp} = 1800$ g/cm³ consist of 95 % particles – 0.040 mm, and A_p as calculated in the previous case, is 0.033 mm.

It is shown in this way that the size representative powder particles can be succesfully estimated from the values of the specific surface and apparent density using the above procedure. The morphology of such particles can be estimated in the following way: m, the number of branches into which the initial one from Fig. 1 is divided can be calculated using Eq. (14) and the data of the apparent densities. For the first powder under consideration (S_{sp}

865

= 300 cm²/g, ρ = 2.40 g/cm³ and A_r = 0.083 mm), $m \approx 4$ and for the second one (S_{sp} = 1800 cm²/g, ρ = 1.00 g/cm³ and A_r = 0.033 mm), $m \approx 15$. As expected, the particles of the first powder are larger and less dendritic, while the ones of the other one are smaller and more dendritic which is accordance with the real situation⁶ regardless of the fact that the calculated representative particles cannot be directly compared to the photographed ones, because they represent the physical equivalent of the set of different real particles.

On the other hand, the precursor of dendrites similar to the particles from Fig. 5 can be obtained during copper electrodeposition.⁸ Hence, it can be concluded that consideration of dendrite branching, a completely unsolved problem,⁹ is also initiated in this paper. Further investigations in this direction are necessery.

Acknowledgements: This work was supported by the Ministry of Sciences, Technology and Development of Republic Serbia under research projects "Electrodeposition of Metal Powders at a Constant and a Periodically Changing Rate" (1806/2002) and "Surface Science and Thin Films" (2018/2002).

ИЗВОД

РЕПРЕЗЕНТАТИВНА ЧЕСТИЦА БАКАРНОГ ПРАХА И ГРАНАЊЕ ДЕНДРИТА БАКРА

К. И. ПОПОВ 1, Н. Д. НИКОЛИЋ 2 и З. РАКОЧЕВИЋ 3

¹ Технолошко-мейіалуршки факулійсій, Универзийсій у Београду, Карнегијева 4, й. йр. 3503, 11001 Београд, ² ИХТМ-Ценйар за елекійрохемију, Његошева 12, й. йр. 473, 11001 Београд и ³ Инсійшйуй за нуклеарне науке Винча, й. йр. 522, 11001 Београд

Електрохемијски исталожени прахови бакра се формирају од честица различитих димензија и морфологије су окарактерисани неким особинама као што су специфична површина и привидна густина (насипна маса). Предложен је поступак одређивања репрезентативне честице праха, која има исте вредности специфичне површине и привидне густине као прах. Предложен поступак такође омогућује објашњење гранања дендрита бакра.

(Примљено 22. јула 2002)

REFERENCES

- K. I. Popov, S. S. Djokić, B. N. Grgur, Fundamental Aspects of Electrometallurgy, Kluwer Academic/Plenum Publisher, New York, 2002, p. 89
- 2. A. Calusaru, Electrodeposition of Metal Powders, Elsevier, Amsterdam-Oxford-New York, 1979, p. 296
- W. Schatt, K. P. Wierters, *Powder Metallurgy Processing and Materials*, European Powder Metallurgy Association, Technical University Dresden, Germany, 1997, p. 8
- 4. K. I. Popov, N. D. Nikolić, Z. Rakočević, J. Serb. Chem. Soc. 67 (2002) No. 8-9
- 5. K. I. Popov, N. D. Nikolić, Z. Rakočević, J. Serb. Chem. Soc. (submitted)
- 6. E. Peissker, J. Powder Metallurgy and Powder Technology 20 (1984) 27
- 7. M. G. Pavlović, Lj. J. Pavlović, E. R. Ivanović, V. Radmilović, K. I. Popov, J. Serb. Chem. Soc. 66 (2001) 923
- 8. K. I. Popov, V. Radmilović, B. N. Grgur, M. G. Pavlović, J. Serb. Chem. Soc. 59 (1994) 119
- K. I. Popov, N. V. Krstajić, M. I. Čekerevac, "The Mechanism of Formation of Coarse and Disperse Electrodeposits", in *Modern Aspects of Electrochemistry*, Vol. 30, R. E. White, B. E. Conway and J. O'. M. Bockris, Eds., Plenum Press, New York, 1996, p. 311.