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*The effect of pulsating potential electrolysis on the porosity of metal deposits**

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Measurements of the porosity of nickel deposits on steel, obtained by pulsating potential electrolysis, have been performed. The porosity of the nickel deposits and the effective overpotentials have been determined as a function of frequency of pulsating potential for selected values of effective current densities. A qualitative discussion of the effect of pulsating potential on the porosity of metal deposits has been presented and the optimum electrolysis conditions have been established.

1. Introduction

In recent years, progress has been made in understanding the effect of pulsating potential on metal deposition on rough surfaces [1, 2]. It was shown that it was possible to prevent the increase of the surface roughness by preventing the expansion of thickness of Nernst's diffusion layer. At very high frequencies, the diffusion layer is thin and follows the microprofile of the surface so closely that the resulting diffusion flux and deposit follow it as well, and there is no amplification of the surface irregularities.

However, on the basis of these facts no conclusions can be drawn concerning the porosity of such a metal deposit. The purpose of this paper is to relate the porosity of metal deposit and the mass-transfer conditions during metal deposition.

2. Statement of the problem

If there is a uniform probability with time of covering the inert substrate, the time dependence of metal deposit porosity, which corresponds to the uncovered part of the surface, is given by

$$\pi = e^{-kit} \tag{1}$$

where π = porosity; k = constant; i = current and t = time. If the covering starts without overlapping, it is possible to determine a constant k as a reciprocal quantity of electricity which corresponds to one monolayer of electrodeposited metal. Equation 1 can then be rewritten as

$$\pi_n = e^{-n} \tag{2}$$

where n is an average number of electrodeposited monolayers. The local thicknesses distribution in this case is a consequence of the overlapping only.

Although Relation 2 is a qualitative one, it can be successfully used for discussing the dependence of the metal deposit porosity on the surface roughness.

Let the local thickness distribution of an n monolayers (average thickness) deposit be

fraction of surface	$1-2\theta$	θ	θ
average thickness of deposit	n	$n+1$	$n-1$

which is caused by non-uniform mass-transfer at the electrode. The porosity of such deposit will be given, according to Relation 2, by

$$\pi = (1-2\theta)e^{-n} + \theta e^{-(n+1)} + \theta e^{-(n-1)}. \tag{3}$$

Dividing Equation 3 with 2 we obtain

$$\pi = \pi_n [1 - 2\theta + \theta(e + e^{-1})]. \tag{4}$$

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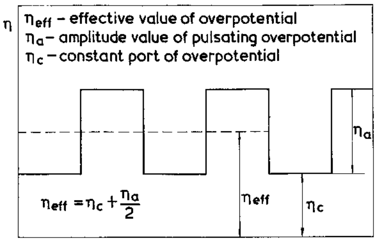

Fig. 1. The shape of input pulsating potential.

It is obvious that because $e + e^{-1} > 2$ for $\theta > 0$, the smoother deposit will be less porous than the rough one. Hence, it is possible to expect, according to Equation 1 a decrease in the porosity of the metal deposit with increasing frequency of pulsating overpotential.

3. Experimental

Nickel was deposited on a steel sheet which was used as a working electrode. The counter and the reference electrodes were pure nickel. The experiments were carried out at room temperature. The steel surface was prepared for electrodeposition in the usual manner. A nickel plating solution of the following composition was used

$NiSO_4 \cdot 7H_2O$	$340\,g\,l^{-1}$
$NiCl_2 \cdot 6H_2O$	$60\,g\,l^{-1}$
H_3BO_4	$40\,g\,l^{-1}$.

The electrolyte was prepared from Podnart chemicals for plating and distilled water. A controlled pulsating potential (Fig. 1) was provided from a Wenking potentiostat driven by a Hewlett-Packard function generator. The electrode was polarized by a constant overpotential (400 mV) in order to avoid the anodic dissolution of steel in the off periods of pulsating potential, because the potential of the steel electrode versus nickel in this solution was −350 mV.

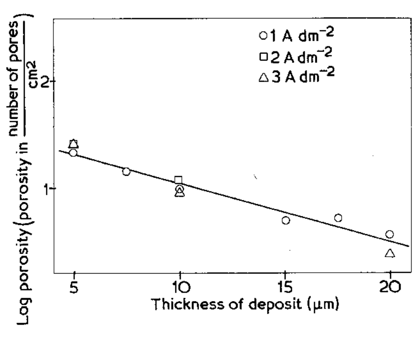

Fig. 2. Relationship between the porosity and thickness of metal deposit for different values of current density at constant overpotential.

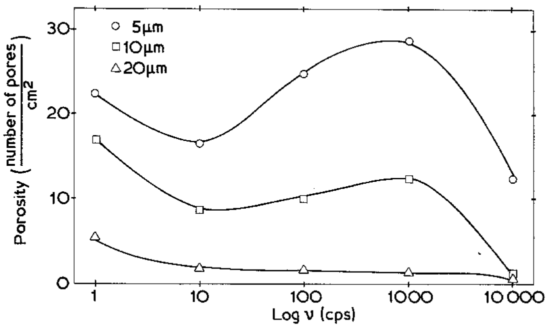

Fig. 3. Relationships between the porosity of metal deposit and the frequency of pulsating potential for an effective current density of 2 A dm^{-2} and different values of metal deposit thickness.

The effective values of current were measured with a d.c. ammeter (Iskra), and the effective values of overpotential were measured by a Hewlett-Packard electronic d.c. voltmeter. The shape of pulsating input potential was controlled by the Tektronix oscilloscope. The adhesion of the deposit was tested by cracking, and the porosity by the standard method [3].

4. Results and discussion

The adhesion of the deposit was satisfactory throughout the work and hence the study was directed to the investigation of the porosity. The dependence of porosity on the thickness of the nickel deposit is shown in Fig. 2. The straight line qualitatively confirms Relation 2. Similar results were obtained for all frequencies of pulsating potential, and for all effective values of current density.

The current efficiency in all experiments was from 94–98% and it was not possible to relate it to any parameter. The frequency dependence of the nickel deposit's porosity is presented in Fig. 3. The frequency dependence of the effective values of overpotential is shown in Fig. 4. The frequency dependence of the porosity of the nickel deposit exhibits a maximum and minimum, while the frequency dependence of the effective overpotential exhibits a minimum only.

This is due to the effect of two factors on the

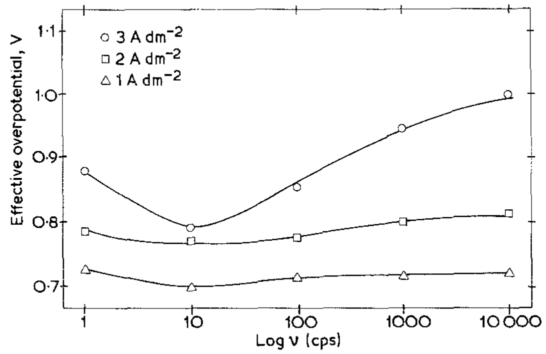

Fig. 4. Relationships between the effective overpotential and frequency of pulsating potential for different values of effective current density.

compactness of the metal deposit. Decreasing the effective overpotential, for the same value of effective current density, leads to smoother (less porous) deposits, and vice versa. In the high frequency region, where the effective value of overpotential is large, a small value of the Nernst's diffusion layer thickness prevents the irregular metal deposit growth. This is in accordance with earlier reported results [1, 4].

The best result obtained in this work was a 10 μm thick nonporous nickel deposit electrodeposited at a current density of 2 A dm^{-2} and a pulsating potential frequency of 10^4 cps.

5. Conclusions

It is shown that a smoother metal deposit will be less porous than a rough one, at the same average thickness, by using a simple mathematical model. On the basis of this result, the frequency dependence of metal deposit porosity obtained by pulsating potential electrodeposition was qualitatively discussed.

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