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Modern Ideas About the Processes Involving the Formation and Growth of the Nuclei of a New Phase Under Potentiostatic Conditions

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The principal advances in the theory and practice concerning the initial stages of the electrocrystallisation of metals are considered. The thermodynamic and kinetic relations for the phase formation processes in electrochemical systems and the influence of the kinetics of the discharge of ions and of the adsorption of surfactants on the stationary rate of nucleation are analysed. The theories of the non-stationary nucleus formation and models taking into account the growth of the nuclei of a new phase are discussed.
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I. INTRODUCTION

The study of the mechanism of the formation and growth of the nuclei of a new phase in the electrodeposition of metals is of great theoretical and practical importance, because many properties of galvanic coatings are established precisely in the initial stages of the process. The development of modern technology requires the formation of thin non-porous current conducting, magnetic, and protecting layers and this is possible only on the basis of a careful study of the characteristics of the formation of a new phase.

A series of reviews and monographs have been published in recent years[1-10] in which the theories of homogeneous and heterogeneous nucleus formation have been analysed in detail. Phase formation under galvanostatic conditions has been studied.[11-28] The interpretation of the results obtained in the study of the electrocrystallisation of silver,[11,12,16] cadmium,[13] tin,[15] copper,[23-25,28] and zinc[26,27] under galvanostatic conditions is complicated by the fact that the systems enumerated, which determine the thermodynamics and kinetics of nucleation, vary in accordance with complex laws; the phase formation process is accompanied by a parallel process in which the electrical double layer is charged, part of the current is consumed on the growth of the nuclei already formed, and the ohmic potential drop can reach a considerable magnitude. The theory of galvanic nucleus formation proposed in a number of studies[13,14,17-22] involves, by virtue of the causes enumerated above, many assumptions, which complicate an adequate description of the real processes. In the present review we shall therefore consider mainly the latest theoretical and practical advances in the electrochemical nucleation of metals applicable to potentiostatic conditions.

II. THERMODYNAMICS OF THE FORMATION OF THE NUCLEI OF A NEW PHASE

The phase formation theory was initially developed for homogeneous systems, for example for the process involving the formation of a drop of liquid from a supersaturated vapour.[2,29-31] The change in the free energy of the system ΔG on formation of the nucleus of a new phase, which is equal to the work of nucleation, consists of the changes in the volume and surface energies:

$$\Delta G = -n\Delta\mu + \varphi(n) = -\frac{4\pi r^3 \Delta\mu}{3V} + 4\pi r^2\sigma \ ,$$

where n is the number of atoms or molecules in the nucleus, r the radius of the nucleus, $\phi(n)$ its surface energy, σ the specific surface energy at the vapour/liquid boundary, V the atomic or molecular volume, and $\Delta\mu$ the difference between the chemical potentials of the supersaturated and equilibrium vapours, i.e. the degree of supersaturation of the system.

The dependence of the work of formation of the drop on its radius is represented by a curve with a maximum,[2] which corresponds to the critical size of the nucleus, for the given degree of supersaturation, defined by the Gibbs–Thomson equation:

$$r_{cr} = 2\sigma V/\Delta\mu \qquad (1)$$

Drops with a radius $r < r_{cr}$ tend to dissolve spontaneously, while nuclei with a radius $r > r_{cr}$ tend to grow by virtue of favourable thermodynamic factors. With increase of the degree of such supersaturation in the system, the critical size of the nuclei and the work of their formation diminish and the $\Delta G(r)$ curve shifts to the origin of coordinates.

Using Eqn.(1), it is possible to formulate an expression for the rate of nucleation:[2]

$$\Delta G = \frac{16\pi\sigma^3 V^2}{3\Delta\mu^2} = \frac{1}{2} n_{cr}\Delta\mu \ , \qquad (2)$$

where the superscript "cr" corresponds to the critical state.

The critical nucleus can be defined in several ways. It is an aggregate of a new phase, which corresponds to one of the following conditions:

(1) It is in a state of metastable equilibrium with the supersaturated parent phase;

(2) its size is such that the probability of further growth is equal to the probability of dissolution;

(3) on fluctuation-induced formation, it requires the consumption of maximum work.

Within the framework of classical nucleation theory, which operates with continuous quantities, namely the size of the nucleus and the work of its formation, these three definitions are equivalent.[32]

Heterogeneous nucleus formation has been examined in a series of studies.[1,2,6,29,31,33] The formal theory presupposes that the nucleus of a liquid on the surface of a solid support has the form of a spherical segment and the change in the energy of the system ΔG^{het} following its formation is proportional to the work of homogeneous nucleation ΔG^{hom}:

$$\Delta G^{het} = \Phi \Delta G^{hom}, \qquad (3)$$

where Φ is the shape factor which is equal to the ratio of the volumes of the spherical segment of the liquid phase on the surface of the support and the sphere of the same radius and depends on the wetting angle. A similar relation is valid also for the formation of crystalline nuclei.

It has been shown[34] that a force which tends to increase the radius of curvature acts along the perimeter of the drop wetting the surface of the support. When account is taken of this phenomenon, calculation of the work of formation of the critical nucleus and of its size yield values 1–2 orders of magnitude higher than those obtained when the changes in only volume and surface energy of the nucleus are considered. Whilst remaining within the framework of the macroscopic thermodynamic theory of the heterogeneous formation of a new phase, it is therefore necessary to take into account the linear tension. Neglect of the linear tension may be the reason why, for example, in the electrolytic formation of a new phase on an extraneous electrode, the calculated sizes of the nuclei are found to be of the order of several molecules or even fractions of a molecule. It is of interest to note that in these and other respects experiment agrees with the macroscopic theory.[34]

The satisfactory agreement between the classical ideas about the nucleation and experiment under the conditions of high supersaturation, which is frequently observed, it can be explained by the fact that there is an internal equilibrium in the nucleus (i.e. there is no chemical potential gradient). In this case the thermodynamic theory can be applied to the description of the nucleation of extremely small crystals. Here one must remember that the properties of such ultradisperse systems (including the surface energy) are no longer the same as those of the macrophases and the radius of curvature or the size of the cluster in the nucleation equations are obtained as a result of the replacement of the real system, consisting of two phases and the surface layer between them, by two bodies—the cluster and the parent medium with distinct interfaces.[35] The determination of the size of the crystals and of the surface energies from experimental nucleation data at high supersaturations therefore yields certain idealised values of the process parameters (we shall assume that the terms "nucleus" and "cluster" are equivalent; we have in mind an aggregate of a new phase consisting of a certain number of atoms or molecules).

On the other hand, numerous investigations of the properties of ultradisperse systems have shown[36,37] that for many metals a number of properties of the macrophase persist down to extremely small dimensions.

The main thermodynamic and kinetic characteristics of phase formation in electrochemical systems were first examined about 50 years ago.[38,39] The specific features of electrochemical nucleations have also been discussed in a number of studies.[1,2,6,40,41] The significant characteristics of electrochemical systems are as follows:[40]

(1) The presence of an electrical double layer (EDL) and an electric charge on the species (ions) arriving on the surface of the electrode and hence the need to take into acount the kinetics of charge transfer;

(2) the adsorption of water molecules, cations, anions, and organic substances on the electrode, which leads to a change in the work of formation of the nuclei and in the kinetics of the discharge of the ions;

(3) there is also a possibility of the presence of layers of partly or completely reduced atoms of the metal deposited (adatoms) formed at potentials more positive than the equilibrium value.[42,43]

We shall consider an ideal system which consists of an inert electrode immersed in the electrolyte (the term "inert" implies the absence of interaction between the deposited metal and the support). At equilibrium the electrode has a potential E_0 and the electrochemical potential of the system $\bar{\mu}_0$ is then defined by the expression[44]

$$\bar{\mu}_0 = \mu_p + zF\psi_0 \ ,$$

where μ is the chemical potential of the ion in solution, ψ_0 the Galvani potential at the metal–solution interface corresponding to E_0 (for simplicity, we shall assume that the external potential is zero), z the ionic charge, and F the Faraday.

When the electrode is polarised by an electric current, a potential E is established at the electrode and the Galvani potential and the electrochemical potential of the system change:

$$\bar{\mu} = \mu_p + zF\psi \ .$$

The quantity

$$\Delta\bar{\mu} = \bar{\mu} - \bar{\mu}_0 = zF(\psi - \psi_0) = zF(E - E_0) = zF\eta \qquad (4)$$

characterises the deviation of the system from equilibrium, i.e. the degree of supersaturation in the system.[45] Eqn.(4) is valid if the chemical potential of the solution does not change when a current flows. Such conditions obtain for an insignificant change in the bulk-phase concentration of the electrolyte and are characteristic of the initial stages of the electrocrystallisation of metals.

The metal nucleus has a potential equal to the electrode potential E and its formation requires the performance of work proportional to the difference between the electrochemical potentials:[1,2,6,40,41,46]

$$\Delta G = \Phi \frac{16\pi\sigma^3 V^2}{3(zF\eta)^2} = \frac{1}{2} n_{cr} zF\eta. \qquad (5)$$

The Gibbs–Thomson equation can be written analogously for electrochemical systems:[46]

$$r_{cr} = \frac{2\sigma V}{zF\eta} \ . \qquad (6)$$

However, there exist other points of view on the nature of the supersaturation in the electrocrystallisation of metals. For example, it has been assumed[11–13,23,24,47] that the energy relations of the nucleation process are determined by the excess number of the adatoms of the deposited metal on the electrode surface and not by the difference between the electrochemical potentials. It has been postulated[11–13] that the concentration of the adatoms depends only on the potential of the cathode:

$$c_{ad} = c_0 \cdot \exp\left(\frac{zF}{RT}\eta\right) , \qquad (7)$$

where c_0 is the concentration of the adatoms at the equilibrium potential and in other studies the need to subtract from the overall overpotential η the overpotential of the transition η_t in order to differentiate the crystallisation overpotential η_c has been noted:[23,24,47]

$$\eta_c = \eta - \eta_t = \frac{RT}{zF} \ln \frac{c_{ad}}{c_0}$$

The work of formation of the nucleus is to be determined from the relation

$$\Delta G = \Phi \frac{16\pi\sigma^3 V^2}{3(zF\eta_c)^2} \ .$$

This approach corresponds to the idea of the independence of the stages involving the discharge of ions with formation of adatoms and the actual process involving the formation of nuclei from the discharged atom present on the surface of the support, which in fact denies the possibility of the formation of its nucleus via the direct incorporation mechanism, which is believed by many workers[10,48] to be the most probable for electrochemical nucleation processes. Furthermore, it has been demonstrated[49] for the formation of copper nuclei on pyrographite from a sulphuric acid electrolyte that the concentration of the adatoms affects only the pre-exponential factor in the rate equation and the work of nucleation is determined by the overpotential of the cathode η.

In the atomistic theory[50,51] the supersaturation is also assumed to be $\Delta\bar{\mu} = zF\eta$ and the work of formation of the critical nucleus is calculated from the formula

$$\Delta G = n_{cr}\Delta\bar{\mu} + \varphi(n_{cr}),$$

where the function $\phi(n_{cr})$ characterises the difference between the energy of an n_{cr}-atomic complex and the overall energy of n_{cr} atoms forming part of an infinite crystal:

$$\varphi(n_{cr}) = n_{cr}\varphi_{1/2} - \sum_{n=1}^{n_{cr}} \varphi_n \ , \qquad (8)$$

where $\phi_{1/2}$ is the work required to separate an atom from the "half-crystal" position and ϕ_n is the work of separating an atom from an n-atomic cluster. In terms of its physical significance, $\phi(n_{cr})$ is equivalent to the surface energy of a complex consisting of n_{cr} atoms.

In contrast to the classical approach, in the given instance the work of formation of the nucleus is not a continuous function of n and the equivalence of the three definitions of the critical nucleus given before therefore breaks down. In the atomistic theory the nucleus is assumed to be critical if its formation requires the expenditure of maximum work. The specific size of the nucleus depends on the structure of the complexes and the interaction forces between the atoms and the support.

The relations between the work of formation of the nucleus, its critical size, and the rate of nucleation have been analysed.[52] Regardless of the approach to the phase formation processes employed, it is possible to formulate the following expressions:

$$\Delta G(n, \Delta\mu) = -n\Delta\mu + F(n, \Delta\mu) \ , \qquad (9)$$

$$J = A(\Delta\mu)\cdot\exp\left[-\frac{\Delta G(n_{cr}, \Delta\mu)}{RT}\right] , \qquad (10)$$

where the number of atoms in the nucleus n is a function of the degree of supersaturation, $F(n, \Delta\mu)$ is the change in the surface energy of the system on formation of an n-atomic complex, and $A(\Delta\mu)$ is the kinetic factor in the equation for the rate of nucleation J. It follows from Eqn.(9) that

$$\left[\frac{d\Delta G}{d\Delta\mu}\right]_{n=n_{cr}} = -n_{cr} + \left[\frac{dF(n, \Delta\mu)}{d\Delta\mu}\right]_{n=n_{cr}} .$$

After taking logarithms and differentiating Eqn.(10) with respect to $\Delta\mu$ at a constant temperature, the following expression was obtained:

$$n_{cr} = RT\frac{d\ln J}{d\Delta\mu} - RT\frac{d\ln A}{d\Delta\mu} + \left[\frac{dF(n, \Delta\mu)}{d\Delta\mu}\right]_{n=n_{cr}} .$$

When the nucleation processes are considered within narrow ranges of the degree of supersaturation, the changes in the surface energy and the kinetic factor can be neglected:

$$n_{cr} = RT\frac{d\ln J}{d\Delta\mu} \ . \qquad (11)$$

This equation makes it possible to determine the size of the critical nucleus from the experimental dependence of the rate of nucleation of the degree of supersaturation regardless of the nucleus formation model employed. According to the analysis[52] of the influence of the pre-exponential factor in Eqn.(10) and the surface energy $F(n, \Delta\mu)$ on the critical size of the nucleus, the error in the determination of n_{cr} by Eqn.(11) does not exceed 1–2 atoms.

Furthermore, the equations presented above permit the experimental estimation of the limits of applicability of the Gibbs–Thomson equation, since, having determined the rate of nucleation of the crystals for different degrees of supersaturation, it is easy to find the dependence of the critical size of the nucleus on $\Delta\mu$.

III. STATIONARY NUCLEATION KINETICS

The dependence of the stationary rate of nucleation J_0 on the work of formation of nuclei has been obtained in a fundamental investigation:[33]

$$J_0 = D_{cr}\cdot Z(1)\cdot\exp\left(-\frac{\Delta G}{RT}\right) = K_1\cdot\exp\left(-\frac{K_2}{\eta^2}\right) , \qquad (12)$$

where D_{cr} is the flux of atoms becoming attached to the critical nucleus, $Z(1)$ the concentration of single atoms, and K_1 and K_2 are constants. As a result of fluctuations, a set of clusters of different size is formed in the system and their number obeys the Boltzmann distribution, so that the product

$$Z(1)\cdot\exp\left(-\frac{\Delta G}{RT}\right)$$

determines the number of critical nuclei.

The fluctuation theory was developed further in a number of studies.[6,30,41,53–58] Becker and Doring[53] used the kinetic approach to establish the relation between J_0 and ΔG. They examined the formation of kinetic nuclei as a chain of successive reactions involving addition to the cluster of or abstraction from the latter of single atoms and obtained the following equation for the rate of nucleation:

$$J_0 = K_1\left(\frac{\Delta G}{n_{cr}^2 RT}\right)^{1/2}\cdot\exp\left(-\frac{\Delta G}{RT}\right) \ , \qquad (13)$$

where ΔG is defined by Eqn.(2). The multiplier $(\Delta G/n_{cr}^2 RT)^{1/2}$, frequently called the Zel'dovich non-equilibrium factor,[6] characterises the deviation of the stationary size distribution of clusters from the equilibrium distribution. Analogous expressions have been obtained for J_0 in other studies.[41,54,57]

Several investigations,[6,53,55] also based on the approach of Becker and Doring, have been devoted to the kinetics of the formation of crystalline nuclei. The authors of these investigations expressed the frequencies of addition and abstraction in terms of the bonding energies between the nearest neighbours in the cluster and obtained equations for the rate of nucleation analogous to Eqn.(13).

The mathematical procedure for the solution of nucleation problems has been improved in a number of investigations.[30,56,59] The following equation has been obtained for the rate of nucleus formation:

$$J = -D(n_{cr}, t)\cdot Z_e(n_{cr}, t)\cdot\left[\frac{\partial}{\partial n}\left|\frac{Z(n, t)}{Z_e(n, t)}\right|\right]_{n=n_{cr}} , \qquad (14)$$

where $Z_e(n, t)$ is the equilibrium distribution function of the nuclei with respect to sizes and $Z(n, t)$ the number of n-atomic clusters at time t. In order to find the specific form of the function $Z(n, t)$, it is essential to solve the differential equation

$$\frac{\partial Z(n, t)}{\partial t} = \frac{\partial}{\partial n}\left[D(n, t)\cdot Z_e(n, t)\cdot\frac{\partial}{\partial n}\left|\frac{Z(n, t)}{Z_e(n, t)}\right|\right] , \qquad (15)$$

which is a complex mathematical task. However, in the stationary case, where the function $Z(n, t)$ can be assumed to be independent of time, the solution greatly simplifies. The expression for the stationary rate of nucleation, obtained by Frenkel' [30] and Zel'dovich,[56] resembles Eqn.(13), which makes it possible to describe fairly accurately the nucleus formation process in real systems.

However, for the analysis of experimental data obtained with narrow ranges of variation of the degree of supersaturation, the employment of the simpler expression (12) is frequently justified.

In examining the nucleation processes in heterogeneous systems, it is essential to take into account the change in the rate of nucleation as a result of the change in both the work of formation of the nucleus, in accordance with Eqn.(3), and in the frequencies of addition and abstraction of atoms.

The occurrence of heterogeneous nucleation via the mechanism involving the direct incorporation of atoms or molecules in the nucleus is unlikely in the gas phase,[31] so that the presence of adatoms on the support and their diffusion along the surface assume considerable importance. These factors have been examined in a review[2] and it has been shown that the rate of nucleation is higher the lower the activation energy for surface diffusion and the stronger the interaction of the adatoms on the support.

Numerous investigators dealt with the influence of the state of the support on the kinetics of nucleation from solutions.[2, 60–71] Ickert[60] considered the influence of chemical interactions during adsorption and the role of the real surface in processes involving the crystallisation of a new phase. The concept of nucleus formation on active centres, which are understood to be the sites on the surface of the support having an increased free energy, has been examined.[61–71] Nuclei are formed preferentially on these centres. Crystal lattice defects (dislocations, vacancies, and inclusions of extraneous atoms), mechanically damaged sites on the surface, or defects in the oxide layer, which are as a rule present on the surfaces of all the supports, can play the role of the active centres. The activity of the centres can vary within fairly wide limits on the same electrode, centres with the highest activity "working" initially, but, as the degree of supersaturation increases, the less active centres also begin to participate in the nucleation process. If the influence of shielding zones, arising around the growing nuclei,[72] can be neglected in a specific system, then the distribution function for the centres with respect to activities can be determined from the experimental dependence of the number of nuclei on the degree of supersaturation.[73]

The relations of the classical theory examined above can be applied also to nucleation processes in electrochemical systems if the degree of supersaturation is expressed in terms of the overpotential of the cathode in accordance with Eqn.(4). However, Eqn.(12) describes satisfactorily only experimental data obtained in systems with high exchange currents within fairly narrow ranges of overpotentials of the cathode, where it is possible to neglect the influence of the rate of discharge of the ions on the surface of the support. In this case the data on the rate of nucleation fit on the linear plots of $\ln J_0$ against $1/\eta^2$ or $\ln J_0$ against η, from the slopes of which it is possible to determine K_2 in Eqn.(12) or the number of atoms in the critical nucleus.

The description of nucleus formation within wide ranges of overpotentials in systems where the charge transfer stage is important requires allowance for the rate of discharge of the ions. A series of studies have been devoted to this problem.[23,24,46,50,51,74–79] It has been suggested[75] that the current density associated with the attachment of atoms to the critical nucleus, growing via the direct incorporation mechanism, be expressed in terms of the cathodic component of the current i_c:

$$i_c = i_0 \cdot \exp\left(\alpha \frac{zF}{RT}\eta\right)$$

and the following equation has been obtained for the stationery rate of nucleation:

$$J_0 = K_1 \cdot \exp\left(\alpha \frac{zF}{RT}\eta\right) \cdot \exp\left(-\frac{K_2}{\eta^2}\right) ,$$

where α is the electrochemical transfer coefficient and i_0 the exchange current density.

The discharge kinetics have been taken into account analogously in the derivation of equations for J_0 in the region of high overpotentials of the cathode in studies by Milchev and co-workers[50,51] and Chebotin et al.[76] However, this approach is not always justified. The nuclei of the new phase have a considerable surface curvature which affects the kinetics of the discharge of ions on their surface. Equations have been obtained[77] for slow discharge on a curved surface, but the Gibbs–Thomson effect[46] has been taken into account only for the anodic process. A more detailed examination of the kinetics of the discharge of ions on a curved surface has shown that the curvature influences the activation energies for the cathodic and anodic processes.[74,79,80]

The kinetics of the discharge of ions on the curved surfaces of clusters have been taken into account by Danilov and Polukarov.[79] The derivation of equations for the stationary rate of nucleation was based on the kinetic method of Becker and Doring.[53] In the derivation of the expression for the atom addition and abstraction flux densities, the cathodic and anodic components of the current density respectively were employed:

$$i_c = i_0 \cdot \exp\left(\alpha \frac{zF}{RT}\eta\right) \cdot \exp\left(-\alpha \frac{2\sigma V}{rRT}\right) ,$$

$$i_a = i_0 \cdot \exp\left[-(1-\alpha)\frac{zF}{RT}\eta\right] \cdot \exp\left[(1-\alpha)\frac{2\sigma V}{rRT}\right] .$$

The following expressions have been obtained for the rate of nucleation via the mechanism involving the direct incorporation of atoms and nuclei:[79]

$$J_0 = K_1 \left(\frac{\Delta G}{n_{cr}^2 RT}\right)^{1/2} \cdot \exp\left[(1+\alpha)\frac{zF}{RT}\eta\right] \exp\left(-\frac{\Delta G}{RT}\right) . \qquad (16)$$

The work of formation of the nucleus can be expressed in different ways depending on which nucleation parameter has to be determined. For the estimation of the specific surface energy of the nucleus, ΔG is expressed in accordance with the first part of Eqn.(5) and Eqn.(16) is written in the form

$$J_0 = K_1 \eta^2 \cdot \exp\left[(1+\alpha)\frac{zF}{RT}\eta\right] \cdot \exp\left(-\frac{K_2}{\eta^2}\right) . \qquad (17)$$

The constant K_2 is determined from the slope of the experimental plot of the rate of nucleation against the overpotential in terms of the variables $\ln\{J_0\eta^{-2}\exp[-(1+\alpha)zF/RT\eta]\}$ and $1/\eta^2$ and then σ is calculated.[79]

In order to calculate the number of atoms in the critical nucleus n_{cr}, it is necessary to use the second part of Eqn.(5). Eqn.(16) is then transformed into

$$J_0 = K_1 \eta^2 \cdot \exp\left[\left(1+\alpha-\frac{n_{cr}}{2}\right)\frac{zF}{RT}\eta\right]$$

and n_{cr} can be determined from the formula

$$n_{cr} = \frac{RT}{zF}\left(\frac{d\ln J_0}{d\eta} - \frac{2}{\eta}\right) - 1 - \alpha .$$

Expressions have also been published[79] for the stationary rate of two-dimensional nucleation and nucleus formation via the surface diffusion mechanism.

Models not using macroscopic physical quantities have been proposed for the description of nucleation processes in the range of high degrees of supersaturation.[50,51,76,81–83] The atomistic theory of electrochemical nucleation has been developed by Milchev and co-workers.[50,51] The following expression has been obtained for the direct incorporation mechanism:

$$J_0 = K_1(n_{cr}) \cdot Z_0 \cdot \exp[-\varphi(n_{cr})/RT] \cdot \exp\left[(n_{cr} + \alpha)\frac{zF}{RT}\eta\right],$$

where $K_1(n_{cr})$ is a parameter which depends only slightly on the overpotential of the cathode, the function $\phi(n_{cr})$ is defined by Eqn.(8), and Z_0 is the number of active centres on the support. To a first approximation, the dependence of the surface energy on η is neglected and the equation

$$J_0 = K_1 Z_0 \cdot \exp\left[(n_{cr} + \alpha)\frac{zF}{RT}\eta\right] \qquad (18)$$

is used.

The expression

$$J_0 = K_1 Z_0^2 \cdot \exp\left[(n_{cr} + 1)\frac{zF}{RT}\eta\right]$$

has been obtained for the formation of a nucleus via the mechanism involving the surface diffusion of adatoms.[50]

It has been shown[50,51] that the classical and atomistic models of nucleus formation are limiting cases of a single theory and are valid under the conditions of low and high supersaturations respectively. According to the atomistic theory, the number of atoms in the critical nucleus can be arbitrarily small and can even be zero. In this case the critical nucleus is an active centre of the support and addition of one atom to such a centre converts the complex into a stable formation capable of growing spontaneously under the conditions of the given supersaturation. Within the limits of a certain range of values of η, the number of atoms in the nucleus remains constant and then changes abruptly, so that the dependence of the logarithm of the rate of nucleation $\ln J_0$ on the overpotential η should be represented by broken lines. The slope of each section yields n_{cr} and the critical sizes of the nucleus in the neighbouring ranges need not necessarily differ by unity.[45,84]

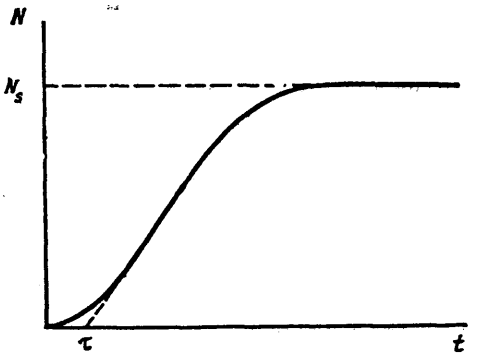
Nucleus formation in the presence on the support of centres with different activities has been examined.[76] Using the main principles of the atomistic theory, the authors obtained the following expression for the stationary rate of nucleation on active centres of the kth kind:

$$J_k = K_k \cdot \exp\left[(m_k + \alpha)\frac{zF}{RT}\eta\right] \cdot \left[1 + a_k \exp\left(\frac{zF}{RT}\eta\right)\right]^{-1} \qquad (19)$$

where K_k is a constant independent of η in the given range of overpotentials, $a_k = [Z_k(1)/Z_{0,k}]_{\eta=0}$, and m_k is the number of atoms in the critical nucleus on the active centres of the kth kind. The numerator of Eqn.(19) yields a linear relation between $\ln J_k$ and η, analogous to that described by Milchev and co-workers,[50,51] while the denominator produces a deviation from it, which may be significant at high overpotentials and for a high adsorption capacity of the support when a_k is fairly large. In the general case, at a given overpotential, there is a set of values of m_k and the overall stationary rate of nucleus formation is determined by the sum of expressions of type (19) with respect to different kinds of active centres.[76]

Extensive experimental data have now accumulated and can be used to test the theoretical calculations for stationary nucleation in electrochemical systems. We shall not dwell on the results obtained within narrow ranges of overpotentials, because they have been examined in detail in a series of reviews.[1,2,4–6,8,9] We shall only mention that their analysis on the basis of the thermodynamic and atomistic models leads to practically identical conclusions and calculations yield similar values of the critical size and of the work of formation of the nuclei.

The determination of data for nucleation kinetics within wide ranges of overpotential is associated with considerable experimental difficulties. The main method of securing information about nucleus formation processes is the determination of the dependence of the number of nuclei of the metal deposited N on the duration of the potential static pulse t (see Figure). The use of the two-pulse method[6,85] enables the nuclei formed during the first pulse to grow further until the attainment of sizes visible under the microscope and makes it possible to count them. The stationary rate of nucleation is determined from the slope of the linear part of the $N(t)$ curve and the thermodynamic process parameters are then evaluated.



Schematic illustration of the dependence of the number of nuclei on the duration of the potentiostatic pulse (τ is the induction period and N_S the limiting number of nuclei).

Valuable results concerning the formation of silver nuclei on vitreous carbon have been obtained.[45,84] The plot of $\ln J_0$ against $1/\eta^2$ exhibits appreciable deviations from linearity, which indicates the inapplicability of Eqn.(12) to the description of the process. Treatment of the results in accordance with the atomistic model showed[45,84] that this theory describes the experiment satisfactorily and makes it possible to estimate the overpotential ranges in which the critical size of the nucleus remains constant: $n_{cr} = 4$ for $\eta = 25–51$ mV, $n_{cr} = 1$ for $\eta = 51–160$ mV, and $n_{cr} = 0$ for $\eta > 160$ mV. However, the results[45,84] can be interpreted also on the basis of the thermodynamic theory.[79] In terms of the variables of Eqn.(17), the experimental data fit satisfactorily on a straight line, from the slope of which it is possible to calculate the constant K_2 and the critical size of the nucleus.

IV. NON-STATIONARY NUCLEUS FORMATION

The stationary course of nucleation can obtain only during a time interval before and after which nucleus formation proceeds under the conditions of a variable rate of nucleation. The increase in the rate of nucleation J in the initial stages of the process is usually attributed to the fact that supersaturation in the system is established not instantaneously but involves the slow formation of a stationary

distribution of clusters with respect to size, the accumulation of the adatoms of the deposited metal, and the time variation of the activity of the extraneous electrode. The decrease in the rate of nucleation which follows the stationary section is due to the exhaustion of the active centres of the support, the overlap of the shielding zones, or the coalescence of the growing crystals, which leads to the termination of the nucleation process.

We shall consider the early stages of nucleus formation. Under the conditions of a constant supersaturation, the nucleation process can be described by the Frenkel'–Zel'dovich equations (14) and (15),[30,56] the most accurate solution of which has been obtained[86] on the assumption that the concentration of the adatoms instantaneously assumes the value corresponding to the given supersaturation [see Eqn.(7)]:

$$J(t)=J_0\left[1+2\sum_{m=1}^{\infty}(-1)^m\cdot\exp\left(-m^2\frac{t}{\tau}\right)\right], \qquad (20)$$

where

$$J_0=D_{cr}\left(\frac{K}{\pi}\right)^{1/2}Z(1)\cdot\exp\left(-\frac{\Delta G}{RT}\right), \qquad (21)$$

$$\tau=4/\pi^2D_{cr}K \qquad (22)$$

Here m are positive integral numbers, τ is the induction period, and K is defined by the expression

$$K=-\frac{1}{2RT}\left[\frac{d^2\Delta G(n)}{dn^2}\right]_{n=n_{cr}}.$$

According to this theory, the main reason for the non-stationary conditions in the early stages of the process is assumed to be the finite rate of establishment of the stationary size distribution of the clusters.

Solutions of Eqn.(15) have been obtained[87,88] taking into account the time-dependent concentration of adatoms using different mathematical approaches. The expression

$$J(t)=\frac{2J_0}{\tau}\sum_{m=1}^{\infty}(-1)^{m+1}m^2\int_0^t c(x)\cdot\exp\left[-\frac{m^2(t-x)}{\tau}\right]dx, \qquad (23)$$

where J_0 and τ are defined by Eqns.(21) and (22), c is the concentration of adatoms varying with time, and x an auxiliary variable, has been obtained.[88]

The equation for the rate of nucleation obtained by Roldugin et al.[87] is

$$J(t)=\frac{J_0}{c_\eta}\left\{c(t)-\exp\left(-\frac{t}{\tau_1}\right)\left[c_0+\int_0^t\frac{dc(x)}{dx}\cdot\exp\left(\frac{x}{\tau_1}\right)dx\right]\right\}, \qquad (24)$$

where τ_1 is the induction period due to the redistribution of clusters with respect to size:

$$\tau_1=\frac{1}{4D_{cr}K}=\frac{16RT\sigma}{i_0zF\eta^2}. \qquad (25)$$

The second part of Eqn.(25) has been obtained taking into account the Gibbs–Thomson effect, according to which the flux of atoms adding to the critical nucleus in electrochemical systems is equal to the product of the surface area of the critical nucleus and the exchange current density and not the cathodic component of the current. This conclusion arises also from the second definition of the critical nucleus given above. Indeed, the probability of the growth of the nucleus is only equal to the probability of dissolution when the equality

$$i_c=i_a=i_0,$$

holds. Many investigators failed to take into account this fact in studying the kinetics of electrochemical nucleation.

The time variation of the concentration of adatoms in Eqn.(24) is defined by the expression[89]

$$c(t)=c_\eta-(c_\eta-c_0)\cdot\exp\left(-\frac{t}{\tau_2}\right),$$

where

$$\tau_2=\frac{zFc_0}{i_0^{ad}}\cdot\exp\left[(1-\alpha)\frac{zF}{RT}\eta\right] \qquad (26)$$

is the induction period due to the finite rate of accumulation of adatoms, c_η and c_0 are the limiting (for the given overpotential) and equilibrium concentrations of adatoms [see Eqn.(7)], and i_0^{ad} is the exchange current density of the adatoms. Evidently τ_1 diminishes and τ_2 increases with increase in the overpotential of the cathode.[87]

Estimation of the duration of the period of non-stationary conditions from Eqns.(25) and (26) yields times of the order of several milliseconds, which is close to the values determined experimentally, while neglect of the Gibbs–Thomson effect in the derivation of Eqn.(25) leads to values which are smaller by 3–5 orders of magnitude than those observed experimentally.

For $\tau_1=\tau_2=\tau$, Eqn.(24) reduces to

$$J(t)=J_0\left[1-\exp\left(-\frac{t}{\tau}\right)-\frac{c_\eta-c_0}{c_\eta}\cdot\frac{t}{\tau}\cdot\exp\left(-\frac{t}{\tau}\right)\right],$$

and if one of the components of the induction period is much greater than the other, we obtain[87]

$$J(t)=J_0\left[1-\exp\left(-\frac{t}{\tau}\right)\right]. \qquad (27)$$

At low overpotentials, the effective induction period is determined by the redistribution of clusters with respect to size and decreases with increasing overpotentials in accordance with Eqn.(25); at $\eta\cong 200$ mV the minimum induction period should be observed and in the region of high supersaturations τ increases with increasing η in accordance with Eqn.(26) and the duration of the non-stationary section is determined by the rate of accumulation of adatoms on the surface of the support.[87] These theoretical estimates have been confirmed by experimental data[84] for the nucleation of silver on vitreous carbons: the relation $\tau(\eta)$ passes through a minimum at overpotentials of ~200 mV.

The influence of the time-dependent supersaturation $\Delta\mu(t)$ on the nucleation kinetics has been analysed by Kashchiev within the framework of the quasi-stationary approximation in two studies[90,91] and the following equations have been obtained:

$$\begin{aligned}J(t)&=J_0(t)\left[1-\frac{\pi^2}{6}n_{cr}(t)\cdot\tau(t)\cdot\frac{d\Delta\mu(t)}{dt}\right],\\ J_0(t)&=D_{cr}(t)\cdot[K(t)]^{1/2}Z_e[n_{cr}(t),t],\\ \tau(t)&=4/\pi^2D_{cr}(t)\cdot K(t),\\ K(t)&=-\frac{1}{2RT}\left[\frac{d^2\Delta G(n,t)}{dn^2}\right]_{n=n_{cr}(t)}.\end{aligned} \qquad (28)$$

These are valid subject to the condition

$$\frac{d\Delta\mu}{dt}<\frac{6}{\pi^2n_{cr}(t)\tau(t)}.$$

Eqns.(20), (23), (24), and (28) were obtained for homogeneous nucleus formation but, by introducing the shape factor into the expression for the work of formation of the nucleus in accordance with Eqn.(3), it is possible to use them for the description of heterogeneous processes.[92]

Aleksandrov and Kedyarov[93] took into account the possibility of nucleation in which several energy barriers are overcome at a constant supersaturation and analysed the influence of the multistage course of the process on the nucleation kinetics. In particular, they showed that, in the

presence of two energy barriers, the extrapolated induction period can be negative.

Milchev[94,95] developed a theory of non-stationary nucleation based on the assumption that the active centres of the support can arise during the operation of the initiating pulse at a rate which depends on the degree of supersaturation. Since the rate of nucleation is proportional to the number of centres active at the given instant, the stationary state is established only after an induction period during which all the active centres which can arise for the given degree of supersaturation are produced. For electrochemical systems, the active centres are, in particular, defects in the oxide layer on the metallic electrode, which exist before the application of the overpotential pulse or which arise during evaporation. The kinetics of the non-stationary nucleation are described by an equation identical in form to Eqn.(27), but the induction period τ should diminish with increase in the overpotential.

Theories of non-stationary nucleation have been tested thoroughly in a number of studies.[95-102] The integral form of Eqns.(20) and (27) in terms of their dimensionless variables $F = (J_0\tau)^{-1}\int_0^\infty J(t)dt$ and $y = t/\tau$ is more convenient for comparison with experimental data:

$$F(y) = y - \frac{\pi^2}{6} + 2\sum_{m=1}^{\infty}(-1)^m m^{-2}\cdot\exp(-m^2 y)\ , \qquad (29)$$

$$F(y) = y - 1 + \exp(-y)\ . \qquad (30)$$

It has been established that Eqn.(29) describes satisfactorily the non-stationary nucleation of mercury,[96-99] silver,[100] and cadmium[97,101] on platinum and of copper on pyrographite,[102] but systematic deviations of experimental data from the theoretical curve are observed in the region of low values of the ratio t/τ. Statistical analysis[95] of the experimental data for the nucleation of mercury on platinum showed that a more accurate description of this process is possible on the basis of the theory taking into account the variation of the number of active centres of the support[94] and the corresponding equation (30).

However, one should note that the same experimental data fit fairly well on the theoretical curves corresponding to Eqns.(29) and (30),[87] because the theoretical relations themselves differ insignificantly. The deviations from them are comparable to the experimental errors and the determination of the nature of the non-stationary conditions (the redistribution of the clusters with respect to size, slow accumulation of adatoms, the manifestation of active centres of the support, etc.) therefore requires additional information. It may be that, for each specific system, the non-stationary conditions in the initial stages of the nucleation process are due to specific causes: the state and nature of the support, the experimental conditions, etc.

In the late stages of nucleation, the rate of the process diminishes from J_0 (if it has been attained) to zero. The causes of this phenomenon have been analysed[72,103-106] on the basis of the concept that the aggregates of the new phase are initiated on the active centres of the support.

The phenomenon of such saturation in the formation of mercury nuclei on platinum has been explained[106] by the energetic homogeneity of the surface of the cathode. The possibility of explaining this finding from the standpoint of the concept of the development and overlap of shielding zones arising around the growing nuclei has been demonstrated.[72,103] These models have been generalised in a study[104] according to which the rate of nucleation is given by the relation

$$J(t) = \frac{dN(t)}{dt} = J_0\frac{Z_0(t)}{Z_0(0)} = J_0\frac{S(t)}{S(0)}\ ,$$

where $Z_0(t)$ is the number of unoccupied active centres and $S(t)$ the surface area of the support not covered by shielding zones. At $t \to \infty$ we have $Z_0(t) \to 0$ and $S(t) \to 0$, which leads to the cessation of the nucleation process. Depending on the experimental conditions, either the exhaustion of the active centres or the overlap of the shielding zone play the decisive role.

The first case is described by the equation

$$N(t) = N_s\{1 - \exp[-J_0(t-\tau)/N_s]\}\ ,$$

where $N_S = Z_0(0)$. When the shielding zones play the decisive role, the following expression has been obtained:

$$N(t) = N_s\gamma\left\{\Gamma\left(\frac{2q+2}{2q+1}\right)\frac{J_0(t-\tau)}{N_s}\right\}\ ,$$

where Γ and γ are the complete and incomplete gamma-functions.

The quantities $N(t)$, N_S, J_0, and τ are determined directly from experimental plots of the number of nuclei against the duration of the pulse (see Figure) and the parameter q is found from the slope of the plot of $\ln N_S$ against $\ln J_0$.[104] In terms of the dimensionless variables $N(t)/N_S$ and $J_0(t-\tau)/N_S$, it is possible to determine the mechanism of the saturation process. For example, it has been established that, during the formation of mercury nuclei on platinum[105-107] and of copper nuclei on pyrographite,[102] the main role is played by the process involving the overlap of the shielding zones, while in the presence of surfactants the saturation during the nucleation of copper is caused by the exhaustion of the active centres of the support.[102]

V. STATISTICAL ANALYSIS OF NUCLEATION PROCESSES

One of the methods for the experimental study of nucleation kinetics involves the measurement of the time and probability of the appearance of the first nucleus. A random fluctuation process obeys the Poisson law and the probability of the appearance of at least one nucleus is given by[108]

$$P_{\geq 1} = 1 - \exp[-N(t)]\ ,$$

where $N(t)$ is the average number of nuclei formed at a given overpotential during time t. If there is no induction period, then $N(t) = J_0 t$ and the average expectation time for the nucleus, which can be readily determined experimentally, is given by the formula

$$\bar{t}_1 = \int_0^\infty t\,dP_{\geq 1}(t) = \frac{1}{J_0}\ .$$

The stationary rate of nucleation J_0 can be determined analogously from the probability of the formation of m nuclei:

$$P_{\geq m+1} = 1 - \exp(-J_0 t)\cdot\sum_{k=0}^{m}(J_0 t)^k/m!\ ,$$

$$\bar{t}_{m+1} = \int_0^\infty t\,dP_{\geq m+1}(t) = \frac{m+1}{J_0}\ .$$

However, in this case it is necessary to demonstrate that the process involving the appearance of m nuclei is random and obeys the Poisson law; this is not always true. For example it has been shown[45,65] that, in the nucleation of silver on vitreous carbon, deviations are observed from the Poisson law for the distribution of distances between nearest nuclei, due to the mutual influence of the growing crystallites.

If the stationary state is attained after an induction period τ, then the probability $P_{\geq 1}$ is given by the expression

$$P_{\geq 1} = 1 - \exp\left[-\int_0^t J(t)\,dt\right] .$$

Knowing the theoretical relation

$$J(t) = J_0 F(t, \tau) ,$$

where $F(t, \tau)$ is a function of time and τ, it is possible to estimate the stationary rates of nucleation and the induction period from the coordinates of the point of inflection P_i and t_i on the experimental plots of the probability of the appearance of the nucleus against time for a constant overpotential. The period τ is calculated from the relation

$$P_i = 1 - \exp\left\{-\left[\int_0^{t_i} F(t, \tau)\,dt\right] \cdot F^{-2}(t_i, \tau)\left[\frac{dF(t, \tau)}{dt}\right]_{t=t_i}\right\}$$

and then the stationary rate of nucleation is evaluated[108] from the formula

$$J_0 = -\ln(1 - P_i)/\int_0^{t_i} F(t, \tau)\,dt$$

A somewhat different mathematical procedure for the determination of J_0 and τ has been used by Milchev and Tsakova.[95] The product $J_0\tau$ is calculated from the formula

$$J_0\tau = \left[\frac{d^2F(y)}{dy^2}\right]_{y=y_i} \cdot \left[\frac{dF(y)}{dy}\right]^{-2}_{y=y_i} , \qquad (31)$$

where $F(y) = N(t)/J_0\tau$ and $y = t/\tau$. The ordinate of the point of inflection in the $P_{\geq 1}(t)$ relation is given by the expression

$$P_i = 1 - \exp\left\{-\left[\frac{d^2F(y)}{dy^2}\right]_{y=y_i} \cdot \left[\frac{dF(y)}{dy}\right]^{-2}_{y=y_i} \cdot F(y_i)\right\} ,$$

on the basis of which the calibration curve $P_i(y)$ is plotted, provided that the theoretical relation $F(y)$ is known. Next the values of P_i and t_i are determined from the experimental relation between the probability of the formation of the nucleus and the duration of the potential static pulse and then $y_i = t_i/\tau$ is found with the aid of the calibration curve, the induction period τ is calculated, and the stationary rate of nucleation is evaluated from Eqn.(31).[95]

The theoretical relations (29) and (30) have been tested experimentally[95,101,108] for the nucleation of mercury and cadmium on platinum; satisfactory agreement has been found between the values of J_0 and τ determined from the experimental $N(t)$ relations and the values calculated from the results of statistical analysis.

Fairly numerous studies have been carried out recently on the statistical analysis of the processes involving the formation and growth of nuclei.[1,2,10,109–115] but their detailed examination would require too much space. We shall only note that the methods developed for the calculation of the spatial and temporal distribution of the nucleation steps permit a deeper understanding of the mechanism of nucleus formation and the analysis of the nature of the active centres of the support and of their influences on the kinetics and thermodynamics of nucleation.

VI. THE INFLUENCE OF SURFACTANTS ON THE FORMATION AND GROWTH OF NUCLEI

Surfactants have been used widely and for a long time in the cathodic deposition of metals and alloys to control the physicomechanical and structural properties of galvanic deposits. The theoretical and experimental studies of the influence of surfactants on various stages of electrochemical processes have been thoroughly described in a series of reviews and monographs,[116–119] but their action on phase formation processes has been studied to a much lesser extent.[2,24,73,107,120–125]

It has been shown[120,121] that the adsorption of surfactants in the system can alter the work of formation of nuclei and their critical size by altering the surface energy at the nucleus/electrolyte and nucleus/support interfaces (which is accompanied by a change in the wetting angle and the shape factor).

The influence of saponin on the nucleation of mercury on platinum has been studied[122] and it has been shown that, with increase in the concentration of the additive in solution, the stationary rate of nucleus formation and the number of nuclei N_S in the region of saturation on the $N-t$ curve decrease (see Figure), but the work of nucleation remains almost unchanged under these conditions. According to electrocapillary measurements, no appreciable adsorption of saponin on mercury was observed in the experimental range of potentials and concentrations of the additive, and the authors therefore explain the decrease of J_0 and N_S in terms of the blocking of the active centres of the support. It was suggested that the same centres are active in relation to both adsorption and phase formation processes. Other workers,[107] investigating the mechanism of the influence of poly(propylene glycol) on the nucleation of mercury on platinum, arrived at analogous conclusions.

The influence of acrylamide (AA) and acrylonitrile (AN) on the galvanostatic initiation of the zinc crystals on pyrographite has been investigated.[26,27] Calculation[27] showed that AN increases significantly ΔG as a consequence of its strong adsorption on the surface of the support and, after the introduction into the electrolyte of a combined additive comprising a mixture of AN and AA, the work of nucleation remains almost unchanged compared with the pure zinc sulphate solution. This finding was explained by the simultaneous adsorption of the surfactant on the nuclei and the support, which cancels out the changes in ΔG. However, these calculations, based on the separation of the crystallisation and transition overpotentials, are open to doubt because in the same study it is concluded that the size of the critical nucleus decreases after the adsorption of AN, which is inconsistent with the observed increase of ΔG.

The study of the influence of polyacrylamide (PAA) and acrylic acid (AAC) on the electrocrystallisation of copper under potentiostatic conditions[73,125] showed that PAA is adsorbed only on nuclei of specific size and is not adsorbed on the support, which leads to an increase of N_S, while the initial sections of the $N(t)$ curves in the presence of PAA coincide for the given overpotential. This effect has been explained by the decreased rate of growth of the shielding zone arising around the growing crystallites. In contrast to PAA, AAC is adsorbed on the pyrographite support and eliminates active centres, which decreases J_0 and N_S and also increases the period of non-stationary conditions.

Thus the majority of investigators have concluded that the influence of surfactants on the initial stages of electrocrystallisation is manifested mainly by the inversion of the ratio of the rates of formation and growth of the nuclei of the new phase as a result of the blocking of the active centres of the

support and the inhibition of the discharge of ions on the surfaces of the growing crystallites.

VII. MODELS OF NUCLEATION TAKING INTO ACCOUNT THE GROWTH OF NUCLEI

The study of the character of the growth of nuclei can yield important information about the nucleation processes.[1,2] Analysis of the potentiostatic current–time relations (transients) has been recently used increasingly to determine the phase formation relations. The theory governing the growth of two-dimensional layers[10,127–139] and three-dimensional crystals has been confirmed by experimental studies of electrocrystallisation on dislocation-free phases of silver single crystals[10,140–146] and the formation of anodic films[147–154] and metallic nuclei,[155–159] and by mathematical modelling.[139,160–165] Investigators have devoted much attention to the role of processes involving mass transfer to the growing nuclei.[166–173]

In the present review we shall confine ourselves to the analysis of the most important studies of the three-dimensional nucleus formation and growth, which occur widely in processes involving the deposition of galvanic coatings on supports made of a different material. A general model taking into account the two-dimensional initiation and subsequent three-dimensional growth of crystals has been proposed.[174–177]

The relations governing the growth of nuclei were analysed for the first time by Sheludko and Bliznakov,[126] who derived the relation between the current associated with the growth of a single semispherical nucleus I_1 and time t for different rate-limiting stages. Under the conditions of slow discharge of ions, the current is proportional to t^2, while in processes subject to diffusional and ohmic control it is proportional to $t^{1/2}$, but the character of the dependence of the current on the potential differs significantly, which permits the experimental differentiation of the above growth mechanisms.

In the further development of the theory, the growth of an ensemble of nuclei was examined. For the diffusional growth regions, satisfactory results were provided by the model based on local semispherical diffusion;[178] corrections have been applied[17,80,179] for the initial radius of the nucleus and the Gibbs–Thomson effect. The experimental $I(t)$ relations were interpreted on the assumption of the independent increase of N for the crystallites, i.e. it was assumed that the overall current is equal to the sum of the individual currents associated with the growth of the nuclei. The following expression is then obtained for the instantaneous nucleation (the formation of N nuclei at a rate greatly exceeding the rate of their growth):

$$I_N(t) = NI_1(t),$$

while for progressive nucleation (when the rate of nucleus formation and growth are comparable)

$$I_N(t) = J_1 Z_0 I_1(t) \cdot t,$$

where J_1 is the specific (referred to one active centre) rate of nucleation and $I_1(t)$ the current associated with the growth of a single nucleus. An experimental test showed[17,80,178–184] that, despite the satisfactory agreement between experiment and theory in the description of the growth of single nuclei, we have $NI_1(t) > I_N(t)$ even in the initial stages of the process, which indicates a significant mutual influence of the growing nuclei.

Scharifker and Hills[185] took into account the overlap of the semispherical diffusion zones arising around the growing crystallites and obtained the following expression for the current associated with the growth of N nuclei formed simultaneously:

$$I_N(t) = zFc_v\left(\frac{D}{\pi t}\right)^{1/2} \cdot [1 - \exp(\pi NkDt)], \qquad (32)$$

where c_v is the volume concentration of the electrolyte, D the diffusion coefficient, and k the rate constant for the growth of the zone:

$$k = (8\pi c_v V)^{1/2}.$$

For progressive nucleation, the current is described by the expression

$$I_N(t) = zFc_v\left(\frac{D}{\pi t}\right)^{1/2} \cdot \left[1 - \exp\left(-\frac{2}{3}\pi J_1 Z_0 kDt^3\right)\right]. \qquad (33)$$

The plots of the growth current, corresponding to Eqns.(32) and (33), pass through a maximum, whose coordinate I_m and t_m can be readily found from the condition that the derivatives of the current with respect to time are zero. The product

$$I_m^2 t_m = \delta D(zFc_v)^2,$$

where δ is a numerical multiplier equal to 0.1629 for instantaneous nucleation and 0.2598 for progressive nucleation, does not contain the quantities N and J_1Z_0 and is therefore a diagnostic criterion of the initial mechanism.[185] Furthermore, instantaneous and progressive nucleation can be distinguished on the basis of the experimental $I(t)$ relations plotted in terms of the variables $(I/I_m)^2$ and t/t_m and one can then calculate the quantities N and J_1Z_0. If the initiation ceases as a result of the overlap of the diffusion zones, then the limiting number of nuclei is given by the expression

$$N_s = \left(\frac{3J_1Z_0}{8kD}\right)^{1/2}.$$

Comparison of the relations obtained with the experimental data for the nucleation of lead on zinc oxide and of copper sulphide on copper[185] demonstrated a satisfactory agreement between theory and experiment.

The theory was developed further by Scharifker and Mostany.[186] In their study of diffusion-controlled nucleation on a limited number of active centres of the support, the authors of the above investigation were able to derive a system of transcendental equations, whose solution permits the independent calculation of J_1 and Z_0 from the experimental coordinates of the maximum on the current transient. Yet another advantage of this theory is the possibility of describing a diffusion-controlled potentiostatic initiation and growth process in a general form, where the instantaneous and progressive nucleation are limiting special cases.

Analysis of the current transients for the lead nucleation process on structureless carbon[187] demonstrated that the number of active centres on which the nuclei are formed increases with increasing overpotential but is almost independent of the electrolyte concentration. Furthermore, the concentration dependence of the rate of nucleation permits the conclusion that the atoms are directly incorporated in the nucleus without the intermediate deposition of adatoms. Treatment of the experimental data in accordance with the classical and atomistic nucleation theories leads to virtually identical critical sizes of the nucleus ($n_{cr} < 1$).

An interesting approach in the analysis of the formation and growth of nuclei was employed by Isaev and Baraboshkin.[188] Equations permitting the description of the nucleation processes under the conditions of diffusional and kinetic control of growth were derived on the basis of Kolmogorov's theory. If the instantaneous nucleation takes place under the conditions of slow discharge of ions, then the current is defined by the expression

$$I = 2i_g x_1 \omega(x_1),$$

where

$$i_g = i_0 \cdot \exp\left(\alpha \frac{zF}{RT}\eta\right) - i_0 \cdot \exp\left[-(1-\alpha)\frac{zF}{RT}\eta\right]$$

and $\omega(x_1)$ is the tabulated Dawson integral:

$$\omega(x_1) = \exp(-x_1^2) \cdot \int_0^{x_1} \exp(x^2)\,dx,$$

and the variable x_1 is defined by the expression

$$x_1 = i_g V (\pi N)^{1/2} t / zF.$$

The $I(x_1)$ relation has a maximum at $x_1 = 1.50$, which corresponds to the product $x_1\omega(x_1) = 0.64$ and the degree of surface coverage of the electrode by the growing deposit $\theta = 0.90$.

For diffusional control of growth, x_2 is described by the expression

$$x_2^2 = 2Dc_v V \cdot \pi N t \left[1 - \exp\left(-\frac{zF}{RT}\eta\right)\right]$$

and the following equation is valid for the current:

$$I = 2zFDc_v(\pi N)^{1/2} \cdot \omega(x_2)\left[1 - \exp\left(-\frac{zF}{RT}\eta\right)\right].$$

When $x_2 = 0.92$, a current maximum corresponding to $\omega(x_2) = 0.54$ and $\theta = 0.57$ is observed.

For progressive nucleus formation with kinetic control, the following equation has been obtained:

$$I = 3i_g \omega_2(x_3),$$

where

$$\omega_2(x_3) = \exp(-x_3^3) \cdot \int_0^{x_3} (x_3^3 - x^3) \cdot \exp(3x_3x^2 - 2x^3)\,dx,$$

$$x_3^3 = \frac{i_g^2 V^2 \pi J_0}{3(zF)^2} t^3$$

Here the quantities $x_3 = 1.34$, $\omega_2(x_3) = 0.44$, and $\theta = 0.91$ correspond to the current maximum.

If the rate of the process is limited by bulk diffusion, then the following relation holds:

$$I = zF\left\{4Dc_v\left[1 - \exp\left(-\frac{zF}{RT}\eta\right)\right]^{3/4}\right\} \cdot \left(\frac{\pi J_0}{V}\right)^{1/4} \omega_4(x_4),$$

where

$$\omega_4(x_4) = \exp(-x_4^4) \cdot \int_0^{x_4} (x_4^3 - x^3) \cdot \exp(2x_4^2x^2 - x^4)\,dx,$$

$$x_4^4 = Dc_v V \pi J_0 \left[1 - \exp\left(-\frac{zF}{RT}\eta\right)\right] \cdot t^2.$$

In this case $x_4 = 1.08$, $\omega_4(x_4) = 0.36$, and $\theta = 0.4$ correspond to the current maximum.

The equations obtained make it possible to infer the mechanism of nucleation (instantaneous or progressive), to deduce the factor controlling the growth of nuclei (slow discharge of ions or volume diffusion), and to calculate the degree of coverage of the electrode by the deposit and the parameters of the initiation process.

The method of current transients has been used[189–193] to investigate the influence of the degree of surface coverage of the electrode by adatoms on the kinetics of three-dimensional nucleation. At potentials more positive than the equilibrium potential for the deposition of lead on the (111) and (100) faces of silver single crystals, a certain definite number of adatoms were deposited, an overpotential pulse was applied, and the time variation of the current was measured. The transients were treated on the assumption that the nucleation is progressive with diffusional control of the growth of semispherical nuclei in accordance with the theory developed in a number of investigations[180–183,194–196] and the rate of initiation of lead crystals was calculated. It was shown that, with increase in the degree of surface coverage by the adatoms, the rate of nucleation diminishes and does not increase as should have been expected.

This non-trivial fact was explained as follows: previously it had been established that the structures of the sorption layer of the adatoms and of the bulk phase of the metal differ appreciably from one another.[189,190,192] The formation of a three-dimensional nucleus therefore requires a rearrangement of the adsorption layer, whose rate depends on the density, symmetry, and ideality of the two-dimensional film. The dependence of the rate of nucleation on the potential at which the adsorption layer was formed on the surface can also be associated with the decrease of the number of active centres of the support as a result of the two-dimensional association of the adatoms or the adsorption of microimpurities.

According to the calculation based on the atomistic model of nucleation, the critical nucleus consists of 11 and 13 atoms for overpotentials in the range 10–20 mV on the (111) and (100) faces of silver single crystals respectively. Since the rate of initiation on the (100) face is much higher than on the (111) plane and the work of formation of nuclei is approximately the same, one may conclude that the preliminary maintenance of the electrode at potentials more positive than the equilibrium value influences mainly the kinetic factor in Eqn.(18) for the rate of nucleation.[193] It is therefore quite evident that, in the study of nucleus formation on supports made of a different material, it is necessary to take into account the possibility of the formation of adsorption layers or two-dimensional nuclei even in the anodic range of potentials.

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The data considered in the review show that during recent years there has been a significant expansion of the range of studies on the initial stages in electrocrystallisation. New trends have arisen in research, in particular, a more logical allowance has been made for the specific features of the electrochemical reactions in the crystal initiation processes, a method has been developed for the analysis of the time variation of the current whereby one can estimate the number of nuclei generated and infer the mechanism of their growth, which splendidly supplements the classical two-pulse method. Interesting results have been obtained in the study of the dependence of the rate of initiation of crystal formation on the degree of coverage by adsorption layers made up of atoms of the metal deposited in the range of potentials more positive than the equilibrium potential of the phase. Systematic research has been begun on the influence of surfactants in the stage involving the initiation and growth of crystals.

The model ideas in the studies described are based on the assumption the absence of interaction between the nuclei formed. However, under the conditions of high supersaturation, which usually obtain in the electrodeposition of metals, the processes involving the coalescence of the nuclei with formation of aggregates are apparently entirely probable. There is no doubt that further study of the influence of surfactants and of the multistage occurrence of electrochemical reactions on nucleation processes will yield useful data both for the theory of electrochemical phase formation and for the practical deposition of galvanic coatings.

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