An experimental study of zinc morphology in alkaline electrolyte at low direct and pulsating overpotentials

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Abstract

A possible mechanism of the formation of spongy zinc electrodeposits is considered. The confirmation of the proposed semiquantitative mathematical model is performed in zinc electrodeposition onto copper wire from a 0.1 M zincate solution in 1.0 M KOH at room temperature. It was shown by SEM analysis of the deposit that the spongy growth was caused by mass transfer limitations under low nucleation rate conditions. In this situation, amplification of the surface inequalities on the independently growing grains takes place leading to the formation of the spherical agglomerate of filaments, which form a spongy deposit. Also, it was shown that in the case of a square-wave pulsating overpotential regime, the deposits are less agglomerated than the ones obtained in the case of a direct overpotential regime. This effect is more pronounced at a higher pulse-to-pulse ratio. This is explained by dissolution of filaments, based on the mathematical model of pulsating overpotential. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

It is well known that smooth zinc deposits cannot be obtained from alkaline zincate solutions at constant overpotentials [1,2]. There are three distinct types of zinc deposits reported in the literature [2–5]. At low overpotentials, a spongy deposit is obtained, while at higher overpotentials near the limiting current, a boulder type of deposit is formed and upon further deposition the boulders preferentially grow into dendrites. The mechanisms of dendritic growth initiation and dendritic growth, as well as of nondendritic amplification of surface roughness have already been quantitatively described [2,6–10]. On the other hand, the mechanism of spongy deposit formation was discussed only in a qualitative way [1,3,5,11–14], mainly for spongy zinc from zincate alkaline solutions. Popov and Krstajić [15] presented the first quantitative explanations of the spongy growth mechanism. The very initial stage of spongy deposit growth was demonstrated by the physical simulation of the process [16] and under real experimental conditions at low [17] and high overpotentials [18].

However smooth deposits can be obtained by using pulsating current [19], reversing current [20] and pulsating overpotential electrodeposition [21]. It has been reported that the optimum frequency range in electrodeposition is 10–100 Hz [22].

The zinc electrode in alkaline solution is interesting, mainly because this metal is widely used in electrochemical power sources. However, a short cycle life caused by its disperse deposit limits its applicability in that field.

The purpose of this paper is to illustrate in detail the origin of the spongy zinc deposit at direct low overpotentials and to demonstrate the validity of the proposed spongy growth mechanism [15] and to show the advantage of using a pulsating overpotential for the elimination of agglomerates during zinc deposition.

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2. Experimental

The electrolyte used throughout this work was 0.1 mol dm\(^{-3}\) zincate solution in 1 mol dm\(^{-3}\) KOH. The solution was prepared from AR-grade reagents and triply-distilled water. Concentrated zincate stock solution was made by dissolving ZnO in concentrated CO\(_2\)-free KOH solution at 80–90°C in a flask under reflux in a nitrogen atmosphere. After dilution, the solution was analysed for zinc by EDTA-titration and for KOH by acidimetric titration. All experiments were carried out in a three-compartment glass cell at 25.0 ± 0.1°C with a tube for bubbling nitrogen. Zinc was deposited onto a stationary vertical copper cathode. Prior to each experiment, the surface of the electrode was polished mechanically with silicon carbide paper (grits 180, 320 and 600) and then with alumina powders (1.0 and 0.3 μm) and etched in 80% H\(_2\)SO\(_4\) solution. The counter electrode was a high purity (99.99%) zinc plate and the reference was a Hg|HgO electrode connected to a Luggin capillary via a salt bridge of the test solution. The experiments with constant overpotential electrolysis consisted of setting the electrode at a constant potential negative to the reversible potential of zinc by means of a PAR-173-potentiaostat for a chosen period of time. A PAR-276-programmer was employed to perform square pulsating overpotential experiments, and a Tektronix (type 564B) oscilloscope was employed to determine the ohmic drop correction. After a period of deposition, the electrode was taken out of the cell, washed and dried. The morphology of the deposits was investigated using a Jeol JSM-35 TEX scanning electron microscope.

3. Results and discussion

Contrary to the majority of other metals, disperse zinc deposits can be obtained at quite low overpotentials. In that case during the first deposition stage, the compact amorphous grains are formed and start to grow at energetically preferred sites on the copper substrate. The mechanism is based on the assumption of spherical diffusion controlled deposition on the independently growing grains.

The radius of the initial stable nucleus is given by:

\[
 r_0 = \frac{2\sigma V}{nF} \tag{1}
\]

and is extremely low even at low overpotentials [23]. The function of nucleus growth versus time and overpotential is given by [4]:

\[
 r = r_0 + \frac{V}{nF} j_0 ft \approx \frac{V}{nF} j_0 ft \tag{2}
\]

The spherical diffusion control of deposition can be established if

\[
 N \leq \frac{1}{(4r)^3} \tag{3}
\]

assuming that around each grain with the radius \(r\), growing under spherical diffusion control, a diffusion layer of the same thickness is formed. In this case the diffusion layers of different grains do not overlap [15] and Eq. (3) is satisfied.

The relation between \(\eta\) and \(j\) is given by

\[
 j = \frac{j_0 f}{1 + \frac{j_0}{j_L} f t} \tag{4}
\]

and at low overpotentials deposition will be diffusion controlled if

\[
 \frac{j_0}{j_L} \gg 1 \tag{5}
\]

Eq. (5) is satisfied for zinc deposition from zincate alkaline solution [2,23]. The diffusion limited current to the growing grain is given by

\[
 j_{L,S} = \frac{nFDc_0}{r} \tag{6}
\]

\[
 j_{L,S} = j_L \frac{\delta}{r} \tag{7}
\]

At the very beginning of the deposition, Eq. (5) is not satisfied. At a constant overpotential \(\eta\), at 20 mV, the grains that grow under activation control are shown in Fig. 1. The dimensions and number density of nuclei depend on duration and deposition overpotentials.

If we adopt the proposed assumption, for some cases [24]:

\[
 j \geq 0.2 j_L \tag{8}
\]

the process enters mixed control, and by combining Eqs. (4), (7) and (8), one obtains

\[
 r_c = \frac{j_L \delta}{j_0 4f_1 - 5f_2} \tag{9}
\]

where \(r_c\) is the value of the radius of the growing nucleus when the process becomes mixed controlled.

From Eqs. (2) and (9) it follows that \(r_c\) will be reached at:

\[
 t_c = \frac{j_0}{j_L} \frac{4f_1 - 5f_2}{nF} \tag{10}
\]

Then a spherical mixed control can be operative around the whole nucleus, sufficiently far from the other ones and amplification of the surface roughness, or rather, of surface irregularities on the growing nucleus take place [23,25] (Fig. 2), just as in the case of deposition onto stationary wire electrodes in mixed or diffusion control [21,26,27].
The moment when the growth of surface irregularities begins inside the spherical diffusion layer of separately growing nuclei is shown in Fig. 3 for $\eta = 20$ and $\eta = 30$ mV.

The induction time values calculated from Eq. (10) for $\eta = 20$ and 30 mV and $j_L = 10^{-2}$ A cm$^{-2}$, $j_0 = 10^{-1}$ A cm$^{-2}$, $2.3\eta_0 = 120$ mV dec$^{-1}$, $2.3\eta = 40$ mV dec$^{-1}$ [2,23], $\delta = 2 \times 10^{-2}$ cm and $V = 9.15$ cm$^3$ mol$^{-1}$ for the surface imperfect polycrystalline Cu substrate are $0.5 < t < 1.5$ min. The calculated values of induction time correspond mostly within an order of magnitude to the induction time values obtained in the real system ($t_i < 15$ min, Fig. 3).

The cases of radial growth of surface irregularities inside the spherical diffusion layer are shown in Figs. 4 and 5.

During further deposition, these surface protrusions continue to grow keeping characteristic sponge shapes. After longer deposition times, assimilation of the separate growing sponge groups occurs and the whole electrode area becomes covered with a disperse zinc sponge deposit.

Typical deposits obtained by the square wave pulsating overpotential are shown in Fig. 6. It is obvious that the deposits become less disperse and less agglomerated by increasing the ‘off’ period. The following analysis will explain this phenomenon. It is well known that the reversible potential difference between a surface with a radius of curvature, $r$, and a planar one is [6]:

$$\Delta E = \frac{2\sigma V}{Fr}$$

(11)

This makes the equilibrium potential of spongy zinc deposits from 7 to 10 mV more negative than that of zinc foil [20,28,29]. During the pauses in the potential program, the tips of curvature characterised by small radii are dissolved faster than the flat surface. In the case of the square-wave pulsating overpotential, assuming that the surface concentration in pulsating overpotential deposition does not vary with time at sufficiently high frequencies, it is easy to show that the current response to the input overpotential is given by [22]:

$$j = nFD \frac{\partial c(0, t)}{\partial x}$$

$$= j_0 \left(1 - \frac{j_0}{j_L} \right) \exp \left( \frac{\eta_0 c}{\eta_0} \right) - j_0 \exp \left( - \frac{\eta_0 c}{\eta_0} \right)$$

for $mT_p < t \leq (m + 1)T_p$ (12a)

and

$$j = nFD \frac{\partial c(0, t)}{\partial x} = - j_0 \frac{j_0}{j_L}$$

for $\left( m + \frac{1}{p+1} \right)T_p < t \leq (m + 1)T_p$ (12b)

Eq. (12) is valid for flat electrode surfaces or protrusions with sufficiently large tip radii, where the surface energy term [6] can be neglected. If it cannot be neglected, the surface energy term affects the reaction rate [30] and Eq. (12) becomes:

![Fig. 2. Schematic presentation of spherical diffusion layer establishment around independently growing nucleus.](image)
\[ j = nFD \frac{\partial c(0, t)}{\partial x} \]

\[ = j_0 \left( 1 - \frac{j_{av}}{j_L} \right) \exp \left( \frac{\eta_A}{\eta_{0,c}} \right) - j_0 \exp \left( \frac{2 \sigma V}{RTr} \right) \exp \left( \frac{\eta_A}{\eta_{0,a}} \right) \]

\[ \text{for } mT_p < t \leq \left( m + \frac{1}{p+1} \right) T_p \quad (13a) \]

and

\[ j = nFD \frac{\partial c(0, t)}{\partial x} = j_0 \left( 1 - \frac{j_{av}}{j_L} \right) - j_0 \exp \left( \frac{2 \sigma V}{RTr} \right) \]

\[ \text{for } \left( m + \frac{1}{p+1} \right) T_p < t \leq (m + 1)T_p \quad (13b) \]

The difference between the current density at the tip of the irregularities and the flat surface during the ‘off’ period, if \( j_{av} \approx j_L \), which is satisfied in most cases of irregularity growth, is given by:

\[ \Delta j = j_0 - j_0 \exp \left( \frac{2 \sigma V}{RTr} \right) \]

(14)

The change in height of surface protrusions with tip radius \( r \), relative to the flat surface is then given by [24]:

\[ \frac{dh}{dt} = \frac{\Delta j V}{zF} \]

(15)
and finally,

\[ h = h_0 + \frac{V_j}{zF} \left[ 1 - \exp \left( \frac{2\sigma V_j}{RT} \right) \right] t \]  

(16)

where

\[ \left( m + \frac{1}{p + 1} \right) T_p < t \leq (m + 1) T_p \]  

(17)

Eq. (16) presents the height of the irregularities with tip radius \( r \) as a function of time, relative to the flat surface, or the protrusion with sufficiently large \( r \). It is obvious that irregularities with very low tip radii can be dissolved completely during the pause. This means that branching of irregularities can be prevented in square-wave pulsating overpotential deposition. Obviously, the larger \( p \) is, the greater the degree of dissolution, as follows from Eq. (16). The effect is more pronounced if \( \eta_A \) remains constant and \( p \) increases, as shown in Fig. 6.

Hence, it can be concluded that at low direct overpotentials spongy growth is due to the amplification of surface protrusions directly inside the spherical diffusion layer formed around each independently growing grain.

Deposits obtained by pulsating overpotential are more compact than deposits obtained in the direct overpotential regime. The above discussion and experimental confirmation show that the filaments and the growing grains can be dissolved completely during a sufficiently high pause to pulse ratios. This is in accordance with the fact that surfaces with low tip radii have a more negative reversible potential than flat surfaces, which lead to selective dissolution of deposits during pause.

4. Nomenclature

- \( c \): concentration
- \( c_0 \): bulk concentration
- \( D \): diffusion coefficient
- \( F \): Faraday constant
- \( f \): exchange current density
- \( f_1 \): limiting current density
- \( f_2 \): exchange current density
- \( \eta \): limiting current density under spherical diffusion control
- \( h \): height of protrusion
- \( h_0 \): initial height of protrusion
- \( j \): current density
- \( j_0 \): exchange current density
- \( j_L \): limiting current density
- \( m \): integer
- \( n \): no. of electrons
- \( N \): no. of nuclei
- \( p \): pause-to-pulse ratio
- \( r \): radius of growing nucleus
- \( r_0 \): radius of critical nucleus
radius of growing nucleus at which deposition becomes mixed controlled
\( T \) temperature
\( T_p \) period
\( t \) time
\( t_i \) induction time for spongy growth initiation
\( V \) molar volume
\( x \) coordinate in horizontal direction
\( \sigma \) surface energy
\( \delta \) thickness of the diffusion layer
\( \eta \) overpotential
\( \eta_A \) amplitude overpotential
\( 2.3\eta_{0,c} \) slope of the cathodic Tafel line
\( 2.3\eta_{0,a} \) slope of the anodic Tafel line

References