

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. 1. A FORMULATION OF THE PROBLEM

A. I. NESTERENKO

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Ukrainian State Chemical-Technological University
(8, Gagarin Ave., Dnipropetrovsk 49005, Ukraine; e-mail: ugxtu@dicht.dp.ua)

A mathematical description of the evolution of the structure and composition of a multiphase diffusion layer in the process of diffusion of the element of saturation into a metal substrate is carried out. This description allows for the existence of the following possible situations: a) the appearance of a new phase layer in the composition of a multiphase diffusion layer and b) the disappearance of a layer of a phase present in a multiphase diffusion layer. The possibility of existence of non-ideal boundary conditions on the external surface of a metal is taken into account as well. It is shown that each phase of a multiphase diffusion layer has a region of homogeneity. It is proved that the coordinates of phase boundaries strongly depend on the correctness of the initial diffusion parameters, which are set at the formulation of the problem. Therefore, the dependence of the coordinates of phase boundaries on time is an integral indication which can be used when ascertaining the adequacy of results obtained from the simulation of the kinetics of diffusion processes and the experimental data of a microstructure analysis. The conditions of appearance and disappearance of a continuous phase layer are analyzed. The estimate of the critical thickness of a continuous phase layer appearing or disappearing during the diffusion experiment is conducted. The numerical solutions of the model problems concerning the evolution of the structure and composition of a multiphase diffusion layer during the diffusion saturation are obtained. The computer simulation results have shown a possibility of consideration of the following model situations: 1) appearance of a new phase layer; 2) disappearance of a phase layer; 3) consecutive appearance of phase layers.

Introduction

Multiphase diffusion layers, appearing on a metal surface as a result of its diffusion saturation with elements of high diffusion mobility, usually have high values of useful characteristics (heat resistance, endurance, hardness, etc.). They depend on the presence or lacking of various phase layers of the “the saturation element — the substrate metal” system in a multiphase diffusion layer as well as on their thickness. Theoretically, if diffusion saturation is infinitely long, the number of phases in a diffusion layer equals the number of binary

compounds present at the equilibrium diagram of the “the saturation element — the substrate metal” system at the temperature of a diffusion layer formation plus one phase being a solid solution of the saturation element in the metal substrate. Practically, the lacking of some phases in a diffusion layer is often observed. In [1], this is considered to be a result of the existence of a latent period with the nucleation of centers of a new phase being the limiting process as well as a considerable variance in rates of growth of coexisting phases. But the consecutive appearance of phases, delay in the appearance of new ones, and disappearance of those having been a part of the diffusion layer can be a result of realization of boundary conditions more complicated than the ideal ones on the saturation surface. Let’s consider some typical cases of change of the phase structure of the diffusion layer caused by non-ideal conditions of the mass transfer process on the saturation surface.

Problem Formulation

Let a multiphase layer consist of Q phase layers at any time and let Q depend on the diffusion situation. The diffusion of the saturation element in each phase is described by the system of equations

$$\frac{\partial C_q}{\partial t} = D_q \frac{\partial^2 C_q}{\partial x^2}, \quad q = 1, 2, \dots, Q, \quad \Gamma_{q-1} \leq x \leq \Gamma_q,$$

$$\Gamma_0(0) = 0, \quad \Gamma_Q(t) = l, \quad (1.1)$$

where C_q, D_q indicate the diffusion coefficient and the saturation element concentration in the q th phase layer, respectively; q — the number of a phase (counted off from the saturation surface $x = 0$); Γ_q — the right boundary coordinate of the q th phase; l — the thickness

of the diffusion area; x — the coordinate counted off from the exterior surface of the metal (the saturation surface) depthward.

Boundary conditions associated with any method of diffusion saturation are generally given by:

$$C(x, 0) = \varphi(x), \quad (1.2)$$

$$C_1(0, t) = C_1(\Gamma_0, t) = f(t), \quad (1.3)$$

$$C_Q(l, t) = C_Q(\Gamma_Q, t) = \phi(t). \quad (1.4)$$

The conditions met at movable phase boundaries are

$$C_q(\Gamma_{q-1}, t) = C_q^{q-1}, \quad q = 2, 3, \dots, Q;$$

$$C_q(\Gamma_q, t) = C_q^{q+1}, \quad q = 1, 2, \dots, Q - 1. \quad (1.5)$$

All diffusion processes in the multiphase system are interconnected since, at each movable interface, the conditions of mass balance are to be realized: at the left boundary of the q th phase,

$$-D_{q-1} \frac{\partial C_{q-1}}{\partial x} \Big|_{\Gamma_{q-1}} = -D_q \frac{\partial C_q}{\partial x} \Big|_{\Gamma_{q-1}} +$$

$$+ (C_{q-1}^q - C_q^{q-1}) \frac{\partial \Gamma_{q-1}}{\partial t}, \quad q = 2, 3, \dots, Q;$$

at the right boundary of the q th phase,

$$-D_q \frac{\partial C_q}{\partial x} \Big|_{\Gamma_q} = -D_{q+1} \frac{\partial C_{q+1}}{\partial x} \Big|_{\Gamma_q} +$$

$$(C_q^{q+1} - C_{q+1}^q) \frac{\partial \Gamma_q}{\partial t}, \quad q = 1, 2, \dots, Q - 1. \quad (1.6)$$

In the boundary conditions (5), (6), the values of the saturation element concentration at the movable boundaries of the q th phase C_q^{q-1} and C_q^{q+1} remain constant during the whole process of diffusion saturation and are equal to the equilibrium values of the concentration in the q th phase according to the equilibrium state diagram. The correctness of this statement is proved by the fact that diffusion in a multiphase system includes two processes: a) diffusion inside the phase (within the q th phase); b) interphase diffusion (in the neighborhood of the phase boundaries). As was shown in [1], since the diffusion activation energy

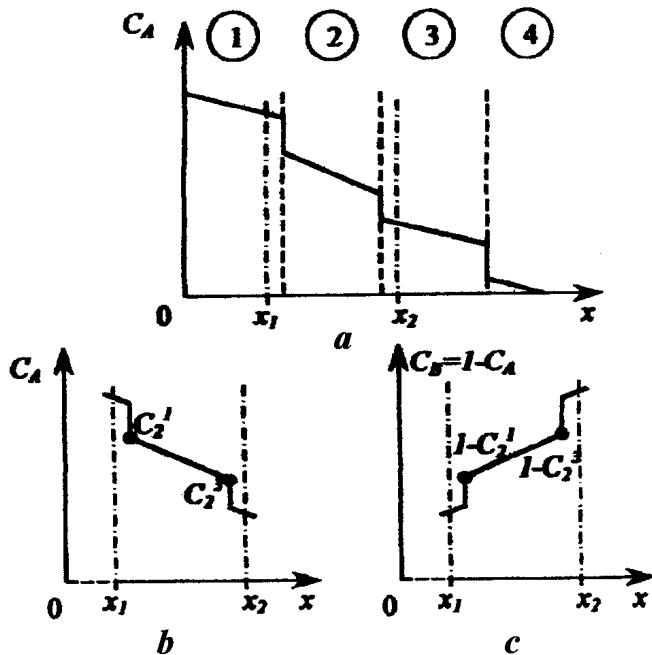
within the phase is higher than that at the boundary, the interphase diffusion process runs much faster than diffusion within the phase. Therefore, at the boundaries of each phase layer, the equilibrium concentration values are realized which remain constant under isothermal conditions according to the equilibrium state diagram.

Special consideration should be given to the problem of the existence of a region of homogeneity. In [2], the method of geometric thermodynamics is used to show that a stable chemical compound A_mB_n with its own lattice in a binary system A – B should be considered as an independent component dividing the system A – B into the subsystems A – A_mB_n and A_mB_n – B. As a result, the region of homogeneity on the basis of this compound includes two regions: the solid solution of A in A_mB_n and that of B in A_mB_n , both formed on the basis of the lattice A_mB_n . Moreover, the basic impossibility of the existence of possible components (we keep the nondissociated compound A_mB_n in mind) in a heterogeneous system, i.e. “the basic impossibility for the equilibrium state diagram with simple eutectic to exist” is proved in [2]. Hence, there exist no chemical compounds without a region of homogeneity.

It can be concluded from the kinetic ideas of diffusion processes running during the formation of multiphase layers. Let's prove this.

Since physical-chemical characteristics change stepwise at an interface, the stable chemical compound A_mB_n in the system A – B should be considered as an individual component. It is only the fact of the diffusion activation energy of the compound A_mB_n in A or B being much higher than that of isolated atoms (it implies that diffusion of A_mB_n is practically impossible) that allows us to consider diffusion in the system A – B in the binary approximation. As any substance, the compound A_mB_n has a non-ideal crystal lattice (including lattice vacancies, dislocations, grain and block boundaries), so the elements A and B can diffuse in it. One can hardly imagine a substance of absolute rigidity (though it is not in contrast to Gibbs's rule), i.e. a substance which absolutely doesn't dissolve the substances A or B and has absolute diffusive impenetrability. This fact alone implies the impossibility of presence of the pure phase A_mB_n in a diffusion heterogeneous system.

Let's analyze a fragment of a multiphase binary system, limited by the coordinates x_1 and x_2 (Figure, a). If $C_2^1 = C_2^3$, then neither A nor B can diffuse through layer 2 of the phase 2 (named as the substance A_mB_n), which is in contrast to the fact of the evolution of all phases including A_mB_n under the diffusion saturation. Hence, there must exist some level of solubility of the



Model scheme of a fragment of the concentration profile of a multiphase diffusion layer

substance A in the chemical compound A_mB_n . In other words, the condition $C_2^1 \neq C_2^3$ — must be realized, i.e. there exists a region of homogeneity of A_mB_n . Let's define this conclusion more accurately.

Let the concentration value C_2^3 correspond to the stoichiometric composition of A_mB_n . Then the concentration excess $\Delta C_2 = (C_2^1 - C_2^3)$ (Figure, b) within the considered phase (phase 2) can be treated as the surplus concentration of non-reacted atoms A diffusing in the compound A_mB_n . But this conflicts with the condition $\sum_1^2 C_i = 1$, since for the stoichiometric composition of A_mB_n , $C_A + C_B = 1$.

Moreover, allowing for the process of mutual diffusion in the system A — B, one cannot regard concentration values C_2^1 as corresponding to the stoichiometric composition of A_mB_n . The same conclusion can be drawn after a similar argumentation concerning the component B (Figure, c).

Therefore, the concentration value corresponding to the stoichiometric composition lies somewhere between C_2^1 and C_2^3 and the thickness of the layer of the stoichiometric composition of A_mB_n in the case discussed is commensurate to the lattice spacing. Hence, according to Figure, a to the left from the stoichiometric composition zone, there exists a region depleted with the element B, while to the right — the one depleted with

the element A. That is, $(C_2^1 - C_A^{A_mB_n})$ is the miscibility limit for A in A_mB_n and $(1 - C_2^3 - C_B^{A_mB_n})$ is that for B in A_mB_n .

Thus, the region of homogeneity of the compound A_mB_n has non-zero width and consists of regions of the solid solution of A in A_mB_n and that of B in A_mB_n .

Since phases have usually narrow regions of homogeneity, the assumption concerning the diffusion coefficient being constant within every phase cannot be treated as oversimplified [1]. At a fixed temperature, the diffusion coefficient is determined by a short-range order alone. That is why, for a phase with a sufficiently narrow region of homogeneity (diluted solid solution), the effective diffusion coefficient D_q is close to its actual value though generally speaking, the latter must depend on the composition rather than correspond to its average value within the considered phase. It is worth noting that allowing for the dependence of diffusion coefficients on the concentration is not a principal obstruction for a simulation using the additional grid method [3,4] and can be performed if its quantitative expression is available. Hence, the diffusion in a system including Q phase layers is completely described by Eqs. (1.1)—(1.6).

The very principle of diffusion isothermal saturation results in the fact that the flux of the saturation element through a layer of a higher intermetallide cannot be lower than the flux through each successive layer of any lower intermetallide. Otherwise, the layer of a higher intermetallide will be dissolved. Taking into account that phases have sufficiently narrow regions of homogeneity, this flux can be characterized [1] with the product $D_q \Delta C_q$, where $\Delta C_q = C_q^{q-1} - C_q^{q+1}$ denotes the width of the region of homogeneity of the q th phase. One can prove that allowing for a complicated dependence of the evolution of each phase on the characteristics of coexisting phases, even a formal mathematical formulation gives a single collection of values D_q and ΔC_q for each phase of the multiphase system.

Let's consider the evolution of the composition and structure of the system formed when the element A diffuses into the metal B, which results in the generation of a four-phase system: the highest intermetallide (phase 1), successively lower ones (phases 2, 3), and the solid solution of A in B (phase 4). The values of the equilibrium concentrations at the phase boundaries and the diffusion coefficients (m^2/s) in the phases of this model system are taken equal to

$$C_1^0 = 0.4, C_1^2 = 0.3, C_2^1 = 0.23, C_2^3 = 0.16,$$

$$C_3^2 = 0.12, C_3^4 = 0.06, C_4^3 = 0.03, C_4(\infty, t) = 0,$$

$$D_1 = 7 \times 10^{-14}, D_2 = 8.6 \times 10^{-14},$$

$$D_3 = 12.5 \times 10^{-14}, D_4 = 13.3 \times 10^{-14}.$$

Assuming these values to be exact, we'll introduce an error only in those parameters which correspond to one of the "middle" phases, for example to the phase 2, i.e. in D_2 and $\Delta C_2 = C_2^1 - C_2^3$. An error in the latter parameter is introduced by variation of C_2^3 . Referencing to the actual information was carried out by comparison of the evolution of the coordinates of phase boundaries. Simulation of the system of equations (1.1) — (1.6) was fulfilled by the auxiliary grid method [3, 4]. Two cases were considered: a four-phase diffusion layer grows under the assumption of the ideal boundary condition being realized upon the saturation surface $C(0, t) = C_1^0$ while an error is introduced into the description of the second phase: i) $D_2' = 1.5D_2$, ii) $\Delta C_2' = \Delta C_2/1.5$ (D_2' and $\Delta C_2'$ are incorrect values of the diffusion coefficient and the concentration in the second phase). As follows from the computation results, the maximal error in the values of the coordinates of phase boundaries appears in cases i) and ii) at the phase boundary $\Gamma_2(40\%)$ while it is equal to 5–8% at the boundaries Γ_1 and Γ_3 . Thus, the phase boundaries coordinates are very sensitive to the correctness of specifying the parameter $D_q \Delta C_q$. That's why the dependence of the motion of phase boundaries on time is an integral indication characterizing the correctness of specifying all the parameters of the diffusion system. It can be used when estimating the agreement between the results of mathematical simulation of the diffusion kinetics and experimental information which can be easily obtained from the data on microstructure analysis of real diffusion layers.

Existence Conditions for a Continuous Phase Layer Being a Part of a Multi-phase Diffusion Layer

Special consideration should be given to the condition of appearance or disappearance of a phase layer, as well as to the estimation of the critical thickness of a continuous phase layer appearing or disappearing during the diffusion experiment.

Making no use of the assumption about linearity of the concentration distribution within any phase layer, let's still take advantage of the parameter $G_q =$

$D_q \Delta C_q / \Delta \Gamma_q$ (here, $\Delta \Gamma_q = \Gamma_q - \Gamma_{q-1}$ is the thickness of the q th phase layer at time t). Then we can state that, in each previous phase (the compound containing a larger amount of the saturation element), this parameter must meet the condition $G_q \geq G_{q+1}$.

Let the parameter value for the q th phase satisfy the condition $D_q \Delta C_q < D_{q+1} \Delta C_{q+1} < D_{q-1} \Delta C_{q-1}$. From the mathematical point of view, the quantity $\Delta \Gamma_q$ can be indefinitely small. Then we can state that, at any small finite values of D_q and ΔC_q (in the presence of the previous phase containing a larger amount of the diffusant) starting from the moment close to $t = 0$ (the beginning of the saturation), there will exist a layer of the q th phase even if having very small thickness. In the course of time, the layers of the phases $(q-1)$ and $(q+1)$ will grow resulting in a decrease of G_{q-1} and G_{q+1} . This results in a decrease of G_q and consequently an increase of $\Delta \Gamma_q$. Then we can draw a conclusion that, in spite of the difference in the values of the parameters $D_q \Delta C_q$, all the phases present at the equilibrium diagram exist in the diffusion area practically from the beginning of the saturation as continuous growing layers. But this fact conflicts with the experimental data. We recall that this conclusion was drawn under the condition that there exist continuous phase layers of however small finite thickness. But continuous phase layers having thickness lower than 1 μm were not observed experimentally [1]. It is worth adding that the estimation of the thickness of the surface interphase layer situated under the saturation surface and influenced by peculiarities of the exchange processes running through it gives the same value, 1 μm [5]. This implies that, at a thickness in the order of 1 μm , a continuous phase layer becomes unstable. This can be explained in the following way.

The surface energy of an phase boundaries can be neglected only in case where its radius of curvature approaches infinity (a flat boundary). If the radius of curvature r of a phase boundary is finite, then the equilibrium value of the concentration at the boundary $C_q^{q+1}(r)$ is much higher and is given by the Gibbs—Thomson equation

$$C_q^{q+1}(r) = C_q^{q+1}(\infty) \exp\left(\frac{2\sigma V_a}{RT} \frac{1}{r}\right), \quad (1.7)$$

where $C_q^{q+1}(\infty)$ — the equilibrium value of concentration according to the equilibrium state diagram, σ — the surface energy, V_a — the atomic volume of the q th phase, R — the molar gas constant, T — the absolute temperature.

Let the q th phase layer dissolve in the process of diffusion annealing and becomes much narrower than the layers of the neighboring phases ($q - 1$) and ($q + 1$). When the thickness of the q th phase layer decreases to the proportions of $\Delta\Gamma_{qk}$ which is commensurate with structural defects dimensions, there appears a possibility of its local perforation. Then, in neighborhood of this perforation, the radius of curvature of the interface becomes very small, of the order of $r \approx \Delta\Gamma_{qk}/2$, which results in a sudden increase of the equilibrium concentration $C_q^{q+1}(r)$ according to (1.7). Thus, in turn, results in the acceleration of dissolution of the q th phase and the appearance of new perforations in it.

The mechanism of instability appearance in the continuous layer of the q th phase was considered here ex contrario. At the diffusion saturation when G_{q-1} and G_{q+1} have such values that $\Delta\Gamma_q < \Delta\Gamma_{qk}$, the continuous layer of the q th phase is absent while, in the phase ($q + 1$) near the boundary Γ_{q-1} (practically coinciding with Γ_q at that moment), heterophase fluctuations result in the appearance and decay of the q th phase nuclei. That is, a dynamic equilibrium is established in this diffusion area [1].

In the absence of a flat boundary between the phases ($q - 1$) and ($q + 1$), i.e. in the isolated volume of the phase ($q + 1$), some of the q th phase nuclei would be above-critical and consequently they would not decay and would go on growing under the conditions of present oversaturation $C_{q+1} > C_{q+1}^q$. But the q th phase nuclei appear directly nearby the flat boundary Γ_{q-1} (according to (7), the concentration $C_{q+1}^q = C_{q+1}^q(\infty)$ at Γ_{q-1} is much lower than the equilibrium concentration $C_q^{q+1}(r)$ on the surface of the nuclei even if the latter is "above-critical"). Therefore, this stage of the diffusion zone evolution can be imagined in the following way: all phases except the q th one are present and evolve; nuclei of the q th phase "twinkle" (arise and decay) in front of the flat boundary Γ_{q-1} . This process lasts until G_{q-1} and G_{q+1} take on such values that $\Delta\Gamma_q = \Delta\Gamma_{qk}$, i.e. until the increase of the q th phase nuclei and their association forming a continuous layer become possible. That is why the algorithm of mathematical simulation of the appearance or disappearance of a phase layer being a part of a

multiphase diffusion layer is based upon the condition $\Delta\Gamma_{qk} = 1 \mu\text{m}$.

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

О. І. Нестеренко

Резюме

Проведено математичний опис еволюції структури та складу багатофазного дифузійного шару в процесі дифузії елементу насичення в метал основи. Цей опис проведено з урахуванням можливих ситуацій: а) появи шару нової фази в складі багатофазного дифузійного шару, б) зникнення шару фази, що вже була в складі багатофазного дифузійного шару. Врахована також можливість існування неідеальних межових умов на зовнішній поверхні металу. Показано, що кожна фаза багатофазного дифузійного шару має область гомогенності. Доведено, що координати міжфазних меж сильно залежать від коректності вихідних дифузійних параметрів, які задаються при постановці задачі. Тому залежність координат міжфазних меж від часу є збірною ознакою і може бути використана при констатації адекватності результатів математичного моделювання кінетики дифузійних процесів та експериментальних даних мікроструктурного аналізу. Проаналізовано умови виникнення та зникнення суцільного шару фази. Проведено оцінку критичної товщини суцільного шару фази, який виникає або зникає в процесі дифузійного експерименту. Одержано числові розв'язки модельних задач про еволюцію структури та складу багатофазного дифузійного шару в процесі дифузійного насичення. Результати комп'ютерного моделювання показали можливість розгляду таких модельних ситуацій: 1) поява шару нової фази, 2) зникнення шару фази, 3) послідовна поява шарів фаз.