

Journal of Mining and Metallurgy, 39 (1–2) B (2003) 167 - 175.

EXCHANGE CURRENT DENSITIES AT ELECTROCHEMICAL PHASE FORMATION FROM MOLTEN SALTS

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(Received 23 January 2003; accepted 3 March 2003)

Abstract

The processes of nucleation, growth and phase formation during electrodeposition from molten salts have been studied. Theoretical methods for the determination of nucleation and growth parameters, particularly exchange current densities at the melt/new phase cluster interface, are considered.

Keywords: nucleation, growth, new phase, melt, deposit, exchange current density

1. Introduction

Exchange current density at the melt/new phase interface is the main kinetic parameter that determines the rate of electrochemical phase formation during electrodeposition. The influence of the current density on the nucleation rate, growth rate of new phase, and induction time of nucleation is considered in this paper. Exchange current densities at the melt/deposit interface are high in many cases and the rate of electrodeposition process is limited by the rate of the mass transfer stage in the bulk of the melt (diffusion or migration of ions to be deposited). In this case, the exchange current densities can be determined as the small clusters of new phase are growing [1]. All these reasons require a more detailed analysis of exchange current densities at the melt/new phase interface. In our paper, theoretical methods of the determination of exchange current densities at the melt/new phase interface are studied for the processes of nucleation, growth and phase formation.

2. Theoretical fundamentals

2.1. Nucleation

The process of electrochemical nucleation can be presented as the series of bimolecular reactions between ions being deposited and clusters of the new phase (deposit). Then this process can be described by the basic kinetics Fokker-Plank (FP) equation [2, 3]:

$$\frac{\partial Z}{\partial t} = \frac{\partial^2}{\partial g^2} (BZ) - \frac{\partial}{\partial g} (AZ) \quad (1)$$

where $Z(g, t)$ is the concentration of clusters consisting of g atoms. Coefficients A and B are expressed as:

$$A = v_1 - v_2, \quad 2B = v_1 + v_2 \quad (2)$$

where $v_1(g, t)$ and $v_2(g, t)$ are frequencies at which ions join or leave a cluster of size g , respectively. Coefficient A is the mean rate of growth of the clusters and can be written as follows:

$$A = \left\langle \frac{dg}{dt} \right\rangle = \frac{\langle I_g \rangle}{ze} = \frac{s(g)}{ze} \langle i_g \rangle \quad (3)$$

where I_g and i_g are current and current density at the melt/cluster interface, respectively, and $s(g)$ is the area of the melt/cluster interface.

The solution of the FP equation for potentiostatic conditions of electrodeposition can be expressed as [4-6]:

$$J(t) = J_{st} \left[1 + 2 \sum_{n=1}^{\infty} (-1)^n \exp(-n^2 t / \tau) \right] \quad (4)$$

where $J(t)$ is nucleation rate, J_{st} is steady-state nucleation rate and τ is nucleation induction time needed to establish a steady-state distribution of subcritical clusters.

The steady-state nucleation rate is equal to:

$$J_{st} = K_1 \exp(-K_2 / \eta^2) \quad (5)$$

where K_1 and K_2 are nucleation constants, kTK_2/η^2 is the work of formation of critical cluster.

Let us examine the case when the nucleation process is limited by the transfer of ions across the melt/new phase interface. Using the theory of absolute reaction rates, coefficient A in the FP equation can be expressed in the form [7]:

$$A = \frac{i_0 s(g)}{ze} \left\{ \exp[\alpha f(\eta - \eta_p)] - \exp[(1 - \alpha)f(\eta_p - \eta)] \right\} \quad (6)$$

where i_0 is exchange current density at the melt/cluster interface, α is transfer coefficient, $f = ze/kT$, $\eta_p = 2\sigma v/ze$ and r is the radius of cluster.

The parameter B is equal to:

$$B(g_c) = i_0 s(g_c) / ze \quad (7)$$

where g_c is the critical size of cluster. Thus, the exchange current is determined by the frequencies of joining of ions into a critical cluster.

After integrating Eq.(4) the following expression for the number of nuclei forming on the electrode surface is obtained [5]:

$$N(t) = J_{st} \left[t - \frac{\pi^2}{6} \tau - 2\tau \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} \exp(-n^2 t/\tau) \right] \quad (8)$$

Nucleation induction time is equal [4]:

$$\tau = \frac{I}{\pi^2 z_n^2 B(g_c)} \quad (9)$$

where z_n is non-equilibrium factor (Zeldovich factor), $z_n^2 = f\eta/6\pi g_c$ [7]. At long times equation (8) transforms to a linear one (Fig. 1):

$$N(t) = J_{st} \left[t - \frac{\pi^2}{6} \tau \right] \quad (10)$$

This equation gives an opportunity to determine steady-state nucleation rate and nucleation induction time τ .

This method allows to find τ and, accordingly, i_0 (exchange current density at the melt/new phase interface) with the help of experimental dependencies of the number of nuclei $N(t)$ being formed. This method was applied for the electrodeposition of Ag from nitrate melts [8].

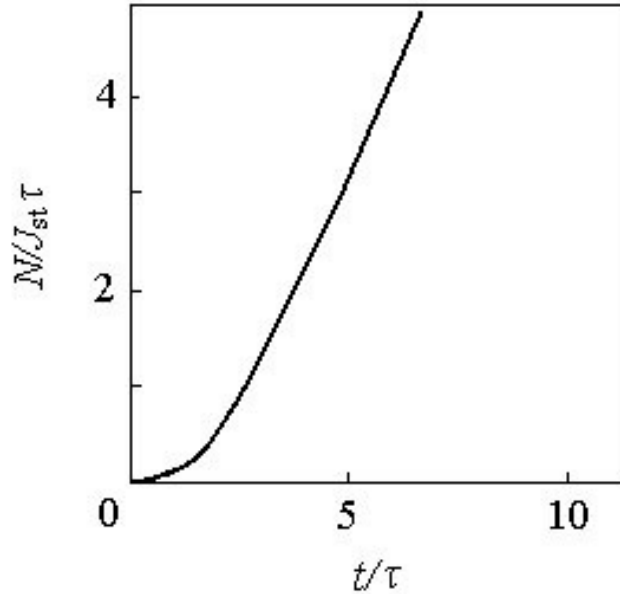


Figure 1. Correlation between the number of nuclei and time according to Eq. (8).

2.2. New phase growth

The most precise method to determine exchange current densities at the melt/new phase interface is studying the initial stages of growth of a single cluster under potentiostatic or galvanostatic conditions. In melts the growth of cluster of a new phase is usually controlled by mixed kinetics. Two cases will be considered: the growth of cluster is controlled by the transfer and migration of ions in the bulk of the melt to the cluster surface (case 1), and by the transfer and diffusion of ions in the bulk of the melt to the cluster surface (case 2). The electrochemical cluster growth in melts was studied in works [1,9,10]. The first case occurs when electrodepositing from individual molten salts (for example, during the electrodeposition of silver on platinum from the $AgNO_3$ melt). The second case occurs during electrodeposition from mixed salts (for example, Ag in the melt $AgNO_3+KNO_3+NaNO_3$).

In the first case, the equation for the current density of growth of a single cluster has the form [10]:

$$i_g = i_0 \left\{ \exp[\alpha f(\eta - \eta_p - \eta_\Omega)] - \exp[(1 - \alpha)f(\eta_p + \eta_\Omega - \eta)] \right\} \quad (11)$$

where η_Ω is ohmic drop in the melt near the growing cluster, $\eta_\Omega = i_g t / k_e$, k_e is the specific

conductivity of the melt.

If the growth of a new phase is controlled by ion transfer and by the diffusion of ions in the bulk of the melt to the cluster surface, then [11]

$$i_g = i_0 \left\{ \frac{c_{sr}}{c_0} \exp[\alpha f(\eta - \eta_p)] - \exp[(1 - \alpha)f(\eta_p - \eta)] \right\} \quad (12)$$

where c_{sr} is the concentration of ions being deposited near the cluster surface, c_0 is the bulk concentration of depositing ions, and c_{sr} is determined by the conditions of hemispherical diffusion. In stationary approximation one can write:

$$i_g = zeD \frac{c_0 - c_{sr}}{r} \quad (13)$$

where D is the diffusion coefficient of ions being deposited.

As one can see from equation (11) and (12), the growth of small clusters is controlled by ion-transfer kinetics and the growth of large ones – by migration or diffusion. At small overpotentials from equation (11) we have:

$$i_g = \frac{\eta - \eta_p}{(1/fi_0) + (r/k_e)} \quad (14)$$

Using the Nernst equation and equation for the balance of electrode current we can derive the equation for overpotential under galvanostatic conditions [12, 13]:

$$\frac{d\eta}{dt} = \frac{i - I_g / s}{C_d + zefZ(1,0)\exp f\eta} \quad (15)$$

where i is current density, s is the area of electrode, C_d is double layer capacity, $Z(1, 0)$ is the concentration of single ad-atoms. These equations can be applied to study the initial stages of growth of the single clusters of new phase under galvanostatic conditions. The calculated dependencies of overpotential upon time for growing single cluster of silver on platinum during electrodeposition from the $AgNO_3$ melt are shown in Fig. 2 [12].

2.3. Phase formation

Kinetic limitations at the melt/deposit interface (exchange current density) can be also investigated during the stage of formation of continuous electrodeposit. Let us consider the formation of electrodeposit by means of nucleation, growth and overlap of clusters of new phase under potentiostatic conditions. The degree of overlap of nuclei

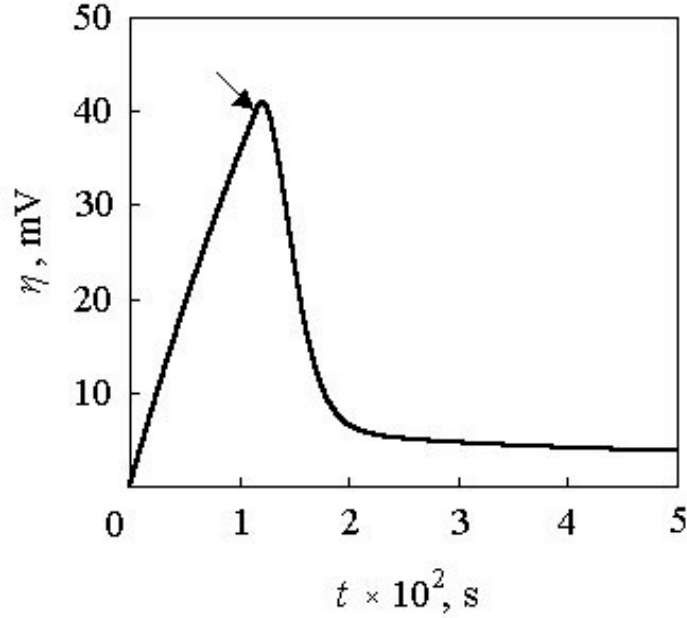


Figure 2. Time dependencies of the growth overpotential for single cluster of new phase during the electrodeposition of silver on platinum from the AgNO_3 melt, $i=5 \times 10^{-4} \text{ A} \times \text{cm}^{-2}$, $i_0=10^3 \text{ A} \times \text{cm}^{-2}$. The arrow on the curve shows the moment of appearance of critical cluster.

increases during electrodeposition, and the size of the melt/deposit interface also varies. So the continuous layer of deposit is formed after some time (Fig. 3). This process can be analyzed on the basis of Kolmogorov theory [14]. According to this theory, the coverage of the electrode surface by the deposit is equal to:

$$\theta(t) = 1 - \exp \left[-\pi \int_0^t J(\tau) r^2(\tau, t) d\tau \right] \quad (16)$$

where $r(\tau, t)$ is the radius of nucleus at time t , τ is the time of appearance of this nucleus. Relationships similar to (16) are valid for any section of the deposit in a plane parallel to the electrode surface taking into account the variation of radius of nuclei. Integration of equation (16) over these sections gives the volume of the deposit and, accordingly, the charge needed for its formation (q). Having determined q we can find the current density as follows: $i = dq/dt$. It must be noted that the current transients have a characteristic maximum. Let us consider the cases of instantaneous and progressive nucleation of a new phase. The growth of the deposit is limited by the transfer of ions (kinetic regime), or by the diffusion of ions.



Figure 3. The formation of a three-dimensional deposit.

Dependencies $q(t)$ and $i(t)$ were calculated in Ref. [15] and they are shown in Fig. 4. We can write dependencies $q(t)$ and $i(t)$ for the kinetic regime of growth of a new phase. For instantaneous nucleation we have the following equation:

$$q = \frac{ze}{\nu(\pi n)^{1/2}} [x - \omega(x)] \quad (17)$$

where ν is the volume of one atom of the deposit, n is the number of nuclei per unit area of the electrode, $x = 2(\pi n)^{1/2} r$, $\omega(x)$ is the Dawson's integral:

$$\begin{aligned} \omega(x) &= \exp(-x^2) \int_0^x \exp \xi^2 d\xi \\ i &= 2i_g x \omega(x) \\ \frac{dr}{dt} &= \frac{i_g \nu}{ze} = k_1 \end{aligned} \quad (18)$$

For progressive nucleation we have:

$$\begin{aligned} q &= \frac{ze}{\nu} \left(\frac{3k_1}{\pi J} \right)^{1/3} \omega_1(y) \\ \omega_1(y) &= y - \exp(-y^3) \int_0^y \exp(3y\xi^2 - 2\xi^3) d\xi \\ y^3 &= \frac{\pi}{3} J k_1^2 t^3 \\ i &= 3 \frac{ze}{\nu} k_1 \omega_2(y) \\ \omega_2(y) &= \exp(-y^3) \int_0^y (y^2 - \xi^2) \exp(3y\xi^2 - 2\xi^3) d\xi \end{aligned} \quad (19)$$

$$\quad (20)$$

Processing the results of i - t curves one can find the parameters of nucleation (n and J) and the kinetic parameter of growth of new phase (k_1) and, consequently, the exchange current density at the melt/deposit interface. Detailed information can be found in Ref. [15].

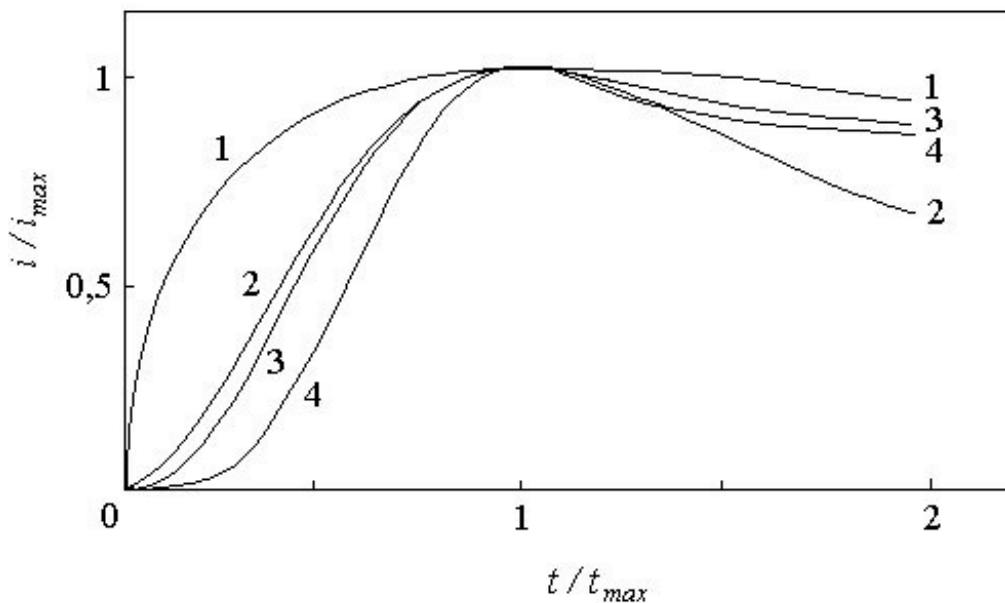


Figure 4. Current transients for: (1) instantaneous nucleation and diffusion-controlled growth, (2) progressive nucleation and diffusion-controlled growth, (3) instantaneous nucleation and kinetically controlled growth and (4) progressive nucleation and kinetically controlled growth.

3. Conclusions

To summarize, let us note that exchange current densities at the melt/new deposit interface can be determined by studying the processes of nucleation, growth and formation of a new phase. The most convenient method is to study the initial stages of growth of single nucleus. In this case, the current is concentrated at growing nuclei and the influence of surface conditions of the electrode upon this process is minimal. It must be noted that the exchange current density at the melt/deposit (cluster of new phase) interface is defined to a great extent by the surface state of cluster.

Typical parameters for the electrodeposition of silver on platinum from nitrate melts

have the following values: $C_d=8\cdot 10^{-5}$ F·cm⁻², $Z(l,0)=1.2\cdot 10^{13}$ cm⁻², $k_e=0.88$ Ω⁻¹·cm⁻¹, $\sigma=10^{-5}$ J·cm⁻², the size of critical cluster $r_c\sim 10^{-7}$ cm, Zeldovich factor $z_n\sim 10^{-1}$ [12]. Exchange current density at the melt/silver interface is $i_0\sim(10^2\div 10^3)$ A·cm⁻² [1, 15]. If exchange current density at the melt/cluster of new phase interface is $i_0=10^3$ A·cm⁻², so the frequency of ion joining the critical cluster will be $B(g_c)\sim 10^8$ s⁻¹. Exchange current density at aqueous-solution-of-silver-nitrate/cluster interface is ~ 10 A·cm⁻² [16].

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