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The relationship between the effective current density and the effective overpotential in copper deposition by the pulsating potential

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The relationship between the effective current density and the effective overpotential in copper deposition by pulsating potential has been established experimentally. It has been shown that due to non-linearity of the steady state polarization curve, the value of the effective current density is not dependent on the value of the effective overpotential only, but on the ratio between the pulse and the pause duration too. Effective values of current density for the constant pulse-to-pause ratio are functions of the input pulsating potential frequency for a given value of the effective overpotential.

When a frequency dependence of effective values has been experimentally studied it has been found that the effective current density at a given constant value of the effective overpotential is a function with a maximum, while the effective overpotential at a given constant value of the effective current density is a function with a minimum. Digital simulation of copper deposition by the pulsating potential gave qualitatively the same picture. Discussion of phenomena has been presented.

1. Introduction

It is well known that metal deposits of higher quality can be obtained by deposition with pulsating currents, as compared to metal deposits obtained with common d.c. procedure, with all other parametes of the process comparable [1]. Similar effect can be obtained by pulsating potentials [2]. Recently, it was pointed out that it is possible to synthesize in advance an optimal pulsating programme for current density in the process of metal deposition using methods of the modern control theory [3]. The optimal pulsating programme is based either on a minimum time or on a minimum energy criterion.* Successful application of the modern control theory, however, requires a linear mathematical model of the process, but in metal deposition the current density is not linearly related to the overpotential when a practical range of current densities is considered. Hence, an approach through the application of the control theory is rather difficult. From that point of view this paper presents a heuristic approach to parameter optimization problems of metal deposition with pulsating potentials.

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* These criteria are defined as the shortest possible time, or the lowest possible energy required to obtain the specified amount of the metal deposit of a desired quality.

The purpose of this paper is to study experimentally copper deposition with rectangular periodic pulsating potentials in order to analyse an effect of the non-linearity of the system on effective values of current and overpotential at various values of parameters determining the pulsating potential (amplitude, pulse-to-pause ratio and frequency). It was expected that functions of effective values of current and overpotential on parameters determining the pulsating potential would point out a possibility of the optimization of the system. A mathematical model of the system is proposed and the digital simulation together with experimental results is used to check its validity.

2. Experimental

A standard quasi-potentiostatic method is used with the electronic interrupter of the working electrode circuit. The electrolyte used was 0·5 M $CuSO_4$ with 50 g l^{-1} H_2SO_4 and 50 g l^{-1} C_2H_5OH. The electrolyte was prepared from reagent grade chemicals and distilled water. A two-electrode cell was used. Copper was deposited on the copper sheet which was used as a working electrode. A copper electrode with an area approximately 50 times larger than that of the working electrode was used as both the counter and reference electrode.

Effective values of currents were measured with a d.c. ammeter and compared with values calculated from measured weights of copper deposits. Therefore, a requirement for good quality of copper deposit was strictly followed through the experiments. Effective values of overpotential were measured with an electronic voltmeter, while the shape of the pulsating input potential was controlled by the oscilloscope.

All experiments were performed at room temperature.

3. Results

A typical steady state polarization curve for copper deposition is presented in Fig. 1.

Due to non-linearity of the polarization curve, different values of the effective current density correspond to the single value of the effective overpotential if different shapes of the input pulsating potential are applied. For example, if Fig. 1 is considered the current density of $4{\cdot}5 \times 10^{-3}$ A cm^{-2} corresponds to the overpotential of 0·100 V. If, however, an effective overpotential of 0·100 V is obtained using the pulsating potential with pulses of 0·200 V fol-

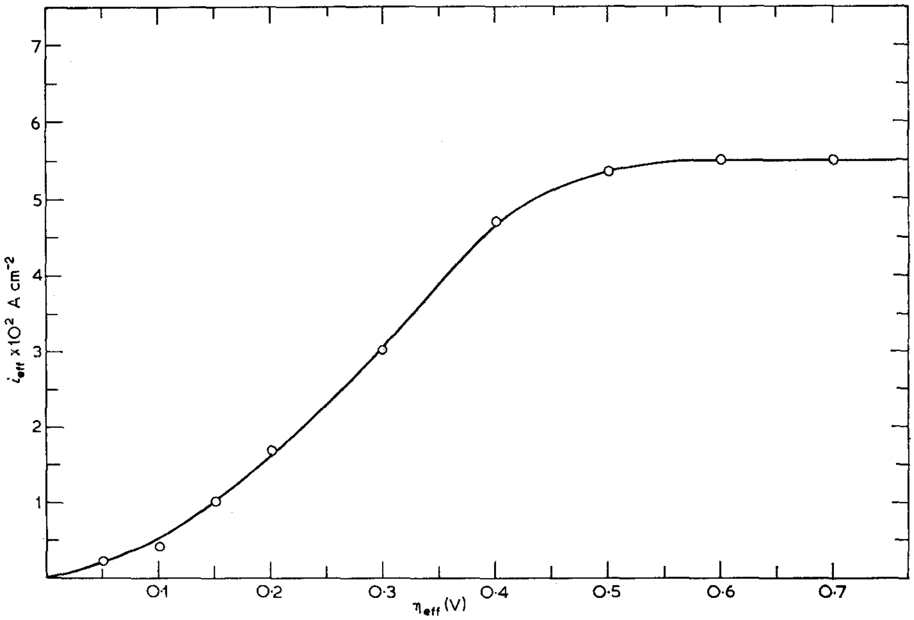

Fig. 1. Experimental steady-state polarization curve for copper deposition.

lowed by the pause of the same duration, an effective current density of $8{\cdot}0 \times 10^{-3}$ A cm^{-2} results. This value is obtained from the curve in Fig. 1 when the value of the current density which corresponds to the overpotential of 0·200 V is divided by two.

It is useful to introduce the parameter $\mathscr{H}$ which defines the pulsating program:

$$\mathscr{H} = \frac{T_i}{T_i + T_p} \qquad (1)$$

where T_i is the duration of the pulse, while T_p is the duration of the pause.

Introducing the parameter $\mathscr{H}$, the effective current density and the effective overpotential are now defined by the following equations:

$$\eta_{eff} = \eta_i \mathscr{H}$$
$$i_{eff} = i_i \mathscr{H} \qquad (2)$$

where: η_{eff} = effective value of the overpotential
i_{eff} = effective value of the current density
η_i = amplitude of the pulsating potential
i_i = current density corresponding to the amplitude of the overpotential from the non-linear relationship given by the curve in Fig. 1.

Using Equations 2 and the curve presented in Fig. 1 one can now relate effective values of the current density and the overpotential for different values of the parameter $\mathscr{H}$ of rectangular, periodic and pulsating potential. These relationships are given in Fig. 2, where the curve from Fig. 1 is given for the sake of comparison. These lines are analogous to the steady state polarization curves and in the following text the term effective polarization curve will be used.

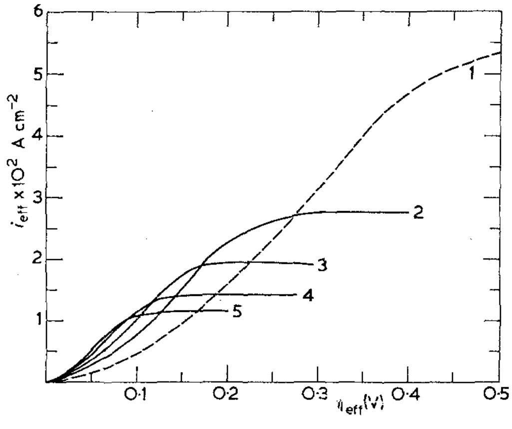

Fig. 2. Calculated relationships between the effective current density and the effective overpotential for different values of the parameter $\mathscr{H}$. 1, steady-state polarization curve; 2, 3, 4 and 5, effective polarization curves for $\mathscr{H}$ equal to $\frac{1}{2}$, $\frac{1}{3}$, $\frac{1}{4}$ and $\frac{1}{5}$, respectively.

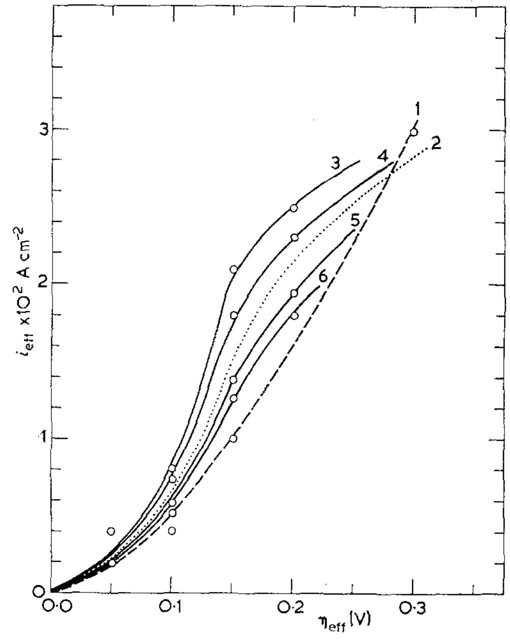

Fig. 3. Experimental relationships between the effective current density and the effective overpotential, for $\mathscr{H} = \frac{1}{2}$ and different duration of pulses. 1, steady-state polarization curve; 2, calculated effective polarization curve; 3, 4, 5 and 6, effective polarization curve for T_i equal to 10^{-1}, 10^{-2}, 10^{-3} and 10^{-4} s respectively.

Experimental effective polarization curves for $\mathscr{H}$ equal to $\frac{1}{2}$, the steady state polarization curve and calculated effective polarization curve for $\mathscr{H}$ equal to $\frac{1}{2}$, are compared in Fig. 3. It is obvious that experimental values of effective current density for the same value of the effective overpotential depend on frequency of the input pulsating potential. The relationships between the effective current density and the frequency of pulsating potential for constant effective overpotential ($\eta_{eff} = 0{\cdot}100$ V) and for different values of the parameter $\mathscr{H}$ are given in Fig. 4. The horizontal line in Fig. 4 corresponds to constant direct current density (4×10^{-3} A cm^{-2}), which is obtained from Fig. 1 for a constant overpotential value of 0·100 V. This pair of values is reflecting steady state conditions of copper deposition with direct current. Differences of values of currents between the curve and the horizontal line in Fig. 4 is a measure of improvement in deposition time obtained when electrolysis with pulsating potential is applied. The effective overpotential at a constant effective current density ($i_{\text{eff}} = 1{\cdot}6 \times 10^{-2}$ A cm^{-2}) as a function of frequency for different values of the parameter $\mathscr{H}$ is presented in Fig. 5, together with the horizontal line which corresponds to the constant overpotential of 0·195 V, which is obtained from the curve in Fig. 1 for constant value of the current density of $1{\cdot}6 \times 10^{-2}$ A cm^{-2}. As in Fig. 4 the differences between values of overpotential at the horizontal line and those at the curves in Fig. 5 reflect the improvement in energy consumption achieved by the use of pulsating potential.

It should be noted that frequency dependencies of the effective current density and the effective overpotential (Figs. 4 and 5) exhibit maximum and minimum, respectively. However, for lower values of the parameter $\mathscr{H}$ ($\frac{1}{4}$ and $\frac{1}{5}$) these relationships could be experimentally obtained in the region of higher frequencies only, since the requirement of good quality of copper deposits was followed. This is in accordance with the fact, that good quality metal deposits at higher values of applied potential are obtained at rather high frequencies, as already reported [2].

4. Digital simulation

Frequency dependencies of the effective current and the effective overpotential could be analysed using the following mathematical model of metal deposition by the pulsating potential with the working electrode circuit disconnected during the pause. It is assumed that the ohmic drop contribution to the measured overpotentials was negligible, and that the diffusion layer thickness was constant during the experiment.

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}$$

$$C(x,0) = C_0$$

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

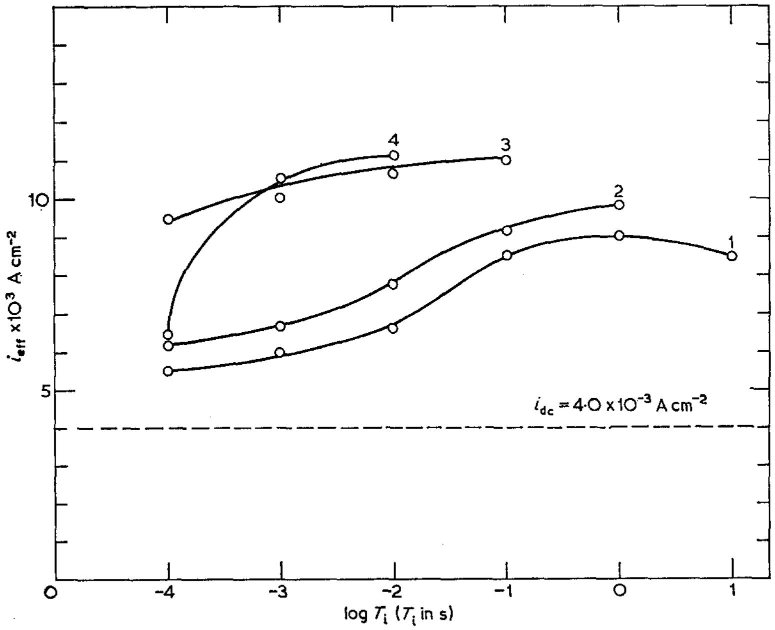

Fig. 4. Relationships between effective values of the current density and the pulse duration for $\eta_{\text{eff}} = 0{\cdot}100$ V and for different values of $\mathscr{H}$. Curves 1, 2, 3 and 4 correspond to the values of $\mathscr{H}$ equal to $\frac{1}{2}$, $\frac{1}{3}$, $\frac{1}{4}$, and $\frac{1}{5}$ respectively.

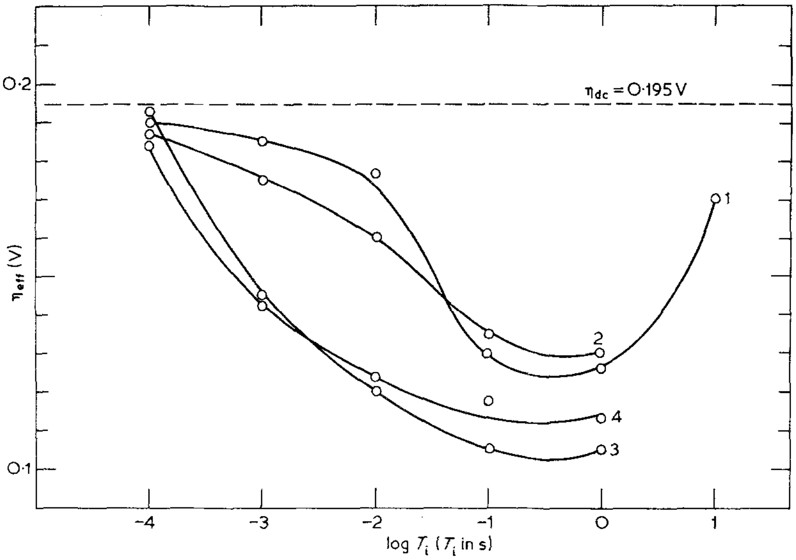

Fig. 5. Relationships between effective values of the overpotential and the pulse duration for $i_{\mathrm{eff}} = 1{\cdot}6 \times 10^{-2}$ A cm^{-2} and for different values of $\mathscr{H}$. Curves 1, 2, 3 and 4 correspond to the values of $\mathscr{H}$ equal to $\frac{1}{2}$, $\frac{1}{3}$, $\frac{1}{4}$ and $\frac{1}{5}$, respectively.

$$C(0,t) = C_s \text{ for } t_{ni} < t \leqslant t_{np}$$

$$\left.\frac{\partial C(x,t)}{\partial x}\right|_{x=0} = 0 \text{ for } t_{np} \leqslant t < t_{(n+1)i}$$

where:

$$t_{ni} = n\,T_i\left(\frac{1-\mathscr{H}}{\mathscr{H}}+1\right)$$

$$n = 0, 1, 2, 3 \ldots$$

$$t_{np} = t_{ni} + \frac{1-\mathscr{H}}{\mathscr{H}}\,T_i$$

C_0 = concentration in the bulk of the solution
C_s = surface concentration, corresponding to the overpotential during the pulse
D = diffusion coefficient
δ = diffusion layer thickness
T_i = the pulse duration

The model does not contain the non-linear relationship between the surface concentration and the overpotential directly. Instead, the surface concentration is calculated from the experimental steady state polarization curve (Fig. 1) for each value of overpotential, with values of diffusion layer thickness of $2{\cdot}2 \times 10^{-2}$ cm, calculated from the plateau of the steady state polarization curve, and the diffusion coefficient of 10^{-5} cm^2 s^{-1}. The mathematical model [3] has been simulated on the digital computer using finite difference approximation (the mesh of 20 points has been used). The results for $\mathscr{H} = \frac{1}{2}$ and $\eta_i = 0{\cdot}200$ V ($\eta_{\mathrm{eff}} = 0{\cdot}100$ V) and corresponding surface concentration $C_s = 0{\cdot}71 \times C_0$ are given in Fig. 6.

The agreement between calculated and experimentally obtained curves, as presented in Fig. 6, is qualitative only. To check the possible effects of the ohmic drop and the change of the δ during the measurement, the relationship η versus log $i/(1-i/i_L)$ was calculated for experimentally obtained values of η and i presented in Fig. 1. Resulting linear relationship indicated negligible ohmic drop and constant δ during the measurement. Possible reasons for discrepancies are as follows:

(i) The value of diffusion layer thickness calculated from the plateau of the polarization curve is probably lower than real value (at lower current densities) under experimental conditions used.

(ii) The surface concentration during the pulse and the pause has almost the same value at high frequencies (Fig. 7), hence the correpond-

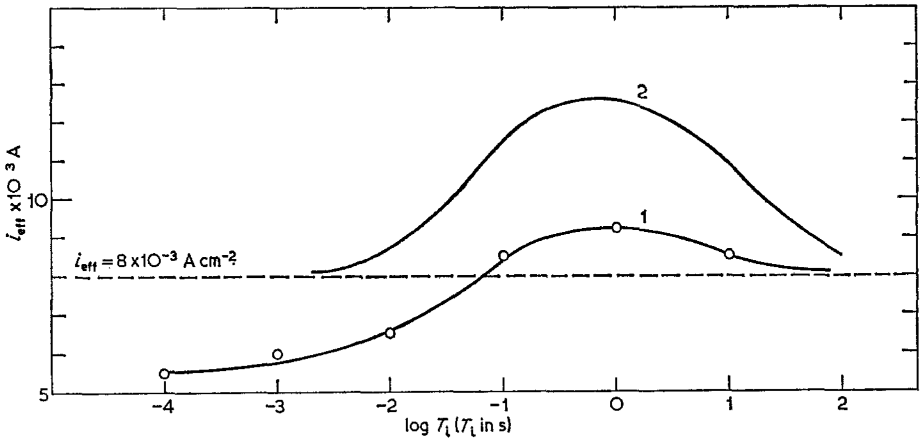

Fig. 6. Experimental (1) and calculated (2) relationship between the effective current density and the pulse duration for η_{eff} = 0·100 V and $\mathscr{H} = \frac{1}{2}$.

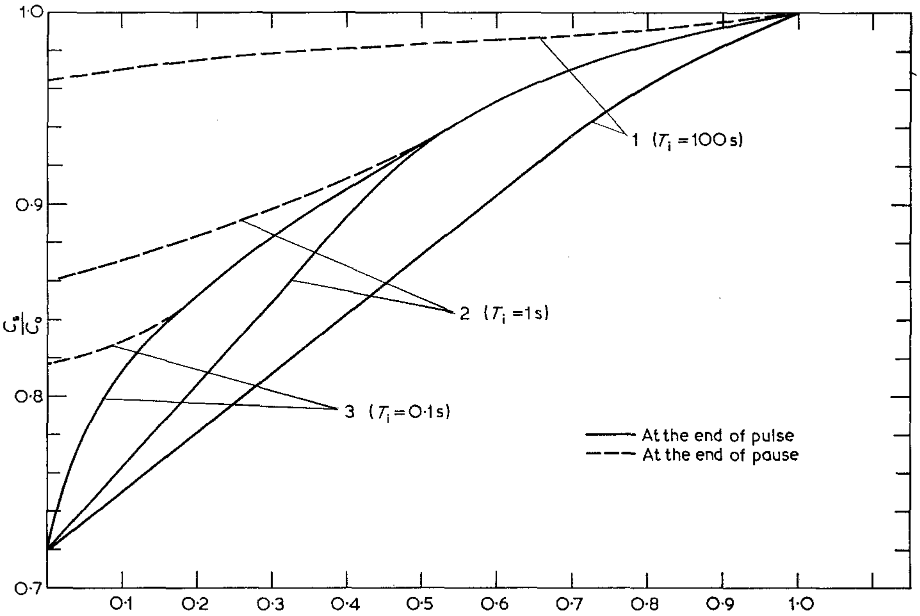

Fig. 7. The concentration distribution in the diffusion layer at the end of *n*th pulse and *n*th pause for different values of T_i (results of the digital simulation).

ing value of the Nernst potential during the pause is contained in the measured value of the effective overpotential.

The concentration distribution in the diffusion layer for different frequencies of the input pulsating potential are given in Fig. 7. This figure enables a qualitative discussion of the frequency dependence of the effective current density. It is obvious that at high frequencies the surface concentration at the end of the pulse and the end of the pause are almost the same until after a number of periods ($T = T_i + T_p$) the concentration distribution in the diffusion layer reaches the steady state shape, which is rather slightly affected by the pulsating potential. At low frequencies, however, the major part of the pulse system behaves as though a constant overpotential is applied although the concentration distribution in the diffusion layer at the end of the pause returns to its initial shape. There is a similar range of medium frequencies where the pause is sufficiently long to enable the system to reach approximately the initial concentration distribution and the pulse duration covers the initial, greatest gradient of the surface concentration.

5. Summary

The relationship between the effective current density and the effective overpotential in copper deposition by the pulsating potential has been analysed experimentally and by digital simulation on the basis of a simple mathematical model. It is shown that the effective current density is dependent not only on the values of the effective overpotential, but also on the ratio of pulse-to-pause duration and on a frequency of the input pulsating potential. The analysis has been restricted to rectangular periodic pulsating potentials. It was found that frequency dependencies of the effective current density and of the effective overpotential exhibit a maximum and a minimum, respectively.

It is expected that further improvement could be achieved if the shape of input potential was not accepted in advance and restricted to rectangular periodic pulses, but was synthesized according to some convenient criterion or performance index. This could be done using methods of the optimal control theory, as already demonstrated in metal deposition with pulsating currents [3].

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