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LOW-DIMENSIONAL SYSTEMS AND SURFACE PHYSICS

Reactive Diffusion in a Binary Solid-State Nanosystem

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Abstract—The kinetics of growth of a new nanosized phase in a binary diffusion couple during isothermal annealing has been investigated with allowance made for the size dependence of kinetic coefficients. It has been demonstrated using this approach that the exponent of the growth rate of the new phase can be nonmonotonic in time and that the growth of the new phase at intermediate stages can be either retarded or accelerated.

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1. INTRODUCTION

The development of new technological processes and objects for subsequent manufacturing of new nanomaterials with desired properties requires solving solution of the problem of an adequate description of physicochemical processes that occur in materials and devices in the course of the interaction with the environment. In this respect, an important role is played by the reactive diffusion, i.e., the phase transformation with the formation and growth of new phases due to the atomic diffusion. Rapid progress in computer engineering makes it possible to use sufficiently accurate methods of numerical simulation for investigating size-induced processes in nanoobjects and for solving the above problem.

A solid-phase reaction in a binary couple is one of the examples of the reactive diffusion and can be treated as a first-order phase transition, namely, as a decomposition in a film in which a new intermediate nanophase grows in the diffusion zone [1–3]. This new phase grows as a result of the atomic diffusion to the surfaces of contact between two materials and the reactions that proceed at the boundaries and the center of the already formed layer of the new phase.

In the general form, the problem associated with the description of the growth of a new phase interlayer remains unsolved and important. The question as to the determination of the state of the new nanophase interlayer remains open because this state, in the general case, differs from the state of final macroscopic products. Moreover, the classical growth theory does not consider the concentration dependences of the kinetic coefficients, which can exist as a result of the deviation from the stoichiometry in nanophases due to the shift in the condition of equilibrium between the new nanophase and the surrounding material. Furthermore, the problems regarding the size dependence of the kinetic coefficients in nanosystems as a result of the arising correlations between the order parameter and the diffusion mean free path of atoms have not been investigated to date.

Experimental investigations of annealings of diffusion couples, as a rule, allow one to determine the time dependences of the thickness of the new phase and have specific limitations in the study of the exponent of the growth rate n as a function of the thickness. These investigations have almost always revealed that there is a stage of parabolic growth [4–6]. The parabolic growth law has also been confirmed by theoretical studies beginning with the works by Wagner and Frenkel' [7–9]. However, the linear growth stage is not always observed in experiments, even though it can been theoretically predicted in the description of the interdiffusion of components with due regard for the deviation of compositions from equilibrium values at the boundary of the growing phase [4]. Recently, Prakash and Sritharan [10] experimentally investigated the nucleation of the interlayer of the Cu_6Sn_5 intermetallic compound in the Cu/Sn–Pb system for 30 days at temperatures in the range 125–175°C and revealed considerable deviations of the calculated exponent of the growth rate n from the values corresponding to the classical growth theory [10]. The deviations from the parabolic growth law were also observed in other experimental works [6]. However, the authors did not allow for the possible size dependence of the diffusion coefficient that can lead to these "anomalies."

The purpose of the present work is to investigate the influence of the size-induced diffusion on the kinetics of initial stages of growth of a new intermediate phase by using analytical solutions and numerical simula-

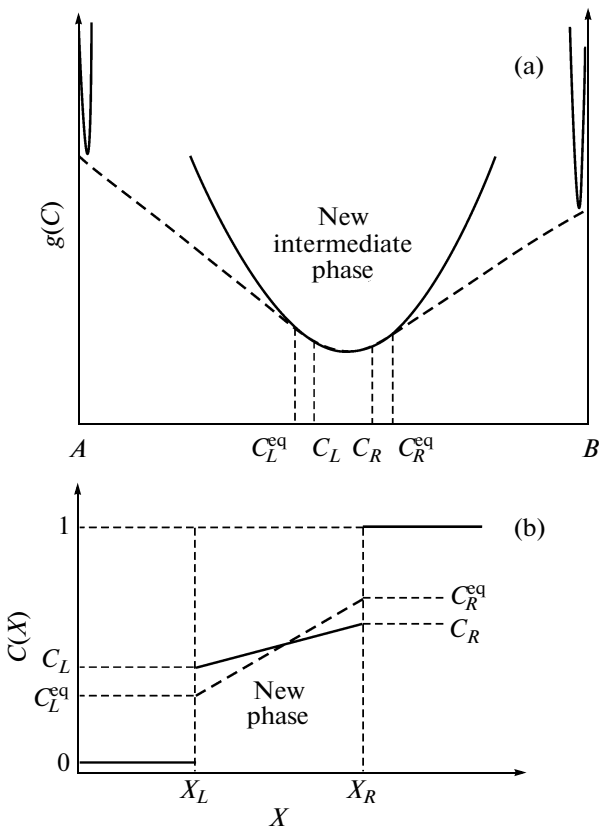

Fig. 1. (a) Qualitative dependences of the Gibbs energy density $g(C)$ for phases on the composition and (b) concentration profiles for the growth of the new phase between insoluble components. Inclined dashed lines connecting the dependences $g(C)$ for the new phase to the dependences for the pure components A and B are common tangents that determine the equilibrium concentrations C_L^{eq} and C_R^{eq} at the boundaries of the new phase. Designations: C_L and C_R are the compositions at the current instant of time, and $\Delta X = X_R - X_L$ is the characteristic thickness of the new phase.

tions. This generalized description of the kinetics of the process leads to nontrivial results and requires the verification of the theory and results with the use of different approaches (in particular, experiments and computer simulations).

2. THE CLASSICAL MODEL OF GROWTH OF ONE PHASE

For completeness of the description and subsequent representation and comparison of the results, we briefly recall the formulation of the problems and methods for their solution for the classical models of growth of one phase. Let us consider the annealing of a binary diffusion couple of mutually insoluble materials A and B, which leads to the nucleation and growth of one new intermediate phase (Fig. 1). It is assumed that, under specific conditions, there exists a narrow range of the concentration homogeneity of the intermediate phase. We assume that the A atoms are located at the left, the B atoms are located at the right, the A atoms in the course of reactive diffusion arrive at the "phase–B component" interface and enter into the reaction with the B atoms, and vice versa. In this formulation, we obtain the process with the one-dimensional diffusion.

In the framework of this growth theory, the growth equation has the form

$$\frac{1}{2}\frac{d\Delta X^2}{dt} = \frac{1}{(1-C_R)C_L}D\frac{\eta\Delta C_{eq}}{(1+\eta)}\left(1-\frac{\eta\Delta C_{eq}}{1+\eta}\right). \quad (1)$$

Here, C_L^{eq} and C_R^{eq} are the equilibrium concentrations at the left and right boundaries of the new phase, respectively; X_L and X_R are the coordinates of the left and right boundaries of the new phase; $\Delta X = X_R - X_L$ is the thickness of the new phase; η is the parameter of the control growth regime; D is the effective interdiffusion coefficient of atoms; $\Delta C_{eq} = C_R^{eq} - C_L^{eq}$ is the concentration width of the new phase; and t is the time of the process after the nucleation of the new-phase interlayer.

Equation (1) at $\eta \longrightarrow 0$ transforms into the relationship for the growth rate of the new phase, which includes not only the flux inside the new phase but also the fluxes at the boundaries of the new phase at the left and right (for the steady-state process, they are considered to be equal to the flux inside the new phase):

$$\begin{cases} C_R = C_R^{eq} - \dfrac{D\Delta C_{eq}}{K_R(\Delta X + D/K_{eff})}, \quad C_R \le C_R^{eq} \\ C_L = C_L^{eq} + \dfrac{D\Delta C_{eq}}{K_L(\Delta X + D/K_{eff})}, \quad C_L \ge C_L^{eq} \\ \dfrac{d\Delta X}{dt} = \dfrac{1}{(1-C_R)C_L}D\dfrac{\Delta C_{eq}}{(1+D/(K_{eff}\Delta X))\Delta X} \\ \times\left(1-\dfrac{\Delta C_{eq}}{1+D/(K_{eff}\Delta X)}\right). \end{cases} \quad (2)$$

Here, we wrote initially the conditions for the compositions and then the growth equation and introduced the designation $K_{eff} = K_L K_R/(K_L + K_R)$, which is the effective reaction rate constant. In this case, we consider the growth of the new phase when the A and B atoms, in actual fact, do not diffuse into the interlayer and grow the new phase at the left and right at the boundaries, where the compositions C_R and C_L do not correspond to the equilibrium values: $C_R < C_R^{eq}$ and $C_L > C_L^{eq}$ (Fig. 1b).

This case takes into account a finiteness of the reaction rate at the boundaries of the new phase (it is also referred to as the reaction-controlled growth). It is assumed that the flux of the A component at the boundary with the new phase J_A is proportional to the deviation of the concentration C_L of the A component from its equilibrium value C_L^{eq} at the left boundary, i.e., $J_A = K_L(C_L^{eq} - C_L)$, and the flux of the B component at the boundary with the new phase J_B is proportional to the deviation of the concentration C_R of the B atoms from the equilibrium value C_R^{eq} at the right boundary, i.e., $J_B = K_R(C_R - C_R^{eq})$. Here, K_L and K_R are the reaction rate constants at the left and right boundaries, respectively [3, 4, 6].

The kinetic coefficients K_L and K_R are proportional to the frequencies of addition of atoms (inversely proportional to the time of addition of atoms at the boundary to the new phase). The time of addition consists of the migration time (drift of atoms along the boundary) and the time of interaction with defects and is determined by the detachment of atoms from the lattice of one phase, the transfer through the interface, and the attachment to the lattice of the new phase [1–3]. Therefore, in my opinion, the reaction rates at the boundaries K_L and K_R, as well as the interdiffusion coefficient D, should depend on the structure of the new phase and the size or thickness of its interlayer. If the total time of the detachment, transfer, and attachment of atoms is longer than the time of the diffusion supply of atoms of both types to the interface, the growth will be controlled by the reactions at the interface. This situation will occur, for example, in the presence of an oxide film at the interface or another barrier layer.

The finiteness of the reaction rate at the boundaries leads to the difference between the equilibrium concentration width of the new phase $\Delta C_{eq} = C_R^{eq} - C_L^{eq}$ that corresponds to the phase diagram and the real concentration width $\Delta C = C_R - C_L$ (Fig. 1b). In the absence of the retardation of the reactions at the left surface, the composition C_L reaches C_L^{eq} (and C_R reaches C_R^{eq} at the right boundary).

For $\eta \ll 1$ and constant parameters D, K_L, and K_R, Eq. (1) has an analytical solution and the characteristic size of the new phase varies linearly with time:

$$\Delta X \cong \Delta X_0 + \frac{K_{eff}\Delta C_{eq}}{(1 - C_R)C_L}(t - t_0). \quad (3)$$

Here, ΔX_0 is the initial thickness of the primary continuous interlayer of the new phase after the nucleation at the instant of time $t = t_0$.

For large values of the parameter of the control regime $\eta \longrightarrow \infty$, Eq. (1) becomes equation for the diffusion-controlled growth of the new phase when the growth rate of the intermediate phase is determined only by the effective interdiffusion coefficient D averaged over the phase for atoms and the thermodynamic stimulus of the phase formation (Fig. 1a), which completely determines the concentration range of homogeneity inside the new phase. The corresponding growth equation is the material balance equation at the mobile boundary of the new phase and can be represented in the form [11]

$$\frac{1}{2}\frac{d\Delta X^2}{dt} = \frac{1 - \Delta C}{(1 - C_R)C_L} D\Delta C. \quad (4)$$

Here, it is assumed that the A and B atoms grow the phase inside the formed interlayer due to the interdiffusion and the thermodynamically equilibrium compositions $C_R = C_R^{eq}$ and $C_L = C_L^{eq}$ are attained at the boundaries (Fig. 1). For a constant value of the heterodiffusion coefficient D, the intermediate phase grows according to the parabolic law

$$(\Delta X)^2 \cong (\Delta X_0)^2 + \frac{2(1 - \Delta C_{eq})D\Delta C_{eq}}{(1 - C_R)C_L}(t - t_0). \quad (5)$$

Consequently, in the general case when the growth rate of the phase layer is determined by both the diffusion transfer and the reaction rate at the interface, there is a crossover from the linear law (3) of growth of the thickness of the new phase $\Delta X \cong \varepsilon t^n$ with the exponent of the growth rate $n = 1$ to the parabolic growth rate (5) with the exponent $n = 1/2$.

Below, we will physically justify the influence of the size effects on the growth of the new phase in the framework of our approach.

3. PHYSICAL FACTORS RESPONSIBLE FOR THE SIZE DEPENDENCE OF THE KINETIC COEFFICIENTS

The physical reason for the existence of the size dependence of the kinetic coefficients can be understood from the following simple considerations briefly summarized in Table 1.

The aforementioned reasons allow us to make the inference that there exists a size (structural) dependence of the kinetic coefficients in the problem associated with the description of the kinetics of growth of the new intermediate phase at the initial stages when the self-consistent organization of the growing material is possible. In the course of the subsequent analysis, the presented data are sufficient for demonstrating

Table 1. Different functional variants for the size dependences of kinetic coefficients (for the diffusion coefficient as an example)

Reason, example, explanation	Dependence of the diffusion coefficient on the thickness of the new nanophase
Concentration correlation of the diffusion coefficients. The shift in the conditions of equilibrium of the coexistence of nanophases leads to the shift in the concentration limits of solubility [12]	$D \approx D_0\{1 + C_{eq}/C_{eq}^{\infty}\}$, where $C_{eq} = C_{eq}(\Delta X)$ is the solubility in the nanophase (the equilibrium concentration of the component inside the nanophase), C_{eq}^{∞} is the solubility in the bulk medium (the equilibrium concentration of the component for an infinite sample), and D_0 is the equilibrium effective coefficient of heterodiffusion for the bulk alloy
In terms of the energy-activated process $D = D_0\exp(-Q/kT)$, where D_0 is preexponential frequency factor and Q is the activation energy for the diffusion process [3]. The correlation between the activation energy Q and the melting temperature T_{melt} has the form $Q \approx 20kT_{melt}$. There exists a size dependence of the melting temperature [13]. This leads to the size dependence of the diffusion coefficient D. Owing to the increase in the ratio of the surface area to the volume of the material, the nitrification of face-centered cubic iron occurs at a sufficiently low temperature of 573 K, whereas the conventional bulk diffusion proceeds at temperatures of the order of 773 K and higher [14]	$T_{melt} = T_{\infty}\{1 - \beta/(2\Delta X)\}$ is the melting temperature, where T_{∞} is the melting temperature of the bulk material and β is the parameter of the material that depends on its shape and the surface tension. Substitution gives the phenomenological evaluation of the size dependence of the diffusion coefficient $D = D_0\exp(-20T_{\infty} \times \{1 - \beta/(2\Delta X)\}/T)$
Spontaneous nitrification, amorphism of nanoalloys and particles. During growth of the new phase, the amorphous phase becomes crystalline [15]	$D \approx (1 - \rho)D_{am} + \rho D_{cr}$, where D_{am} is the diffusion coefficient in the amorphous medium, D_{cr} is the diffusion coefficient in the crystal, and $\rho = \rho(\Delta X)$ is the volume fraction of the crystalline phase
Changes in the crystalline modifications with variations in the thickness of the film [16, 17]. Anisotropy of the diffusion coefficient, which takes on different values along different crystallographic axes even in the same lattice. Different crystal lattices competing with each other can be gradually formed in the new phase	$D \approx (1 - \rho)D_{cr1} + \rho D_{cr2}$, where D_{cr1} is the diffusion coefficient for the first crystalline modification, D_{cr2} is the diffusion coefficient for the second crystalline modification, and $\rho = \rho(\Delta X)$ is the volume fraction of the second crystalline modification
The growth of the new phase is accompanied by the nucleation and growth of grains [12]. The attachment of atoms to the phase and grain boundaries (frequency of attachment jumps) depends on the degree of imperfection of the boundary and on the grain size. The grain size depends on the thickness of the new phase interlayer. As a rule, the grain size is proportional to the thickness of the new phase interlayer	There appears a mutual correlation between the thickness of the intermediate phase, granularity, and kinetic coefficients of attachment of the atoms to the boundary of the new phase $D \approx D_{bulk} + D_{gb}\delta/\Delta X$, where D_{gb} is the grain boundary diffusion coefficient, D_{bulk} is the bulk diffusion coefficient, and δ is the average width of the channel of grain boundary diffusion (the thickness of the surface interlayer between grains of the new phase)

the specific features of different types of the size dependences of the kinetic coefficients. The phenomenological dependences for particular cases of each problem will be the subjects of separate investigations.

We use the functional dependences of the kinetic coefficients on the thickness of the new phase: $D = D(\Delta X)$, $K_{eff} = K_{eff}(\Delta X)$, $\Delta X_{cr} = D/K_{eff} = \Delta X_{cr}(\Delta X)$, and $\eta = \Delta X/\Delta X_{cr} = \eta(\Delta X)$.

The generalized equation of the size-induced growth (relationship (1)) for the cases under consideration can be written in the form

$$\frac{1}{2}\frac{d\Delta X^2}{dt} = \frac{1}{(1 - C_R)C_L}D(\Delta X)\frac{\eta(\Delta X)\Delta C_{eq}}{(1 + \eta(\Delta X))} \times \left(1 - \frac{\eta(\Delta X)\Delta C_{eq}}{1 + \eta(\Delta X)}\right). \quad (6)$$

Table 2. Selected size dependences of the coefficients for the description of the growth of the new intermediate phase in the binary nanosystem

Case	Dependence	$D/D_0 = f(\Delta X)$, $K_{\text{eff}}/K_0 = f(\Delta X)$
Dependences leading to the results qualitatively inconsistent with the classical growth theory, i.e., a nonmonotonic decrease or increase in the exponent $n(t)$		
1	Exponential dependence of the first type	$f = 1 + \exp(-\text{const}_1\Delta X)$
2	Parabolic dependence	$f = \text{const}_2 + \text{const}_3(\Delta X - \text{const}_4\Delta X_0)^2$
Dependences leading to the results qualitatively consistent with the classical growth theory, i.e., a monotonic decrease or increase in the exponent $n(t)$		
3	Exponential dependence of the second type	$f = \text{const}_5 \pm \exp(-\text{const}_6\{1 - \text{const}_7/\Delta X\})$
4	Hyperbolic dependence	$f = \text{const}_8 + \text{const}_9/\Delta X$
5	Linear dependence	$f = \text{const}_{10} + \text{const}_{11}\Delta X$

We investigated different types of the size dependences of the kinetic coefficients D, K, K_L, and K_R (Table 2). We present only symmetric cases when $K_L = K_R = K(\Delta X)$ and $K_{\text{eff}} = K_{\text{eff}}(\Delta X) = 0.5K(\Delta X)$, as well as the cases of similar simultaneous dependences of the diffusion coefficient $D/D_0 = f(\Delta X)$ and the kinetic reaction rate coefficient $K_{\text{eff}}/K_0 = f(\Delta X)$. Here, K_0 is the combined reaction rate constant at the boundary, which for the nanomaterial can be estimated to be $K_0 \approx D_0/\Delta X_{\text{cr}} \approx 10^{-15}\ \text{m}^2\ \text{s}^{-1}/10^{-9}\ \text{m} = 10^{-6}$ m/s. The specific feature of the last case is that the ratio between the size-dependent kinetic coefficients $D/K_{\text{eff}} = D_0/K_0 = \Delta X_{\text{cr}}$ is constant and the phase growth equation (6) in the case of the limiting kinetics becomes dependent not on the coefficient K_{eff} (as for the reaction-controlled growth) but on the size dependence of the diffusion coefficient D (as for the diffusion-controlled growth).

For illustration, we chose only some cases of the decreasing dependences of the kinetic coefficients, namely, case nos. 1–3 (Table 2). Now, we turn to the corresponding results and demonstrate the main differences of this approach from the classical models.

4. SIZE-INDUCED DIFFUSION-LIMITED GROWTH OF THE PHASE

Let us consider the results of the solution to Eq. (6) at $\eta \longrightarrow \infty$, i.e., for the diffusion-controlled growth of the new phase with Eq. (4) in which the diffusion coefficients depends on the size according to Table 2.

Case no. 1 in Table 2 corresponds to the exponential dependence of the first type for the diffusion coefficient D. This case was calculated with the parameters $C_L = C_L^{\text{eq}} = 0.45$, $C_R = C_R^{\text{eq}} = 0.55$, $\Delta X_0 = 10^{-10}$ m, $D_0 = 10^{-14}\ \text{m}^2/\text{s}$, $t_0 = 10^{-10}$ s, and $\text{const}_1 = 10^6$ m. The main results are presented in Fig. 3.

The exponent of the growth rate n nonmonotonically increases (Fig. 2c) from zero initial values to the asymptotic value $n = 0.5$ at long growth times, which coincides with solution (5) to problem (1) according to the classical growth theory for a constant diffusion coefficient.

Case no. 2 in Table 2 corresponds to the parabolic dependence of the diffusion coefficient D. In this case, the parameters chosen for the thicknesses of the new phase were as follows: $\Delta X \le \text{const}_4\Delta X_0$, $C_L = C_L^{\text{eq}} = 0.45$, $C_R = C_R^{\text{eq}} = 0.55$, $\Delta X_0 = 10^{-10}$ m, $D_0 = 10^{-14}\ \text{m}^2/\text{s}$, $t_0 = 10^{-10}$ s, $\text{const}_2 = 0.5$, $\text{const}_3 = 0.0016/\Delta X_0^2$, and $\text{const}_4 = 50$. For the thickness $\Delta X > \text{const}_4\Delta X_0$, the diffusion coefficient D was taken to be $D = \text{const}_2 D_0$. The results are presented in Fig. 3.

It can be seen that the resulting thicknesses of the new phase during the growth have no features and the dependence $\Delta X(t)$ itself is similar to the dependence for the conventional parabolic growth (Fig. 3b). However, the detailed analysis of the exponent n again showed that the growth rate is nonmonotonic (Fig. 3c). Therefore, the influence of the size-induced diffusion can be significant for determining the exponent of the growth rate n and "insignificant" for the time dependence of the thickness of the new phase $\Delta X(t)$.

It should be noted that, although case no. 3 in Table 2 (the exponential dependence of the second type for the diffusion coefficient) leads to a two-stage growth of the new phase interlayer, the exponent of the growth rate n monotonically increases to its asymp-

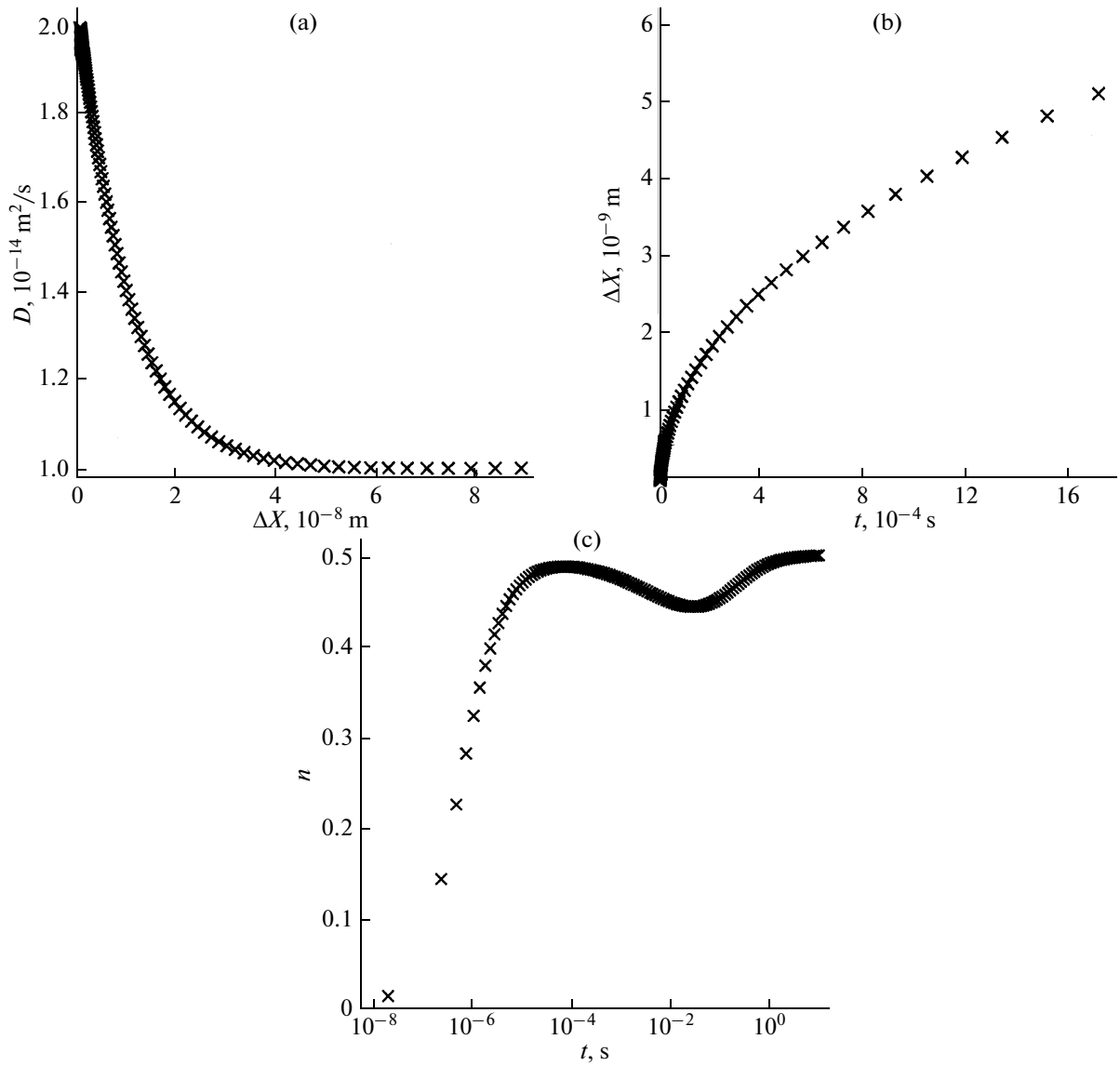

Fig. 2. Kinetics of size-induced growth of the new intermediate phase that is controlled by the rate of interdiffusion of atoms inside the intermediate phase: (a) size dependence of the diffusion coefficient, (b) time dependence of the thickness of the intermediate phase ΔX, and (c) time dependence of the exponent of the growth rate n.

totic value $n = 1/2$ and does not exhibit features for the data typical of metals.

Now, we turn to the main results of the problem regarding the boundary kinetics (Eq. (6)).

5. SIZE-INDUCED GROWTH OF THE NEW PHASE CONTROLLED BY THE BOUNDARY KINETICS

We analyze problem (6) for the cases when there exists a functional dependence of the kinetic coefficients on the size of the new phase (Table 2).

Case no. 2 in Table 2 corresponds to the parabolic dependence of the coefficient K_{eff} on the thickness. In this case, we used the following parameters: $C_L^{\text{eq}} = 0.4$ $(C_L \neq C_L^{\text{eq}})$, $C_R^{\text{eq}} = 0.5$ $(C_R \neq C_R^{\text{eq}})$, $\Delta X_0 = 10^{-10}$ m, $D_0 = 10^{-14}$ m^2/s, $t_0 = 10^{-10}$ s, $K_0 = 10^{-6}$ m/s, $\text{const}_2 = 0.5$, $\text{const}_3 = 0.004/\Delta X_0^2$, and $\text{const}_4 = 50$. For the thickness $\Delta X > \text{const}_4 \Delta X_0$, the coefficient K_{eff} was taken to be $K_{\text{eff}} = \text{const}_2 K_0$. The interdiffusion coefficient D inside the new phase was assumed to be constant and independent of the size: $D = D_0$. The corresponding results are presented in Fig. 4.

As before, we obtain the nonmonotonic bimodal dependence of the exponent of the growth rate n of the new phase due to the size dependence of the kinetic

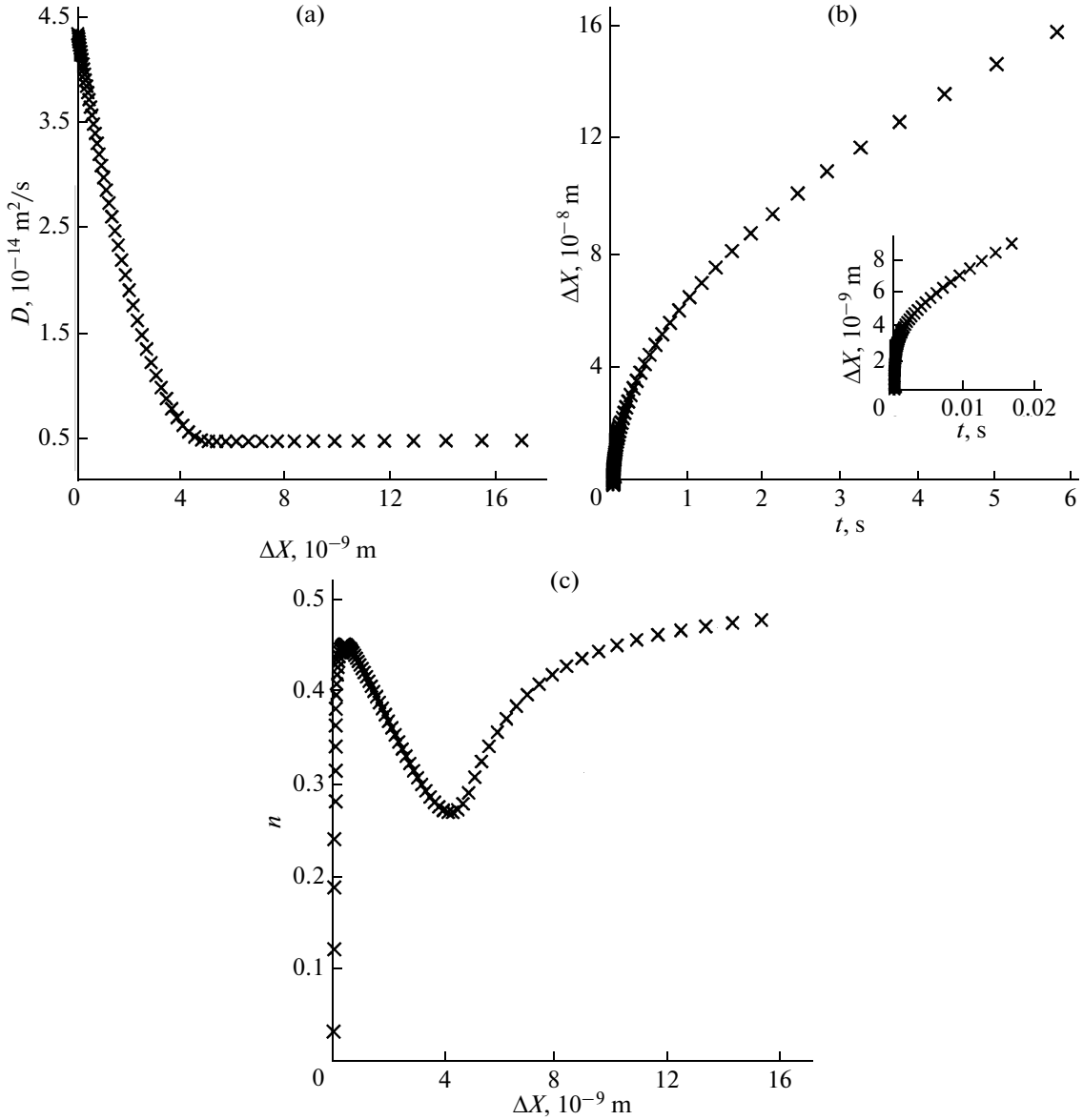

Fig. 3. Kinetics of growth of the new intermediate phase that is controlled by a finite rate of interdiffusion of atoms in the new phase: (a) parabolic dependence of the diffusion coefficient D on the size, (b) time dependence of the thickness of the intermediate phase (the inset shows the initial portion of the dependence), and (c) dependence of the exponent of the growth rate on the thickness of the new phase.

coefficient K_{eff} of the reaction at the boundary between the new and initial phases. The asymptotic value of the exponent n is equal to 0.5 when the kinetic coefficient K_{eff} tends to a constant and the parameter of the control growth regime η becomes considerably larger than unity for thickness of the new phase interlayer that reach and exceed $\Delta X = 10^{-7}$ m (Fig. 4b).

Case no. 2 in Table 2 corresponds to similar parabolic dependences of the quantities K_{eff} and D. In this case, we have $K/D = K_0/D_0$. The corresponding results resemble those obtained in the previous case (the parabolic dependence of the kinetic coefficient K_{eff}) when the dependence of the exponent n on the thickness of the new phase interlayer exhibits a nonmonotonic behavior.

Therefore, the parabolic dependences of the kinetic coefficients lead to a new exponent of the growth rate of the new phase, which exhibits a nonmonotonic dependence on the time and thickness of the new phase interlayer.

Case no. 3 in Table 2 corresponds to the exponential dependence of the second type for the kinetic coefficient K_{eff}. This case was calculated for the following parameters: $C_L^{\text{eq}} = 0.45$, $C_R^{\text{eq}} = 0.55$, $\Delta X_0 =$

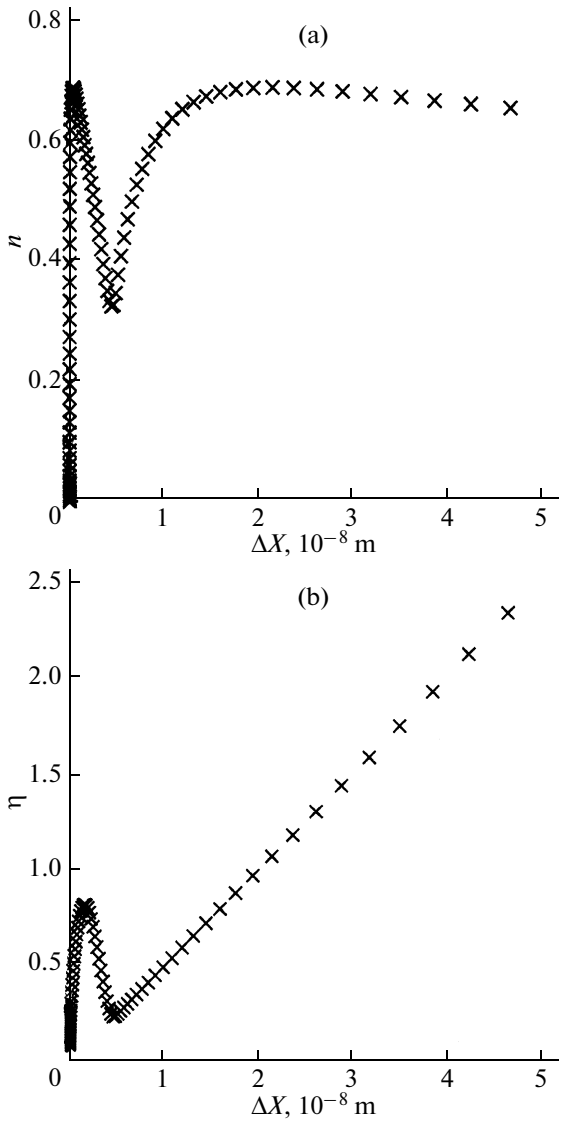

Fig. 4. Growth of the new intermediate phase that is controlled by the boundary kinetics, constant diffusion coefficient, and parabolic size dependence of the coefficient K_{eff}: (a) dependence of the exponent of the growth rate n of the new phase on the thickness of the new phase and (b) dependence of the parameter of the control growth regime η on the thickness of the new phase during the growth.

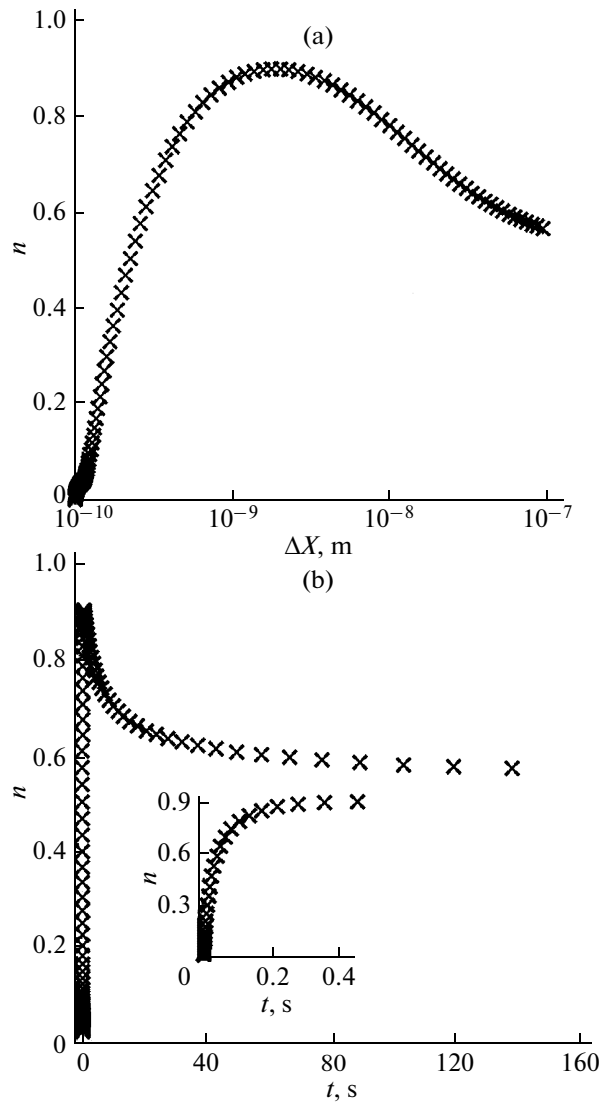

Fig. 5. Growth of the new intermediate phase that is controlled by the boundary kinetics, constant diffusion coefficient, and exponential size dependence of the second type for the coefficient K_{eff}: (a) dependence of the exponent n on the thickness of the new phase and (b) time dependence of the exponent of the growth rate n. The asymptotic value of the exponent n is equal to 0.5. The inset shows the initial portion of the dependence.

10^{-10} m, $K_0 = 10^{-6}$ m/s, $t_0 = 10^{-10}$ s, $\text{const}_5 = 0.01$, $T_\infty = 800$ K, $T = 400$ K, $\text{const}_6 = 18T_\infty/T$, $\text{const}_7 = 10^{-10}$ m, and diffusion coefficient $D = D_0 = 10^{-14}$ m^2/s. The results of the numerical solution to Eq. (6) are presented in Fig. 5.

Case no. 3 in Table 2 corresponds to similar exponential dependences of the second type for the kinetic coefficient K_{eff} and the diffusion coefficient. This case was calculated with the parameters similar to those used in the above calculations. The solution to the growth equation (6) leads to the results characterized by insignificant quantitative differences as compared to the previous case (Fig. 5). The difference is observed in the dependence of the parameter of the control regime η on the thickness of the intermediate phase: this parameter is a monotonically increasing function of the time and thickness, whereas, in the previous case, the corresponding parameter increases nonmonotonically. In this case, the asymptotic value of the exponent of the growth rate n reaches 0.5 and the parameter of the control regime η at long times tends to infinity.

Case nos. 4 and 5 in Table 2 for parameters typical of metals and alloys do not lead to unusual results as compared to those for the classical theory of new phase growth. Therefore, we can argue that even the presence of the size dependence of the kinetic coefficients does not necessarily lead to nonmonotonic features for the exponent of the growth rate. However, "selectivity" of the solutions can make it possible to more accurately solve the "inverse" problem associated with the determination of the kinetic coefficients from experimental data on the curves of growth thickness $\Delta X(t)$ and the exponents of the growth rate n.

6. CONCLUSIONS

Thus, in this paper, we have generalized two problems of the classical theory of intermediate phase growth in the binary diffusion couple with allowance made for the size dependence of the kinetic coefficients. The size dependence has been justified within the microscopic approach and in the context of the phenomenological approximation (Table 1). The inclusion of the size dependence of the kinetic coefficients leads to their variation with time. The results obtained allow one not only to understand the initial stages of growth of the nanophase but also to solve the inverse problem, i.e., to determine the kinetic coefficients from experimental data on the curves of the thickness of the new phase interlayer $\Delta X(t)$, the exponent of the growth rate n, and the average size of grains of the new phase at different temperatures. This analysis has been performed and is the subject of a separate investigation.

The description of the competing growth of several phases in the framework of the proposed approximation is a next important problem.

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