

The determination of the optimum current wave in reversing current metal electrodeposition

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The experimental procedure for the determination of the optimum reversing current wave, producing uniformly distributed polycrystalline deposits, is given. First, deposition at the maximum current density for different periods of RC wave was carried out. The period was increased until a smooth polycrystalline deposit was obtained in the middle of the electrode. Subsequently, the deposition current density was decreased by increasing the anodic-to-cathodic time ratio, in order to obtain a suitable metal distribution on a macroprofile.

Key words: reversing current, optimum current wave, metal electrodeposition.

It was shown recently¹ that the maximum current density in metal electrodeposition by reversing current (RC) in the second range can be related to the period of the RC wave by Eq. (1):

$$j_{av,max} = j_L \frac{1 - \frac{8t_0}{T} \ln \frac{2}{1 + \exp(-T/4t_0)}}{1 - (16/\pi^2) \frac{\exp(-T/4t_0)}{1 + \exp(-T/4t_0)}} \quad (1)$$

and the period of the RC to the anodic-to-cathodic time ratio by Eq. (2):

$$r = \frac{\frac{4t_0}{T} \ln \frac{2}{1 + \exp(-T/4t_0)}}{1 - \frac{4t_0}{T} \ln \frac{2}{1 + \exp(-T/4t_0)}} \quad (2)$$

At the same time, a procedure for the determination of the shape of the optimum current wave was proposed; the first step was the determination of the t_a/t_c ratio producing a uniformly distributed deposit and then the choice of the amplitude current density to obtain the polycrystalline deposit at the maximum possible

deposition rate. It seems to be necessary to find a somewhat different way for the determination of the optimum current wave, if the previous one is not operative. In this case, the first step should be the determination of the t_a/t_c ratio producing a smooth polycrystalline deposit in the middle of the electrode as well as at the edges at the maximum possible deposition rate and after that the choice of the amplitude current density which permits an uniform current density distribution over a macroprofile. The purpose of this paper was to confirm this proposed procedure.

EXPERIMENTAL

Copper was deposited from 0.2 M CuSO₄ in 0.5 M H₂SO₄ in an open cell at room temperature. Doubly-distilled water and p.a. chemicals were used. Copper was deposited by RC in the second range and DC methods on the copper plate electrodes. The counter and reference electrodes were also of pure copper. The limiting diffusion current was determined potentiostatically. The cell was glass of 100 ml and counter electrode was of cylindrical shape which covered the walls of the cell. The cathode was in the centre of cell, always at the same location for each series of experiments. This is important because the optimum current wave can be determined by described procedure for one and the same cell geometry. A controlled current was obtained using a potentiostat (as a galvanostat) and a function generator. The period T was equal to either 4, 9, 12, or 16 s and the average current densities were either 0.41 j_L , 0.56 j_L , or 0.67 j_L . The j_c was equal to j_a in RC deposition. In all experiments the same quantity of metal was deposited, which was 95 mg cm⁻². The morphology of the deposits was investigated by means of a scanning electron microscope (JOEL T20, Japan). Photomicrographs were made under magnifications of $\times 250$, $\times 500$, $\times 750$, and $\times 1000$.

RESULTS AND DISCUSSION

Typical results obtained in this work are shown in Figs. 1-4. The effect of increasing the period T on the quality of the copper deposit is illustrated by Figs. 1 and 2, from which it can be seen that T has opposite effects on the quality of the deposits in the middle and at the edges of electrodes. The deposit grain size decreases with increasing period T , and at 16 s becomes polycrystalline (Fig. 1c). At the same time, the current density distribution over the macroprofile becomes worse (Fig. 2). It should be noted that the deposit from Fig. 2a is homogeneously distributed, but it is granular. Deposited copper of the best quality in the middle of the electrode can be seen in Fig. 1c, showing that the conditions suitable for the deposition of polycrystalline metal are fulfilled.

A better distribution on a macroprofile, compared to that from Fig. 1c, can be obtained by increasing t_a . A fine polycrystalline, well distributed deposit is obtained, as illustrated in Figs. 3a and 3b. The deposit obtained under DC conditions, at the same deposition rate, is shown in Figs. 3c and 3d. It is obvious that the deposits from Figs. 3a and 3b are better than those from Figs. 3c and 3d.

The deposit obtained by further decreasing the average current density, at the same j_A and longer t_a , shown in Fig. 4, confirms that the deposit from Figs. 3a and 3b is really the best one. In this way, the proposed procedure for the determination of the optimum shape of the RC wave is verified. The change from the originally proposed procedure of optimum RC wave shape determination can be explained as follows.²

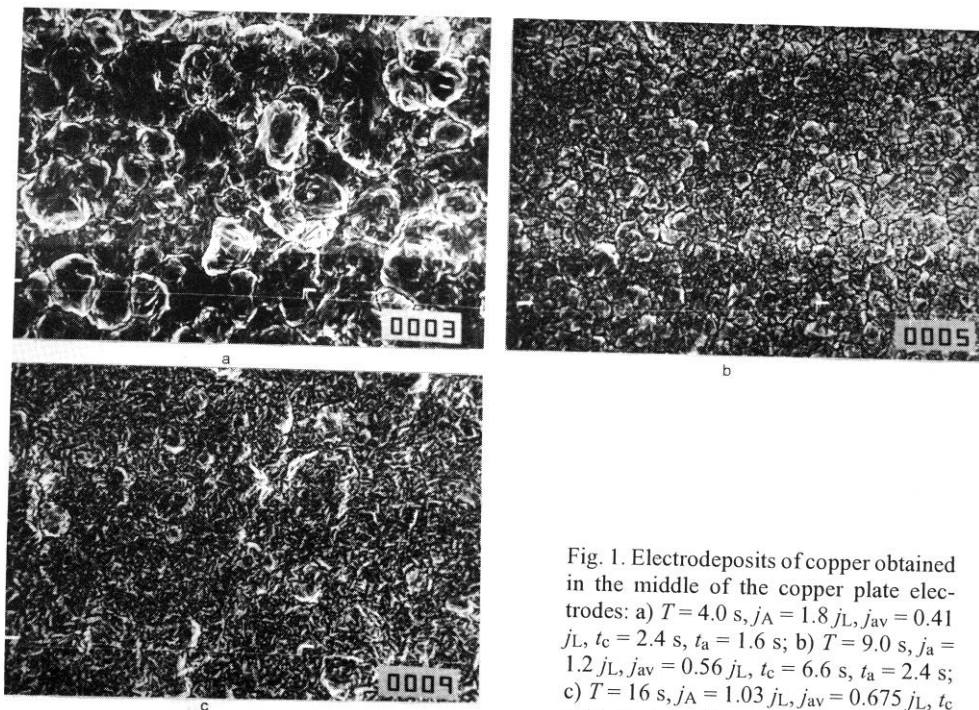


Fig. 1. Electrodeposits of copper obtained in the middle of the copper plate electrodes: a) $T = 4.0$ s, $j_A = 1.8$ j_L , $j_{av} = 0.41$ j_L , $t_c = 2.4$ s, $t_a = 1.6$ s; b) $T = 9.0$ s, $j_a = 1.2$ j_L , $j_{av} = 0.56$ j_L , $t_c = 6.6$ s, $t_a = 2.4$ s; c) $T = 16$ s, $j_A = 1.03$ j_L , $j_{av} = 0.675$ j_L , $t_c = 13.2$ s, $t_a = 2.8$ s.

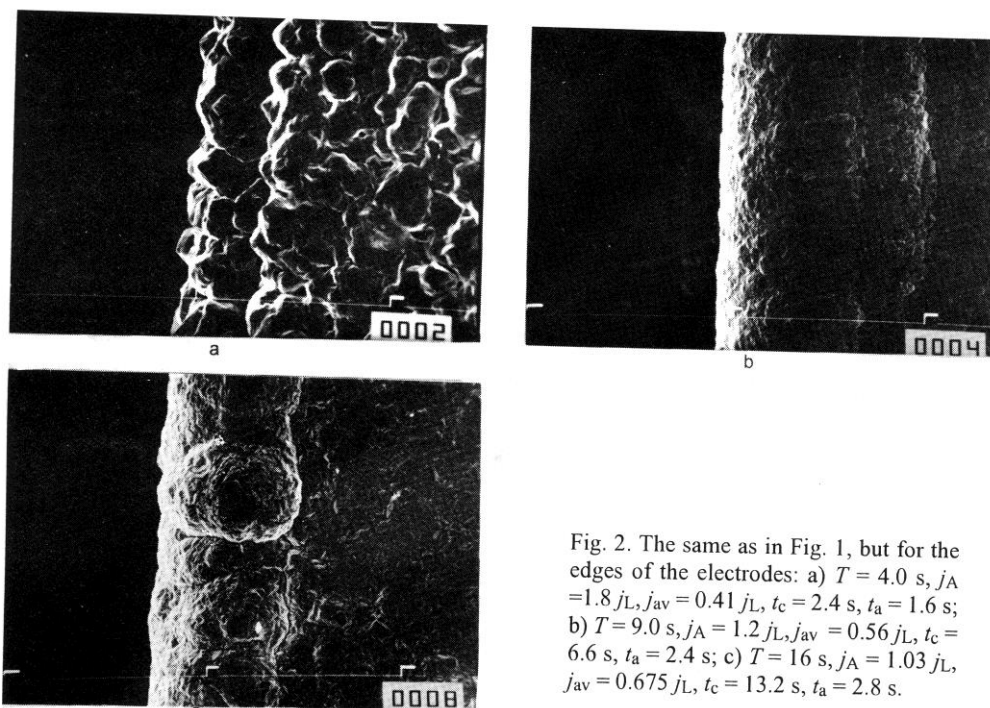


Fig. 2. The same as in Fig. 1, but for the edges of the electrodes: a) $T = 4.0$ s, $j_A = 1.8$ j_L , $j_{av} = 0.41$ j_L , $t_c = 2.4$ s, $t_a = 1.6$ s; b) $T = 9.0$ s, $j_A = 1.2$ j_L , $j_{av} = 0.56$ j_L , $t_c = 6.6$ s, $t_a = 2.4$ s; c) $T = 16$ s, $j_A = 1.03$ j_L , $j_{av} = 0.675$ j_L , $t_c = 13.2$ s, $t_a = 2.8$ s.

The effect of reversing current on the current distribution at a macroprofile can easily be discussed for the case of activation controlled deposition if the Tafel slopes of the anodic and cathodic processes are different, as they are for copper deposition and dissolution in sulfate solutions. With the assumption that the current density in RC deposition is sufficiently high that the effect of the opposite process can be neglected and that deposition on the edge as well as at the middle of the electrode is activation controlled, $j_{c,e}$ is expressed by:

$$j_{c,e} = j_{c,h} \exp\left(\frac{2.3\rho l j_{c,h}}{b_c}\right) \quad (3)$$

and $j_{a,e}$, by analogy can be written in the form:

$$j_{a,e} = j_{a,h} \exp\left(3 \frac{2.3\rho l j_{a,h}}{b_c}\right) \quad (4)$$

since $b_a = b_c/3$. The difference between the current density at the edge and that at the middle of the electrode in cathodic deposition is:

$$\Delta j_c = j_{c,h} \left[\exp\left(\frac{2.3\rho l j_{c,h}}{b_c}\right) - 1 \right] \quad (5)$$

and for the anodic case:

$$\Delta j_a = j_{a,h} \left[\exp\left(3 \frac{2.3\rho l j_{a,h}}{b_c}\right) - 1 \right] \quad (6)$$

It is obvious that for:

$$\Delta j_c t_c = \Delta j_a t_a \quad (7)$$

which occurs when:

$$\frac{t_c}{t_a} = \frac{\exp\left(3 \frac{2.3\rho l j_h}{b_c}\right) - 1}{\exp\left(\frac{2.3\rho l j_h}{b_c}\right) - 1} \quad (8)$$

(if $j_{c,h} = j_{a,h} = j_h$), deposits of equal thickness can be obtained at the edge and at the middle of the electrode. In this way, a completely uniform average current density distribution on the macroprofile can be obtained in RC deposition.

It is obvious that Eq. (8) is valid for copper deposition in the plane parallel arrangement of the electrodes with the electrodes not touching the walls of the cell. In all other cases it can be treated as a qualitative indication that some optimum shape of the RC wave can be determined, but only after the appropriate experiments. On the other hand, the deposit obtained must be polycrystalline, and the deposition process must be carried out in mixed activation-diffusion control. In this situation the coarseness of the electrode surface increases.³ It is obvious that in determination

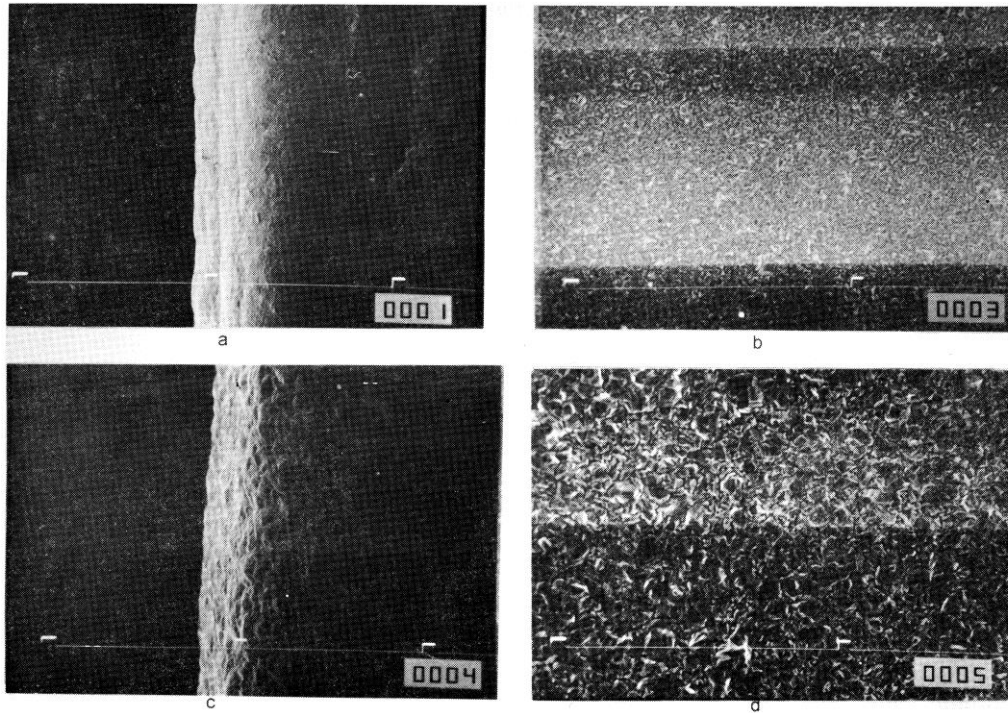


Fig. 3. Electrodeposits of copper in the middle and at the edge of electrode in: a), b) the optimum regime $T = 16$ s, $j_A = 1.03 j_L$, $j_{av} = 0.56 j_L$, $t_c = 12.3$ s, $t_a = 3.7$ s; c), d) the DC regime, $j_{av} = 0.56 j_L$.

of the optimum RC wave shape the effect of the surface coarseness increasing has not yet been considered. Hence, it will be estimated in the following.

The surface concentration changes during the cathodic pulse according to:⁴

$$\frac{c_s}{c_0} = 1 - \frac{j_c}{j_L} f(t) \tag{9}$$

where:

$$f(t) = 1 - \frac{8}{\pi^2} \sum_{k=0}^{\infty} \frac{1}{(2k+1)^2} \exp\left[-\frac{(2k+1)^2 t}{4t_0}\right] \text{ and } t_0 = \frac{\delta^2}{\pi^2 D} \tag{10}$$

In this case:

$$j = j_0 \frac{c_s}{c_0} f_c = j_0 \left(1 - \frac{j_c}{j_L}\right) f_c \tag{11}$$

is also valid and substitution of c_s/c_0 from Eq. (9) in Eq. (11) gives:

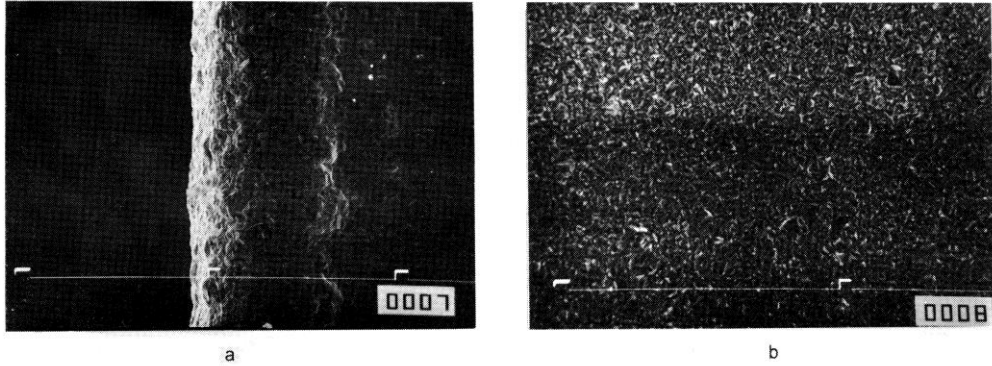


Fig. 4. a), b) The same as in Fig. 3 but for $T = 16$ s, $j_A = 1.03 j_L$, $j_{av} = 0.41 j_L$, $t_c = 11.2$ s, $t_a = 4.8$ s

$$j_t = j_0 f_c \left[1 - \frac{j_t}{j_L} \frac{\delta - h}{\delta} f(t) \right] \quad (12)$$

for the tip of a protrusion and:

$$j_f = j_0 f_c \left[1 - \frac{j_f}{j_L} f(t) \right] \quad (13)$$

for the flat portion of the surface. If all the surface is isopotential, elimination of f_c from Eqns. (11) and (12) and further rearranging produces:

$$j_t = \frac{j_f}{1 - \frac{j_f}{j_L} \frac{h}{\delta} f(t)} \quad (14)$$

The difference in the current densities at the tip of a protrusion and the flat portion of electrode is then given by:

$$\Delta j = j_t - j_f = \frac{j_f^2}{j_L} \frac{h}{\delta} f(t) \quad (15)$$

for $\delta \gg h$.

Now, according to:³

$$\frac{dh}{dt} = \frac{M}{nF\rho} \Delta j \quad (16)$$

which can be written:

$$\frac{dh}{dt} = \frac{j_f^2}{j_L} \frac{V_m}{nF} \frac{h}{\delta} f(t) \quad (17)$$

or in the integral form:

$$h = h_0 \exp\left(\frac{j_f}{j_L} \frac{V_m f(t)}{nF\delta} Q\right) \quad (18)$$

where:

$$F(t) = \int_0^{t_c} f(t) dt \quad (19)$$

Assuming that the surface will dissolve uniformly during the anodic period it is obvious that because $f(0) = 0$ and $f(\infty) = 1$ the increase in surface coarseness in the RC regime will be lower than in the DC regime until the condition:

$$F(t) \leq \frac{1-r}{1+r} \quad (20)$$

is satisfied.

This is because the increase in the surface coarseness will be lower during the cathodic pulse than in the deposition by the corresponding average constant current if the amplitude current is equal to this average value because of the lower deposition time. Taking into account that for optimum RC waves $0.2 < r < 0.7$ is valid,^{1,2} it is obvious that in all RC cases the increase in the surface coarseness will be lower than in the DC case. A longer r means a lower increase in the surface coarseness, as shown Figs. 1-4.

NOTATION

b_a	Slope of the anodic Tafel line
b_c	Slope of the cathodic Tafel line
c	Concentration
c_0	Bulk concentration
c_s	Surface concentration
D	Diffusion coefficient
f_c	$\exp\left(\frac{2.3\eta}{b_c}\right)$
h	Height of a protrusion
h_0	Initial height of a protrusion
j	Current density
j_a	Anodic current density
$j_{a,e}$	Anodic current density at the electrode edge
$j_{a,h}$	Anodic current density at the flat part of the electrode
j_c	Cathodic current density
$j_{c,e}$	Cathodic current density at the electrode edge
$j_{c,h}$	Cathodic current density at the flat part of the electrode
j_f	Current density at the flat portion of the surface

j_L	Limiting diffusion current density
j_0	Exchange current density
l	Distance between the electrodes
n	Number of electrons
M	Molar mass
Q	Quantity of electricity
r	Anodic-to-cathodic time ratio
t	Time
t_a	Anodic time
t_c	Cathodic time
T	Period of RC ware
V_m	Molar volume of metal

Greek letters

δ	Thickness of the diffusion layer
η	Overpotential
ρ	Resistivity of the electrolyte

ИЗВОД

ОДРЕЂИВАЊЕ ОПТИМАЛНОГ ОБЛИКА ТАЛАСА РЕВЕРСНЕ СТРУЈЕ ПРИ
ЕЛЕКТРОХЕМИЈСКОМ ТАЛОЖЕЊУ МЕТАЛА

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Предложен је експериментални поступак за одређивање оптималног облика таласа реверсне струје који даје равномерно распоређен поликристални талог. Прво се врши таложење на максималној густини струје за различите периоде таласа реверсне струје. Период се повећава док се не добије поликристални талог на средини електроде. После тога, густина струје таложења се смањује повећањем односа анодног и катодног времена док се не добије равномерна расподела по макропрофилу.

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