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SHORT COMMUNICATION

The effect of the pause-to-pulse ratio on the morphology of metal powder particles electrodeposited by square-wave pulsating overpotential

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Notation

C	concentration
C_0	bulk concentration
D	diffusion coefficient
F	Faraday constant
h	height of protrusion
h_0	initial height of the protrusion
j	current density
j_{av}	average current density
j_{L}	limiting current density
j_{d}	current density on the tip of a dendrite of height h
$j_{\mathrm{d,av}}$	average j_{d}
j_0	exchange current density
m	integer
p	pause-to-pulse ratio
R	gas constant
r	dendrite tip radius
T	temperature
T_p	period
t	time
V	molar volume
x	co-ordinate in the horizontal direction
z	number of electrons

Greek symbols

β	symmetry factor
δ	thickness of diffusion layer
η	overpotential
η_{A}	amplitude overpotential
$2.3\eta_{0,\mathrm{c}}$	slope of cathodic Tafel line
$2.3\eta_{0,\mathrm{a}}$	slope of anodic Tafel line
σ	surface energy

1. Introduction

It is well known that the deposition conditions such as bath composition, hydrodynamic regime, temperature, current density, exhibit a strong effect on the grain size and the morphology of electrodeposited metal powder particles [1, 2]. On the other hand it has been shown recently [3] that similar effects can be obtained by changing only the shape of the current overpotential waves in metal powder electrodeposition at a periodically changing rate with other conditions constant. This is in accordance with Ibl's observation [4] that, at one and the same average deposition rate (current density), it is possible to create a number of different deposition conditions in the pulsating regimes.

In square-wave pulsating overpotential electrolysis the overpotential amplitude, frequency of pulsation and pause-to-pulse ratio can be varied independently. The purpose of this work is to discuss the effect of the last parameter on the morphology of electrodeposited metal powder particles on the basis of the existing experimental evidence.

2. Basic equations

Square-wave pulsating overpotential is described by [5]:

$$\partial C/\partial t = D\partial^2 C/\partial x^2 \qquad (1)$$

$$C(x, 0) = C_0 \qquad (2)$$

$$C(\delta, t) = C_0 \qquad (3)$$

$$\frac{\partial C(0, t)}{\partial x} = \frac{j_0}{zFD}\left[\frac{C(0, t)}{C_0}\exp\left(\frac{\eta}{\eta_{0,\mathrm{c}}}\right) - \exp\left(\frac{\eta}{\eta_{0,\mathrm{a}}}\right)\right] \qquad (4)$$

where

$$\eta = \begin{cases} \eta_{\mathrm{A}} \text{ for } mT_p < t \leqslant \left[m + \left(\dfrac{1}{p+1}\right)\right] T_p & m = 0, 1, 2, \ldots \\ 0 \text{ for } \left[m + \left(\dfrac{1}{p+1}\right)\right] T_p < t \leqslant (m+1)T_p & m = 0, 1, 2, \ldots \end{cases} \qquad (5)$$

Assuming that the surface concentration in pulsating overpotential deposition does not vary with time, at sufficiently high frequencies it is easy to show that the current response to the input overpotential is given by:

$$j = \begin{cases} j_0\left(1 - \dfrac{j_{\mathrm{av}}}{j_{\mathrm{L}}}\right)\exp(\eta_{\mathrm{A}}/\eta_{0,\mathrm{c}}) - j_0 \exp(-\eta_{\mathrm{A}}/\eta_{0.\mathrm{a}}) \\ \text{for } mT < t \leqslant \left[m + \left(\dfrac{1}{p+1}\right)\right] T_p \\ -j_{\mathrm{av}}\dfrac{j_0}{j_{\mathrm{L}}} \\ \text{for } \left[m + \left(\dfrac{1}{p+1}\right)\right] T_p < t \leqslant (m+1)T_p \end{cases} \qquad (6)$$

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and the average current density is given by

$$j_{\mathrm{av}} = \frac{j_0 \exp\left(\dfrac{\eta_{\mathrm{A}}}{\eta_{0,\mathrm{c}}}\right)}{p + 1 + \dfrac{j_0}{j_{\mathrm{L}}}\left[p + \exp\left(\dfrac{\eta_{\mathrm{A}}}{\eta_{0,\mathrm{c}}}\right)\right]} \tag{7}$$

if the anodic current density is neglected during overpotential pulses, being equal to j_{L} for sufficiently high η_{A} values. The overpotential amplitude can then be obtained in the form

$$\eta_{\mathrm{A}} = \eta_{0,\mathrm{c}} \ln \frac{j_{\mathrm{av}}}{j_0} + \eta_{0,\mathrm{c}} \ln\left(p + 1 + \frac{p j_0}{j_{\mathrm{L}}}\right) + \eta_{0,\mathrm{c}} \times \ln\left[1 \Big/ \left(1 - \frac{j_{\mathrm{av}}}{j_{\mathrm{L}}}\right)\right] \tag{8}$$

3. Discussion

It has been shown [6–10] that the shape of a pulsating overpotential wave has a strong effect on the morphology of metal powder particles. In general, the higher the pause-to-pulse ratio, the less dendritic powder particles are obtained. This can be explained in the following way.

The third term in Equation 8 corresponds to bulk diffusion control. It remains constant for a determined current density regardless of pause-to-pulse ratio, whereas the second term, which with the first one represents the activation part of the overpotential, increases with increasing p. In this way the ratio between overpotential corresponding to bulk diffusion control and activation overpotential can be reduced to the value corresponding to the deposition at lower overpotentials in the constant overpotential regime. So, deposits obtained at η_{A} in pulsating regimes ($p > 0$) are more similar to those obtained at lower overpotentials than at η_{A} in the constant overpotential regime ($p = 0$).

On the other hand [11], the overpotential and current density on the tips of growing dendrites inside the diffusion layer are related by

$$j_{\mathrm{d}} = j_0 \frac{h}{\delta} \exp\left(\frac{\eta_{\mathrm{A}}}{\eta_{0,\mathrm{c}}}\right) \tag{9}$$

and:

$$j_{\mathrm{d,av}} = j_0 \frac{h}{\delta(p+1)} \exp\left(\frac{\eta_{\mathrm{A}}}{\eta_{0,\mathrm{c}}}\right) \tag{10}$$

in the constant overpotential and pulsating overpotential regimes, respectively. This means that dendritic growth is lowered in pulsating overpotential deposition. This is the second reason why dendrites, or powder particles, obtained in pulsating overpotential deposition are more similar to those obtained at lower overpotentials than to those obtained at overpotential amplitude in constant overpotential deposition. For example: powder particles obtained in pulsating overpotential at overpotential amplitude 50 mV, pause-to-pulse ratios 1 : 3 and 1 : 6, and pulse duration 5 ms are more similar to those obtained at 10 mV than those at 50 mV in the constant overpotential regime. (See Figs. 2 and 4 in [9]).

The last effect can also be seen in non-powdered metal deposition by square-wave pulsating overpotential [12]. The fact that powder particles are less dendritic if deposition takes place at higher p, but at one and the same value of overpotential amplitude, is illustrated for Sn [9], Cu [8] and Ag [7] deposition. It can be seen that the effect is more pronounced in Sn and Ag than in the Cu case. This can be explained as follows. Equations 1–6 are valid for flat electrode surfaces or protrusions with sufficiently large tip radii, where the surface energy term [13] can be neglected. If it cannot be neglected, there are two possible cases of the effect of the surface energy term on the reaction rate [14] as shown by Equations 11 and 12.

$$\frac{\partial C}{\partial x} = \frac{j_0}{zFD}\left\{\left(1 - \frac{j_{\mathrm{av}}}{j_{\mathrm{L}}}\right) \exp\left(\frac{\eta}{\eta_{0,\mathrm{c}}}\right) - \exp \frac{2\sigma V}{RTr} \exp\left(\frac{-\eta}{\eta_{0,\mathrm{a}}}\right)\right\} \tag{11}$$

or

$$\frac{\partial C}{\partial x} = \frac{j_0}{zFD}\left\{\left(1 - \frac{j_{\mathrm{av}}}{j_{\mathrm{L}}}\right) \exp\left(-\frac{2\beta\sigma V}{RTr}\right) \exp\left(\frac{-\eta}{\eta_{0,\mathrm{c}}}\right) - \exp\left[\frac{2(1-\beta)\sigma V}{RTr}\right] \exp\left[\exp \frac{-F\eta}{\eta_{0,\mathrm{a}}}\right]\right\} \tag{12}$$

depending on the system under consideration. The right hand side of Equation 4 should be transformed by taking Equations 11 and 12 into account. The output currents during pauses ($\eta = 0$) become

$$j = j_0\left(1 - \frac{j_{\mathrm{av}}}{j_{\mathrm{L}}}\right) - j_0 \exp \frac{2\sigma V}{RTr} \tag{13}$$

and

$$j = -j_0 \exp \frac{2(1-\beta)\sigma V}{RTr} \tag{14}$$

if $r \to 0$.

It is easy to show that the difference between the current density on the flat surface and at the tip of the dendrite during the 'off' period is given by

$$j = j_0 - j_0 \exp \frac{2\sigma V}{RTr} \tag{15}$$

and

$$\Delta j = j_0 - j_0 \exp\left[\frac{2(1-\beta)\sigma V}{RTr}\right] \tag{16}$$

if $j_{\mathrm{av}} \approx j_{\mathrm{L}}$, which leads to

$$h = h_0 + \frac{V j_0}{2F}\left[1 - \exp\left(\frac{2\sigma V}{RTr}\right)\right] t \tag{17}$$

and

$$h = h_0 + \frac{V j_0}{2F}\left[1 - \exp\left(\frac{2(1-\beta)\sigma V}{RTr}\right)\right] t \tag{18}$$

The above equations represent the change of the height of the dendrite with tip radius, r, relative to the flat surface or the protrusion with sufficiently large r. It is obvious that dendrites with very low tip radii can be completely dissolved during the pause. This means that the branching of dendrites can be prevented in square-wave pulsating overpotential deposition. The effect is obviously more pronounced with increasing p and j_0, in accordance with experimental results [2–4]. In this way the effect of the 'off' period on the micromorphology of metal power particles can be explained. It seems that some effect on the macromorphology of powder particles can also be seen. In the case of copper the powder particle size increases with increasing p, while in the cases of Ag and Sn there is an opposite effect. The behaviour of copper is in accordance with the fact that increasing p leads to a decrease of the dendritic character of particles and, hence, to increased particle size.

The behaviour of Ag and Sn can be explained by the fact that anodic current density during the 'off' periods cannot be neglected at sufficiently high j_0 at overpotentials at which the average current is lower than j_L. Because of this the effective quantity of metal deposited can be decreased, leading to lower grain size powder particles.

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