MACROKINETICS OF DIFFUSION MASS TRANSPORT WITH SOLID PHASE REACTION IN BINARY METALLIC SYSTEMS

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A macrokinetic description is presented for diffusion produced by a solid-phase reaction in a binary system. The kinetics of processes on the interphase boundary and diffusion with the phase volumes are considered. The effect of kinetic factors on the growth of intermetallic compounds is studied numerically.

The growth of intermetallic compounds or silicides upon diffusion mass transport accompanied by solid phase reaction (so-called reaction diffusion) may be found in deposition of protective coatings on metals and alloys, upon use of composition materials at high temperatures, and in integrated circuit technology [1]. Reaction diffusion in solids involves three stages: diffusion approach of atoms to the interphase boundary and their removal therefrom, as well as transitions of atoms through the interphase boundary with a corresponding phase transition – readjustment of one crystalline lattice to another [2]. In the case where the limiting stage is the diffusion mass transport, the elemental concentrations on the interphase boundary correspond to equilibrium values. Such a situation is found given a sufficient thickness of intermetallides. For such physical conditions diffusion in a binary system will be described by a Stefan-type problem, from the solution of which there follows a parabolic law of interphase boundary motion [3]. However, in some systems (Cu–Al [4], Fe–Cr, Fe–Mn [5]) the elemental concentrations at the boundary deviate from equilibrium values. The growth of a number of phases ($MoSi_2$, WSi_2, $NbSi_2$, $CrSi_2$, et al.) upon diffusion saturation [5], annealing of thin-film and massive diffusion pairs [1, et al.] occurs linearly with time. Those experimental data indicate that the kinetics of processes occurring on the solid phase boundary play a significant role. The studies [6, 7] considered the case in which growth of the intermetallide is limited by the atomic flux through the interphase boundary, while in [8] the limiting process was the phase transformation rate.

Formulation of the Model. We will consider a case more general than that of [3, 6-8], where the rates of the three processes are comparable. We will also consider the fact that according to electron microscopy data [9] the interphase boundary has a steplike form with amplitude from 30 nm ($CoSi_2$–Si) to 100 nm ($NiSi_2$–Si). We will use the following notation: 1) solid replacement solution based on element A; 2) the intermetallide (Fig. 1). In both phases diffusion is accomplished by a vacancy mechanism. We make the following traditional assumptions: 1) diffusion mass transport is describable in the one-dimensional approximation – the fluxes J_1 and J_2 are directed along the axis Ox; 2) volume diffusion dominates over grain-boundary diffusion; 3) the number of crystalline lattice points per unit volume for phases 1 and 2 is identical: $n_1{}^0 = n_2{}^0$. The second of these assumptions is valid for sufficiently high annealing temperature or saturation of massive specimens as well as for a number of cases of thin film diffusion pairs [10]. The third assumption allows us to neglect change in volume with growth in one phase at the expense of the other. Since the thermal diffusivity coefficient of metals $b \sim 10^{-1}$ cm²/sec, while in the annealing or saturation temperature range the diffusion coefficient $D \sim 10^{-8} - 10^{-7}$ cm²/sec, with the heating zone size $\Delta\ell_T$ significantly exceeds the diffusion zone width $\Delta\ell_d$: $\Delta\ell_T/\Delta\ell_d \sim \sqrt{b/D} \sim 10^3$. In light of this we will consider the process under isothermal conditions.

Transition of atoms through the interphase boundary occurs as a result of exchange of places between atoms A and B, belonging to different phases, and jumping of atoms into a vacant place in the adjacent crystalline lattice [11] (Fig. 1c). This leads to a change in the compositions of the regions near the boundaries. The necessity of distinguishing between atomic transitions through the interphase boundary and a phase transition consisting

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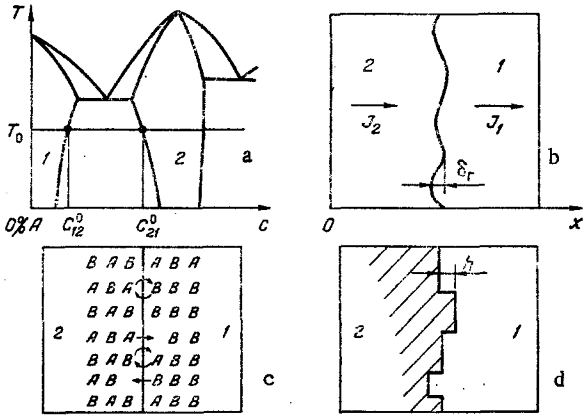

Fig. 1. Schematic diagram of diffusion with solid state reaction in binary system: a) portion of A–B state diagram; b) diffusion zone; c) atomic transitions through interphase boundary (after [11]); d) readjustment of one crystalline lattice to another.

of transformation of one crystalline lattice into another was noted in [2, 11]. The size of the readjustment region h ~ 10*a*, where *a* is the interatomic distance (Fig. 1d).

To construct the model we will use an approach close to the description of growth of a binary crystal from a melt [12]. We divide the boundary region of the diffusion zone into layers of thickness h with planes perpendicular to the axis Ox (Fig. 1d). Each layer is characterized by volume fractions of the phases y_1^k and y_2^k ($y_1^k + y_2^k = 1$) and concentrations of element A c_1^k, c_2^k, where k is the layer number. In the one-dimensional approximation c_1^k and c_2^k depend only on time. Change in phase composition in layer k is caused by both volume diffusion and by atomic redistribution and crystalline lattice readjustment in the contacting portions of phases 1 and 2 belonging to adjacent layers. Motion of the interphase boundary is equivalent to change in the volume fractions of the phases as a result of crystalline lattice readjustment. Within the framework of the model considered the equations for the time change in characteristics of layer k can be written in the following form:

$$\frac{\partial y_1^k}{\partial t} = (y_1^{k+1} - y_1^k)\,u_{21} - (y_1^k - y_1^{k-1})\,u_{12}, \tag{1}$$

$$\frac{\partial y_1^k c_1^k}{\partial t} = \frac{1}{n_1^0 h}(y_1^{k-1}J_1^{k-1} - y_1^k J_1^k) + [(y_1^{k+1} - y_1^k)\,u_{21}c_2^k - (y_1^k - y_1^{k-1})\,u_{12}c_1^k] + (y_1^k - y_1^{k-1})\,(c_2^{k-1}w_{21} - c_1^k w_{12}), \tag{2}$$

$$\frac{\partial y_2^k c_2^k}{\partial t} = \frac{1}{n_2^0 h}(y_2^k J_2^k - y_2^{k+1} J_2^{k+1}) + [(y_2^{k-1} - y_2^k)\,u_{12}c_1^k - (y_2^k - y_2^{k+1})\,u_{21}c_2^k] + (y_2^k - y_2^{k+1})\,(c_1^{k+1}w_{12} - c_2^k w_{21}), \tag{3}$$

where J_i^k, J_i^{k+1} are the densities of the diffusion fluxes supplied to layers k and (k + 1) in phase i; w_{ij} is the frequency of transition of atoms A from phase i into phase j ($i \neq j$) on the boundary, i, j = 1, 2, u_{ij} is the frequency (probability) of readjustment of the crystalline lattice of phase i into phase j, $i \neq j$. Equation (1) describes the change in volume fraction of phase 1 as a result of crystalline lattice readjustment of the second phase into the first (the first term on the right) and the the converse (second term). Equations (2), (3) define the change in concentration of an element due to diffusion (first term on the right), crystalline lattice readjustment (second term), and transition of atoms through the interphase boundary (third term). We will now transform from discrete to continuous variables in Eqs. (1)-(3). To do this we relate the values y_i, c_i, J_i in the layers (k − 1) and (k + 1) with the values in layer k, using expansions of the form $y_i^k \equiv y_i$, $y_i^{k\pm 1} = y_i^k \pm h\,dy_i/\partial x$, etc. Dropping terms of second order smallness, we obtain

$$\frac{\partial y_1}{\partial t} + (p_{12} - p_{21}) \frac{\partial y_1}{\partial x} = 0, \tag{4}$$

$$\frac{\partial y_1 c_1}{\partial t} = -\frac{1}{n_1^0} \frac{\partial y_1 J_1}{\partial x} + [c_2 (p_{21} + s_{21}) - c_1 (p_{12} + s_{12})] \frac{\partial y_1}{\partial x}, \tag{5}$$

$$\frac{\partial y_2 c_2}{\partial t} = -\frac{1}{n_2^0} \frac{\partial y_2 J_2}{\partial x} + [c_2 (p_{21} + s_{21}) - c_1 (p_{12} + s_{12})] \frac{\partial y_2}{\partial x}, \tag{6}$$

where $s_{ij} = hw_{ij}$ is the rate of transition of atoms A from phase i into phase j, $i \neq j$, i, j = 1, 2, while $p_{ij} = hu_{ij}$ is the rate of readjustment of the crystalline lattice of phase i into phase j on the boundary. In Eq. (4) the change in volume fraction of phase 1 is proportional not to the quantity y_i to some power, as is usually assumed in chemical kinetics of heterophase reactions, but to the spatial gradient $\partial y_1/\partial x$. This is true because the phase conversion is localized on the phase boundary. The second terms on the right sides of Eqs. (5) and (6) define the concentration changes due to two processes on the interphase boundary. We note that the model of Eqs. (4)-(6) can also be obtained directly from consideration of elementary processes without dividing the border region into discrete layers.

The probability of transition of atoms A from phase i into phase j ($i \neq j$, i, j = 1, 2) depends on the energy barrier E_{ij}: $w_{ij} \sim w_i \exp(-E_{ij}/RT)$, where w_i is the frequency of oscillation of atoms A in phase i on the interphase boundary. Then $w_{12}/w_{21} \sim (w_1/w_2) \exp[-E_{12} - E_{21})/RT]$. The difference in the activation energies for forward (from phase 1 into phase 2) and reverse transitions is the difference between the chemical potentials of element A $E_{12} - E_{21} = \mu_A^{(1)}[c_1] - \mu_A^{(2)}[c_2]$. If the phase compositions correspond to equilibrium values at a given temperature $c_1 = c_{12}^0$, $c_2 = c_{21}^0$ (Fig. 1a), a macroscopic flow of atoms A through the boundary is absent, $J_s = c_2 s_{21} - c_1 s_{12}$, whence $s_{12}/s_{21} = c_{21}^0/c_{12}^0$. In our further treatment we will consider the quantities s_{12}, s_{21} to be independent of concentration, which is permissible for small deviations from equilibrium. The probability of crystalline lattice readjustment of phase i into phase j ($i \neq j$, i, j = 1, 2) is related to the energy barrier U_{ij}: $u_{ij} \sim u_i \exp(-U_{ij}/RT)$, where u_i is the frequency of heterophase fluctuations in phase i. The ratio of the rates of forward (1 → 2) and reverse (2 → 1) phase conversions $u_{12}/u_{21} \sim (u_1/u_2) \exp[-(U_{12} - U_{21})/RT]$ is determined by the change in the Gibbs potential $\Delta G_{1\to 2} = U_{12} - U_{21}$. Crystalline lattice readjustment occurs when the phase composition deviates beyond the limits of the homogeneity region in the diagram of state (Fig. 1a). Therefore, the rates p_{12}, p_{21} which figures in the macrokinetic model of Eqs. (4)-(6) can be related to the deviation of the phase composition from equilibrium values by the simple expressions

$$p_{12} = \begin{cases} M_{12} (c_1 - c_{12}^0)^{m_{12}} & \text{for} \quad c_1 > c_{12}^0 \\ 0 \ \text{for} \quad c_1 \leqslant c_{12}^0; \end{cases} \qquad p_{21} = \begin{cases} M_{21} (c_{21}^0 - c_2)^{m_{21}} & \text{for} \quad c_2 < c_{21}^0, \\ 0 \ \text{for} \quad c_2 \geqslant c_{21}^0, \end{cases} \tag{7}$$

where M_{ij} and m_{ij} are constants, i, j = 1, 2.

Limiting Cases. We will consider a planar interphase boundary, in which case y_1 is a unit step function $y_1 = 1[x - \Gamma(t)]$, i.e., $y_1 = 0$ for $x < \Gamma$, $y_1 = 1$ for $x > \Gamma$, where $\Gamma(t)$ is the coordinate of the boundary. Its derivatives can be expressed in terms of a δ-function $\partial y_1/\partial x = \delta[1 - \Gamma(t)]$, $\partial y_1/\partial t = -\delta[1 - \Gamma(t)] \times d\Gamma/dt$, where $d\Gamma/dt$ is the rate of motion of the boundary. The concentration of element A on the boundary changes discontinuously from c_2^Γ to c_1^Γ. In the volume of phases 1 and 2 $\partial y_1/\partial x = 0$ and Eqs. (5), (6) reduce to the usual diffusion equation

$$\partial c_i/\partial t = -(1/n_i^0)\, \partial J_i/\partial x, \quad i = 1,\ 2. \tag{8}$$

Integrating Eqs. (5) and (6) from $x = \Gamma - 0$ to $x = \Gamma + 0$, we obtain

$$(1/n_1^0)\, J_1 \big|_{\Gamma+0} = c_1^\Gamma\, d\Gamma/dt + (c_2^\Gamma\, p_{21} - c_1^\Gamma\, p_{12}) + (c_2^\Gamma\, s_{21} - c_1^\Gamma\, s_{12}), \tag{9}$$

$$(1/n_2^0)\, J_2 \big|_{\Gamma-0} = c_2^\Gamma\, d\Gamma/dt + (c_2^\Gamma\, p_{21} - c_1^\Gamma\, p_{12}) + (c_2^\Gamma\, s_{21} - c_1^\Gamma\, s_{12}). \tag{10}$$

These relationships are written in a coordinate system fixed to the moving phase boundary. Subtracting Eq. (9) from Eq. (10), we arrive at the mass balance

$$(1/n_2^0)\, J_2 \big|_{\Gamma-0} - (1/n_1^0)\, J_1 \big|_{\Gamma+0} = (c_2^\Gamma - c_1^\Gamma)\, d\Gamma/dt. \tag{11}$$

When diffusion mass transport is the limiting stage of the process, equilibrium concentrations $c_1^\Gamma = c_{12}^0$, $c_2^\Gamma = c_{21}^0$ are established on the interphase boundary, since any deviations of c_1^Γ, c_2^Γ from c_{12}^0, c_{21}^0 are eliminated due to the high rates of crystalline lattice readjustment and atomic transition through the interphase boundary. In this case Eqs. (8), (11) represent a Stefan-type problem which was analyzed in]3].

If the limiting stage is phase transformation s_{12}, $s_{21} \gg p_{12}$, p_{21} then because of the high rate of atomic redistribution the flux through the interphase boundary $J_s = c_2^\Gamma s_{21} - c_1^\Gamma S_{12} \approx 0$, whence $c_2^\Gamma/c_1^\Gamma = s_{12}/s_{21} = c_{21}^0/c_{12}^0$. Upon growth of the intermetallide due to solid solution the latter near the boundary is supersaturated by element A: $c_2^\Gamma > c_{21}^0$, $c_1^\Gamma > c_{12}^0$. This corresponds to the experimental data of [4] in annealing of diffusion pairs in the α–β system of Cu–Al. From Eqs. (9), (10), (7) there follow the conditions

$$(1/n_1^0)\,J_1\big|_{\Gamma+0} = c_1^\Gamma\,d\Gamma/dt + c_2^\Gamma\,M_{21}\,(c_{21}^0 - c_2^\Gamma)^{m_{21}} - c_1^\Gamma\,M_{12}\,(c_1^\Gamma - c_{12}^0)^{m_{12}}, \tag{12}$$

$$(1/n_2^0)\,J_2\big|_{\Gamma-0} = c_2^\Gamma\,d\Gamma/dt + c_2^\Gamma\,M_{21}\,(c_{21}^0 - c_2^\Gamma)^{m_{21}} - c_1^\Gamma\,M_{12}\,(c_1^\Gamma - c_{12}^0)^{m_{12}}, \tag{13}$$

written in a coordinate system fixed to the interphase boundary. Equations (12), (13) are analogous to those obtained in [8] in a nonmoving coordinate system for growth limited by phase transformation.

In the opposite case, where growth is limited by transition of atoms through the interphase boundary p_{12}, $p_{21} \gg s_{12}$, s_{21}, deviation of the phase compositions beyond the limits c_{12}^0, c_{21}^0 of their stability ranges is eliminated by phase transformation. Then $J_p = c_2 p_{21} - c_1 p_{12} \approx 0$. Under these conditions $c_1^\Gamma < c_{12}^0$, $c_2^\Gamma > c_{21}^0$, which corresponds to growth of a γ-phase or chromization of α-iron. Using the condition $c_{21}^0 s_{21} - c_{12}^0 s_{12} = 0$, from Eqs. (9), (10) we obtain the relationships

$$(1/n_1^0)\,J_1\big|_{\Gamma+0} = c_1^\Gamma\,d\Gamma/dt + (c_2^\Gamma - c_{21}^0)\,s_{21} - (c_1^\Gamma - c_{12}^0)\,s_{12}, \tag{14}$$

$$(1/n_2^0)\,J_2\big|_{\Gamma-0} = c_2^\Gamma\,d\Gamma/dt + (c_2^\Gamma - c_{21}^0)\,s_{21} - (c_1^\Gamma - c_{12}^0)\,s_{12}, \tag{15}$$

written in a coordinate system fixed to the interphase boundary. Equations (14), (15) are close to those of the model of [6], [7] for growth limited by atomic flow at the boundary. If the composition of phase 1 is equal to the solubility limit $c_1(x) = c_{12}^0$ and the intermetallide 2 corresponds to the formula AB, then for p_{12}, $p_{21} \gg s_{12}$, s_{21} each transition of an atom A through the boundary leads to formation of a new elementary cell of phase 2. Such a mechanism was considered in [6].

Diffusion in the Boundary Region. For oriented growth of phases in the diffusion zone, which is found in a number of systems [1, et al.] an elastic coupling of crystalline lattices exists on the interphase boundary. Nonisotropic elastic deformation changes the chemical potential of A atoms, the gradient in which is the diffusion motive force. During diffusion in replacement phases the Kirkendall effect occurs – motion of crystalline lattice planes due to the presence of a vacancy flux. Coupling of the lattices affects the rate of Kirkendall motion in the boundary region. We will consider the changes in diffusion of A atoms with consideration of these facts for a limiting case – a coherent interphase boundary, as is found, for example, in growth of thin monocrystalline layers of $CoSi_2$ and $NiSi_2$ in thin-film diffusion pairs CoSi–Si and NiSi–Si [13, et al.]. The velocities of Kirkendall motion in each phase v_i, i = 1, 2, are determined by the difference between the self-diffusion coefficients of atoms A and B [3, 6]. Difference in the values of v_1, v_2 in the boundary region δ_Γ (Fig. 1b) would cause termination of the coherent coupling. Therefore, in the given situation motion of crystalline lattice planes near the interphase boundary occurs at an identical velocity $v_1 = v_2$. The chemical potential of type k particles (A or B atoms or vacancies) in the nonisotropically-elastically deformed solid changes as compared to the stressed state μ_k^0 [14]:

$$\mu_k = \mu_k^0 - (1/3)\,\sigma_{nn}\omega\rho_k - V\sigma_{mn}\beta_{mn}^k + \bar{R}_k, \tag{16}$$

where σ_{nn} are the diagonal components of the stress tensor σ_{mm}; ω is the mean atomic volume; $\rho_k = (\partial N/\partial N_k)_{\sigma_{mn}, N_l, l \neq k}$ is the number of moles of alloy in the volume V; N_k is the number of moles of particles of type k; $\beta_{mn}^k = (\partial\varepsilon_{mn}/\partial N_k)_{\sigma mn, N\ell \neq k}$ is the elastic compliance tensor; ε_{mn} is the deformation tensor; $\bar{R}_k = (\partial R/\partial N_k)_{\sigma mn, N\ell, \ell \neq k}$ is the partial molar work of elastic deformation; $R = \int V\sigma_{mn}d\varepsilon_{mn}$ is the work involved in elastic deformation of a volume V of the alloy. Symbols for summation over the tensor indices are omitted from Eq. (16). In diffusion by a vacancy mechanism the number of particles per unit volume does not change; $\rho_k = 0$. Defining the quantities R, $\bar{R}_k$, $\beta_{mn}{}^k$ with Hook's law $\varepsilon_{mn} = \delta_{mn}\sigma_{nn}/9K + \left(\sigma_{mn} - \frac{1}{3}\delta_{mn}\sigma_{nn}\right) \Big/ 2G$ [15], where K is the volume compression coefficient, G is the shear modulus, and δ_{mn} is a Kronecker symbol, we obtain:

$$\mu_k = \mu_k^0 + \bar{V}_k\,[(1/9K)\,\sigma_{nn}^2/2 + (1/4G)\,(\sigma_{mn}\sigma_{mn} - \sigma_{nn}^2/3)] +$$
$$+ V\,[(1/9K^2)\,(\sigma_{nn}^2/2)\,(\partial K/\partial N_k) + (1/4G^2)(\sigma_{mn}\sigma_{mn} - \sigma_{nn}^2/3)(\partial G/\partial N_k)].$$

Here $\bar{V}_k = (\partial V/\partial N_k)_{\sigma_{mn}, N_\ell, \ell \neq k}$ is the partial molar volume. The elasticity constants K, G in each phase are practically independent of concentration. Then $\mu_k = \mu_k{}^0 + \bar{V}_k E$, where $E = (1/9K)\,\sigma_{nn}^2/2 + (1/4G)\left(\sigma_{mn}\sigma_{mn} - \frac{1}{3}\sigma_{nn}^2\right)$ is the energy of elastic deformation of a unit volume. For a single atom in phase i, $\mu_k{}^{(i)} = \mu_k{}^{(i)0} + \omega_k{}^{(i)}E_i$, i = 1, 2, where $\omega_k{}^{(i)}$ is the volume of type k particles. For intermetallides in solid replacement solutions $\omega_k{}^{(i)} \approx 1/n_i{}^0$. Then $\nabla\mu_k{}^{(i)} = \nabla\mu_k{}^{(i)0} - f_i/n_i{}^0$, where $f_i = -\nabla E_i$ is the force acting on atoms in the boundary region of phase i, i = 1, 2. We assume that the size of the segments of phases 1 and 2 in the direction perpendicular to the axis Ox in the boundary region δ_Γ is comparable to the step height h (Fig. 1d). In this case the forces f_i change little in the direction perpendicular to Ox, and fall off rapidly with removal from the boundary into the depths of the phases [16]. For a vertical layer of the boundary region δ_Γ we write the condition of force equilibrium $n_1{}^0 y_1 f_1 + n_2{}^0 y_2 f_2 = 0$. The density of the diffusion flux of atoms A in phase i is given by

$$J_i = -n_i^0 L_{AA}^{(i)}\,\nabla\,(\mu_A^{(i)} - \mu_v^{(i)}) - n_i^0 L_{AB}^{(i)}\,\nabla\,(\mu_B^{(i)} - \mu_v^{(i)}) + n_i^0 c_i v_i, \tag{17}$$

where $L_{AA}{}^{(i)}$, $L_{AB}{}^{(i)}$ are kinetic coefficients and the subscript v denotes vacancies. Usually $\nabla\mu_v{}^{(i)} \ll \nabla\mu_A{}^{(i)}$, $\nabla\mu_B{}^{(i)}$, $L_{AB}{}^{(i)} \ll L_{AA}{}^{(i)}$ [3, 6, et al.]. Substituting the expressions obtained for the chemical potentials in Eq. (17) and eliminating f_i, we obtain

$$\begin{gathered} J_i = -n_i^0 D_{ii}\partial c_i/\partial x - n_i^0 D_{ij}\partial c_j/\partial x,\ i \neq j,\ i,\ j = 1, 2, \\ D_{ii} = [c_i D_{Bi}^* + (1 - c_i)\,D_{Ai}^* - c_i\,(D_{Ai}^* - D_{Bi}^*)\,F_{ii}]\,g_i, \quad D_{ij} = c_i\,(D_{Ai}^* - D_{Bi}^*)\,F_{ij} g_j, \end{gathered} \tag{18}$$

$$\begin{gathered} F_{ii} = y_j\,(1 - c_i)\,(D_{Ai}^* - D_{Bi}^*)/W,\ F_{ij} = y_j\,(1 - c_i)(D_{Aj}^* - D_{Bj}^*)/W, \\ W = y_2\,[c_1 D_{A1}^* + (1 - c_1)\,D_{B1}^*] + y_1\,[c_2 D_{A2}^* + (1 - c_2)\,D_{B2}^*],\ i \neq j\ . \end{gathered} \tag{19}$$

Here $D_{Ai}{}^*$, $D_{Bi}{}^*$ are self-diffusion coefficients for elements A and B in phase i, i = 1, 2; $g_i = 1 + \partial \ln\gamma_i/\partial \ln c_i$ is a thermodynamic factor; γ_i, activity coefficients in phase i. The mutual diffusion coefficients D_{11} and D_{22} characterize the effect of the gradient in concentration of element A in phases 1 and 2 on the diffusion flux in the same phase. The nondiagonal coefficients D_{ij} relate the concentration gradient in phase j with the flux in the phase i, i ≠ j, i, j = 1, 2. These are caused by the identical rate of Kirkendall motion in both phases due to the coherent coupling of the crystalline lattices on the interphase boundary. It is evident from Eq. (19) that D_{12}, D_{21} are nonzero only near the boundary. Within the volume of phases 1 and 2 the expressions for D_{11} and D_{22} reduce to Darken's: $D_{ii} = c_i D_{Bi}{}^* + (1 - c_i) D_{Ai}{}^*$.

In the case of an incohrent interphase boundary, which is found for significant differences in crystalline lattice parameters or high phase thickness [1, et al.] elastic stresses are absent. In the boundary region δ_Γ Kirkendall motion within each phase is defined only by the difference between the self-diffusion coefficients of atoms A and B and occurs at velocities v_1 and v_2, respectively. A similar case was considered in [17] for mutual diffusion in a multiphase alloy. Then in Eq. (19) $D_{12} = D_{21} = 0$ and diffusion fluxes are described by the conventional equation $J_i = -n_i{}^0 D_{ii}\partial c_i/\partial x + n_i{}^0 c_i v_i$, and the mutual diffusion coefficients D_{11}, D_{22} are given by Darken's expression.

Numerical Study. The problem of Eqs. (4)-(6) was solved on a computer using finite difference methods. To anneal diffusion pairs, at the boundaries of the computation region with dimensions L a condition of the second sort was posed, $J_{1,2}|_{x=0, x=L} = 0$ (absence of mass exchange with the external medium), while a condition of the third sort was used for saturation $J_2|_{x=0} = H(c_2{}^s - c_2|_{x=0})$, where H is the mass transport coefficient, $c_2{}^s$ is the concentration of element A which would be established on the surface in equilibrium with the external medium. Calculations were performed using the dimensionless quantities z =

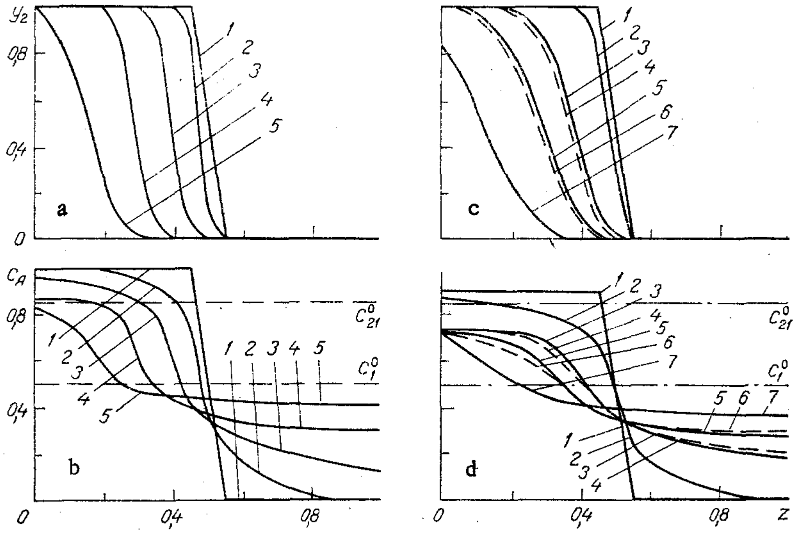

Fig. 2. Results of numerical modeling of growth of solid solution 1 due to intermetallide 2 for $D_0/L:p_0:s_0 = 0.1:6:1$ (a, b) and $D_0/L:p_0:s_0 = 0.2:1:6$ (c, d); a, c) change in volume fraction of phase 2; b, d) change in content of element A. For a, b: 1) 0; 2) 0.1; 3) 0.4; 4) 1.0; 5) 2.0; for c, d: 2, 3) various $\bar{D}_{A1}^* = 1$, $\bar{D}_{B1}^* = 0.5$; $\bar{D}_{A2}^* = 2$, $\bar{D}_{B2}^* = 1$; 4, 6) identical $\bar{D}_{A1}^* = \bar{D}_{B1}^* = 1$, $\bar{D}_{A2}^* = \bar{D}_{B2}^* = 2$; dimensionless self-diffusion coefficients for atoms A and B: 1) 0; 2) 0.1; 3, 4) 0.6; 5, 6) 0.8; 7) 2.0.

x/L, $\tau = t/T_M$, $\bar{s}_{ij} = s_{ij}/s_0$, $\bar{p}_{ij} = p_{ij}/p_0$, $\bar{D}_{ij} = D_{ij}/D_0$, $i = j$, where T_M is the scale of the annealing time ($T_M \sim 1$ h); s_0, p_0, D_0 are characteristic values of the corresponding parameters. For diffusion pair annealing the interphase boundary at $\tau = 0$ is located in the middle of the specimen. Equilibrium $c_{12}{}^0 = 0.5$, $c_{21}{}^0 = 0.85$ and initial $c_1(z, \tau = 0) = 0.1$, $c_2(z, \tau = 0) = 0.9$ concentrations (atomic fractions) were used. Calculation results are shown in Figs. 2, 3, where $C_A = y_1c_1 + y_2c_2$ is the net content of element A in a section perpendicular to the axis Ox. Growth in phase 1 begins when the concentration of element A in phase 2 near the boundary becomes less than the equilibrium value $c_{21}{}^0$ (Fig. 2a, b). For similar rates of diffusion, atomic transition, and crystalline lattice readjustment $D_0/L:p_0:s_0 = 1:1:1$ there is initially an "incubation period," where the interphase boundary does not move. The limiting stage is then atomic redistribution on the interphase boundary. Further phase 1 increases at a constant rate which is limited by readjustment of the crystalline lattice of phase 2 into phase 1 (Fig. 3). For lengthy annealing $c_2{}^\Gamma \to c_{21}{}^0$, the limiting stages becomes diffusion and the linear increase law approaches parabolic (Fig. 3, curve 1). If diffusion is accomplished more slowly than processes on the interphase boundary then the "incubation period" disappears and the growth in phase 2 is limited by phase transformation (the linear portion of curves 2-5, Fig. 3) and then by diffusion (parabolic growth law). The deviation of the boundary concentrations $c_1{}^\Gamma$, $c_2{}^\Gamma$ from their equilibrium values $c_{12}{}^0$, $c_{21}{}^0$ depends on the ratio between the quantities p_0 and s_0. For $p_0 > s_0$ it decreases. Calculations with identical $\bar{D}_{A1}^* = \bar{D}_{B1}^* = 1$, $\bar{D}_{A2}^* = \bar{D}_{B2}^* = 2$ and different $\bar{D}_{A1}^* = 1$, $\bar{D}_{B1}^* = 0.5$, $\bar{D}_{A2}^* = 2$, $\bar{D}_{B2}^* = 1$ self-diffusion coefficients for atoms A and B with the ratio $D_0/L:p_0:s_0 = 0.2:1:6$ show that in the latter case the growth of phase 1 is somewhat retarded due to reduction in

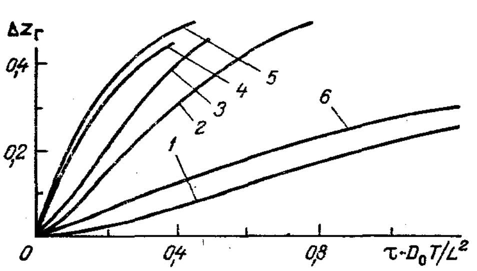

Fig. 3. Kinetics of interphase boundary motion for growth in phase 1 (1-5) and phase 2 (6) in diffusion pair annealing: 1) $D_0/L:p_0:s_0 = 1:1:1$; 2) $D_0/L:p_0:s_0 = 1:3:6$; 3) $D_0/L:p_0:s_0 = 0.1:1:6$; 4) $D_0/L:p_0:s_0 = 0.2:3:6$; 5) $D_0/L:p_0:s_0 = 0.1:6:1$; 6) $D_0/L:p_0:s_0 = 0.2:1:6$.

the mutual diffusion coefficients (Fig. 2c, d). However, the character of the displacement of the interphase boundary with time remains practically unchanged.

NOTATION

J_i, diffusion flow of atoms A; n_i^0, number of lattice points per unit volume; a, interatomic distance; y_i, volume fraction of phase; c_i, concentration of element A; t, τ, dimensional and dimensionless time; x, z, dimensional and dimensionless coordinate; T_M, characteristic time interval; L, characteristic diffusion zone length; δ_Γ, size of boundary region; p_{ij}, rate of phase i crystalline lattice readjustment into phase j; s_{ij}, rate of transition of A atoms from phase i into phase j; Γ, coordinate of planar phase boundary; v_i, Kirkendall velocity; μ_k, chemical potential of particle k; G, shear modulus; ε_{mn}, σ_{mn}, stress and deformation tensors; E, elastic deformation energy per unit volume; D_{Ai}^*, D_{Bi}^*, self-diffusion coefficients for atoms A and B in phase i; γ_i, thermodynamic activity coefficient. Subscripts, phase numbers.

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