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Mathematical model and digital simulation of pulsating overpotential copper electrodeposition

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The relationships between the effective current density and the effective overpotential in copper electrodeposition carried out by pulsating overpotential have been analysed experimentally and by digital simulation on the basis of a simple mathematical model. The agreement between the theoretical and experimental results was satisfactory. The quality of the electrodeposit was also studied.

1. Introduction

It is known that good metal deposits can be obtained by square-wave pulsating overpotential electrolysis. Some results which help towards explaining the effects of the frequency of pulsation on the morphology of metal deposits have been obtained on the basis of a standard mathematical model of potentiostatic electrolysis [1]. The purpose of this paper is to present some experimental results on copper electrodeposition by rectangular, sinusoidal and triangular pulsating overpotentials and to contrast them with those obtained by digital simulation of an improved mathematical model [2].

2. Mathematical model

The pulsating overpotential metal electrodeposition can be described by Equations 1–4.

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \tag{1}$$

$$C(x, 0) = C_o \tag{2}$$

$$C(\delta, t) = C_o \tag{3}$$

$$\left.\frac{\partial C}{\partial x}\right|_{x=0} = \frac{i_0}{nFD} \times \left[\frac{C(0,t)}{C_o} 10^{(\alpha_c F/2{\cdot}3RT)\eta(t)} - 10^{-(\alpha_a F/2{\cdot}3RT)\eta(t)}\right] \tag{4}$$

where the symbols have the meaning usually given to them in electrode kinetics [3]. The computer simulation and experiments have been performed with rectangular (Equation 5), sinusoidal (Equation 6) and triangular (Equation 7) pulsating overpotentials

$$\eta(t) = \begin{cases} \eta_A & kT \leqslant t \leqslant (2k+1)\dfrac{T}{2} \\ 0 & (2k+1)\dfrac{T}{2} \leqslant t \leqslant (k+1)T \end{cases} \tag{5}$$

$$k = 0, 1, 2, \ldots$$

$$\eta(t) = \frac{\eta_A}{2} + \frac{\eta_A}{2}\sin\frac{2\pi t}{T} \tag{6}$$

$$\eta(t) = \begin{cases} \dfrac{2\eta_A}{T}\left(t - kt + \dfrac{T}{4}\right); \\ \qquad \dfrac{4k-1}{4}T \leqslant t \leqslant \dfrac{4k+1}{T}T \\ -\dfrac{2\eta_A}{T}\left(t - kt - 3\dfrac{T}{4}\right); \\ \qquad \dfrac{4k+1}{4}T \leqslant t \leqslant \dfrac{4k+3}{4}T \end{cases} \tag{7}$$

$$k = 0, 1, 2, \ldots$$

where η_A is the amplitude value and T is the period of the pulsating overpotential. The effective values of current density and overpotential are given by Equations 8 and 9.

$$i_{\text{eff}} = \frac{nFD}{T}\int_0^T \frac{\partial C}{\partial x}(0, t)\,\mathrm{d}t \tag{8}$$

$$\eta_{\text{eff}} = \frac{1}{T}\int_0^T \eta(t)\,\mathrm{d}t \tag{9}$$

3. Experimental

A controlled pulsating overpotential was applied to the electrode to be investigated by a potentiostat driven by a function generator at its input, with the output voltage applied to the experimental cell. The shape of the pulsating overpotential was controlled by a cathode-ray oscilloscope, and the effective values of current densities and overpotentials were measured by appropriate d.c. instruments. The electrolyte was 0·1 mol dm^{-3} $CuSO_4$ in 0·5 mol dm^{-3} H_2SO_4. All experiments have been carried out at room temperature. The counter and reference electrode were plates of electrolytic copper.

Copper was deposited on a platinum electrode (in the measurements of the effective current density – effective overpotential relationships), on a copper sheet (in the determination of the current efficiency) and on a steel wire plated with copper from copper pyrophosphate bath (in the determination of the quality of electrodeposited copper). At the end of an experiment the wires were washed free of electrolyte, sealed in wax and metallographic samples of their cross-sections were made by cutting them and polishing in the usual manner. Photomicrographs have been made using magnifications of x 100 and x 500.

4. Digital simulation

The behaviour of the system has been simulated on a digital computer using the finite difference approximation. The central difference approximation for second order spatial derivatives has been used:

$$\left.\frac{\partial^2 C}{\partial x^2}\right|_{x=x_i} = \frac{C_{i-1} - 2C_i + C_{i+1}}{\Delta x^2} \tag{10}$$

$$i = 2, 3, \ldots, 19$$

where C_i is the value of the concentration at the point $x = x_i$ and $\Delta x = \delta/N$. A mesh of $N = 20$ points has been used. The boundary conditions at the points $i = 1$ and $i = 20$ are expressed in the following way:

$$\frac{C_2 - C_1}{\Delta x} = \frac{i_o}{nFD}\left[\frac{C_1}{C_o}\,10^{(\alpha_c F/2{\cdot}3RT)\eta(t)} - 10^{-(\alpha_a F/2{\cdot}3RT)\eta(t)}\right] \tag{11}$$

$$C_{20} = C_o \tag{12}$$

In this way the partial differential Equation (1) with corresponding boundary conditions (Equations 3 and 4) is replaced by a system of 20 time-dependent ordinary differential equations which is solved by the standard Runge-Kuta procedure.

The following values of physical constants are used:

$C_o = 1{\cdot}10^{-4}$ mol cm^{-3} $\quad D = 10^{-5}$ cm^2 s^{-1}

$n = 2$ $\quad i_o = 1{\cdot}10^{-3}$ A cm^{-2}

$F = 10^5$ A s mol^{-1} $\quad \delta = 3{\cdot}0 \times 10^{-2}$ cm

$\dfrac{\alpha_c F}{2{\cdot}3RT} = \dfrac{1}{120}$ mV^{-1} $\quad \dfrac{\alpha_a F}{2{\cdot}3RT} = \dfrac{1}{40}$ mV^{-1}.

5. Results and discussion

Experimental effective polarization curves for rectangular, sinusoidal and triangular pulsating overpotentials are shown in Figs. 1, 2 and 3 respectively. These results are very similar to the results obtained by Chernenko *et al.* [4] for current reversal. Practically no differences in polarization curves can be observed for different modes of pulsation, except for a small decrease of effective current density for one and the same value of effective overpotential going from rectangular to triangular pulsating overpotential. The effective limiting diffusion current density is reached at an effective overpotential of 200 mV in each case. The values of these current densities at low frequencies are almost the same as the stationary limiting diffusion current density. Increasing the frequency leads to smaller values of effective limiting current densities. This could be due to some deformation of the shape of the pulsating overpotential at higher frequencies. All these values are, however, larger than the value of cur-

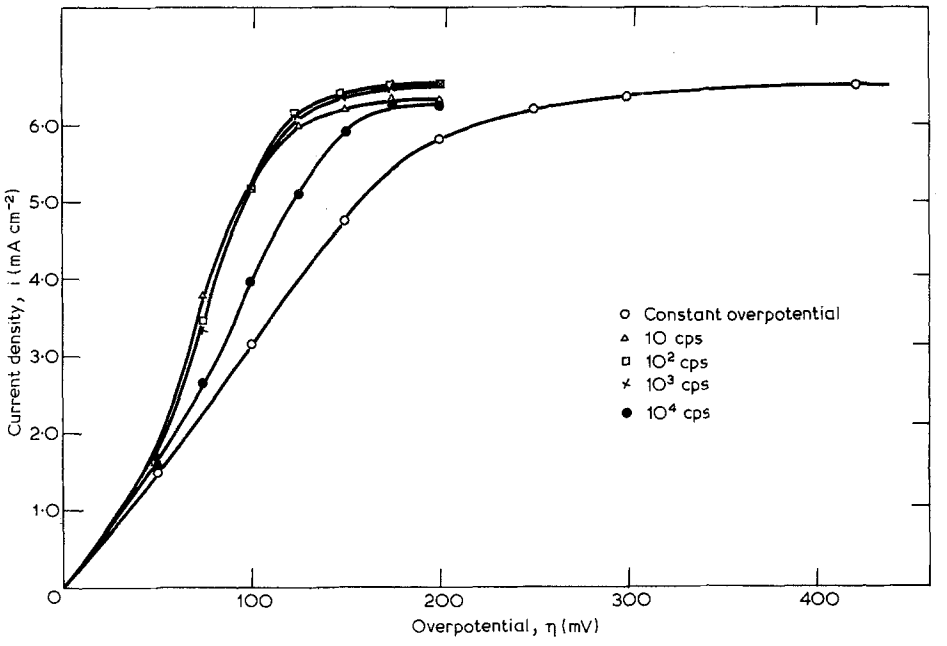

Fig. 1. Stationary polarization curve and polarization curves of effective values for different frequencies of rectangular pulsating overpotential.

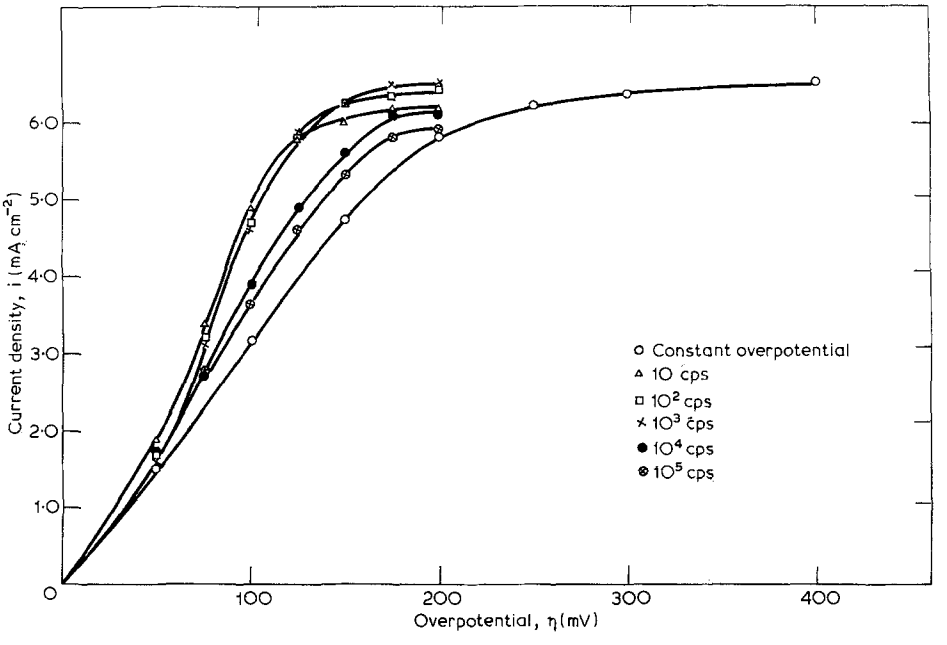

Fig. 2. Stationary polarization curve and polarization curves of effective values for different frequencies of sinusoidal pulsating overpotential.

rent density obtained at a constant overpotential of 200 mV. The current efficiency was near 100% in all experiments.

The effective polarization curves for 10 c/s and the stationary polarization curve obtained by digital simulation are compared with the experimentally obtained results in Fig. 4. The agreement between the theoretical and experimental results is fair. This is considered as a proof of the validity of the mathematical model used to de-

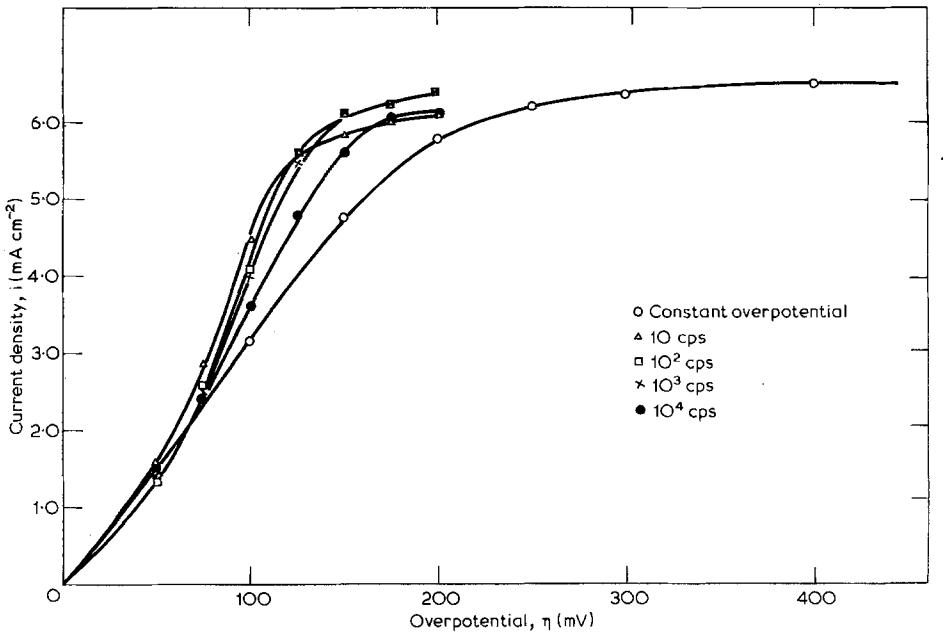

Fig. 3. Stationary polarization curve and polarization curves of effective values for different frequencies of triangular pulsating overpotential.

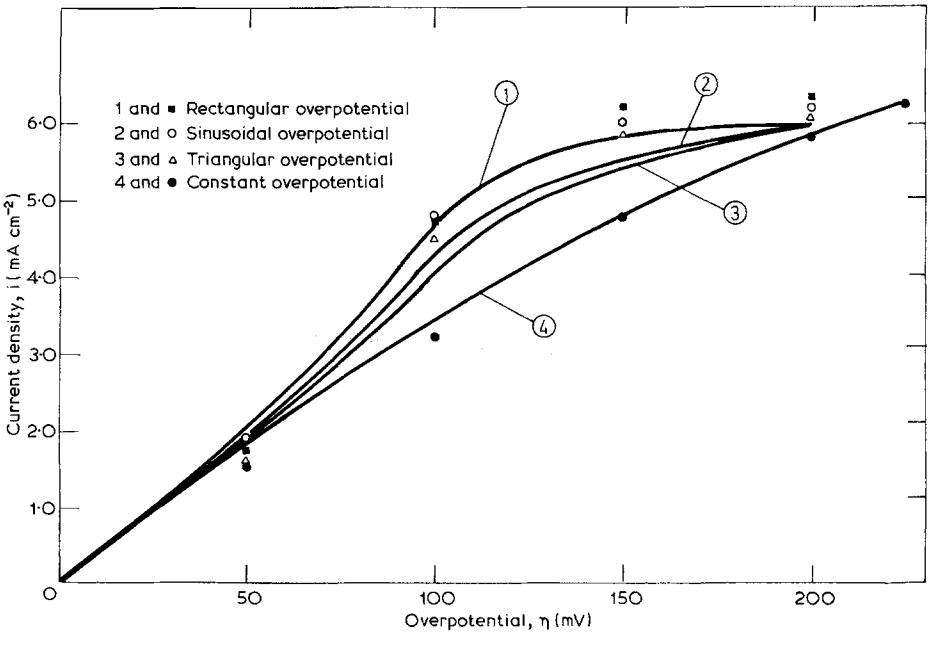

Fig. 4. Comparison of the calculated (lines) and experimental values (points) for stationary polarization curve and polarization corves of effective values for different shapes of pulsating overpotentials; frequency 10 c/s.

scribe the pulsating overpotential copper electrodeposition.

The effect of frequency of pulsating overpotential on the morphology of the copper deposits in each case was the same as reported earlier [1] for square-wave pulsating potentials. This is important since the sine-wave function is much easier to obtain than the square, or triangular

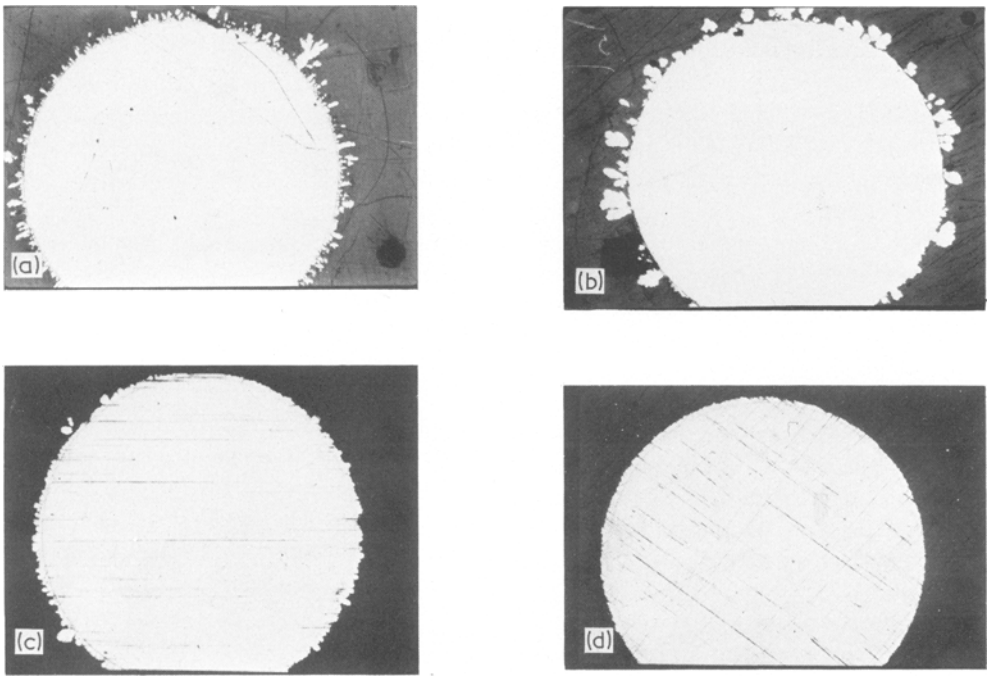

Plate 1. Copper deposits obtained by sinusoidal pulsating overpotential at effective overpotential of 200 mV (amplitude 400 mV). Frequencies: (a) 10^2 c/s (b) 10^3 c/s (c) 10^4 c/s (d) 10^5 c/s. Magnification X 100.

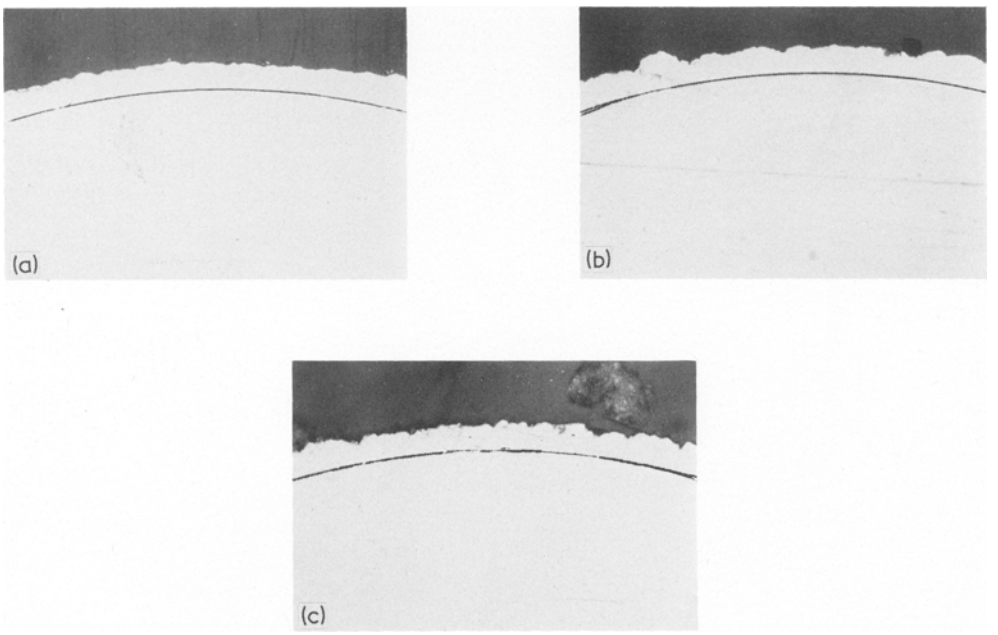

Plate 2. (a) Copper deposit obtained by sinusoidal pulsating overpotential at effective overpotential of 200 mV and frequency of 10^5 c/s. Magnification X 500. (b) Copper deposit obtained by constant overpotential of 200 mV. Magnification X 500. (c) Copper deposit obtained by rectangular pulsating overpotential at effective overpotential of 116 mV and frequency of 10^3 c/s. Magnification X 500.

ones. Typical results for sinusoidal pulsating overpotentials are shown in Plate 1. In Plate 2 a comparison is made between the copper deposits obtained at the same effective current density and the same effective overpotential for pulsating and constant overpotential electrolysis. Smoother copper deposits (Plate 2a) can be obtained using sinusoidal pulsating overpotentials of frequency 10^5 c/s and an effective overpotential of 200 mV, than by the same constant overpotential electrolysis (Plate 2b) at a 2% higher current density. Using a rectangular pulsating overpotential of 10^3 c/s and an effective overpotential of 116 mV it is possible to obtain smoother copper deposits (Plate 2c) than with a constant overpotential of 200 mV for the same current density. In this case the square-wave pulsating overpotential is chosen from among the three pulsating overpotential shapes used, because it is then possible to obtain the desired effective current density at the lowest value of effective overpotential. A frequency of 10^3 c/s is chosen because it gives the best effect of frequency on the morphology of the metal deposit at the same values of effective (and amplitude) overpotentials. By this pulsating overpotential regime it was possible to carry out the electrodeposition of copper at a 40% smaller energy consumption compared to the constant overpotential electrolysis at the same current density. The results presented above indicate various possibilities for improving copper electrodeposition by using pulsating overpotentials.

6. Conclusion

From the technological point of view, the most important result obtained from this work is the lowering of energy consumption for electrondeposition at the same current density and the same, or better quality of metal deposits. This fact could be of great importance in metal refining and plating.

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