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Electrochemical nucleation of mercury on platinum in the presence of organic additives

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The electrochemical nucleation of mercury on a platinum electrode has been studied in the presence of some organic compounds used in the deposition of bright galvanic coatings. It is established that these organic additives do not affect the thermodynamics of the nucleation process but block the electrode surface, thus decreasing the rate of nucleus formation. It is found that the growth of the stable metal clusters is inhibited in the presence of the organic substances which leads to a marked increase of the maximal number of nuclei formed on the electrode surface.

1. Introduction

The presence of organic compounds in an electrochemical system may cause significant changes in the properties of both the electrolyte solution and the 'electrode–electrolyte' interface. It is obvious that these changes also essentially affect the kinetics of nucleation and growth of a new phase. For this reason many organic compounds are used to optimize the practical processes of electrochemical plating. Of course, in most cases these substances are chosen empirically without knowing the actual mechanism of their influence on the nucleus formation and on the growth of stable clusters in the advanced stages of electrodeposition. The solution of this problem, in the case of a complex industrial electrolyte, is an extremely difficult task. Thus, the aim of this study is to examine the effect of some organic compounds on the nucleation and growth kinetics in a more simple, model electrochemical system.

2. Experimental details

The electrochemical system consisted of a platinum single crystal working electrode and a 1 M aqueous solution of $Hg_2(NO_3)_2$ kept at 308 K. Bulk mercury was used as counter and reference electrode and all overpotentials, η, are referred to its equilibrium potential E_0 ($\eta = E_0 - E$). The construction of the electrochemical cell provided the possibility for microscopic observation of the working electrode. This electrochemical system has been used in many experimental studies [1–6] of the nucleation kinetics mainly because of the good reproducibility of the experimental results and the reliability of the data obtained for the nucleation parameters.

The organic compounds used in this study were components of a composite additive (CA) for bright copper plating containing polypropyleneglycol type of polymers (PPG), safronic dyes (SD) and sulfo-organic aliphatic compounds (SAC) with a disulphide group [7]. The results from an investigation of the nucleation kinetics of mercury on platinum in the presence of PPG have already been reported elsewhere [4]. Here we present data on the influence of SD, SAC* and CA (PPG + SD + SAC) on the initial stage of mercury electrodeposition. All concentrations, C, of the additives are referred to the corresponding optimal concentrations, C_0, used in the industrial electrolyte for bright copper plating.

The nucleation kinetics were studied by means of a triple pulse potentiostatic technique [1–6] allowing visualization and counting of the metal clusters formed on the electrode surface. Thus it was possible to obtain 'number of nuclei (N) vs time (t)' relationships for different overpotentials, η.

3. Results and discussion

The $N(t)$ experiment provides information on two basic characteristics of the nucleation process (Fig. 1) – the steady state nucleation rate, I_{st}, given by the slope, dN/dt, of the linear part of the $N(t)$ dependence and the saturation number of nuclei obtained from the plateau of the $N(t)$ relationship.

3.1. *Steady state nucleation rate in the presence of organic compounds*

The steady state rate of nucleus formation can be presented in the form:

$$I_{st} = N_0 \omega_k \exp(-A_k/kT) \qquad (1)$$

where N_0 is the number of active sites on the electrode surface, ω_k is the frequency of attachment of single ions to the critical nucleus and A_k is the nucleation work.

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* The studies in the presence of SAC were commenced with the assistance of A. Danilov (visiting research fellow from the Institute of Physical Chemistry, Academy of Sciences of USSR) and some experimental results are reported in [8].

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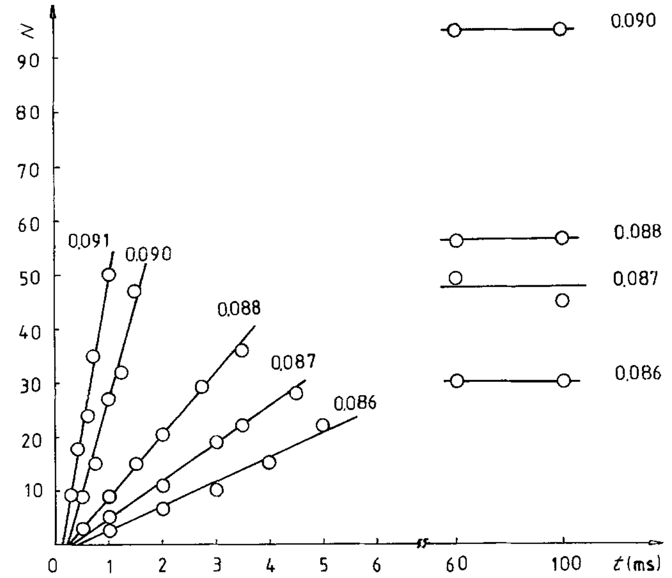

Fig. 1. Number of nuclei–times relationships obtained in 1 M $Hg_2(NO_3)_2$ at different overpotentials marked by figures in V.

In principle the presence of organic compounds in an electrochemical system may affect I_{st} in three different ways: (a) by adsorbing on the nucleus surface, thus decreasing the specific surface energy and, therefore, decreasing both the thermodynamic barrier, A_k, for nucleus formation and the size, n_k, of the critical nucleus; (b) by adsorbing on the electrode surface thus decreasing the number, N_0, of free active sites for nucleus formation; (c) by changing the structure of the electrical double layer thus changing the frequency, ω_k.

The effect of the organic compounds on the size, n_k, of the critical nucleus can be found by studying the overpotential dependence of the steady nucleation rate. Bearing in mind that

$$A_k = \phi(n_k) - n_k ze\eta \quad (2)$$

and

$$\omega_k = K \exp(\alpha ze\eta/kT) \quad (3)$$

for I_{st} one obtains [6]

$$I_{st} = N_0 K \exp[-\phi(n_k)/kT] \exp[(n_k + \alpha)ze\eta/kT] \quad (4)$$

where α is the transition coefficient, $\phi(n_k)$ is an energetic measure for the 'nucleus–substrate' and the 'nucleus–mother phase' interaction and K is a frequency factor.

As is seen from Equation 4 the quantity n_k can be determined directly from the slope of an experimental $\ln I_{st}$ vs η plot. Figure 2 presents data for the steady state nucleation rate obtained in the base electrolyte (pure 1 M $Hg_2(NO_3)_2$) and in the presence of the different organic compounds. The constant slope $d \ln I_{st}/d\eta$ of the straight lines shows that the size of the critical nucleus is influenced neither by CA nor by its components SD, SAC and PPG. This means that the organic compounds do not affect the thermodynamics of the nucleation process. This result is not

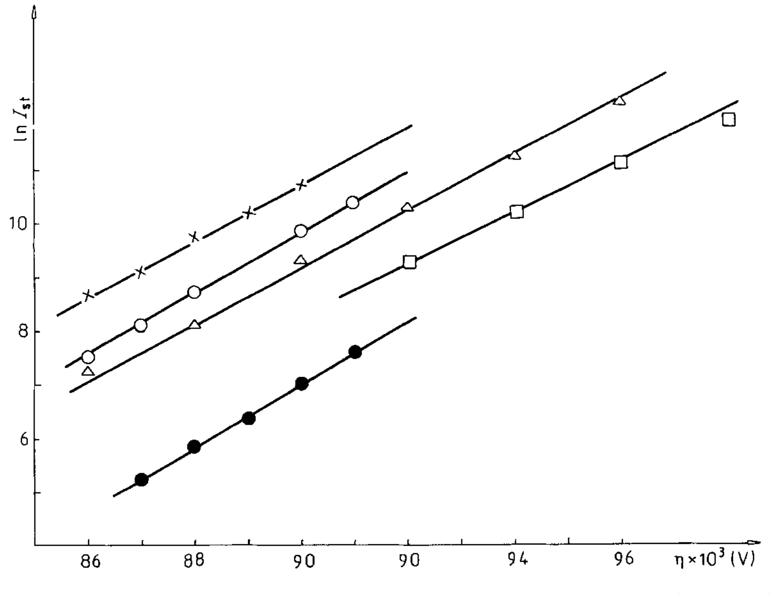

Fig. 2. Overpotential dependence of the steady state nucleation rate I_{st} obtained in pure 1 M $Hg_2(NO_3)_2$ (×) and in the presence of SD (○), SAC (△) and CA (●). The data for PPG (□) are taken from [4].

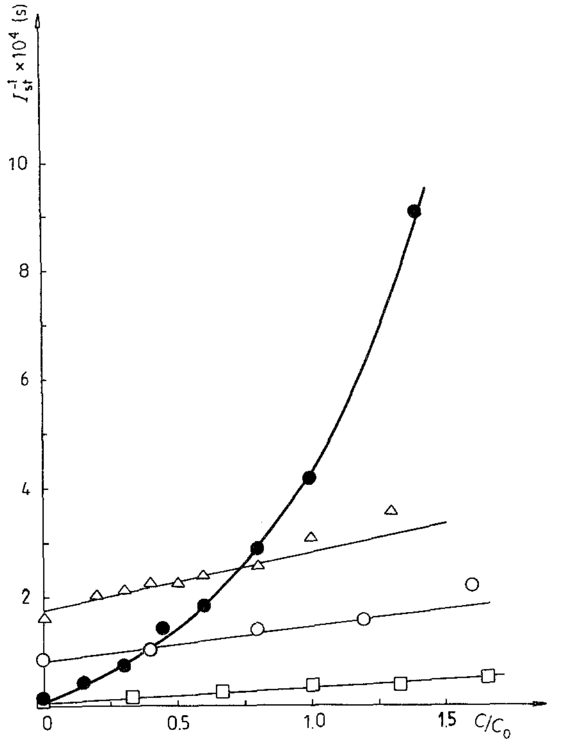

Fig. 3. Concentration dependence of the steady state nucleation rate, I_{st}, obtained in the presence of PPG (□) [4], SD (○), SAC (△) and CA (●).

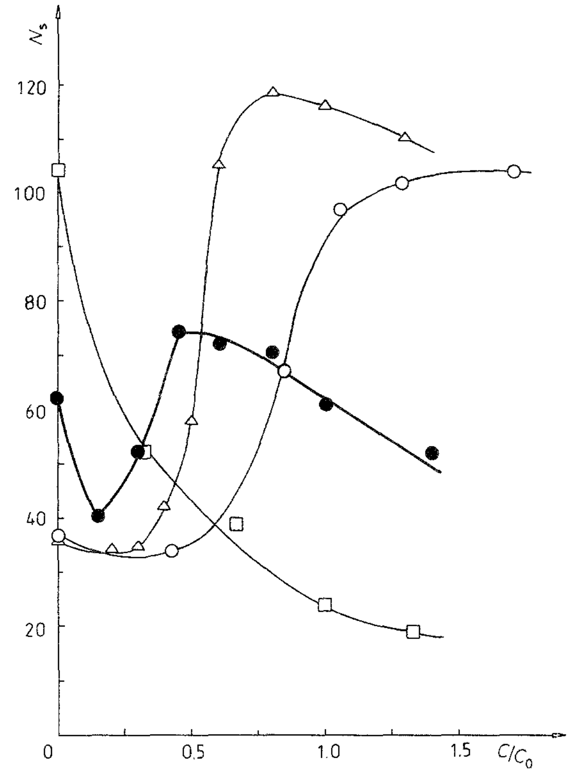

Fig. 4. Concentration dependence of the saturation number of nuclei, N_s, obtained in the presence of PPG (□) [4], SD (○), SAC (△) and CA (●).

very surprising bearing in mind that the critical nucleus consists of only 6 atoms. Therefore it seems useless to comment upon adsorption of the much bigger organic molecules on its 'surface'.

Let us now consider the possibility for adsorption of the organic compounds on the working electrode. In this case the steady state nucleation rate will be

$$I_{st} = I_{st}^0(1 - \theta) \tag{5}$$

where I_{st}^0 is given by Equation 4 and $\theta = N_0^a/N_0$, N_0^a being the number of active sites occupied by the organic molecules. If θ is expressed by a Langmuir type of adsorption isotherm

$$\theta = c/(c + B) \tag{6}$$

for I_{st} one obtains

$$I_{st} = I_{st}^0 B/(c + B) \tag{7}$$

where c is the concentration of the organic compounds and B is an adsorption constant.

Equation 7 shows that the data for I_{st} should be linear in I_{st}^{-1} vs c coordinates. As is seen in Fig. 3 this is true for the case of SD, SAC and PPG. However the data for I_{st} obtained in the presence of the composite additive (points in Fig. 3) show a much stronger concentration dependence. This might be due to some interaction between the adsorbed organic components (SD, SAC and PPG) leading to an increased blocking of the electrode surface.

It is to be noted that the above interpretation of the experimental results is based on the assumption that the decrease of I_{st} is due only to the blocking of the electrode surface by the adsorbed organic species. In fact, the overall decrease of I_{st} may also reflect some changes of the quantity ω_k in the presence of the organic compounds. However such effects can not be distinguished in the framework of the present study.

3.2. *The saturation number of nuclei in the presence of organic compounds*

Let us first note that the saturation number of nuclei, N_s, is a complex quantity depending essentially on both the nucleation kinetics and the growth of the supercritical clusters. In fact, there are two different processes determining the value of N_s – the direct exhaustion of active sites by the nuclei appearing on the electrode surface and the spreading and overlap of nucleation exclusion zones arising around the growing stable clusters.

It is to be noted that the nucleation exclusion zones may have different physical natures – diffusion zones [9] when nucleation occurs in dilute electrolytes and zones of reduced overpotential [10] when nucleation occurs in concentrated electrolytes. In both cases, however, the spread of the nucleation exclusion zones depends on the growth kinetics of the stable clusters.

In principle, the presence of organic compounds in the electrochemical system may influence N_s in two different ways: on the one hand the organic molecules can block the electrode surface thus decreasing the number of free active sites and, therefore, decreasing N_s; on the other hand the organic compounds can hinder the growth of the supercritical clusters thus hindering the spread of the nucleation exclusion zones. The last effect will increase the number of free active sites and therefore will increase N_s. Thus, both overall increase or decrease of N_s could be expected in the presence of organic compounds depending on the prevailing influence of the two competitive factors.

Figure 4 shows the experimentally observed concentration dependences of N_s found in the presence of the separate organic additives. The continuous decrease of N_s when increasing the concentration of PPG (squares in Fig. 4) is direct evidence for the blocking effect of this compound [4]. The effect of SD and SAC (circles and triangles in Fig. 4) is, however, much more complicated. Thus, at low concentrations of these substances only a slight decrease of N_s is observed. On increasing c_{SD} and c_{SAC}, N_s markedly increases, probably because of the hindered spread of the nucleation exclusion zones. The plateau and the slight decrease in the $N_s(c)$ relationship found at high concentrations of SD and SAC obviously reflect the compensation of the two competitive processes. Concerning the concentration dependence of N_s in the presence of CA (points in Fig. 4), this seems to be a result of a complicated superposition of the $N_s(c)$ relationships of the three different components – PPG, SD and SAC.

4. Conclusions

Thus far it has been established that the organic compounds used in this study do not influence the thermodynamics of mercury nucleation on a platinum cathode. It has been found that the composite additive (CA) as well as the three separate components (PPG, SD and SAC) block the electrode surface thus decreasing the steady state rate of nucleus formation. Also, the rising parts of the $N_s(c)$ relationships give evidence for hindering of the growth kinetics of the stable clusters in the presence of SD, SAC and CA.

These results, although obtained in a model system and under potentiostatic conditions, may be used to draw some preliminary conclusions about the mechanism of influence of the organic additives during the process of practical metal plating. Thus, bearing in mind that under galvanostatic conditions all limitations of the growth kinetics cause an increase of the overpotential it is clear that the presence of organic additives in the electrolyte will strongly increase the rate of nucleus formation. This increases the number of nuclei formed on the electrode surface. The effect is enhanced because of the impeded spread of the nucleation exclusion zones, this leading to an increase in the number of free active sites for nucleus formation. As a result a great number of small metal clusters are formed which is an important requirement for the deposition of bright corrosion-protective metal coatings.

Acknowledgements

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