PHYSICS AND CHEMISTRY OF SOLID STATE
V. 23, No. 2 (2022) pp. 335-340

Section: Physics

DOI: 10.15330/pcss.23.2.335-340

Vasyl Stefanyk Precarpathian National University

ФІЗИКА І ХІМІЯ ТВЕРДОГО ТІЛА
Т. 23, № 2 (2022) С. 335-340

Фізико-математичні науки

UDC 538.931 ISSN 1729-4428

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Quantitative Estimate of the Contribution of the Surface Diffusion Process to Mass Transfer during Electrochemical Deposition of Metals

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In this study, an attempt was made to quantify the contribution of the surface diffusion process to mass transfer during electrochemical deposition of metals. The maximum density of nucleation centers is calculated, at which only diffuse overgrowth of a continuous layer of a new phase is possible. The time of diffusion overgrowth of a continuous monomolecular layer of a new phase is calculated. The results of independent experiments on the determination of boundery diffusion coefficients in a two-layer platinum-nickel thin-film system are analyzed. The value of the boundery diffusion coefficient of nickel at a temperature of 393 K was found. The part of mass transfer due to surface diffusion of physically adsorbed atoms in relation to the total mass transfer during electrochemical deposition of metals has been quantified. It is proved that the role of the surface diffusion process in the formation of the coating during electrochemical deposition of metals is insignificant. It is shown that this is an indirect proof of the formation of an amorphous coating structure during electrochemical deposition of metal.

Key words: surface diffusion, nucleation process, surface diffusion coefficient, monomolecular layer, growth rate of nucleus of a new phase, layer overgrowth time, electrochemical deposition.

Received 25 January 2022; Accepted 23 May 2022.

Introduction

In numerous works on the theory of electrochemical deposition of metals, the whole process is divided into stages: 1) the transfer of metal ions through the electric double layer; 2) the formation of neutral atoms of the metal that deposition on the surface of the base metal; 3) surface diffusion of deposited atoms on the surface of the base metal to the most energetically advantageous places (nucleation centers) and the growth of supercritical nuclei of the new phase. (Even when the deposition metal is the same as the base metal, the new phase will be called the formation on its surface of supercritical nucleus, which grow, overlap and turn into a continuous monomolecular layer).

Surface diffusion is a separate stage in the chain of successive stages of mass transfer. It would seem that, being the slowest, surface diffusion will limit the whole process of electrochemical deposition, and, as a consequence, will determine all the growth kinetics of the new phase. However, this is not the case, at least for the reason that the formation of neutral atoms on the surface of the base metal goes hand in hand with the process of surface diffusion of atoms that have been physadsorbed before. In addition, if the layer of the new phase overgrown as a result of only surface diffusion, then this layer would be closer to the crystal structure because it is the most energetically beneficial for the atom that diffuses on the surface. At the same time, it was experimentally proved [1, 2] that during electrochemical deposition the layer of the new phase has an amorphous structure, which can later turn into crystalline under the action of thermal fluctuations.

Therefore, it can be argued that the process of surface diffusion is not limiting. However, it is necessary to know: how significant is the share of mass transfer, which is carried out by surface diffusion.

To date, there is no quantitative estimate of surface diffusion kinetics at lower 0.3 $T_{\text{пл}}$ temperatures. There is no method of appropriate calculation. The problem is complicated by the lack of data on surface diffusion coefficients at the temperature of electrochemical deposition of metals. Therefore, in the current study, an attempt was made:

1) to develop an algorithm for calculating mass transfer in the process of surface diffusion;

2) predict the value of the surface diffusion coefficient at the temperature of electrochemical deposition of metals;

3) evaluate the contribution of surface diffusion in the process of mass transfer during electrochemical deposition of metals.

I. Diffusion overgrowth of layer of the new phase

The appearance of nuclei of a new phase and their growth occurs [3] in the transverse direction along the interfacial boundary in the absence of normal growth. At large concentration gradients [4], normal nucleus growth outside the critical thickness is prohibited. Thus, the nuclei of a new phase grow only along the deposition surface and do not grow in a direction perpendicular to the latter

The dependence of the part X of the surface occupied by the nuclei of a new phase on time $t$shoulde described by the Kolmogorov-Avrami equation [5]:

$$X = 1 - exp\left[-kNt^{''}\right], \tag{1}$$

Here k - coefficient determined by the growth rate of the nuclei of a new phase; N - concentration of nucleation centers; n - Avrami index, which is determined by the dimension of the system and the nature of the distribution of nucleation centers.

We assume that the nucleation centers are dristributed randomly, the nuclei have the shape of a disks, the growth rate of each nucleus is constant, and the interphase boundary is two-dimensional.

In this case, as shown in [6], the Kolmogorov-Avrami equation takes the form:

$$C(t) = exp(-N\pi G^2 t^2), \tag{2}$$

that is the Avrami index $n = 2$.

Let the degree of overgrowth of the new phase exceed 99 % of the total surface area. Then equation (2) will be written: $exp(-N\pi G^2 t_3^2) = 0.01$.

Or, after logarithmization:

$$N\pi G^2 t_3^2 = 4.605, \tag{3}$$

here t_3 - the time of the whole overgrowth of layer of the new phase as a result of surface diffusion..

First, determine the order of magnitude of the concentration of nucleation centers. In order to be able to speak about of surface diffusion as a result of accidental wandering of atoms on the interphase surface, it is necessary that the minimum diffusion path be at least about interatomic distances of the crystal lattice of the metal [7].

It follows that the average distance between the centers of neighboring nucleus should be at least:

$$\overline{\lambda} \geq 40\delta, \tag{4}$$

Here δ - the interatomic distance (crystal lattice parameter).

If the concentration of nucleation centers is equal N, then on average one center has a surface area $\frac{1}{N}$. This means that the average distance between the centers is equal to:

$$\overline{\lambda} = \frac{1}{\sqrt{N}}, \tag{5}$$

Then from (4) and (5) we have:

$$N \leq \frac{1}{\overline{\lambda}^2} = \frac{1}{1600\delta^2}$$

If we take $\delta = 5 \cdot 10^{-10} m$, the maximum density N_{max} of nucleation centers, at which exclusively diffuse overgrowth of a continuous layer of a new phase is possible, will be equal to:

$$N_{max} = 2.5 \cdot 10^{15} \mathrm{m}^{-2}, \tag{6}$$

Then, on the one hand, the diffusion path (value [7] of about $\sqrt{Dt_3^2}$), according to the above considerations, is equal to half the average distance between the centers of the nuclei - $\frac{\bar{\lambda}}{2}$.

On the other hand, if the growth rate G of nuclei is constant, then during the time t_3 (the time of the whole overgrowth of layer of the new phase as a result of surface diffusion) the interphase boundary will pass on average Gt_3, which is also equal to half the average distance between nuclei centers -$\frac{\bar{\lambda}}{2}$. Then you can write:

$$Gt_3 = \sqrt{Dt_3}, \tag{7}$$

Substitute (7) in (3) and take into account (6). Then we have: $N_{max}\pi D t_3 = 4.605$.

Hence, for the time of diffusion overgrowth of the whole layer of the new phase, we finally have:

$$t = \frac{4.605}{\pi N_{max} D}, \tag{8}$$

here D - the surface diffusion coefficient.

According to (8), the time of diffusion overgrowth of the whole layer of the new phase is greater, the lower the density of the nucleation centers and the lower the surface diffusion coefficient.

II. Estimation of the value of the surface diffusion coefficient

In volume diffusion [8], atoms move only through defects (exchange of places, vacancies, internodes) by the mechanism of random wanderings. Boundary diffusion is similar to "… street traffic on the street, which is limited by fixed walls…" [8]. Surface diffusion is limited only by the surface on which it is carried out. As shown in [8], the coefficients of volume diffusion D_V, grain boundary diffusion D_B and surface diffusion D_F must satisfy the inequalities: $D_V < D_B < D_F$.

Fisher [9] made a number of assumptions that simplify the problem, and obtained an equation to describe surface diffusion:

$$C = C^0 \frac{exp\left(-\sqrt{\frac{4D_V}{\pi t}}\right)}{\sqrt{\delta D_B}} \cdot x \cdot erf \frac{x}{\sqrt{D_V t}} .$$

Here C^0 - the average value of concentration at the moment $t = 0$; C - the concentration of atoms that have diffused over time t; δ - the thickness of the surface diffusion layer.

In the assumption that $\delta = 5 \cdot 10^{-10} m$ (a monomolecular layer is formed on the surface), an estimate was performed which showed that the boundary diffusion coefficient can exceed the volume diffusion coefficient by 10^5 times.

Diffusion coefficients in a two-layer thin-film system $Pt - Ni$ were determined by Auger spectroscopy [10], by directly measuring the amount of substance accumulated on the free surface of the film during diffusion annealing. According to the model adopted in [10], the diffusion of nickel from one layer to another proceeds along the grain boundaries, followed by a more accelerated transfier of diffusing atoms on the free surface.

In this case, the solution for the surface concentration of the component has the form:

$$1 - \bar{C}_{so} = exp\left(\frac{k'\delta}{2\delta'} \cdot \frac{l}{L} \cdot \frac{\bar{D}_B \tau}{l^2}\right).$$

Here $\bar{C}_{S0}$- the average surface concentration of the diffusing component; $\bar{D}_B$ - the average boundary diffusion coefficient of the component; τ - annealing time of the sample at constant temperature; l - the thickness of the layer of material in which the diffusion is studied; L - grain size; δ' - the thickness of the analyzed layer; δ - the thickness of the grain boundary.

$$k' = C_B / C_S$$

Here C_B- the he concentration of the diffuser in the investigated layer; C_S- the concentration of diffuser on the free surface.

The volume diffusion coefficient of nickel (for the temperature range 1314 K – 1674 K) can be determined [10] by the formula:

$$D_v = 4.9 \cdot 10^{-2} \cdot exp\left(-\frac{55700}{RT}\right).$$

Extrapolation of this dependence to the temperature range 523 - 623 K gives the value of the volume diffusion coefficient $D_V = 2{,}2 \cdot 10^{-25} \frac{m^2}{s}$.

As shown by the results of the experiment [10], the value of the boundary diffusion coefficient in the temperature range 523 - 623 K (see Table 1) is much higher than the value of the volume diffusion coefficient.

Table 1

Dependence of the boundery diffusion coefficient of nickel from the temperature.

T, K	$D_V, \frac{m^2}{s}$
523	$8 \cdot 10^{-18}$
573	$2 \cdot 10^{-17}$
623	$3{,}16 \cdot 10^{-17}$

The activation energy of the boundery diffusion of nickel in the temperature range 523 - 623 K is equal to $Q = 41400$ J / mol [10].

The more detailed account of the peculiarities of this diffusion experiment carried out in [11] allowed to obtain a more correct formula for calculating the boundery diffusion:

$$D_1 = H \frac{\delta' L}{\delta} \left(\frac{D_1}{D_2} l_2 + l_1\right) \cdot \left(\frac{l_2}{l_1} + \frac{1}{1 + \frac{D_1 l_2}{D_2 l_1}}\right)$$

Here H - the value calculated from the slope of the experimental curves at small values t; D_1, D_2 - diffusion coefficients in the first and second films, respectively; l_1, l_2 - the thickness of the first and second films, respectively. The calculation of the boundery diffusion coefficient according to this formula allowed to obtain the following data: $D_B = 5{,}6 \cdot 10^{-18} \frac{m^2}{s}$ at 523 K.

The dependence of the diffusion coefficient on the temperature according to Arrenius is:

$$D = D_0 exp\left(-\frac{Q}{RT}\right) .$$

Here D - the diffusion coefficient at temperature T; D_0 - coefficient; Q - activation energy; R - universal gas constant.

After logarithming the Arrenius equation we have:

$$lgD = lgD_0 - \frac{Q \cdot lne}{R} \cdot \frac{1}{T}.$$

Then in the coordinates $lg\, D - \frac{1}{T}$ the dependence of Arrenius will look like a straight line.

We use the value of the boundery diffusion coefficient of nickel at temperatures 523K - 623 K, as well as the activation energy of boundery diffusion $Q = 41400 \ \frac{J}{mol}$ for quantitative estimate of the boundery diffusion coefficient of nickel at a temperature (T = 393 K) characteristic of electrochemical deposition of metals (Fig. 1).

Extrapolation of the Arrenius dependence to the region of low temperatures (393 K), carried out on the basis of experimental data of [10] and [11], gives the values of the coefficients of boundery diffusion of nickel, which are equal to $2.28 \cdot 10^{-19}$ m^2/s to $3.22 \cdot 10^{-19}$ m^2/s. These values will be used as a basis for quantitative estimate the role of surface diffusion in mass transfer during electrochemical deposition of metals.

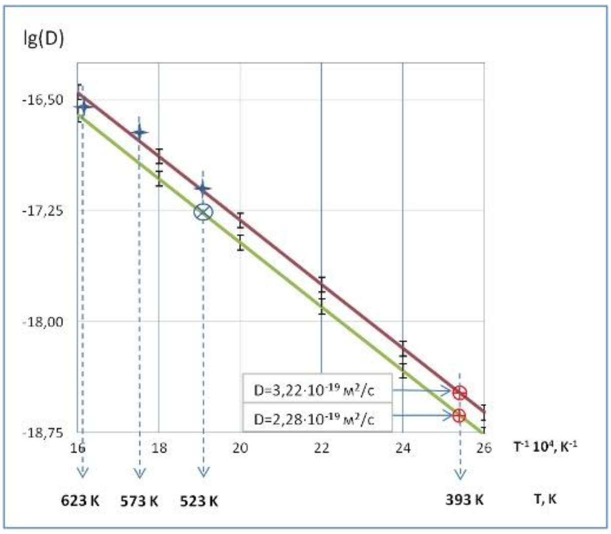

Fig. 1. Dependence of the boundery diffusion coefficient of nickel on temperature: ✦ - data [10]; ⊗ - data [11]; ⊕ - values of extrapolated by [10] and [11] coefficients of boundery diffusion at the temperature o f the process of electrodeposition of metals (T = 393 K).

III. Calculation the part of the mass transfer carried out by surface diffusion during electrochemical deposition of metals

The density of electric current in electrolytes during electrochemical deposition of metals is equal to:

$$j = e^{+}n^{+}u^{+} + e^{-}n^{-}u^{-}.$$

Here e^{+}, e^{-} - the absolute value of charge carriers positive and negative, respectively; n^{+}, n^{-} - the number of positive and negative charge carriers per unit volume, respectively; u^{+}, u^{-} - speeds of the directed movement which have positive and negative charge carriers under action electric field, respectively.

It follows that in the electrochemical deposition of metals, the flow of metal ions creates a current density equal to half the density of the electric current j. Consequently, the number n_a of metal atoms that are deposited per unit area per unit time is equal to: $n_a = \frac{j}{2e}$.

Here e = 1.6·10^{19} C - the magnitude of the elementary charge.

During the time t of electrochemical deposition on the unit area of the base metal deposited N_a atoms:

$$N_a = n_0 t = \frac{jt}{2e}, \tag{9}$$

The time of diffusion overgrowth of the whole layer of the new phase is determined by equation (8). According to the calculations given in paragraph II, the layer of the new phase can be considered a monomolecular layer. And if the distance between the atoms is equal $\delta = 5 \cdot 10^{-10} m$, then the unit surface area of the monomolecular layer will consist N_m of atoms, ie:

$$N_m = \frac{1}{\delta^2} = 4 \cdot 10^{18} \mathrm{m}^{-2}, \tag{10}$$

Thus, (8) determines the time $t_3$of diffusion overgrowth of the whole layer of the new phase on the surface of the base metal at the selected density of nucleation centers $N \leq N_{max}$ (see paragraph II), as well as using the value obtained in paragraph III of the boundery diffusion coefficient. During this time, the process of surface diffusion transferred N_m atoms. The value N_m is defined in (10). Substituting the time t_3 in (9), we can determine the number of atoms N_a that were deposited during the diffusion overgrowth of the monomolecular layer of the new phase. As part of the formalism of the current review, $N_m$atoms participated in the process of surface diffusion from the place of their deposition to the interphase boundaries of the growing nuclei of the new phase. At the same time, $(N_a - N_m)$ atoms "did not participate" in the process of surface diffusion.

Then the part of mass transfer carried out by surface diffusion during electrochemical deposition of metals can be defined as $\varepsilon = \frac{N_m}{N_a}$.

Taking into account (8) - (10) the last equation is finally written:

$$\varepsilon = \frac{N_m}{N_a} = \frac{1.28}{4.605} \cdot \frac{\pi N D}{j} = 0.873 \frac{ND}{j} \tag{11}$$

As can be seen from (11), the role of surface diffusion will decrease with decreasing density of nucleation centers of the new phase and increasing the density of electric current of the process of electrochemical deposition of metals.

We make quantitative estimates of the magnitude ε of the traditional for the process of electrochemical deposition densities of electric current and different densities of nucleation centers of the new phase. According to [8], the surface diffusion coefficient at temperature (T = 393 K) will be $D < 2{,}28 \cdot 10^{-19} \frac{m^2}{s}$. The results of calculations according to formula (11) are shown in Table 2.

The dependences of the part ε of mass transfer carried out by surface diffusion on the current density during electrochemical deposition of nickel are shown in Fig. 2 and are hyperbolas.

The first of them (curve 1-2) is based on the diffusion coefficient calculated in this paper, and shows that part of the surface diffusion in the total mass transfer during electrochemical deposition of nickel does not exceed $2{,}1 \cdot 10^{-4}\%$. Even if we use the value of the diffusion coefficient $D_B = 5{,}6 \cdot 10^{-18} \frac{m^2}{s}$, obtained in [11] for a temperature of 523 K (curve 3-4), the value ε does not exceed $2{,}4 \cdot 10^{-3}\%$. Domain between curves 1-2 and 3-4 in Fig. 2 is the range of possible values ε within the values of the diffusion coefficient from the calculated obtained in this work at 393 K, to deliberately inflated (because it corresponds to a temperature of 523K), obtained independently [11].

Table 2

The part ε of mass transfer, which is carried out by surface diffusion during electrochemical deposition of nickel for different densities of nucleation centers of the new phase and different current densities.

j, A/м^2 **N**, м$^{-2}$	125	250	500	625	750
$2.5 \cdot 10^{15}$	$3.98 \cdot 10^{-4}$ %	$1.99 \cdot 10^{-4}$%	$9.95 \cdot 10^{-5}$ %	$7.96 \cdot 10^{-5}$ %	$6.63 \cdot 10^{-5}$ %
10^{14}	$1.59 \cdot 10^{-5}$ %	$7.96 \cdot 10^{-6}$ %	$3.98 \cdot 10^{-6}$ %	$3.18 \cdot 10^{-6}$ %	$2.65 \cdot 10^{-6}$ %
10^{13}	$1.59 \cdot 10^{-6}$ %	$7.96 \cdot 10^{-7}$ %	$3.98 \cdot 10^{-7}$ %	$3.18 \cdot 10^{-7}$ %	$2.65 \cdot 10^{-7}$ %

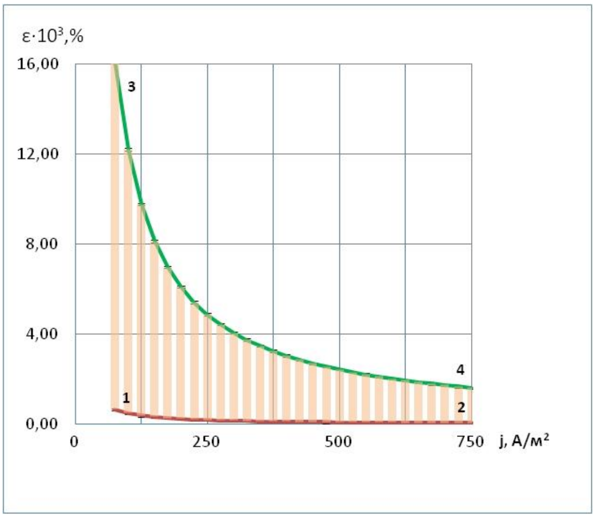

Fig. 2. Quantitative estimate of the contribution of the surface diffusion process to mass transfer during electrochemical deposition of metals.

Conclusions

1. At the temperature of electrochemical deposition of metals, the role of the surface diffusion process was negligent. The part of mass transfer, which is carried out by surface diffusion, in comparison with the total mass transfer during electrochemical deposition of metals does not exceed the value $\varepsilon \le 2{,}5 \cdot 10^{-3}$%.

2. The value of the coefficient of boundery diffusion of nickel at a temperature of 393 K is in the range from $2.28 \cdot 10^{-19}$ m^2/s to $3.22 \cdot 10^{-19}$ m^2/s.

3. As follows from item 1-2 of the Conclusions, the formation of the coating during electrochemical deposition of metal occurs at speeds that significantly exceed the speed of diffusion processes at this temperature. But it is the diffusion growth of the new phase that creates an ordered (crystalline) structure. Therefore, the negligibly small role of diffusion processes may be one of the evidences of the formation of the amorphous structure of the coating during electrochemical deposition of metal.

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Кількісна оцінка внеску процесу поверхневої дифузії в масоперенесення при електрохімічному осадженні металів

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У цьому дослідженні зроблена спроба кількісно оцінити внесок процесу поверхневої дифузії в масоперенесення при електрохімічному осадженні металів. Розрахована максимальна густина центрів зародження, при якій можливо виключно дифузійне заростання суцільного шару нової фази. Розраховано час дифузійного заростання суцільного мономолекулярного шару нової фази. Проаналізовано результати незалежних експериментів по знаходженню коефіцієнтів граничної дифузії в двошаровій тонкоплівковій системі платина – нікель. Знайдено значення коефіцієнта граничної дифузії нікелю при температурі 393 К. Зроблена кількісна оцінка частки масоперенесення за рахунок поверхневої дифузії фізадсорбованих атомів відносно загального масоперенесення при електрохімічному осадженні металів. Доведено, що роль процесу поверхневої дифузії в формуванні покриття при електрохімічному осадженні металів є нехтовно малою. Показано, що це є непрямим доказом формування аморфної структури покриття при електрохімічному осадженні металу.

Ключові слова: поверхнева дифузія, процес зародження, коефіцієнт поверхневої дифузії, мономолекулярний шар, швидкість росту зародків нової фази, час заростання шару, електрохімічне осадження.