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STRUCTURE, PHASE TRANSFORMATIONS, AND DIFFUSION

Growth Kinetics of Nanoshells of the Intermediate Phase with Allowance for Finite Reaction Rates at Interphase Boundaries

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Abstract—Growth kinetics of the intermediate phase upon reaction diffusion in core–shell systems with simultaneous allowance for barriers at interphase boundaries, curvature, and concentration dependence of the interdiffusion coefficient inside the phase has been analyzed. It has been shown that the throughput capacity of interphase boundaries can change in the process of growth of the phase (both monotonically and nonmonotonically) and the concentration-range width of the phase likewise changes in a nonmonotonic manner.

Keywords: diffusion, reaction, boundary kinetics, intermetallic compounds, linear–parabolic law of growth

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1. INTRODUCTION

Solid-phase reactions that result in the formation of an interlayer of intermetallic compound or other intermediate phase with a narrow range of homogeneity are most often modeled in the configuration of a plane diffusion pair A/B, a plane thin layer A/B, or a multilayer film A/B/A...B/A/B. As early as in the 1970s, with the development of microelectronics, it became urgent to predict the initial stages of such solid-phase reactions. In works of Pines [1], Geguzin [2], Gösele and Tu [3], Dybkov [4], etc., the existence of the linear–parabolic law of growth of plane layers of the intermediate phase was long ago established without considering the phenomena of nucleation, grain-boundary diffusion, and the exhaustion of one of the components. The linear–parabolic growth is formally described by an equation of the growth of the intermediate-phase thickness Δx

$$\frac{d\Delta x}{dt} = \frac{c_\gamma - c_\alpha}{(c_\gamma - c_\beta)(c_\beta - c_\alpha)}\frac{\bar{D}\Delta c}{\Delta x + \lambda}, \tag{1}$$

where $\bar{D}$ is the average interdiffusion coefficient inside the phase interlayer; Δc is the equilibrium width of the concentration range of homogeneity; and c_α, c_γ, and c_β are the atomic fractions of atoms of sort B in the parent α and γ phases and intermediate β phase. The parameter λ plays the role of the characteristic thickness of the phase upon transition from the linear to the parabolic regime. At $\Delta x \ll \lambda$ the rate of growth of the phase proves to be constant (linear growth), whereas at $\Delta x \gg \lambda$ the rate of growth is inversely proportional to the phase-interlayer thickness (parabolic growth). According to Pines, the presence of the linear regime is caused by barriers at interphase boundaries (at one or at both). It is for due account of the barrier that Pines introduced the term "external diffusion" [1] in order to distinguish transitions of atoms through boundaries and ordinary diffusion (inside phases). In the linear regime, the delay time of atoms at interphase boundaries exceeds the time of migration of atoms from one boundary to another through the phase interlayer. Using the terminology of chemical kinetics the flux density through the interphase boundary can be written as

$$J = \pm\frac{1}{\Omega}K\left(c - c^{\text{eq}}\right), \tag{2}$$

where K is the reaction-rate coefficient at the interphase boundary (dimensionality m/s), c is the atomic concentration (molar fraction of the component) near the interphase boundary which in the general case varies with time and differs from the equilibrium concentration c^{eq} at the boundary determined by the rule of common tangent, and Ω is the atomic volume. Note that, in all of the models we know, the deviation from the equilibrium concentration is considered only from the side of the intermediate phase. Meanwhile, the deviation is present on both sides of the boundary (the corresponding theory is suggested in [5, 6]). This approach was conducted most rigorously in [3], in which reaction rates on both interphase boundaries were taken into account, then were used to analyze the growth of two intermediate layers with formulation of a criterion for the suppression and growth of phases. In particular, it was shown that the characteristic length

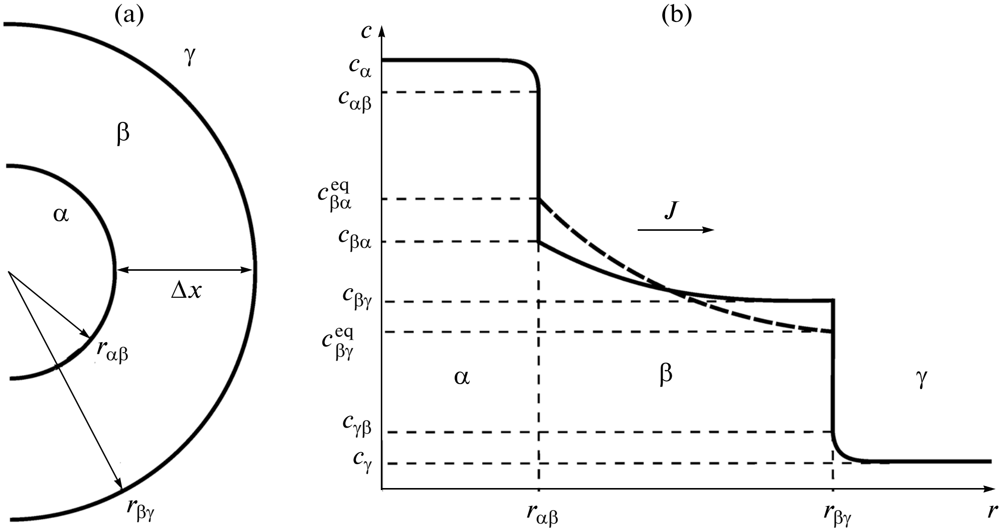

Fig. 1. (a) Growth of the intermediate β phase in the radially symmetric "α core–γ shell" binary system and (b) the corresponding radial concentration profile without (dotted line) and with allowance for reaction rate at the interphase boundary.

of a transition from the linear to the parabolic growth in formula (1) is equal to

$$\lambda = \frac{\bar{D}}{K^{\text{eff}}_{\text{plane}}}, \tag{3}$$

where

$$K^{\text{eff}}_{\text{plane}} = \frac{K_{\alpha\beta}K_{\beta\gamma}}{K_{\alpha\beta} + K_{\beta\gamma}} \quad \left(\text{i.e. } \frac{1}{K^{\text{eff}}_{\text{plane}}} = \frac{1}{K_{\alpha\beta}} + \frac{1}{K_{\beta\gamma}}\right), \tag{4}$$

where K_{ij} is the reaction-rate coefficient at the boundary of phases i and j. In this case, the inverse quantity can be called the resistance of the boundary. For this reason, formula (4) is equivalent to the rule of series connection of resistances.

In many real systems (powder mixtures, composites, nanostructures of the core–shell type) contact between reagents is not a plane. In this work, we suggest the extension of the above scheme to the case of reaction diffusion in spherical nanosystems of the α core– γ shell type (Fig. 1a). In this instance, even at the initial stage of the reaction, the thickness of the phase layer can be comparable with radii of the curvature, and densities of diffusion flows at internal and external boundaries of the layer will differ substantially. Meanwhile, the equality of flux densities at the both boundaries and inside the phase was the main consequence of the quasi-stationary approximation resulted in Eqs. (3) and (4). Therefore, it can be expected that efficient reaction-rate coefficients can be dependent not only on the material constants (properties of the interphase boundary), but also on the time-varying internal and external radii of the interlayer $r_{\alpha\beta}$ and $r_{\beta\gamma}$.

The transition from plane to spherical geometry of the contact likewise can lead to other effects connected first with the stresses that arise in core–shell structures. Recently, these effects were investigated in detail in [7] and were well explained in [8]. In our work, we focus on the role of finite reaction rates, taking the molar volumes of the phases to be equal.

2. FORMULATION OF THE MODEL

Let us assume that the process of interdiffusion inside the phase is quasi-stationary; i.e., the total flow of each of the components through all concentric spherical surfaces is identical (naturally, it varies with time):

$$I = -\frac{D}{\Omega}\frac{\partial c}{\partial r}4\pi r^2 = \text{const}(r). \tag{5}$$

Let us consider two models that differ in the behavior of interdiffusion coefficients inside the phase. In the first model, the interdiffusion coefficient inside the phase is constant ($D = \text{const}$) and, in the second, the interdiffusion coefficient depends strongly on the concentration inside a narrow range of homogeneity ($D = D(c)$). Most often, the diffusion coefficient exhibits a sharp minimum when the concentration is stoichiometric. For this reason, when the concentration range inside the phase varies with time, the diffusion coefficient averaged over this range will be inconstant. It is this change in the concentration range that occurs in the case of delay of atoms at the interphase boundary. In other words, immediately after the intermediate phase was formed, the concentration in it is more likely to be uniform everywhere and, as the phase expands, the boundary concentrations tend to the equilibrium values that are determined by the common-tangent rule. Correspondingly, the concentration range expands, tending to the equilibrium (Fig. 1b).

Model 1 (D = const)

Let us consider the growth in the β-phase spherical interlayer in the α/core–γ shell system with interphase αβ internal and βγ external boundaries in the form of concentric spheres with radii $r_{\alpha\beta}$ and $r_{\beta\gamma}$, respectively (Fig. 1a). As in most of the previous works [1–4], the concentration at boundaries on the side of the parent α and γ phases will be taken to be almost equilibrium and equal to concentrations of the following phases: $c_{\alpha\beta} \sim c_\alpha$ and $c_{\gamma\beta} \sim c_\gamma$ (Fig. 1b). However, actual concentrations at internal ($c_{\beta\alpha}$) and external ($c_{\beta\gamma}$) boundaries on the side of the intermediate phase can differ significantly from the corresponding equilibrium values $c_{\beta\alpha}^{\text{eq}}$ and $c_{\beta\gamma}^{\text{eq}}$ of the intermediate phase.

From the condition of quasi-stability in this model $\frac{d}{dr}\left(r^2\frac{dc}{dr}\right) = 0$ and boundary conditions $c(r_{\alpha\beta}) = c_{\beta\alpha}$ and $c(r_{\beta\gamma}) = c_{\beta\gamma}$ it is easy to obtain a dependence of the concentration on radius $c(r) = \frac{c_{\beta\alpha} - c_{\beta\gamma}}{r}\frac{r_{\alpha\beta}r_{\beta\gamma}}{r_{\beta\gamma} - r_{\alpha\beta}} + \frac{c_{\beta\gamma}r_{\beta\gamma} - c_{\beta\alpha}r_{\beta\alpha}}{r_{\beta\gamma} - r_{\alpha\beta}}$, the flux density through the β phase $j = \frac{D}{\Omega}\frac{c_{\beta\alpha} - c_{\beta\gamma}}{r_{\beta\gamma} - r_{\alpha\beta}}\frac{r_{\alpha\beta}r_{\beta\gamma}}{r^2}$, and the total diffusion flow

$$I = \frac{D}{\Omega}\frac{c_{\beta\alpha} - c_{\beta\gamma}}{r_{\beta\gamma} - r_{\alpha\beta}}4\pi r_{\alpha\beta}r_{\beta\gamma}. \tag{6}$$

According to the condition of quasi-stability, the same total flow should pass through the both interphase boundaries as follows:

$$K_{\alpha\beta}\left(c_{\beta\alpha}^{\text{eq}} - c_{\beta\alpha}\right)4\pi r_{\alpha\beta}^2 = D\frac{c_{\beta\alpha} - c_{\beta\gamma}}{r_{\beta\gamma} - r_{\alpha\beta}}4\pi r_{\alpha\beta}r_{\beta\gamma}, \tag{7}$$

$$K_{\beta\gamma}\left(c_{\beta\gamma} - c_{\beta\gamma}^{\text{eq}}\right)4\pi r_{\beta\gamma}^2 = D\frac{c_{\beta\alpha} - c_{\beta\gamma}}{r_{\beta\gamma} - r_{\alpha\beta}}4\pi r_{\alpha\beta}r_{\beta\gamma}. \tag{8}$$

Equations (7) and (8) can be considered to be an algebraic system of equations in unknowns $c_{\beta\alpha}$ and $c_{\beta\gamma}$. Because in calculations deviations of concentrations from the equilibrium values are more convenient to operate, below, we use the change of variables

$$c_{\beta\alpha} = c_{\beta\alpha}^{\text{eq}} - \delta c_{\beta\alpha}, \quad c_{\beta\gamma} = c_{\beta\gamma}^{\text{eq}} + \delta c_{\beta\gamma}. \tag{9}$$

From (7) and (8), we obtain

$$\begin{cases} \delta c_{\beta\alpha} = \dfrac{D\Delta c^{\text{eq}} r_{\beta\gamma}}{K_{\alpha\beta}r_{\alpha\beta}\left[\left(r_{\beta\gamma} - r_{\alpha\beta}\right) + D/K^{\text{eff}}\right]} \\ \delta c_{\beta\gamma} = \dfrac{D\Delta c^{\text{eq}} r_{\alpha\beta}}{K_{\beta\gamma}r_{\beta\gamma}\left[\left(r_{\beta\gamma} - r_{\alpha\beta}\right) + D/K^{\text{eff}}\right]} \end{cases}, \tag{10}$$

where $\Delta c^{\text{eq}} = c_{\beta\alpha}^{\text{eq}} - c_{\beta\gamma}^{\text{eq}}$ and the effective reaction-rate coefficient at interphase boundaries (4) with allowance for the radial symmetry of the system will have the form

$$K^{\text{eff}} = \frac{K_{\alpha\beta}r_{\alpha\beta}K_{\beta\gamma}r_{\beta\gamma}}{K_{\alpha\beta}r_{\alpha\beta}^2 + K_{\beta\gamma}r_{\beta\gamma}^2}. \tag{11}$$

It is easy to see that, in the case of plane diffusion pair where radii of the curvature tend to infinity and are almost equal to each other, the expression for K^{eff} transforms into the expression for $K_{\text{plane}}^{\text{eff}}$ in formula (4) used in [3].

Substituting (9) and (10) into Eq. (6), we obtain the following equation of the total flow through the phase

$$I = \frac{1}{\Omega}\frac{D\Delta c^{\text{eq}}}{\left(r_{\beta\gamma} - r_{\alpha\beta}\right) + \dfrac{D}{K^{\text{eff}}}}4\pi r_{\alpha\beta}r_{\beta\gamma}. \tag{12}$$

To determine growth kinetics of the phase, we use the equations of balance of flows at moving boundaries whose general form is as follows $\frac{dr_{ij}}{dt} = \frac{\Omega j_j - \Omega j_i}{c_j - c_i}$. Taking into account the lack of flows in parent phases we obtain

$$\frac{dr_{\alpha\beta}}{dt} = -\frac{1}{c_{\beta\alpha}}\frac{r_{\beta\gamma}}{r_{\alpha\beta}}\frac{D\Delta c^{\text{eq}}}{\left(r_{\beta\gamma} - r_{\alpha\beta}\right) + D/K^{\text{eff}}}; \tag{13}$$

$$\frac{dr_{\beta\gamma}}{dt} = \frac{1}{\left(1 - c_{\beta\gamma}\right)}\frac{r_{\alpha\beta}}{r_{\beta\gamma}}\frac{D\Delta c^{\text{eq}}}{\left(r_{\beta\gamma} - r_{\alpha\beta}\right) + D/K^{\text{eff}}}. \tag{14}$$

Model 2 (D = D(c))

Let the diffusion coefficient be dependent on the concentration even at small deviations from the stoichiometry. In this case, no simple hyperbolic dependence of the concentration on the radius is obtained, whereas the approximation of quasi-stability continues to work and in any concentric cross section of the phase, according to the approximation, the flux density is inversely proportional to the square of radius and the total flow is constant along the radius, which allows one to make the following transformations:

$$I = -\frac{D(c)}{\Omega}\frac{\partial c}{\partial r}4\pi r^2$$

$$= -\frac{1}{\Omega}\frac{\displaystyle\int_{r_{\alpha\beta}}^{r_{\beta\gamma}} D(c)\frac{\partial c}{\partial r}r^2\frac{dr}{r^2}}{\displaystyle\int_{r_{\alpha\beta}}^{r_{\beta\gamma}}\frac{dr}{r^2}}4\pi = -\frac{1}{\Omega}\frac{\displaystyle\int_{c_{\beta\alpha}}^{c_{\beta\gamma}} D(c)\,dc}{r_{\beta\gamma} - r_{\alpha\beta}}4\pi r_{\alpha\beta}r_{\beta\gamma}. \tag{15}$$

Thus, as distinguished from formula (6) of Model 1, in formula (15) the radial change in the diffusion coefficient as a function of the concentration is taken into account. The quantity $\int_{c_{\beta\alpha}}^{c_{\beta\gamma}} D(c)\,dc$ is the Wagner integral coefficient that appears more often in the form of

$\int_{c_{\beta\alpha}}^{c_{\beta\gamma}} D(c)\,dc = \bar{D}^{\text{noneq}}\Delta c$, where $\bar{D}^{\text{noneq}}$ differs from $\bar{D}$ in formula (1) by the fact that the concentration range $\Delta c = c_{\beta\alpha} - c_{\beta\gamma}$ over which integration is carried out is not equilibrium and varies with time.

In the first approximation the dependence $D(c)$ can be represented by the parabola

$$D(c) = D_{\min} + p(c - c_s)^2, \tag{16}$$

where c_s is the stoichiometric composition of the β phase. The average diffusion coefficient is obtained via integration within the boundary concentrations as follows:

$$\bar{D}^{\text{noneq}} = \frac{1}{c_{\beta\alpha} - c_{\beta\gamma}} \int_{c_{\beta\alpha}}^{c_{\beta\gamma}} D(c)\,dc. \tag{17}$$

After the substitution of the parabolic dependence (16) into the expression (17) and integration, we obtain the following expression for the average diffusion coefficient:

$$\begin{aligned}\bar{D}^{\text{noneq}} &= D_{\min} \\ &+ \frac{p}{3}\left[(c_{\beta\gamma} - c_s)^2 + (c_{\beta\gamma} - c_s)(c_{\beta\alpha} - c_s) + (c_{\beta\alpha} - c_s)^2\right].\end{aligned} \tag{18}$$

Equations (7) and (8) with allowance of (18) can be considered as a system of algebraic equations in three unknowns $c_{\beta\alpha}$, $c_{\beta\gamma}$, and $\bar{D}^{\text{noneq}}$. As a result of simple and rather cumbersome transformations, we can arrive at the cubic equation for the average diffusion coefficient $\bar{D}^{\text{noneq}}$ as a function of radii $r_{\alpha\beta}$ and $r_{\beta\gamma}$ as follows:

$$a\left(\bar{D}^{\text{noneq}}\right)^3 + b\left(\bar{D}^{\text{noneq}}\right)^2 + c\left(\bar{D}^{\text{noneq}}\right) + d = 0. \tag{19}$$

Expressions for constants of Eq. (19) are presented in the appendix.

The cubic equation (19) can have three solutions, although, as calculations have shown, there is only one root that yields the continuous dependence of $\bar{D}^{\text{noneq}}$ throughout the process of phase growth (in the model for conjugating roots on intervals of solutions the heuristic procedure was used). When physical constants are specified correctly, Eq. (19) exhibits the only (real and positive) solution.

3. RESULTS AND DISCUSSION

In order to analyze a possible influence of the concentration dependence of the diffusion coefficient on the kinetics of phase growth, we solved Eqs. (13) and (14) numerically with a constant diffusion coefficient D (Model 1) or with the average diffusion coefficient $\bar{D}^{\text{noneq}}$ determined from Eq. (19) (Model 2). These models can be compared correctly if the diffusion coefficient averaged over the equilibrium concentration range ($\bar{D}$) is equal to the diffusion coefficient D in Model 1. In this case, the shape of the concentration dependence $D(c)$ is determined by one of two interrelated parameters $D_{\min}$ and p from expression (18) at specified equilibrium concentrations $c_{\beta\alpha}^{\text{eq}}$ and $c_{\beta\gamma}^{\text{eq}}$. Since it is evident that when $D_{\min}$ tends to the average diffusion coefficient $\bar{D} = D$ the curvature of the parabola approaches zero ($p \to 0$), Model 1 is the limiting case of Model 2.

Upon initiation no nucleation stage was taken into account, and the presence of finite reaction rate at boundaries made it possible to formally start calculations from the zero thickness of the phase: $r_{\alpha\beta}(t = 0) = r_{\beta\gamma}(t = 0) = r_0$. The condition of stop of the calculations was the almost complete exhaustion of the core material ($r_{\alpha\beta} < 10^{-10}$ m). The values chosen for the parameters of simulation were as follows: $r_0 = 10^{-8}$ m, $c_{\beta\alpha}^{\text{eq}} = 0.55$; $c_{\beta\gamma}^{\text{eq}} = 0.45$; $D = \bar{D} = 10^{-18}$ m^2/s, $D_{\min} = 2 \times 10^{-19}$ m^2/s, $K_{\beta\gamma} = 10^{-9}$ m/s, and $K_{\alpha\beta}/K_{\beta\gamma} = 1$. When choosing the order of magnitude for the initial radius, we proceeded from real experiments on the reaction diffusion in nanoparticles [7, 8]. The concentration range is characteristic of phases with the NiAl-type structure *B*2. Diffusion coefficients are typical of moderate temperatures of reactions. Orders of magnitude for reaction-rate coefficients are taken from [9].

The allowance for finite reaction rate introduces in a natural manner the characteristic size λ (formula (3)). The other parameter of the same dimensionality is the initial core radius r_0. For this reason, it can be expected that the kinetics of reaction can be determined by the dimensionless-ratio value λ/r_0. In this case, λ can be estimated using the coefficient K^{eff} obtained at initial radii.

Figure 2a displays a time dependence of reduced (by division into initial particle radius r_0) dimensionless radii of internal ($\xi_{\alpha\beta} = r_{\alpha\beta}/r_0$) and external ($\xi_{\beta\gamma} = r_{\beta\gamma}/r_0$) boundaries of a new compound (an increase in the external and a decrease in the internal radius of the interlayer). When the system changes in size, the kinetics of growth is self-simulating; i.e., when the ratio λ/r_0 is constant, the dependence $\xi_{\beta\gamma}(\xi_{\alpha\beta})$ will be the same for different initial particle radii r_0 (Fig. 2b).

Growth in the reaction rate at one of interphase boundaries results in the acceleration of the process of phase formation, and this effect is more significant when the rate changes at the internal boundary, as its throughput capacity is additionally controlled by a smaller area of the interface. At $K_{\alpha\beta} \gg K_{\beta\gamma}$, saturation of the reaction zone occurs by the internal component and the controlling role is passed on to the external boundary.

Irrespective of the ratio of reaction rates at the boundaries, a change in the width of the concentration range of the phase Δc in the process of interlayer

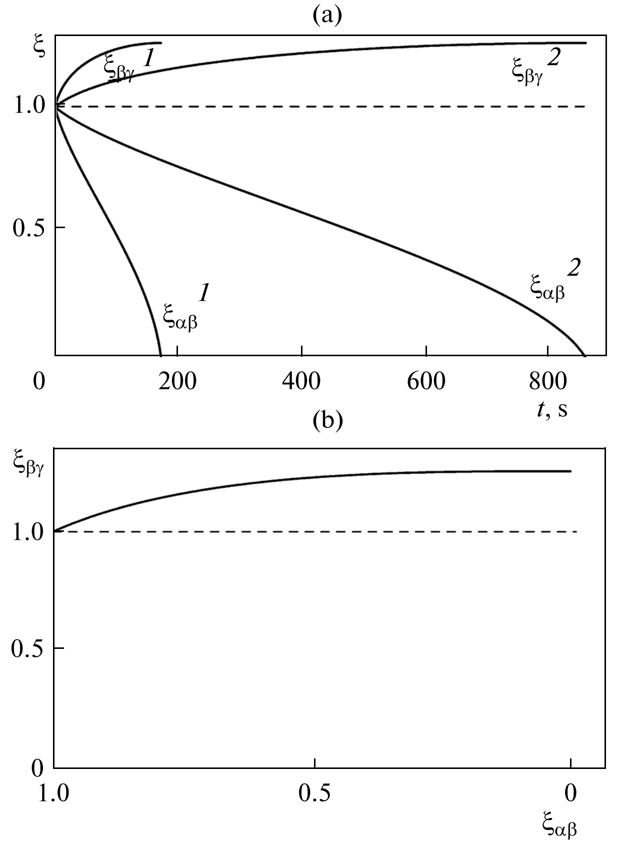

Fig. 2. Kinetics of changes in the dimensionless radii of internal $\xi_{\alpha\beta}$ and external $\xi_{\beta\gamma}$ boundaries of the phase (a) on the time t and (b) on the internal radius $\xi_{\alpha\beta}$. Calculations were conducted at the same λ/r_0 for the two cases: (*1*) $D = 10^{-18}$ m^2/s, $r_0 = 10^{-8}$ m and (*2*) $D = 5 \times 10^{-18}$ m^2/s, $r_0 = 5 \times 10^{-8}$ m.

growth exhibits the general tendency; it first grows beginning from zero and then again tends to zero. In other words, the relative width of the concentration range $\eta = \Delta c/\Delta c^{\mathrm{eq}}$ first increases; then, as the core material is exhausted (a reduction in the internal radius), it again decreases to zero (Fig. 3a).

A simple analysis of formulas (9), (10), and (11) discloses the character of changes in the boundary concentrations in the process of phase growth and the cause of the nonmonotonic behavior of the concentration-range width. At the initial time instant (when internal and external radii are close to each other), the concentrations at both boundaries are nearly coincident and are determined only by the relationship between resistances of these boundaries as follows:

$$c_{\beta\alpha}(t=0) = c_{\beta\gamma}(t=0) = \frac{K_{\alpha\beta}c_{\beta\alpha}^{\mathrm{eq}} + K_{\beta\gamma}c_{\beta\gamma}^{\mathrm{eq}}}{K_{\alpha\beta} + K_{\beta\gamma}}. \qquad (20)$$

Depending on the ratio $K_{\alpha\beta}/K_{\beta\gamma}$, concentrations at the boundaries at the initial time instant can be higher or lower than the stoichiometric values due to excess ($(K_{\alpha\beta}/K_{\beta\gamma}) > 1$) or shortage ($(K_{\alpha\beta}/K_{\beta\gamma}) < 1$) of one of the components because of different throughput capacity of the boundaries (Fig. 3b). In particular, if the resistances of the boundaries are identical, the initial concentrations are at the center of the range of homogeneity (Fig. 3b, curve *2*). The allowance for nucleation stage can change this conclusion, because the probability of nucleation depends, in particular, on the concentration. However, if the growth controlled by the reaction at the boundary comes after nucleation, the system itself would set the concentration from formula (20).

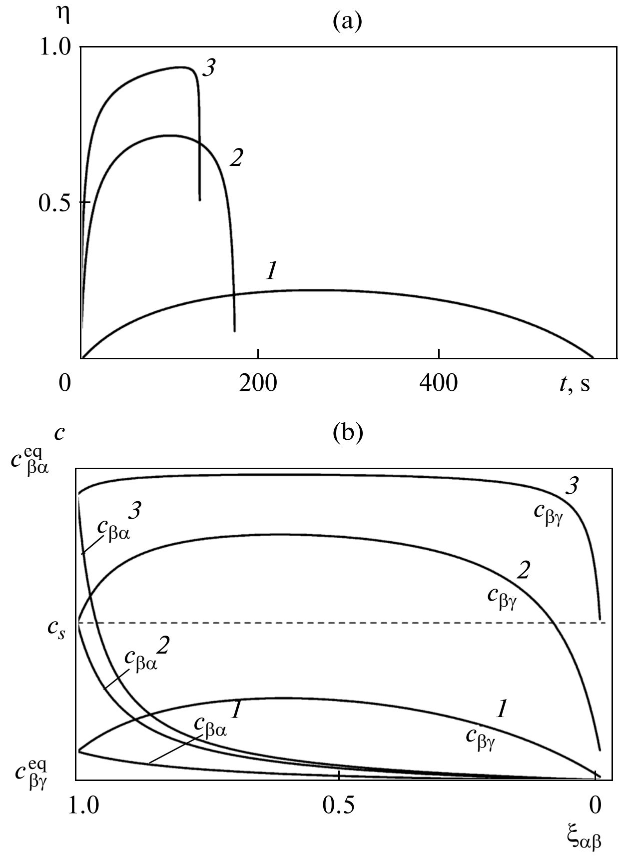

Fig. 3. (a) Dependence of relative width η of concentration range on time t and (b) dependences of concentrations $c_{\beta\alpha}$ at internal and $c_{\beta\gamma}$ at external boundaries on the internal radius $\xi_{\alpha\beta}$ for different relationships between reaction rates at interphase boundaries when $K_{\alpha\beta}$ changes: (*1*) $K_{\alpha\beta}/K_{\beta\gamma} = 0.1$, (*2*) $K_{\alpha\beta}/K_{\beta\gamma} = 1$, and (*3*) $K_{\alpha\beta}/K_{\beta\gamma} = 10$. Model 1.

As the phase grows, the range width $\Delta c = \Delta c^{\mathrm{eq}} - \delta c_{\beta\alpha} - \delta c_{\beta\gamma}$ increases. However, as distinguished from the case of plane diffusion pair, concentrations themselves tend optionally to their equilibrium values, which, as was already noted above, results in the nonmonotonic behavior of the concentration-range width; i.e., enhancement is replaced by a drop to zero (Fig. 3b). This behavior is explained by the dependence of the effective reaction-rate coefficient (11) on both radii. In particular, upon the exhaustion of the initial core when the internal radius (and the internal interface area) approaches zero, the effective reaction rate likewise tends to zero. In this case, as follows from formulas (10), the concentrations at both the internal and external radii tend to the same equilibrium value at the contact of the intermediate phase with the shell, $c^{eq}_{\beta\gamma}$ ($c_{\beta\gamma} \to c^{eq}_{\beta\gamma} + 0 = c^{eq}_{\beta\gamma}$, $c_{\beta\alpha} \to c^{eq}_{\beta\alpha} - \Delta c^{eq} = c^{eq}_{\beta\gamma}$). Correspondingly, the range width $\Delta c = c_{\beta\alpha} - c_{\beta\gamma}$ approaches zero, and the concentration of the phase becomes as low as possible and is almost equal to $c^{eq}_{\beta\gamma}$.

As a rule (as can seen from Fig. 4a), the effective reaction rate falls off with time, whereas at a high reaction rate, nonmonotonic behavior arises at the internal boundary. At the initial stage (when internal and external radii differ slightly), a higher relative rate at the internal boundary provides the active inflow of the core material and rapid growth of the phase. As the core material is exhausted, the total internal interface area through which diffusion flow should pass is reduced. For this reason, when the local throughput capacity of the boundary $K_{\alpha\beta}$ is invariable, its total throughput capacity K^{eff} begins to diminish (Fig. 4a). This leads to the additional delay of atoms at the boundary and, correspondingly, intensifies the nonequilibrium state, increasing the deviation of the concentration from the equilibrium (and decreasing the concentration range $\Delta c \to 0$).

This means that, in terms of conduction and resistances, when the internal radius approaches zero, the effective resistance of the both boundaries $1/K^{eff}$ (as the quantity inverse to the conduction K^{eff}) is approximately equal to $\frac{r_{\beta\gamma}}{K_{\alpha\beta} r_{\alpha\beta}}$ and tends to infinity, while the rate of this tendency is determined by changes precisely in the internal boundary. It follows from this that, depending on the magnitude of the ratio between resistances of internal and external boundaries, either monotonic or nonmonotonic growth of the effective resistance with time can be expected. More precisely, at $K_{\alpha\beta}/K_{\beta\gamma} < 1$, the effective resistance will only increase, since the insufficient conduction of the internal boundary at the initial stage ($K_{\alpha\beta} < K_{\beta\gamma}$) will only enhance, since the internal interface area diminishes. At $K_{\alpha\beta}/K_{\beta\gamma} > 1$, the excess conduction of the internal interface ($K_{\alpha\beta} > K_{\beta\gamma}$) can sometimes compensate for a large external interface area, i.e., the effective resistance $1/K^{eff}$ will have an extreme that corresponds to the time instant of a transition to the prevalence of the effectiveness of the external boundary because of the advantage of the area.

The behavior of concentrations and effective reaction rate at boundaries in Models 1 and 2 is qualitatively similar. However, the deviation of the concentration from the stoichiometry at the initial time instant of phase growth (when the diffusion coefficient in Model 2 depends on the concentration) is the cause of a nonmonotonic behavior of its time average value (Fig. 4b). In other words, $\bar{D}^{noneq}(\xi_{\alpha\beta})$ will not correspond to the minimum of the concentration dependence (16). In the process of extension of the concentration range and coverage of the stoichiometric section, the average diffusion coefficient $\bar{D}^{noneq}$ will drop off. At the last stage, due to a shift in the concentration range to one of equilibrium concentrations, $\bar{D}^{noneq}$ again increases and becomes maximum. Thus, upon the dissymmetry of the reaction rates at the boundaries, the average diffusion coefficient proves to be not merely variable, but also changes in a nonmonotonic manner (Fig. 4b, curves *1*, *3*). In the case of the symmetry of reaction rates ($K_{\alpha\beta}/K_{\beta\gamma} = 1$) at the initial stage of growth, the system is in the section of stoichiometric concentrations with the minimum diffusion coefficient that, as the concentration range expands, does not decrease, i.e., the function $\bar{D}^{noneq}(\xi_{\alpha\beta})$ increases monotonically (Fig. 4b, curve *2*). The

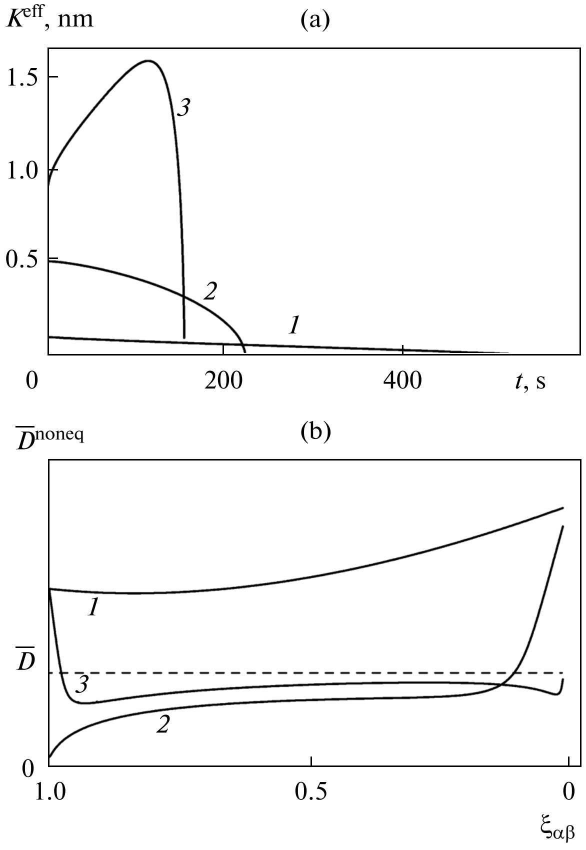

Fig. 4. Dependences of (a) effective reaction-rate coefficient K^{eff} on time t and (b) average diffusion coefficient $\bar{D}^{noneq}$ on the internal radius $\xi_{\alpha\beta}$ for different relationships between reaction rates at interphase boundaries when $K_{\alpha\beta}$ changes: (*1*) $K_{\alpha\beta}/K_{\beta\gamma} = 0.1$, (*2*) $K_{\alpha\beta}/K_{\beta\gamma} = 1$, and (*3*) $K_{\alpha\beta}/K_{\beta\gamma} = 10$. Model 2.

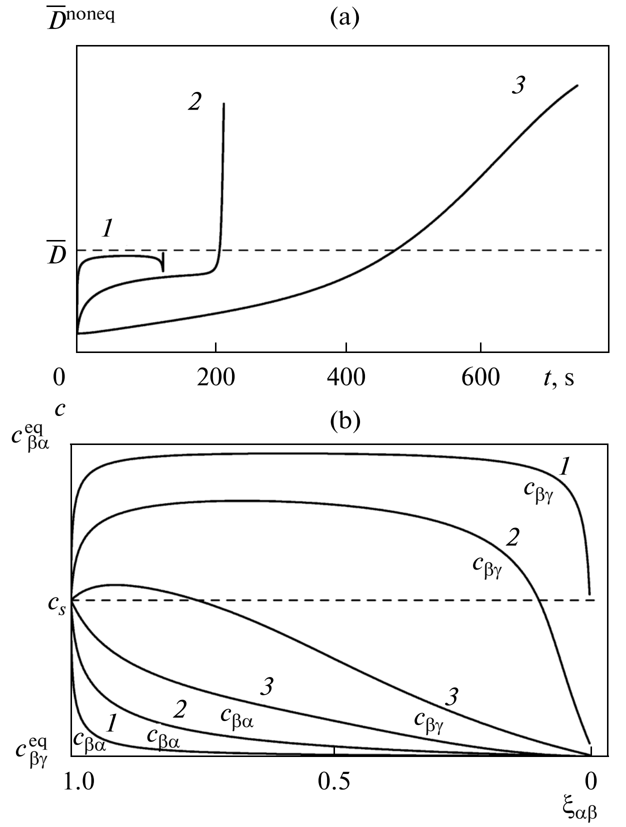

Fig. 5. Dependences of (a) average diffusion coefficient $\bar{D}^{\text{noneq}}$ on time t and of (b) concentrations $c_{\beta\alpha}$ at internal and $c_{\beta\gamma}$ at external boundaries on internal radius $\xi_{\alpha\beta}$ for different reaction rates at interphase boundaries when the ratio $K_{\alpha\beta}/K_{\beta\gamma} = 1$ is fixed: (*1*) $K_{\alpha\beta} = 10^{-8}$ m/s, (*2*) $K_{\alpha\beta} = 10^{-9}$ m/s, and (*3*) $K_{\alpha\beta} = 10^{-10}$ m/s. Model 2.

achievement of the minimum value by the average diffusion coefficient at the last stage of exhaustion of the core, irrespective of the relationship of the parameters, corresponds to the general principle of maximum liberation of the Gibbs energy in nonequilibrium processes.

Enhancement in the concentration dependence of the diffusion coefficient is reached by decreasing $D_{\min}$ to zero or increasing p (provided that $D_{\min}$ is positive in all cases with the exception of spinodal decomposition), and the behavior of the average diffusion coefficient in the process of phase growth, $\bar{D}^{\text{noneq}}(\xi_{\alpha\beta})$, is similar to dependence (2) in Fig. 4b and even becomes sharper, while at the initial time of growth it tends to zero. In contrast to this, when $D_{\min} \to \bar{D}$, the concentration dependence becomes insignificant, i.e., $\bar{D}^{\text{noneq}}(\xi_{\alpha\beta})$ degenerates into the straight line ($\bar{D}^{\text{noneq}}(\xi_{\alpha\beta}) = \bar{D} = D$), and Model 1 transforms into Model 2.

Recall that, in this work, two assumptions are used. One of them (concentration dependence of the diffusion coefficient) determines the difference between Models 1 and 2 and was analyzed in detail above. The second assumption (allowance for finite reaction rate at interphase boundaries) is taken into account in terms of the effective reaction-rate coefficient at interphase boundaries (11). With high reaction rates at both boundaries Models 1 and 2 describe ordinary growth of the intermediate pair without a delay of atoms at the boundaries. In this case, the reaction zone is instantaneously saturated with the material and the concentration range expands to the equilibrium (Fig. 5b, curve *1*) with the result that the average diffusion coefficient tends to the $\bar{D}$ value averaged over the equilibrium range (Fig. 5a, curve *1*). At the final stage of the phase formation, a local minimum appears due to the effect of a small throughput capacity of the internal interface because of an abruptly diminishing area (analog of the situation in Fig. 4b, curve *3*). With low reaction rates at both boundaries, growth in the phase is increasingly controlled by delay of atoms at phase boundaries, which not only slows down the process of phase formation (Fig. 5a, curve *3*), but also determines the narrowness of the real concentration range of the phase (Fig. 5b, curve *3*).

The investigation of the law of phase growth became the next logical step in our analysis. The time dependence of the phase width $\Delta x = r_{\beta\gamma} - r_{\alpha\beta}$ is approximated with a good accuracy by the power dependence $\Delta x \sim t^m$. In this case, at $K_{\alpha\beta}/K_{\beta\gamma} = 1$ when the effective reaction-rate coefficient K^{eff} increases, the growth index m approaches asymptotically to 0.5 (parabolic growth controlled by diffusion) and when K^{eff} decreases, the index m tends to 1 (linear growth controlled by boundary kinetics). When particles increase in size, the tendency to the parabolic law intensifies. An insignificant enhancement in m at the initial stage of growth confirms the effect of reaction rate at the boundary for a narrow phase and at the final stage supports the effect of a small throughput capacity of the internal boundary.

All the above considerations were obtained in the assumption of the quasi-stability of the process. At the last stage of exhaustion of the core, when the rate of contraction of the internal boundary becomes very high, the approximation of quasi-stability will cease to hold because the concentration profile will have no time to respond to rapid motion of the boundary. In this case, however, the rate of changes in the phase volume is low (because at the last stage the internal radius is very small) and, thus, a violence in the regime of quasi-stability will only have time to influence the parameters of the internal boundary rather than those of the external boundary.

The practical value of the suggested model can be considered to be the possibility to predict the complete time (τ) of the reaction until one of the components is exhausted. If the time law of phase growth is $\Delta x \sim t^m$, then the time τ for the interlayer thickness ΔX to be formed should obey the law $\tau \sim \Delta X^{1/m}$. Because the width of the phase is determined by the particle size, $\ln(\tau) \sim \frac{1}{m}\ln(r_0)$. For diffusion-controlled reactions, this time is approximately quadratic in the initial core radius (parabolic law of phase growth with $m = 0.5$), whereas for reactions with boundary kinetics, the time depends linearly on the radius (linear law with $m = 1$).

In order to take into account both approximations of Model 2 (concentration-dependent diffusion coefficient and effective rate at boundaries), we use the dimensionless characteristics parameter λ/r_0. Numerical calculations show (Fig. 6a) that, at a fixed value of λ, the dependence $\tau(r_0)$ is linear at $r_0 \ll \lambda$ (growth index $m[r_0 < \lambda] \to 1$) and transforms into a quadratic dependence at $r_0 \gg \lambda$ (growth index $m[r_0 > \lambda] \to 0.5$). It is natural that, for $\lambda < 10^{-9}$ m, at all physically reasonable initial core sizes, the process remains diffusion-controlled (with the exception of last time instants of the exhaustion of the core when the small throughput capacity of the contracting internal boundary again only controls the reaction at the internal interface for a short final period). On the other hand, for $\lambda > 10^{-3}$ m, in all physically reasonable cases, the kinetics of the reaction will be controlled at the boundaries (Fig. 6b).

The finite reaction rate can be especially important at the interphase boundary between an IM compound and a gas phase in view of the fact that at a low partial pressure of the reagent supply of atoms onto the boundary can be limited. The effect of partial pressure on the phase growth in spherical and cylindrical hollow shells was taken into account in our recent work [10] in which the driving force of the reaction at both the stage of formation of oxide and the stage of its reduction was taken to be time-independent. The generalization of growth kinetics with finite reaction rate at the boundary suggested in this work can be applied to the development of the approach proposed in [10].

If the diffusion coefficient depends strongly on the concentration, then, because of changes in the concentration-range width, the effective diffusion coefficient changes; i.e., at the initial stage of growth of the phase interlayer, it is lower than the average coefficient in the equilibrium concentration range and is higher at the final stage. In most cases, a monotonic increase is observed. The nonmonotonic behavior is caused by a difference between reaction rates at internal and external interfaces and by a decrease in the throughput capacity of the internal boundary in large systems and at low diffusion coefficients.

Our results are obtained within the simplest parabolic approximation for diffusion coefficients. As a matter of fact, the increase in diffusion coefficient with a deviation from the stoichiometry is first directly proportional to the concentration of the defects arising with this deviation (atoms in foreign sublattices, structure vacancies). The deviation from the stoichiometry results in more intricate nonparabolic dependences of the concentration of defects [11–13], the consideration of which leads to mathematical difficulties, although the qualitative result remains unaltered.

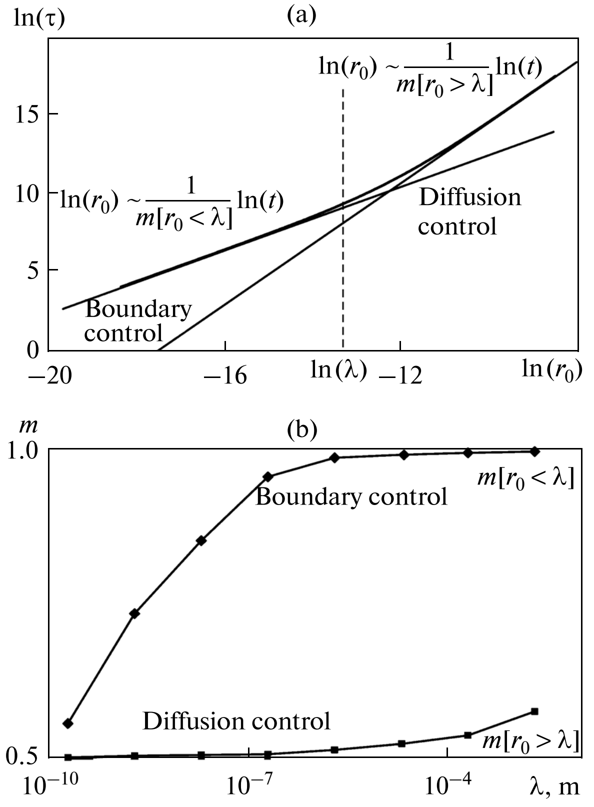

Fig. 6. (a) Dependences of time τ on initial particle radius r_0 at fixed parameter $\lambda = 2 \times 10^{-6}$ m with the growth index of the phase $m[r_0 < \lambda] = 0.983$ for the case of boundary control and $m[r_0 > \lambda] = 0.5$ for the case of diffusion control and (b) dependences of index m on characteristic size λ. Model 1.

4. CONCLUSIONS

(1) The Pines–Geguzin–Gösele–Tu approach of the allowance for finite reaction rates has been generalized to the case of growth of the spherical phase interlayer, and the effective reaction-rate coefficient K^{eff} proves to be dependent on the time-varying external and internal radii with the result that K^{eff} decreases to zero, as the core is exhausted and the internal interphase boundary is contracted.

(2) The strong concentration dependence of the diffusion coefficient in the intermediate phase in combination with the limited reaction rate at boundaries can change substantially the concentration range of the phase and, correspondingly, alter the actual diffusion coefficient in the process of growth.

(3) Following growth in the plane layer of the phase, if its concentration range increases monotoni-

cally to the equilibrium and boundary concentrations tend to equilibrium values, in the case of growth of a layer in the core–shell system, the concentration range behaves in a nonmonotonic manner beginning to approach zero as the core is exhausted.

(4) The dependence of the time of the exhaustion of the core on the size proves to be linear for fairly small sizes and quadratic for fairly large sizes.

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APPENDIX

Let us derive expressions for constants of the cubic equation (19). We substitute expressions characteristic of concentrations at interphase boundaries into the equation for average diffusion coefficient $\bar{D}^{\text{noneq}} = D_{\min} + \frac{\delta}{3}\left[(c_{\beta\gamma} - c_s)^2 + (c_{\beta\gamma} - c_s)(c_{\beta\alpha} - c_s) + (c_{\beta\alpha} - c_s)^2\right]$ as follows:

$$\begin{cases} c_{\beta\alpha} = c_{\beta\alpha}^{\text{eq}} - \dfrac{\bar{D}^{\text{noneq}}\Delta c^{\text{eq}} r_{\beta\gamma}}{K_{\alpha\beta} r_{\alpha\beta}\left[\Delta x + \bar{D}^{noneq}/K^{\text{eff}}\right]} \\ c_{\beta\gamma} = c_{\beta\gamma}^{\text{eq}} + \dfrac{\bar{D}^{\text{noneq}}\Delta c^{\text{eq}} r_{\alpha\beta}}{K_{\beta\gamma} r_{\beta\gamma}\left[\Delta x + \bar{D}^{\text{noneq}}/K^{\text{eff}}\right]} \end{cases}.$$

As a result, we obtain the following equation:

$$\bar{D}^{\text{noneq}} = \left(\frac{\bar{D}^{\text{noneq}}\Delta c^{\text{eq}}}{K^{\text{eff}}\Delta x + \bar{D}^{\text{noneq}}}\right)^2 M + \frac{\bar{D}^{\text{noneq}}\Delta c^{\text{eq}}}{K^{\text{eff}}\Delta x + \bar{D}^{\text{noneq}}} N + L,$$

where M, N, and L are determined as

$$M = \frac{\delta}{3}\left[\left(\frac{K_{\alpha\beta} r_{\alpha\beta}^2 - K_{\beta\gamma} r_{\beta\gamma}^2}{K_{\alpha\beta} r_{\alpha\beta}^2 + K_{\beta\gamma} r_{\beta\gamma}^2}\right)^2 + \frac{K^{\text{eff}\,2}}{K_{\alpha\beta} K_{\beta\gamma}}\right];$$

$$N = \frac{\delta}{3}\left[(2 - 3c_s)\frac{K_{\alpha\beta} r_{\alpha\beta}^2 - K_{\beta\gamma} r_{\beta\gamma}^2}{K_{\alpha\beta} r_{\alpha\beta}^2 + K_{\beta\gamma} r_{\beta\gamma}^2} - \frac{K_{\alpha\beta} r_{\alpha\beta}^2 c_{\beta\alpha}^{\text{eq}} - K_{\beta\gamma} r_{\beta\gamma}^2 c_{\beta\gamma}^{\text{eq}}}{K_{\alpha\beta} r_{\alpha\beta}^2 + K_{\beta\gamma} r_{\beta\gamma}^2}\right];$$

$$L = D_{\min} + \frac{\delta}{3}\left(1 + 3c_s^2 - 3c_s - c_{\beta\alpha}^{\text{eq}} c_{\beta\gamma}^{\text{eq}}\right).$$

Solving this equation for $\bar{D}^{\text{noneq}}$, we obtain the cubic equation in the general form $a\left(\bar{D}^{\text{noneq}}\right)^3 + b\left(\bar{D}^{\text{noneq}}\right)^2 + c\left(\bar{D}^{\text{noneq}}\right) + d = 0$, the constants of which are determined as $a = 1$, $b = 2K^{\text{eff}}\Delta x - \Delta c^{\text{eq}}\left(\Delta c^{\text{eq}} M - N\right) - L$, $c = K^{\text{eff}}\Delta x(K^{\text{eff}}\Delta x - \Delta c^{\text{eq}} N -- 2L)$, and $d = -K^{\text{eff}2}\Delta x^2 L$.

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