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The effect of the overpotential of deposition on the porosity of metal deposits

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The porosity of copper deposits on steel obtained by constant and pulsating overpotential electrolysis has been investigated and determined as a function of the overpotential of deposition. Optimal conditions for copper plating on steel from pyrophosphate baths have been established.

1. Introduction

In a recent paper [1] it was shown that depending on the conditions different quantities of electrodeposited metal are required to obtain the same coverage of an inert substrate with electrodeposited metal. These quantities depend on overpotential, and effective overpotential and frequency in standard potentiostatic, and pulsating overpotential deposition respectively. Following the same reasoning it could be expected that for the same quantity of metal deposit, different coverages of the substrate should be obtained as a function of the above variables.

If the porosity of the metal deposit is taken as the uncovered part of the inert electrode surface, an increase in the coverage leads to a decrease in the porosity of the deposits. Therefore, on the basis of results presented in the previous paper [1] optimal conditions for the deposition of nonporous deposits can be found easily. For the same average deposit thickness the relationship between the porosity and the overpotential of deposition could be established. The minimum porosity would correspond to the best plating conditions.

It is the purpose of this paper to check these ideas in the case of copper plating on steel from a pyrophosphate bath by constant and pulsating overpotential, and to offer some phenomenological observations in the area of pulsating overpotential electrodeposition.

2. Experimental

Copper was deposited on steel (0·04% C, 0·32% Mn, 0·014% P, 0·019% S, 0·055% Al) sheet which served as a working electrode. The counter and reference electrodes were pure copper. The steel surface was prepared for electrodeposition in the usual manner. The experiments were carried out at room temperature without stirring. A standard copper pyrophosphate bath with the following composition was used [2]: 160 g l^{-1} of $K_4P_2O_7 \cdot 10H_2O$; 103·5 g l^{-1} of $K_2HPO_4 \cdot 12H_2O$; 40 g l^{-1} of $CuSO_4 \cdot 5H_2O$; 3·5 g l^{-1} of Rochelle salt; at pH 7·5–8·9.

For this bath a current density in the range from 0·5–1·0 A dm^{-2} is recommended. The electrolyte solution was prepared from Podnart chemicals for plating and distilled water. The shape of the pulsating overpotential was the same as reported earlier [1]. In pulsating overpotential deposition the cathode was polarized by 100 mV from the reversible potential and the pulses were superimposed on that potential. A d.c. polarization served to prevent anodic dissolution of the steel during off-periods. The pulsation frequency of 10^4 cps was used, because at lower frequencies a yellow layer appears at the electrolyte surface adjacent to the cathode. The porosity of the deposit was tested by the ferroxyl test [3]. The current efficiency in all experiments was from 85–95%. It was not possible to relate it to any parameter although it showed a tendency to increase with decreasing current density.

3. Results and discussion

Stationary and effective polarization curves are presented in Fig. 1, from which relationships

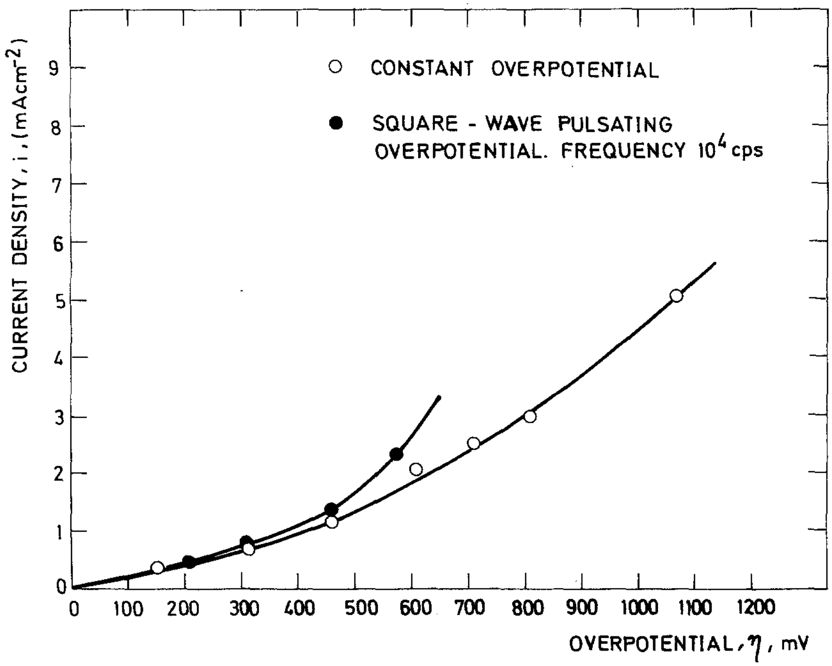

Fig. 1. Polarization curves for constant and pulsating overpotential copper deposition.

between overpotential and current density can be seen. In Fig. 2 the porosity of a 1 μm thick deposit as a function of overpotential (and effective overpotential) is shown. Each point represents an average of five independent measurements. The well-defined minima of porosity of copper deposits on steel can be completely explained on the basis of earlier reported theory [1] given for the mechanism of the formation of thin metal films on an inert electrode. According to the theory [1], these minima represent optimal plating conditions, in constant and pulsating overpotential deposition. In constant overpotential deposition at overpotentials lower than the optimal one, current densities on steel are low compared to current densities on formed copper film. This leads to non-uniform flux distribution and consequently to very porous deposits. At higher overpotentials the difference between the current densities of copper deposition on steel and copper becomes smaller. At these

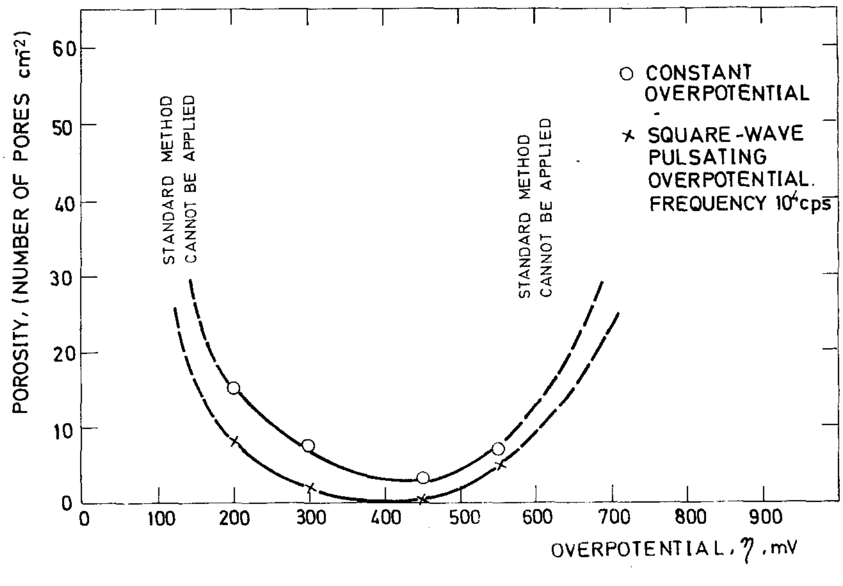

Fig. 2. Relationships between the porosities of 1 μm thick copper deposits on steel and the overpotential (effective overpotential) of deposition.

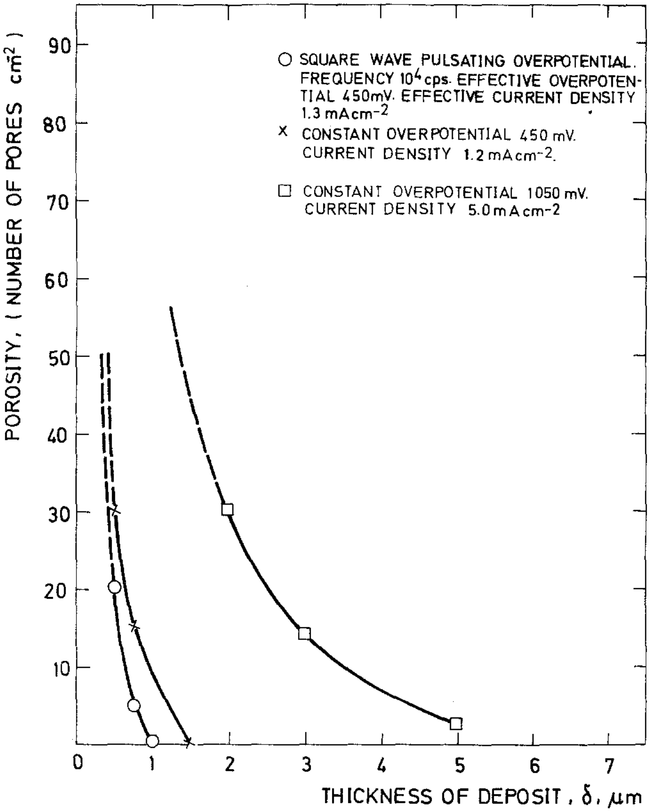

Fig. 3. Relationships between the porosities and thicknesses of copper deposits on steel, obtained under various conditions of deposition.

overpotentials deposition on copper enters mixed control, and this leads to non-uniform flux distribution and a more porous deposit.

The effects of pulsating overpotential on the porosity of deposits clearly show that the above explanation is valid. Deposits obtained at the optimal effective overpotential are deposited at an actual overpotential which has an amplitude which is two times larger. At that overpotential very porous deposits are obtained in constant overpotential deposition. In the case of pulsating overpotential, the current densities on steel and copper become comparable, and pulsation prevents non-uniform flux distribution [4] on copper. This is the mechanism by which the pulsating overpotential deposition gives less porous deposits. This effect of pulsation on porosity was observed only in the case of a square-wave pulsating overpotential.

Relationships between porosity and thickness of metal deposits obtained under various conditions of deposition are shown in Fig. 3. These deposits were obtained at overpotentials which correspond to minima of porosity–overpotential relationships (optimal conditions for constant and pulsating overpotential deposition) and at an overpotential which corresponds to a current density in the recommended current density range [2], which gives the least porous deposits [5]. It is seen from Fig. 3 that deposits obtained under optimal conditions show the same porosity at a several times lower thickness, compared to those obtained by using the recommended current density. As the porosity is the same for much thinner deposits, it should be possible to reduce copper consumption in the plating process. At the same time, because of the much lower current density and overpotential of deposition, for approximately the same times of electrolysis, these processes can be carried out with a large reduction in specific energy consumption.

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