JOURNAL OF APPLIED ELECTROCHEMISTRY 9 (1978) 19–23

Electrodeposition of zinc on copper from alkaline zincate solutions

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Received 26 March 1977

Experiments have been carried out on the deposition of zinc by constant and pulsating overpotential from alkaline zincate solutions. In pulsating overpotential deposition the amplitude values of overpotential used were smaller than the critical overpotential for dendritic growth. The transformation of the form of the zinc deposit from spongy to dendritic in constant overpotential electrodeposition is shown. The possibility of obtaining smooth deposits in pulsating overpotential electrodeposition is also shown.

1. Introduction

It is well known that smooth zinc deposits cannot be obtained practically from alkaline zincate solutions by constant overpotential or constant current electrolysis. Smooth deposits can be obtained by using pulsating current [1], reversing current [2] and pulsating overpotential electrodeposition [3]. These results are very difficult to compare with each other, since no data exist on average values of current and overpotential.

It was recently shown that a complete understanding of the electrolysis with periodically changing rate is possible only on the basis of average and effective polarization curves [4, 5]. On the other hand, an improvement of our understanding of the electrodeposition of the first monolayers on inert substrates has been made [6, 7]. On the basis of these results, it should be possible to obtain compact and smooth zinc deposits in pulsating overpotential electrodeposition.

The purpose of the work described here was to discuss the electrodeposition of zinc from alkaline zincate solutions in terms of average values of overpotential and current density in pulsating overpotential electrodeposition and to try to obtain compact and smooth zinc deposits.

2. Experimental

Zinc was deposited on a platinum electrode (in the measurements of the average current density–average overpotential relationships) and on copper wire (in the determinations of the quality of electrodeposited zinc). The measurements of average current density on platinum were performed after sufficiently long times of deposition, when coverage was complete.

The electrolyte used was $50\,g\,l^{-1}$ ZnO in 10 N KOH. The electrodeposition of zinc was carried out by constant and square-wave pulsating overpotential, at room temperature, in an open cell. The potentiostat, pulse generator and the procedure for preparing the metallographic samples were similar to those which have been described previously [4]. Counter and reference electrodes were of electrolytic zinc. Photomicrographs have been made using a magnification of $\times$ 100.

3. Results and discussion

The stationary polarization curve and polarization curves corresponding to average values are presented in Fig. 1. The shapes of the average values polarization curves are very similar to those reported earlier [4, 5]. The results of the mor-

*Presented at the 4th Yugoslav Symposium on Electrochemistry, June 1975, Dubrovnik, Yugoslavia.

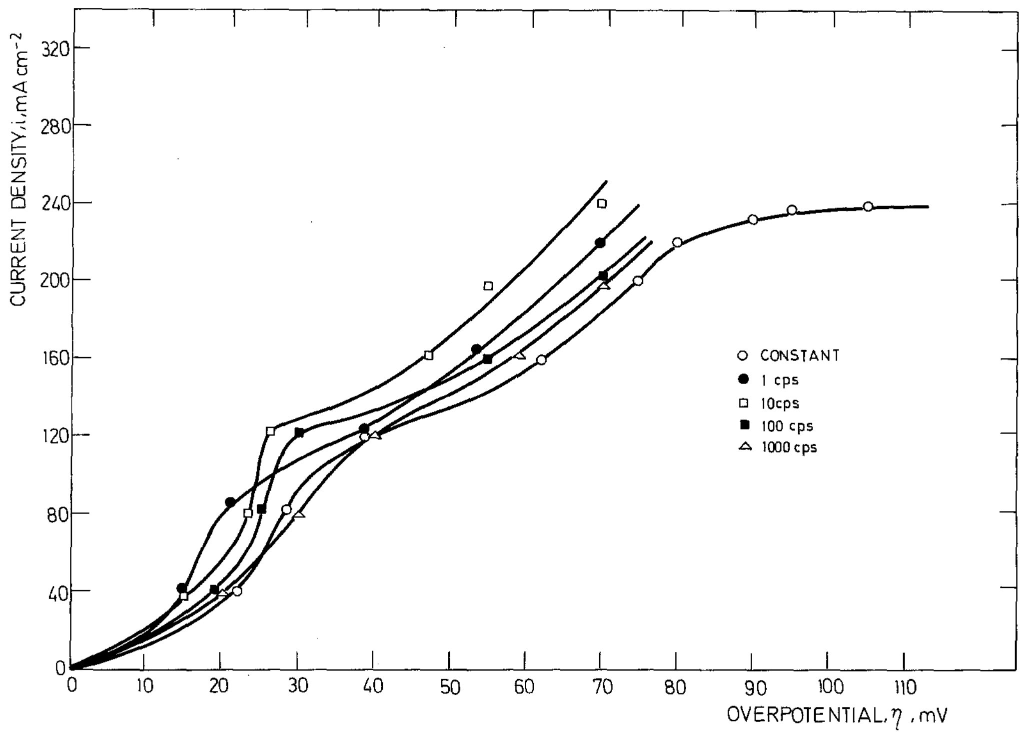

Fig. 1. Constant overpotential polarization curve and average values polarization curves.

phologies of the zinc deposits are presented in Figs. 2–4.

In Fig. 2, typical deposits obtained by constant overpotential deposition are shown. In experimental conditions like these in a nickel–zinc cell with soluble zinc anodes, p.a. chemicals, distilled water, an open cell [8], smooth zinc deposits cannot be obtained by constant overpotential deposition. These results cannot be compared with results obtained under more rigorous experimental conditions, (for example, those of Bockris *et al.* [9]). They can be used for comparison with the deposits obtained by pulsating overpotential deposition under the same experimental conditions.

The change in quality of the zinc deposits with increasing overpotential can be discussed taking into account two effects; (a) the effect of overpotential on the deposition of the first metal monolayers on an inert substrate [6, 7]; and (b) the effect of overpotential on dendritic growth [10–12].

It was recently shown [6, 7] that the quantity of metal deposit, required to obtain the same coverage of an inert electrode, is a function of the overpotential of deposition. At low overpotentials this can be due to different current densities of deposition on an inert substrate and on deposited metal film at the same value of overpotential [13], resulting in porous or spongy deposits.

Increasing overpotential leads to the formation of more compact first monolayers, but dendritic growth starts because of the onset of concentration polarization [10–12, 14]. The critical overpotential for dendritic growth in these experiments was ~ 75 mV. Despić and Popov [3] discussed the effect of frequency of pulsation on the morphology of zinc deposits at overpotential amplitudes larger than the critical one for dendritic growth. Regardless of the necessity of extending these investigations, especially in terms of the kinetic-thermodynamic conditions of dendritic growth [11], only results obtained for amplitude overpotentials lower than the critical one will be referred to in this paper. In Fig. 3 the zinc deposits obtained at an average current density of 4 mA cm^{-2} at different frequencies of pulsation are presented. The zinc deposits obtained at a frequency of 10 Hz at different current den-

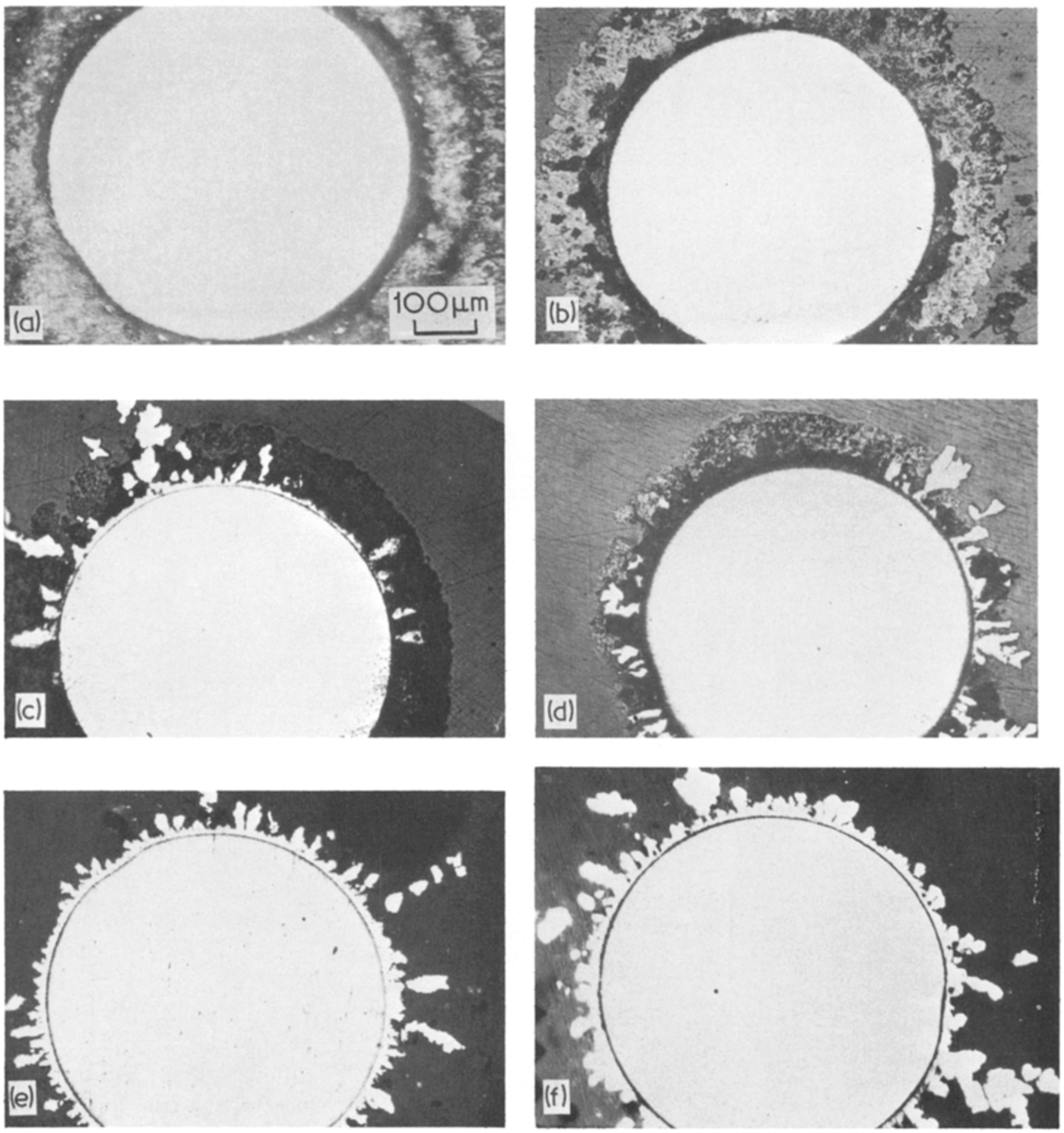

Fig. 2. Zinc deposits obtained by constant overpotential electrodeposition at different values of overpotential, η (mV), initial current density, i (mA cm^{-2}) and duration of electrolysis, t (min). (a) $i = 4{\cdot}0$; $\eta = 22$; $t = 40$ (b) $i = 16{\cdot}0$; $\eta = 62$; $t = 60$ (c) $i = 20{\cdot}0$; $\eta = 75$; $t = 96$ (d) $i = 22{\cdot}1$; $\eta = 80$; $t = 80$ (e) $i = 23{\cdot}7$; $\eta = 95$; $t = 80$ (f) $i = 23{\cdot}9$; $\eta = 105$; $t = 80$.

sities are shown in Fig. 4. It is seen from Figs. 3 and 4, that regardless of frequency of pulsation and overpotential amplitude (if the amplitudes of the overpotentials are smaller than the critical overpotential for dendritic growth) compact and relatively smooth zinc deposits are obtained. This can be explained as follows: as was shown earlier [6, 7], in pulsating overpotential metal electrodeposition the average current density of deposition on an inert substrate increases faster with increasing overpotential than the average current density of deposition on a formed deposit, compared with constant overpotential deposition. In this way, more compact deposits are formed under pulsating overpotential conditions compared to constant overpotential electrolysis. On the

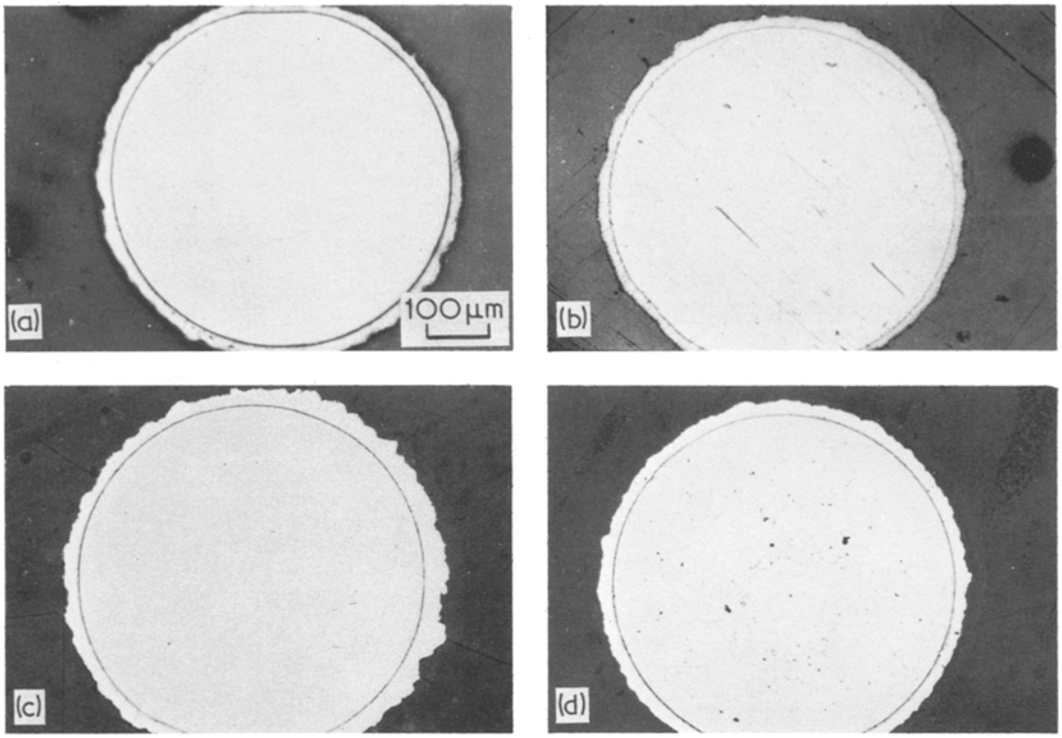

Fig. 3. Zinc deposits obtained by pulsating overpotential at an average current density of 4 mA cm^{-2} for 4 h of deposition at different values of frequency, ν (Hz), and overpotential amplitude, η_A (mV). (a) $\nu = 1$; $\eta_A = 30$ (b) $\nu = 10$; $\eta_A = 30$ (c) $\nu = 100$; $\eta_A = 38$ (d) $\nu = 1000$ Hz; $\eta_A = 40$.

other hand, during the 'off' periods the dispersed deposit dissolves because of the Kelvin effect. It is well known [14] that the reversible potential of a surface with radius of curvature, r, would depart from that of a planar surface by the quantity

$$E_r = \frac{2\alpha V}{Fr} \tag{1}$$

where α is the interfacial energy between metal and solution and F Faraday's constant. Hence, it could be expected that in pulsating conditions in the pauses of pulsating overpotential, metal dissolves at the points where the radius of curvature is small. At the same time the deposition of an equivalent amount of metal at the points where the radius of curvature is large can be expected.

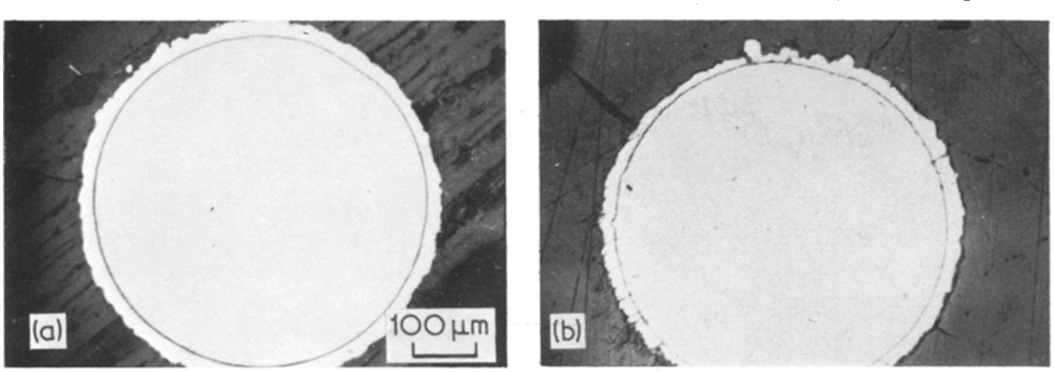

Fig. 4. Zinc deposits obtained by pulsating overpotential at a frequency of 10 Hz and different values of initial current density, i (mA cm^{-2}), overpotential amplitude, η_A (mV), and time of electrolysis, t (min). (a) $i = 7{\cdot}9$; $\eta_A = 47$; $t = 120$ (b) $i = 12{\cdot}3$; $\eta_A = 53$; $t = 80$.

Hence the Kelvin effect during the pauses will stimulate the formation of smooth metal deposits. Because compact deposits are obtained at all applied current densities and frequencies, the optimal conditions of pulsating overpotential deposition can be defined using energy considerations. It was recently shown [5] that specific energy consumption in square-wave pulsating overpotential electrolysis is proportional to the amplitude value of the pulsating overpotential. The amplitude overpotential is two times larger than the average one if 'off' and 'on' times are equal. Hence, it is seen from Fig. 1 that smaller amplitude values are required, to obtain the same current density, at low frequencies of pulsation. Consequently, for one and the same current density, the depostion of compact zinc will be carried out with smaller specific energy consumption at low than at high frequencies of pulsating overpotential.

Acknowledgements

The authors are indebted to the N.S.F. (U.S.A.) for its sponsorship under the PL-480 Programme and to the Fund for Research of the SR of Serbia, whose material support has made this work possible.

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