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The effect of pulsating potential on the morphology of metal deposits obtained by mass-transport controlled electrodeposition

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Experiments have been carried out on the deposition of copper and zinc by imposing pulsating cathodic overpotentials of varying frequency on the electrodes. In the potential region, where the resulting currents were large enough to produce complete concentration polarization at the electrode, it was shown that at very low frequency ($\sim$10 cps) deposits exhibited surface roughness increasing with time in a manner similar to that seen in d.c. deposition. With increasing frequency an ever smoother deposit was obtained, and at high frequencies ($\sim$10,000 cps) no increase in surface roughness could be noted. A theory has been developed for reversible electrodes ascribing this effect to the capacity of the pulsating potential to give an effective diffusion layer of constant thickness determined primarily by the frequency. At very high frequencies the diffusion layer is thin and follows the micro-profile of the surface so closely that the diffusion flux and the resulting deposit are even and no surface irregularity is amplified.

Introduction

In plating practice it has been known for a relatively long time that under otherwise comparable conditions the application of periodically changing currents leads to improvements in the quality of the deposits [1]. Reversing currents, sinusoidal a.c. superimposed on a direct cathodic deposition current or pulsating currents have been used. The latter have been shown to affect the quality of deposit, for example on charging silver–zinc cells [2, 3, 4], silver oxide electrode [5], depositing zinc from alkaline zincate solutions [6], or copper from an acid copper sulphate bath [7]. Romanov was the first to carry out an extensive quantitative study [2] by observing the appearance and measuring the yield of dendritic zinc deposits from alkaline zincate solutions by varying the parameters of the pulsating current and comparing this with the appearance of dendrites in d.c. electrolysis of the same systems. A somewhat unexpected result was obtained: a much delayed appearance of dendrites compared with the time of appearance under d.c. polarization was found at very low frequencies; however, as the frequency was increased reduction of the time of appearance down to that for d.c. was obtained.

In the present investigation it was realized that controlled current pulses have a considerable shortcoming from the point of view of analysing the phenomenon. The double layer capacity consumes part of the current in the 'on' period of the pulse and releases it in the 'off' period thus smearing out the current wave. This effect is more pronounced the higher the frequency and at very high frequency, while pulsating in the outer circuit, the current approaches d.c. as far as the electrode process is concerned. This fact could probably explain the trend of increasing dendrite yield at increasing frequency found by Romanov.

Hence, it was realized that to study the effect of pulsating cathodic deposition one should use a pulsating cathodic potential between the reversible electrode potential and an overpotential sufficiently large that the resulting currents may be considered as partially or totally diffusion controlled. The results of such a study are reported below.

Experimental

A controlled pulsating potential was provided to the electrode to be investigated from a Wenking potentiostat driven by a square wave generator at the input, with the output voltage applied to the experimental cell. The counter-electrode was of the same material as the investigated electrode but of much larger surface area so that it could be considered to be unpolarized and used as the reference electrode. The ohmic drop between the electrodes has been neglected.*

The electrolytes used were 0·5 M $CuSO_4$ and 1·5 M zincate in 5·0 M KOH for copper and zinc deposition respectively. Copper was deposited on gramophone record negatives with well-defined triangularly shaped elevations some 40 μm high (comparable to that shown in Fig. 2). The electrolyte was immobilized at the electrode surface by adding agar to the solution. Zinc was deposited onto a wire electrode in a freely moving solution. After some time of deposition the sample was washed free of electrolyte, put in wax and a metallographic sample was made by cutting and polishing in the usual manner. Photomicrographs were made using a magnification 750 × for copper and 120 × for zinc.

Results

Typical results are shown in Plates 1 and 2. Dendrites were obtained for d.c. deposition and at low frequencies at 0·6 V and 0·1 V overpotential for coper and zinc respectively. Increasing frequency led to a progressively smoother deposit.

The ratio of the maximum elevation to the average thickness of the zinc deposit (calculated from the amount of metal deposited per cm^2 of geometric surface area) is plotted *v.* frequency of pulsation in Fig. 1 after 1 h of deposition.

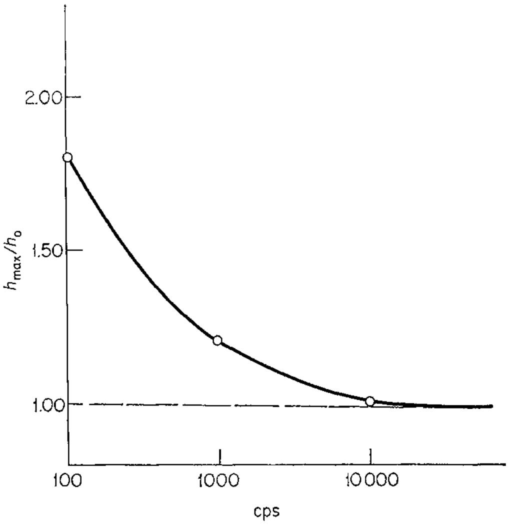

Fig. 1. The ratio of the maximum elevation to the average thickness of the zinc deposit as a function of frequency of the pulsating overpotential of 0·1 V.

Discussion

A pulsating large overpotential causes a periodic formation of a diffusion layer in the 'on' period and its relaxation in the 'off' period. For amplification of surface roughness to appear it is necessary that the diffusion layer should start diverging from the micro-profile of the surface. A model representation of the latter phenomenon was obtained by a computer calculation of the isoconcentration line of $C = 0{\cdot}5\ C_0$, from Fick's second law solved for a triangular elevation and for the sudden application of complete concentration polarization by d.c. The result is shown in Fig. 2. The diffusion flux of the depositing ions only becomes uneven and larger at elevations rather than at recesses when the diffusion layer diverges from the microprofile. Relaxation of the diffusion layer certainly delays this process.

In order to assess the extent of this effect Fick's second law was solved for the common

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* This is justified by the fact that in the current density range employed it could not be larger than 20 mV, of the several hundred mV overpotential used.

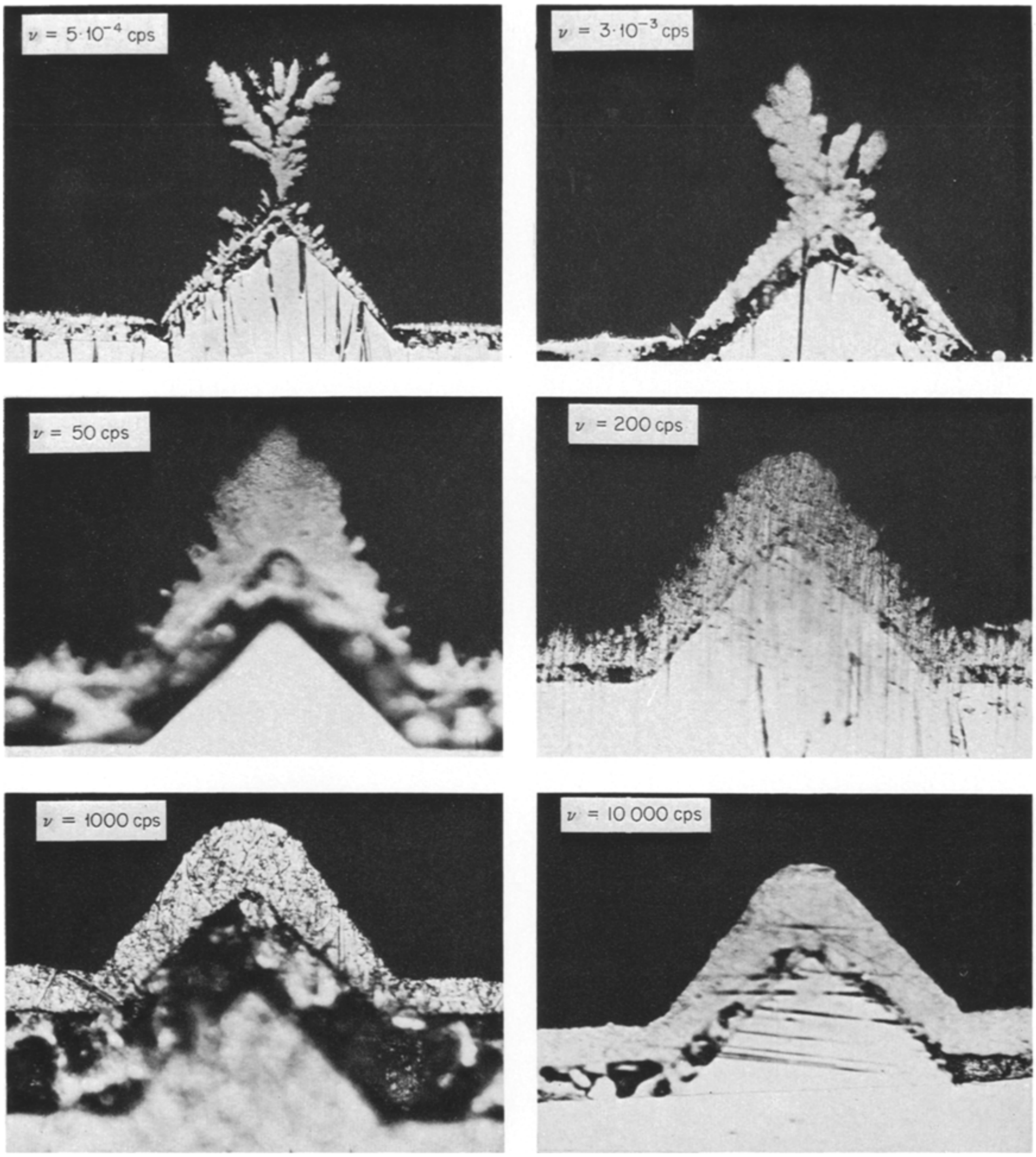

Plate 1 Photomicrographs of copper deposits onto a triangularly shaped irregularity (40 μm high) obtained by a pulsating cathodic overpotential of varying frequency. (magn. 750 ×)

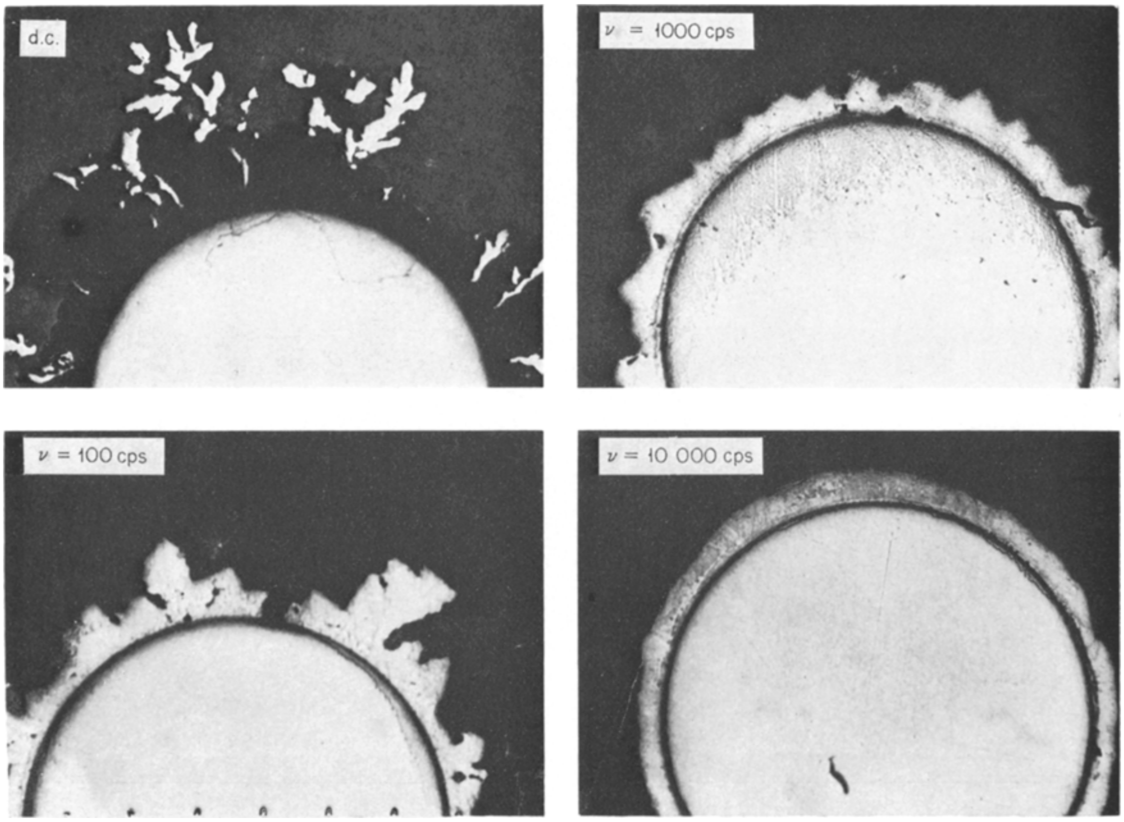

Plate 2 Photomicrographs of zinc deposited onto copper wire by a pulsating overpotential of varying frequency. (magn. 120 ×)

case of linear diffusion to an ideally reversible electrode but with a boundary condition at $x = 0$ oscillating between the bulk concentration value, C^0 in any 'off' period and some much smaller value C^s in the 'on' period of the overpotential pulse. Hence, the boundary conditions could be written as

$$C[0, (2n+1)\tau] = C^0 \tag{1}$$

$$C[0, 2n\tau] = C^s \tag{2}$$

where τ is the duration of the pulse,

$$C(x, 0) = C^0 \tag{3}$$

$$C(x, t)_{x\to\infty} = C^0. \tag{4}$$

C^s is related to the overpotential by the Nernst equation, i.e.

$$C^s = C^0 \exp\left(\frac{zF\eta}{RT}\right). \tag{5}$$

The solution gives the concentration of the depositing substance at the end of an 'on' and an 'off' period as a function of distance from the electrode surface and of time in the n^{th} period as

$$C_{\text{on}} = C[x, (2n+1)\tau] = \frac{2C_0}{\pi}\left[\int_0^{\frac{x}{2D^{1/2}[(2n+1)\tau]^{1/2}}} e^{-u^2}du + \right.$$
$$\left. + \int_{\frac{x}{2D^{1/2}(2n\tau)^{1/2}}}^{\frac{x}{2D^{1/2}[(2n-1)\tau]^{1/2}}} e^{-u^2}du + \quad + \int_{\frac{x}{2D^{1/2}(2\tau)^{1/2}}}^{\frac{x}{2D^{1/2}(2n\tau)^{\frac{1}{2}}}} e^{-u^2}du \right] \tag{6}$$

and

$$C_{\text{off}} = C[x, 2n\tau] = \frac{2C_0}{\pi}\left[\int_0^{\frac{x}{2D^{1/2}(2n\tau)^{1/2}}} e^{-u^2}du + \right.$$
$$\left. + \int_{\frac{x}{2D^{1/2}[(2n-2)\tau]^{1/2}}}^{\frac{x}{2D^{1/2}[(2n-2)\tau]^{1/2}}} e^{-u^2}du \quad + \int_{\frac{x}{2D^{1/2}\tau^{1/2}}}^{\infty} e^{-u^2}du \right] \tag{7}$$

The Nernst diffusion layer thickness δ_N is determined as

$$\delta_N = \frac{C^0}{(\partial c/\partial x)_{x=0}} \tag{8}$$

From the differentiation of (6) and introduction into (8) it follows that

$$\delta_N = \frac{D^{1/2}\pi^{1/2}\tau^{1/2}}{\left[\frac{1}{(2n+1)^{1/2}} - \frac{1}{(2n)^{1/2}} + \frac{1}{(2n-1)^{1/2}} - \ldots + 1\right]} = \frac{D^{1/2}\pi^{1/2}\tau^{1/2}}{q}. \tag{9}$$

Computer analysis has shown that the sum in the denominator is asymptotic to a value $q = 0{\cdot}606$. Hence, the diffusion layer thickness after the n^{th} pulse is not much different from that at the end of the first pulse. Thus, the latter can be taken as a good enough criterion of the diffusion situation for a pulsating potential.

The pulse duration τ being the inverse of the frequency ν, one can write

$$\delta_N = \frac{D^{1/2}\pi^{1/2}}{0{\cdot}606\,\nu^{1/2}} = K\nu^{-1/2}. \tag{10}$$

Important conclusions follow:

(a) irrespective of how still the solution is, the diffusion layer boundary for a pulsating potential does not expand, but stays fixed at a distance determined solely by the pulse frequency. A computer calculation analogous to that leading to Fig. 2, carried out for two different frequencies, shows that after a very large number of pulses the isoconcentration lines stay close to the surface

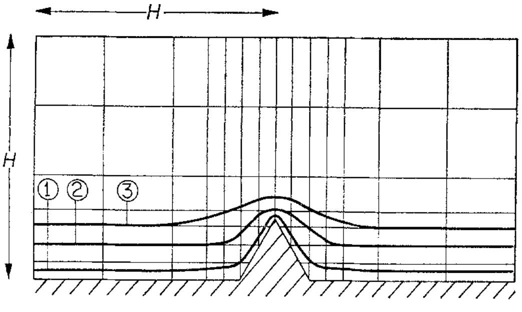

Fig. 2. Computer calculation of the iso-concentration lines of C = 0.5 C_0, made by application of the method of finite differences to solving Fick's second law for a model diffusion field of dimensions Hx2H in which there is a triangular protrusion. Iso-concentration lines are those after time intervals from the onset of total concentration polarisation at the surface, of 0.1 H^2/D (1); 5 H^2/D (2) and 10 H^2/D (3), where D is the diffusion coefficient.

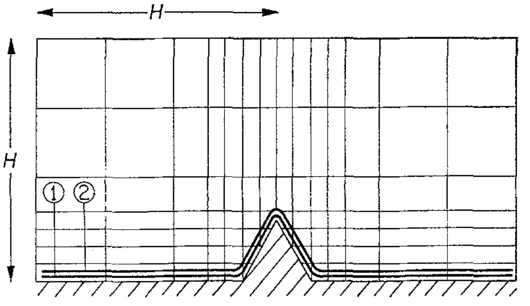

Fig. 3. Iso-concentration lines obtained for the same system as that in fig. 2 but with potential pulsating at a frequency of $100(D/H^2)$ cps. Line (1) pertains to the time interval of $0.1\ H^2/D$ and line (2) to times $\geqslant 5(H^2/D)$ from the onset of pulsating concentration polarisation.

profile (Fig. 3.) Hence, this appears to be a new manner of holding the diffusion layer thickness constant, additional to the known hydrodynamic means.

(b) by making v sufficiently large, δ_N can be made so small as to follow the surface microprofile as closely as desired; the order of magnitude of the surface irregularities is then not amplified.

The latter can be interpreted as follows. The difference in the supply of depositing ions between linear diffusion and, for example, spherical diffusion around tips of irregularities, can be considered to become appreciable when the diffusion layer thickness becomes of the same order of magnitude as the radius of curvature of the tips. Hence, at a certain frequency giving a diffusion layer of thickness defined by equation (10), all irregularities can be divided into those which are and those which are not amplified. The situation is represented by the graph in Fig. 4.

If a microscopic investigation similar to the one reported above can reveal only amplification of irregularities with radii larger than 1 μm, then it is obvious that this should be seen only at frequencies below 5,000 cps. This conclusion is in very good accordance with experimental findings.

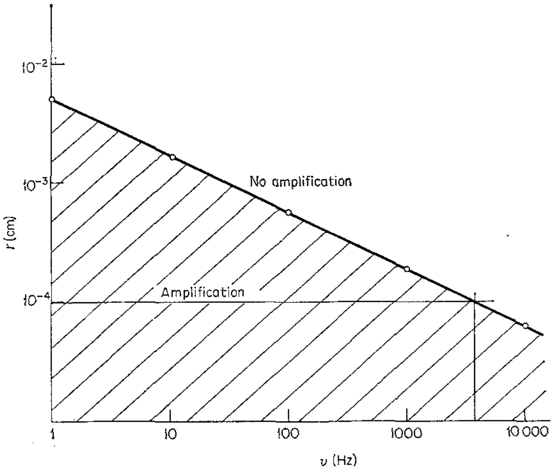

Fig. 4. The frequency dependence of the appearance of amplification of surface roughness. r- the radius of curvature of a surface irregularity.

The above conclusions have significant practical implications for electrowinning and electrorefining of metals as well as for plating. These will be discussed in another paper.

Acknowledgments

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