

INFLUENCE OF A VARIATION OF THE PHASE COMPOSITION OF A MULTIPHASE DIFFUSION LAYER ON THE EVOLUTION OF PHASE BOUNDARIES ACCOMPANIED BY CHEMICAL REACTIONS ON THEM.

2. A SIMULATION OF DIFFUSION

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We consider the features of the kinetics of the phase boundaries of a multiphase diffusion layer under the conditions of diffusion growth of phase layers and diffusion homogenization. A mathematical description of the evolution of the structure and composition of a multiphase diffusion layer is carried out allowing for non-ideal boundary conditions on the external surface of a metal. Consideration is given to a model problem concerning the formation and evolution of a multiphase diffusion layer in the "the saturation element — the substrate metal" system which consists of four phase layers. It is demonstrated that a multiphase diffusion layer can include two, three, or four phases depending on the boundary conditions on the external surface of a metal. It is proved that diffusion of the saturation element into the substrate metal is accompanied by the appearance of a new phase layer in the composition of the multiphase diffusion layer. In this case, a violation of the parabolic law of the growth of phases is observed. This law is also violated under the conditions of the disappearance of a phase layer during diffusion homogenization. The successive appearance of phases in the composition of a multiphase diffusion layer gives rise to a violation of the parabolic law of the growth of phases as well. We analyzed and generalized the features of the violation of this parabolic law in all these cases. The results of computer simulation in the "nitrogen — iron" and "silicon — molybdenum" systems are in good agreement with the experimental data.

The Function of Real Exchange Conditions

Allowing for real conditions of the formation of multiphase diffusion layers makes the boundary conditions of the diffusion problem much more complicated, that's why obtaining an analytic solution becomes practically impossible. But the investigation of the complicated time-dependent boundary conditions allows one to control the structure and composition of multiphase diffusion layers. Let's consider the influence of non-ideal boundary conditions on the formation of a model multiphase layer on the surface of a metal substrate.

Let the diffusion saturation be accompanied by the formation of three phases of the intermetallide of the saturation element with the substrate element and a transitional layer, being a continuous series of solid solutions of the saturation element in the substrate metal. Moreover, the phases of this system have such physical-chemical characteristics that the parameter $D_q \Delta C_q$ [1] which is the product of the diffusion coefficient and the width of the region of homogeneity of the q th phase, meets the condition

$$D_1 \Delta C_1 \gg D_2 \Delta C_2 \geq D_3 \Delta C_3 \geq D_4 \Delta C_4, \quad (2.1)$$

where ΔC_4 is the miscibility limit of the saturation element in the substrate metal.

Let's analyze the evolution of the structure and composition of a multiphase diffusion layer formed on the surface when various boundary conditions reflecting peculiarities of different saturation methods are realized on the saturation surface. For example, let the diffusant concentration $C_1(0, t)$ on the saturation surface remain constant or change stepwise depending on time (Fig. 1). Diffusion processes in each phase are described by the system of equations [2, (1.1)—(1.6)]. In this case, $Q = 4$ and Eqs. (1.2) and (1.4) in [2] take the form (to make it obvious, we suppose that the saturation element is absent in the substrate metal at the start time, i.e. it is not an alloying agent)

$$C_4(x, 0) = 0, \quad (2.2)$$

$$C_4(\Gamma_Q) = C_4(\infty, t) = 0. \quad (2.3)$$

According to (2.1), the diffusion coefficients (m^2/s) and the equilibrium concentrations at the movable boundaries can be taken equal to:

$$D_1 = 7 \cdot 10^{-13}, \quad D_2 = 8 \cdot 10^{-15},$$

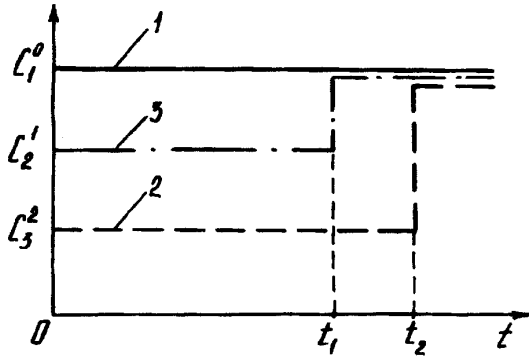


Fig. 1. Temporal variation of the diffusant concentration on the external surface of a metal (the model scheme of the 1st, 2nd, and 3rd variants of saturation)

$$D_3 = 2.25 \cdot 10^{-14}, \quad D_4 = 1.33 \cdot 10^{-14}$$

$$C_1^0 = 0.4, \quad C_1^2 = 0.3, \quad C_2^1 = 0.23,$$

$$C_2^3 = 0.16, \quad C_3^2 = 0.12,$$

$$C_3^4 = 0.08, \quad C_4^3 = 0.03, \quad C_4^5 = 0.$$

Let the diffusant concentration on the saturation surface vary as a time function in three variants depending on a model mode of the saturation (curves 1–3 in Fig. 1). The stated problem (1.1), (1.3), (1.5), (1.6), (2.2), (2.3) was solved using the additional grid method [3, 4]. The computation results for the concentrations profile and the evolution of the interphases are given in Fig. 2.

Though the same diffusant saturated the same substrate metal at the same temperature in all these cases, these processes resulted in the formation of the diffusion layers having different structure and composition.

If the boundary conditions realized on the saturation surface correspond to Fig. 1, curve 1, the diffusion zone practically includes the only layer of the highest intermetallide (Fig. 2), while the phase of the solid solution of the saturation element in the substrate metal is absent as well as phase 2, and phase 3 represents a very thin layer that slowly increases. It means that $\Delta\Gamma_3$ exceeds the critical thickness, but $G_1 \approx G_4$.

In the second case (Fig. 1, curve 2), the diffusion zone consists of the layers of the 1st, 3rd, and 4th phases. One can control the thickness of these phases varying the duration t_2 of the period when the diffusant concentration on the saturation surface remains constant and equals C_3^2 (Fig. 1).

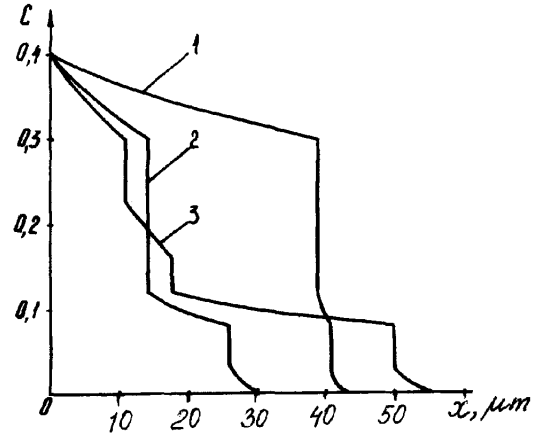


Fig. 2. Concentration profiles for three cases of saturation: a) C_1^0 , b) C_3^2 , 10.9 h + C_1^0 , c) C_2^1 28.3 h + C_1^0 ; at time moments: 1 – 1 h, 2 – 11.2, 3 – 28.4

Appearance of a New Phase in a Multiphase Diffusion Layer

If boundary conditions on the saturation surface conform to the third variant (Fig. 1, curve 3), the formed layer includes developed layers of all four phases of the considered system “the saturation element – the substrate metal”. In this case, one can control the thickness of the phase layers changing t_1 . Thus, nonordinary conditions of saturation, i.e. the step-type change of the diffusant concentration on the saturation surface, result in a violation of the parabolic law starting from the time point preceding the appearance of the phase containing the most amount of the diffusant (Fig. 3). The layer of phase 1 rapidly increases at once after its appearance in comparison with the layers of phases 2 and 3. It results from the realization of condition (2.1) and the fact that layers of phases 2 and 3 are sufficiently developed (17 μm and 33 μm , respectively).

But it doesn’t “rescue” the second phase though a decrease of the thickness of its layer results in an increase of the parameter G_2 and, consequently, in an acceleration of the motion of the interphase Γ_2 , which conflicts with the parabolic law of growth (Fig. 3). A further increase of the layer of phase 1 causes a similar violation of the law of movement of the interphase Γ_3 . The absence of the second phase in the evolving diffusion layer and a decrease (because of the growth of the first phase layer) of the parameter G_1 to values

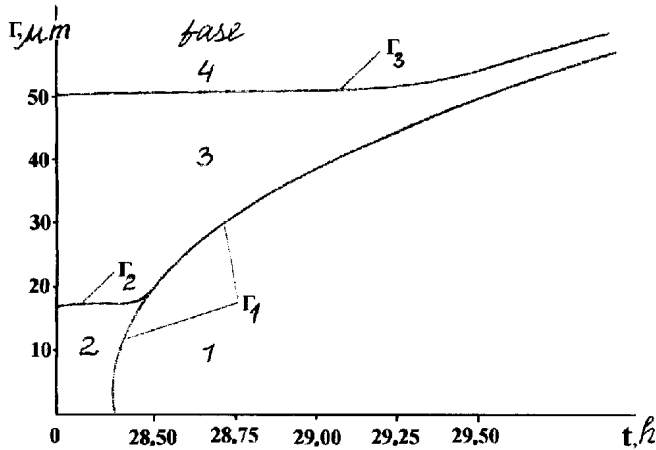


Fig. 3. Evolution of the phase boundaries at the saturation in the third case: C_2^1 28.3 h + C_1^0 . A fragment

commensurate to G_3 (which increases by the same reason as G_2 did at the beginning of our consideration) enable the third phase to “survive” (Fig. 3, $t=29$ hours and later). Increasing G_3 gives rise to an acceleration of the motion of the interphase Γ_3 and as a result to a violation of the parabolic law of the growth of phases. It is naturally to assume that this law is also violated for the boundary Γ_1 , and it is really observed (Fig. 4) during the period from the appearance of the first phase to $t=29.5$ h, but is not accentuated because of the rapid increase of the first phase. These divergences of Γ_1 from the parabola (a time-dependent deceleration) coincide with sudden departures of the motion dependences of Γ_2 and Γ_3 (an acceleration) from the parabolic law (compare Fig. 3 and Fig. 4).

Disappearance of Phase Layers at Diffusion Homogenization

Allowing for the fact that, in [1], the appearance of new phase layers in a multiphase diffusion layer was accompanied by a violation of the law of parabolic growth, it’s logically to assume that deviations from this law must be observed when a phase layer disappears. Let’s consider homogenization in a system consisting of a layer of the phase mostly enriched with the diffusant, which is included in an infinite metal substrate (for example, a layer of $MoSi_2$ between two Mo plates of infinite thickness). As for the investigation of the DACRI (diffusion accompanied by chemical reactions on phase boundaries) kinetics, the problem is well-posed: on the one hand, there exists the single mass-transfer process —

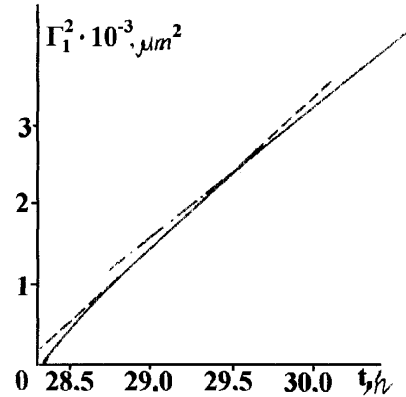


Fig. 4. Dependence of the growth of the first phase at the saturation in the third case (C_2^1 28.3 h + C_1^0); dotted lines are auxiliary

DACRI (i.e. it is the limiting one); on the other hand, the boundary conditions at the external surfaces ($-\infty; +\infty$) are constant (equal to zero). This problem is symmetric and can be described by the system of equations (1.1)—(1.6), but (1.2)—(1.4) must be rewritten as

$$C(x, 0) = \begin{cases} C_1^0, & \text{at } 0 < x < \Gamma_1, \\ 0, & \text{at } \Gamma_1 < x < \infty, \end{cases}$$

$$\frac{\partial C_1}{\partial x} \Big|_{\Gamma_0=0} = 0, \quad C_4(\infty, t) = 0.$$

The computation results correlate well with those of the independent experiment [5] (Fig. 5,c) ($T = 1723$ K, $D_2 = 11.6 \cdot 10^{-12}$, $D_3 = 9.3 \cdot 10^{-15}$, $D_4 = 7.2 \cdot 10^{-16}$ m^2/s). To make the model consideration more evident, it was carried out at 1723 K. All the constants correspond to the “silicon—molybdenum” system [6].

The simulation results (Fig. 5) allow us to draw a conclusion that the disappearance of a phase layer is accompanied by a violation of the parabolic law of the motion of phase boundaries. Diffusion of the element (silicon) from phase 1 which is mostly enriched with the former depthward the matrix, results in the appearance and growth of phases 2 and 3 (less enriched with the diffusant) as well as the solid solution in the metal substrate (phase 4).

Homogenization of each phase (except the first one, being homogeneous from the very beginning) results in the growth of the second and third phases at the expense of the first one. At once after the disappearance of the first phase layer, one can observe a further growth of the second phase during a certain period of time Δt_q

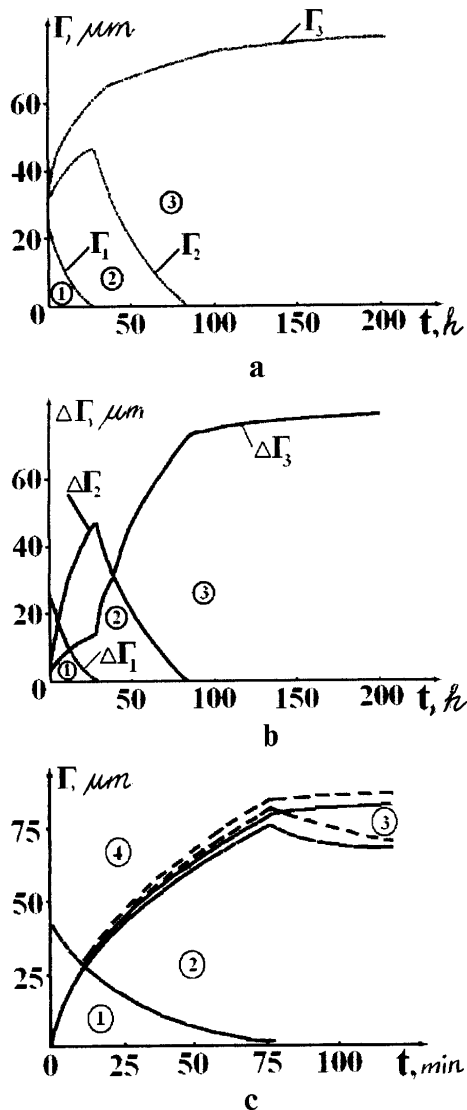


Fig. 5. Temporal variations of the interphase coordinates (a), the thickness of phase layers at the homogenization in the "the layer of phase 1 between semiinfinite plates of phase 4" system (b) and the interphase coordinates (solid lines— computation; dotted line — experiment [5])

(different for the remained phases). It is caused by oversaturation because of the existence of a region of homogeneity in phase 2 (Fig. 5). But the flow of the diffusant to the interphase Γ_2 decreases and so does the rate of the interphase Γ_3 , which becomes equal to zero when the flow of the diffusant from phase 2 to the boundary and that from the boundary to phase 3 get balanced. A deceleration of the phase boundary movement is the more sudden, the narrower the region of homogeneity of the remained phase mostly enriched with

the diffusant is (phase 2 at a time) and the smaller the jump of the concentration at the boundary Γ_2 is. After this moment, the layers of the nonhomogenized phases (phase 3) go on growing at the expense of the dissolution of the phase mostly enriched with the diffusant (phase 2). An increase of the thickness $\Delta\Gamma_3$ of the third phase layer promotes a decrease of the dissolution rate of phase 2 as well as a sudden deceleration of the movement of the interphase Γ_3 . The first process results in the change of sign of the second-order derivative of the interphase motion variation with time (interphase Γ_2 at a time), while the second one gives rise to a sudden change of the curvature of the line joining two different curves (see $\Gamma_3(t)$ at $t = 32 \div 38$ h, Fig. 5,a). The features of the phase evolution are common. It can be demonstrated if observing the evolution of phase 3 (after the disappearance of phase 2), which occurs identically. Deviations from the parabolic law of the growth of phases are observed especially clearly in the diagram representing the variation of the thickness of the phase layers (Fig. 5,b).

Successive Appearance of Phases

In certain systems, one can observe the successive appearance of phases under diffusion saturation. The delayed appearance of an intermediate phase (the existence of a latent period) results [1] from a specific character of the relationship between the parameters G_q , as well as the existence of the critical thickness $\Delta\Gamma_{qk}$ required for the existence of a continuous phase layer.

But the latent period of a new phase appearance can be also observed at the kinetic stage [7] when the limiting processes are those of exchange on the surface of a sample, rather than diffusion. As a result, the flow of the diffusant atoms through the saturation surface (which is controlled by these processes) remains lower during a certain period of time than it could be if performed by the diffusion depthward the matrix. It gives rise to the realization of such conditions just near the saturation surface, which disable the appearance of a phase more enriched with the diffusant than the existing one, which is possibly growing. As the thickness of this phase layer increases, the diffusion flow of the saturation element atoms depthward the matrix decreases (and so does the parameter G). Near the saturation surface, there can arise the conditions allowing the appearance of the new q -th phase which will be the successive one according to the equilibrium diagram if $j|_{x=0+0} \geq G_{qk} > G_{q+1}$, where $j|_{x=0+0}$ represents the flow of the diffusant atoms through the saturation surface.

Let's examine the kinetics of diffusion processes during the saturation accompanied by the successive appearance of phases, for instance the nitriding of iron. Moreover, in addition to solving the direct problem — the determination of the evolution of the concentration profile and phase boundaries, let's try to solve the inverse problem — searching for the quantitative description of the boundary condition on the saturation surface. It is worth noting that solving the inverse problem is rather difficult since the unknowns are not only the constants contained in the boundary conditions but the form of the function itself. Under such transcendental conditions, it is hard to imagine an algorithm allowing one to guarantee the convergence of the inverse problem solution to the proper one. That's why we shall prescribe arbitrarily the function that gives the boundary condition and then we'll determine the constants contained in it, periodically comparing the solution of the direct problem with the experimental data.

The examination of the equilibrium diagram of the “iron — nitrogen” system indicates that, in the temperature range from 823 to 1073 K, the nitriding can be accompanied by the existence of three or four phases [6]. Let's consider the most difficult case — the nitriding of iron at 873 K when the covering represents the layers of four phases: 1 — ε ; 2 — γ' ; 3 — γ ; 4 — α — the solid solution of nitrogen in iron.

Diffusion of nitrogen in the phases is given by the system of equations (1.1)–(1.6). Under the condition that nitrogen is practically absent in the initial sample and the latter has dimensions much higher than that of the diffusion zone, Eqs. (1.2) and (1.4) can be rewritten as

$$C_Q(x, 0) = 0, \tag{2.4}$$

$$C_Q(\infty, t) = 0. \tag{2.5}$$

According to Table, the parameters $D_q \Delta C_q$ in the phases are related in such a way that, in the presence of all the phases of the system in the diffusion zone,

the layers of the phases ε and γ will be the thinnest ones, especially those of the γ -phase, which conflicts with the experimental data. Thus, the experimental results in [8] indicate the contrary: the phases ε and γ are of considerable thickness while the thickness of the γ' -phase is insignificant.

It means that a mistake was made when defining the diffusion coefficients. Moreover, allowing for a close interconnection of the evolution of each phase with that of the coexisting ones, we cannot state that the mistake appeared when calculating the diffusion coefficients in the γ - or ε -phases. This fact was proved by the computation using the method given in [1] and the research data [9]. It is worth noting that the represented refined values of the effective diffusion coefficients cannot be considered as the exact ones because the used data are obtained by the diffusion experiment with the boundary conditions different from those realized at the diffusion welding of samples which is required by the method given in [1]. According to Table, a substantial mistake appeared when calculating the diffusion coefficient in the γ -phase. Mistakes in other phases are insignificant. The parameter $D_q \Delta C_q$ is practically the same for all the phases and, in case where the saturation is limited only by diffusion in phases, all the phases would appear in the composition of the covering practically simultaneously, which conflicts with the experimental results. Thus, the limiting processes for the nitriding of iron are the exchange processes running on the saturation surface. This fact forbids us to make use of the presumption about nitrogen concentration being constant on the external surface of the sample. On the contrary, it rather indicates that nitrogen concentration on the external surface of the sample is time-dependent. It is more plausible to make an assumption that the flow of nitrogen atoms is held constant on the external surface. Then (1.3) can be rewritten as

$$-D_q \frac{\partial C}{\partial x} \Big|_{x=0+0} = E, \tag{2.6}$$

where E is a certain constant.

Parameters and their refined values in the phases of the “iron-nitrogen” system at $T = 873$ K

Phase number	Phase	Parameters in the phases of the system				Refined values	
		$D_q \cdot 10^{12}, \text{ m/s}^2$	$\Delta C_q, \text{ mass \% [6]}$	$D_q \Delta C_q \cdot 10^{14}, \frac{\text{m}^2 \cdot \text{mass\%}}{\text{s}}$	Source	$D_q \cdot 10^{12}$	$D_q \Delta C_q \cdot 10^{14}, \frac{\text{m}^2 \cdot \text{mass\%}}{\text{s}}$
4	α	1.6	0.1	16	[8]	0.75	7.5
3	γ	$8 \cdot 10^{-4}$	0.29	$2.32 \cdot 10^{-2}$	[8]	0.15	4.35
2	γ'	$4.56 \cdot 10^{-1}$	0.76	34.7	[9]	$4.76 \cdot 10^{-2}$	3.61
1	ε	$4.73 \cdot 10^{-2}$	0.93	4.4	[9]	$6.05 \cdot 10^{-2}$	5.6

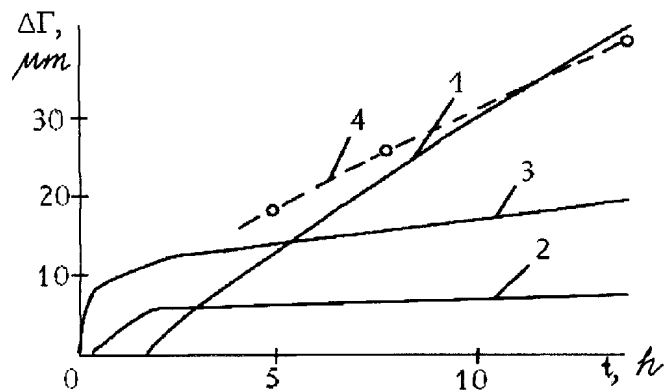


Fig. 6. Temporal variation of the thickness of the phase layers at their successive appearance: 1, 2, 3 — phase numbers; 4 — experiment [9]

Then problem (1.1), (1.5), (1.6), (2.4)—(2.6) is closed. The solution of this system of equations simulating the nitriding of iron was obtained using the additional grid method [3, 4]. The simulation results correlate satisfactorily with the experimental data [9] at $E = 8.2 \cdot 10^{-9}$ mass%·m·s.

The examination of the simulation results indicates that though the nitriding is limited by the processes of mass exchange rather than diffusion, the appearance of each successive phase (more enriched with the diffusant) in the composition of the diffusion layer is accompanied by a sudden change in the dependence of the thickness of the phase layer, having been mostly enriched before, and by its jump into another curve (Fig. 6). After a certain delay due to i) diffusant mobility in phases, ii) development of phases, and iii) the size of their regions of homogeneity, it also affects the growth law of those phase layers which are not situated in the immediate neighborhood of the appeared phase (Fig. 6, curve 3 at $t = 2.5 \div 3$ h).

Thus, if the process in the “iron—nitrogen” system were limited by diffusion, all the phases (according to [1]) would appear practically simultaneously since the parameters $D_q \Delta C_q$ are slightly different (Table). It means that, in this case, the successive appearance of phase layers is caused only by the kinetics of the mass transfer processes at the saturation surface.

Conclusions

The delayed appearance of new phase layers or disappearance of those having been a part of a multiphase diffusion layer can be caused not only by the kinetics of their initiation limited by diffusion, but

also by the kinetics of the mass transfer processes on the saturation surface. Thus, the conditions of the exchange at the saturation surface strongly influence the formation of the structure and composition of a multiphase diffusion layer. It implies that one can control the latter changing the conditions of saturation. Their variety is proved by numerical methods of saturation.

The appearance of a new phase layer in the composition of a multiphase diffusion layer (no matter where it appears — inside the layer or on its external surface) is accompanied by a sudden change of the dependence of the neighboring phase thickness and its jump to another curve. A jump of the second-order derivative of the phase layer thickness with time is observed. So the parabolic law of the growth of phases is violated.

The homogenization of a multiphase diffusion layer is accompanied by the disappearance of the phase layers, which also results in the violation of the parabolic law of the growth of phases. The temporal dependence of an increase of the thicknesses of phase layers changes suddenly and jumps to another curve just after the disappearance of the phase mostly enriched with the diffusant. Moreover, for the phase mostly enriched with the diffusant among those remained, the sign of the second-order derivative of the phase layer thickness with respect to time becomes positive.

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ВПЛИВ ЗМІНИ ФАЗОВОГО СКЛАДУ БАГАТОФАЗНОГО ДИФУЗІЙНОГО ШАРУ НА ЕВОЛЮЦІЮ МІЖФАЗНИХ МЕЖ ПРИ ДИФУЗІЇ, ЩО СУПРОВОДЖУЄТЬСЯ ХІМІЧНИМИ РЕАКЦІЯМИ НА НИХ.

2. МОДЕЛЮВАННЯ ДИФУЗІЇ

О. І. Нестеренко

Резюме

Розглянуто особливості кінетики руху міжфазних меж багатофазного дифузійного шару в процесах дифузійного росту шарів фаз та дифузійної гомогенізації. Проведено математичний опис еволюції структури та складу багатофазного дифузійного шару з урахуванням неідеалізованих межових умов на зовнішній поверхні металу. Розглянуто модельну задачу формування та еволюції багатофазного дифузійно-

го шару в системі “елемент насичення — метал основи”, що складається з чотирьох шарів фаз. Показано, що в залежності від межових умов на зовнішній поверхні металу багатофазний дифузійний шар може складатися з двох, трьох або чотирьох фаз. Показано, що при дифузії елементу насичення в метал основи спостерігається поява шару нової фази в складі багатофазного дифузійного шару. В цьому випадку спостерігається порушення закону параболічного росту фаз. Зникнення шару фази при дифузійній гомогенізації також веде до порушення закону параболічного росту фаз. Послідовна поява фаз в складі багатофазного дифузійного шару також призводить до порушення закону параболічного росту фаз. Особливості порушення закону параболічного росту фаз для всіх трьох випадків проаналізовано та узагальнено. Результати комп'ютерного моделювання в системах “азот—залізо” та “кремній—молібден” добре узгоджуються з експериментальними даними.