distribution can be assessed from the quasi-one-dimensional solution (10). In this case the ratio of the total flux J_g in the gaseous phase to the total flux J_s over the surface of the channel does not depend on the longitudinal coordinate x and has the form

$$J_s/J_g = \frac{3t}{b}\left(1 - \frac{2}{6-a}\right), \tag{15}$$

while in the purely one-dimensional case (which is realized, e.g., at $\lambda = 0$) this ratio is 2t/b. From a comparison of this value with (15) it follows that when the two-dimensionality is taken into account, i.e., when there is not local equilibrium between the bulk and adsorbed phases, the contributions are redistributed to the benefit of the gaseous phase.

NOTATION

L, channel length, r_0, channel radius; x, ρ, dimensionless longitudinal and radial coordinates; c, numerical density of the admixture in a gaseous phase; n_0, the total number of particles in a gaseous phase; c_s, dimensionless numerical density of the admixture in the adsorption phase (degree of occupation); σ, diameter of the adsorbate molecules; λ, constant of radioactive decay; D, D_s, diffusion coefficient in the gaseous phase and over the channel surface, respectively; v_i, thermal velocity of the admixture molecules in the gaseous phase; 1/β, adsorption time; J_s, total diffusion flow over the channel surface; J_g, total diffusion flow in the gaseous phase.

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MACROKINETICS OF INTERMETALLIC COMPOUND FORMATION IN THE DIFFUSION ZONE

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A macrokinetic model is developed for reaction diffusion in binary metallic systems for situations when the phase composition of the diffusion zone does not correspond to the equilibrium phase diagram.

Investigation of the formation of intermetallides and silicides during diffusion mass transfer with solid phase transformations is associated with the development of integral circuit technology, the perfection of methods of superposing protective coatings on metals, etc. It is established experimentally that the phase composition of the diffusion zone during the annealing of thin-film and bulk diffusion pairs of the metal—metal (Ni—Al, Co—Al, Cr—Al, Au—Al, Cu—Sn, etc.) and metal (Co, Ni, Pd, Pt, Cr, Ti, V, W, Mo, Nb, Ta, Zr, etc.)-silicon types does not correspond to an isothermal section of the equilibrium phase diagram [1-3]. For instance, only Ni_2Si out of the six equilibrium phases (Ni_3Si, Ni_5Si_2, Ni_2Si, Ni_3Si_2, NiSi, $NiSi_2$) is formed in the Ni—Si system at the annealing temperature 200-350°C [4], while only Pd_2Si of the four phases (Pd_3Si, Pd_5Si_2, Pd_2Si, PdSi) [5] is formed in the Pd-Si pair at 200-600°C, and which grow until exhaustion of one of the initial elements. The absence of thin interlayers of the remaining phases is confirmed by using scanning electron microscopy [3-5]. Analogous facts, the absence of intermediate compounds, are observed during growth of $MoSi_2$, $TiSi_2$, $NbSi_2$, WSi_2 during silicon saturation of infusible metals

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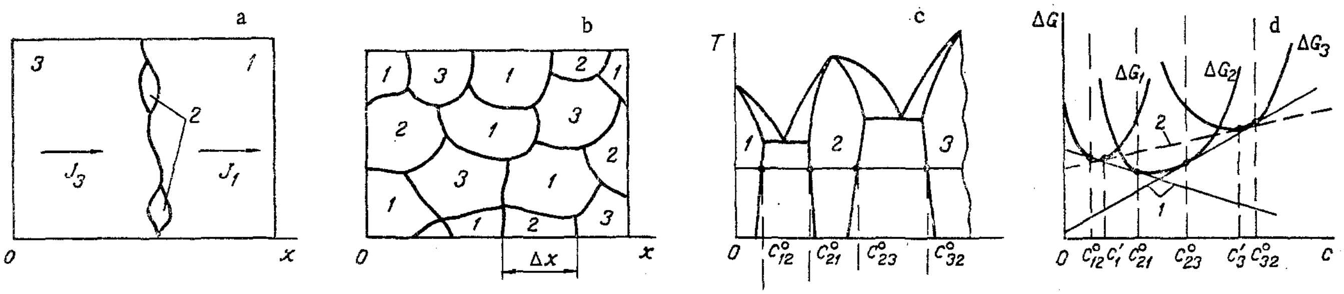

Fig. 1. Diagram of reactive diffusion in a binary system: a) diffusion zone; b) chaotic location of macrosections of three phases; c) fragment of the phase diagram; d) dependent of the free energy on the composition; 1) stable; 2) metastable equilibrium.

from the external medium [6, 7]. The phenomenon of "explosive" formation of certain silicides of the rare-earth metals [8] and PdSi phase in the diffusion pair Pd_2Si—Si [5] when a certain temperature is reached is known. The facts presented indicate the substantial influence of the kinetics of seed formation. The following processes occur in the multiphase diffusion zone: diffusion in the bulk of each phase, atom passages through the interphasal boundary, phase transformations, i.e., rebuilding of the crystalline lattices [9], as well as the occurrence of new intermetallic compounds. The role of the last factor is investigated inadequately in the literature. Two approaches are known to the explanation of the experimental data. When phase growth is limited by diffusion mass transfer, thin (on the order of the dimension of the critical seed) interlayers of all the equilibrium phases are rapidly formed in the diffusion zone. Certain compounds are not thickened in practice for a definite relationship between the $D_i \Delta c_i$ for different phases, where D_i is the coefficient of mutual diffusion, Δc_i is the width of the homogeneity domain, and i is the phase number [10, 11]. For growth limited by atom fluxes through interphasal boundaries, one of the phases can turn out to be kinetically unstable and vanish completely [12]. However because of the high velocity of seed formation, a thin layer of this phase again occurs. The situation when growth is limited by the kinetics of a phase transformation is examined in [13] for the case of two phases without taking account of the origination of a third compound.

A more general model, as compared with [10-13], is proposed in this paper, in which the rates of all the four processes described above are commensurate. It is an extension of the approach developed in [14] to the case of three phases. It is also taken into account that the interphasal boundaries have a step or wave shape [2, 5, etc.] according to raster electron microscopy data. The contact of the solid replacement solution on the basis of the metal B (phase 1) and the intermetallide 3 (Fig. 1a) is examined. There is one intermediate compound, the intermetallide 2 (Fig. 1c), between the phases 1-3 in the A-B equilibrium diagram. Sections of the new phase 2 can occur in the diffusion zone (Fig. 1a). Such a situation corresponds, say, to $NiSi_2$ formation in the diffusion pair NiSi—Si [3, 4]. The seeding sections of the intermetallic compounds have the shape of discs of thickness $h_{cr} \sim 10a$, where a is the interatomic spacing [15]. The characteristic feature of the situation under consideration is that, in contrast to a multicomponent system, seeds of a new intermetallide are formed in a binary system only on interphasal boundary of the initial phases.

Atom transitions from one phase into another occur on all the interphasal boundaries (1-2, 2-3, 1-3). Diffusion in the intermetallides 2 and 3 and the solid replacement solution 1 proceeds by a vacancy mechanism. As in [14], we assume for simplicity: 1) bulk diffusion predominates over grain-boundary diffusion; 2) the number of crystalline lattice sites per unit volume of all three phases is identical: $n^o_1 = n^o_2 = n^o_3$; 3) diffusion mass transfer is examined in a one-dimensional approximation, the J_i fluxes, i = 1 - 3, are directed only along the Ox axis (Fig. 1a). The first assumption is valid for bulk specimens at a sufficiently high temperature, as well as in a number of systems, for thin-film diffusion pairs [16]. The second condition permits neglecting volume changes during reaction diffusion in the multiphase diffusion zone. Phase transformation occurs at the contact sites of phases 1 and 2, 2 and 3, i.e., rebuilding of one crystalline lattice into another. Two "competing" kinds of crystalline lattice rebuilding occur on the boundary between the intermetallide 3 and the solid solution 1: growth of phase 3 due to phase 1 (or vice versa), and formation of the seeds of a new intermetallide 2. It is taken into account in the model that the seeds of phase 2 can occur both from the phase 1 side with probability ν_{12} and the phase 3

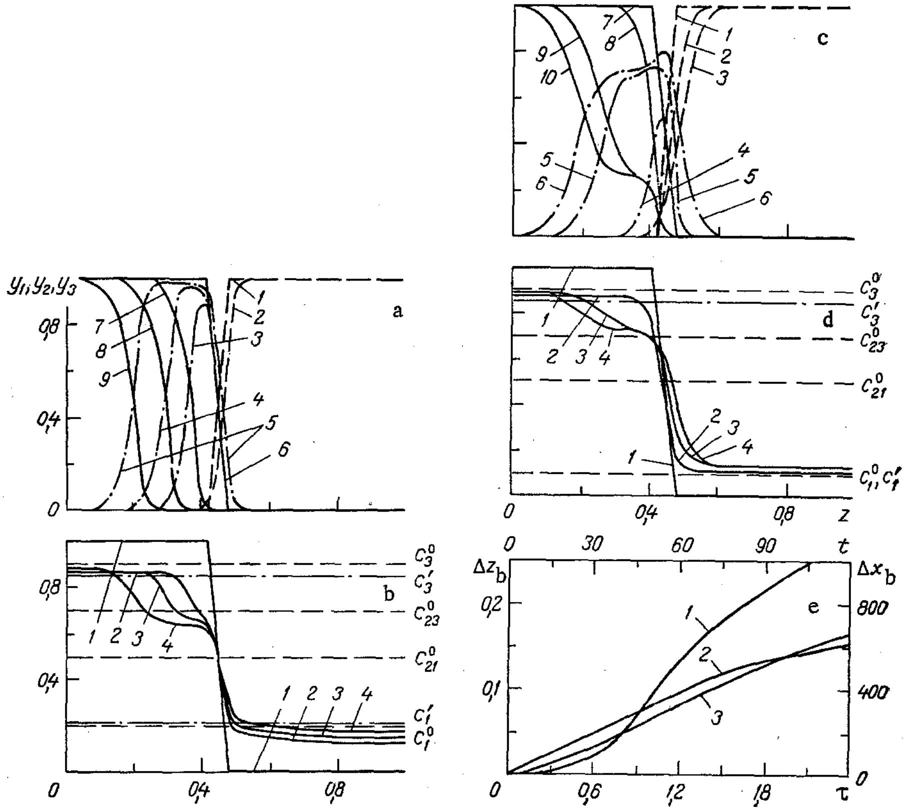

Fig. 2. Numerical modeling of formation of the new intermetallide 2 during annealing of a diffusion pair at a high (a and b) and low (c and d) rate of seed formation; a and c are bulk fractions of the phases in the transverse section and b and d are the content of the element A: at τ 1, 2) y_1; 3-5) y_2; 6-9) y_3; 1, 6) $\tau = 0$; 3, 7) 1.0; 4, 8) 1.4; 2, 5, 9) 2.0; b: 1) $\tau = 0$; 2) 1.0; 3) 1.4; 4) 2.0; c: 1-3) y_1; 4-6) y_2; 7-9) y_3; 7) $\tau = 0$; 4, 8) 3.0; 2, 5, 9(7.5; 3, 6, 10) 10.0; d: 1) $\tau = 0$; 2) 3.0; 3) 7.5; 4) 10.0; e) kinetics of new phase growth for cases a and b: 1) boundary shift of phases 2 and 3 (in dimensionless coordinates; 2) experimental data [2], and 3) numerical computation of V–Si$_2$ (nm) phase thickening in the thin-film pair V–Si. t in min.

side with probability ν_{32}. In a first approximation the rebuilding of the crystalline lattice on the boundary of phases 1 and 2 occurs independently of the phase transformation on adjacent sections of the boundary of phases 3 and 1, etc. In this connection we examine the chaotic distribution of macroscopic sections of grains of all three phases (Fig. 1b). The grain magnitude Δx considerably exceeds the size of the critical seed of phase 2. Such a situation corresponds to annealing a multiphase alloy or a composite material by diffusion saturation. Motion of the 1-2, 2-3, 1-3 phase boundaries is equivalent to a change in the bulk fractions of these phases y_i, i = 1-3 in time in a section perpendicular to the Ox axis ($y_1 + y_2 + y_3 = 1$). It is governed only by rebuildings of the crystalline lattices at the appropriate interphase boundaries. By analogy with a two-phase diffusion zone [14], the expressions for changes in the bulk fractions of phases 1 and 3 in time take on the form

$$\partial y_1/\partial t + (p_{12} - p_{21})\,\alpha_{21} + (p_{13} - p_{31} + q_{12})\,\alpha_{31} = 0, \quad \partial y_3/\partial t + (p_{32} - p_{23})\,\alpha_{32} + \\ + (p_{31} - p_{13} + q_{32})\,\alpha_{31} = 0. \tag{1}$$

Here p_{ij} is the rate of crystalline lattice rebuilding of the phase i into the phase j, i ≠ j, j = 1-3 [14]; $q_{12} = h_{cr}\nu_{12}$, $q_{32} = h_{cr}\nu_{32}$ are the rates of formation of critical seeds of the intermetallide 2 from phase 1 and phase 3, and α_{ij} is the probability of i-th and j-th phase contact.

The concentrations of the element A in all the phases c_i, i = 1-3 are determined by both diffusion mass transfer in the bulk of each phase and by processes on the interphase boundaries, the atom redistribution and rebuilding of crystalline lattices. Using the analogy with the case of two phases [14], we obtain

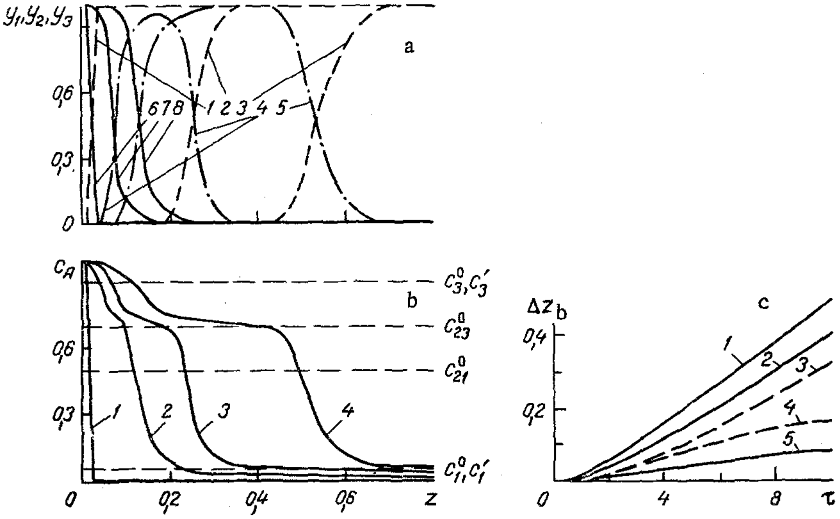

Fig. 3. Formation of the new phase 2 during saturation from the external medium: a) bulk fractions of the phases for $\bar{H}_3 = 10$ [1-3) y_1; 4, 5) y_2; 6-8) y_3; 1, 6) $\tau = 0$; 2, 4, 7) 5.0; 3, 5, 8) 10.0]; b) content of the element A [1) $\tau = 0$; 2) 3.0; 3) 5.0; 4) 10.0]; c) kinetics of boundary motion (1 is boundary of phases 1 and 2 for $\bar{H}_3 = 6$ and 10; 2 and 3 are growth of the phase 2; 4 and 5 are growth of the phase 3; 2 and 5 are for $\bar{H}_3 = 10$, and 3 and 4 for 6).

$$\begin{aligned}
\partial y_1 c_1/\partial t &= -(1/n_1^0)\,\partial J_1/\partial x + (f_{21}+g_{21})\,\alpha_{21} + (f_{31}+g_{31}-r_{12})\,\alpha_{31},\\
\partial y_2 c_2/\partial t &= -(1/n_2^0)\,\partial J_2/\partial x - (f_{21}+g_{21})\,\alpha_{21} + (f_{32}+g_{32})\,\alpha_{32} + (r_{12}+r_{32})\,\alpha_{31},\\
\partial y_3 c_3/\partial t &= -(1/n_3^0)\,\partial J_3/\partial x - (f_{32}+g_{32})\,\alpha_{32} - (f_{31}+g_{31}+r_{32})\,\alpha_{31},
\end{aligned} \tag{2}$$

where J_i is the diffusion flux density in the i-th phase, and n_i^0 is the number of crystalline lattice sites per unit volume, i = 1-3. The quantities f_{ij}, i, j = 1-3 are fluxes of atoms A through the phase boundaries $f_{ij} = c_i s_{ij} - c_j s_{ji}$, where s_{ij} is the rate of transition of atoms A from phase i to phase j [14]; $g_{ij}=c_i p_{ij}-c_j p_{ji}$, $r_{12}=c_1 q_{12}$, $r_{32}=c_3 q_{32}$. The system (2) describes the change in concentration of the element A in the the three phases because of the bulk diffusion (the first components in the right sides), the atom redistribution, the crystalline lattice rebuilding, and the seed formation for the new phase 2 at the appropriate boundaries (remaining components). Since the macroscopic grain sections of the three phases are arranged chaotically, the quantities α_{21}, α_{31}, α_{32} are connected by the relationships

$$\alpha_{31}+\alpha_{32}=|\partial y_3/\partial x|,\quad \alpha_{21}+\alpha_{32}=|\partial y_2/\partial x|,\quad \alpha_{21}+\alpha_{31}=|\partial y_1/\partial x| \tag{3}$$

with spatial gradients of the bulk fractions of the phases $\partial y_i/\partial x$, i = 1-3. The systems (1) - (3) are closed and describe diffusion with phase transformations for an arbitrary arrangement of the macrosections of the three phases. Equations (1) and (2) can also be obtained by partitioning the diffusion zone into discrete layers of thickness h_{cr} and writing the mass balance for each layer as this is done in [14] for two phases.

In the case when phase 3 is on the left and phase 1 is on the right (Fig. 1a), $\partial y_3/\partial x \leq 0$, $\partial y_1/\partial x \geq 0$, the systems (1)-(3) simplify. Substituting the values α_{21}, α_{31}, α_{32} from (3) into (2) and (1), we obtain in matrix form

$$\frac{\partial Y}{\partial t}=E\frac{\partial Y}{\partial x},\quad Y=\mathrm{colon}(y_1,\ y_3), \tag{4}$$

$$\frac{\partial ZC}{\partial t}=\frac{\partial}{\partial x}ZD\frac{\partial C}{\partial x}+F\frac{\partial Y}{\partial x},\quad z_{ij}=\delta_{ij}y_i, \tag{5}$$

where C = colon($c_1 c_2 c_3$) is the concentration vector, z_{ij} are elements of the matrix Z, and δ_{ij} is the Kronecker delta. The expressions obtained in [14] for the diffusion fluxes J_i, i = 1-3 are utilized when going over from (2) to (5). The non-diagonal elements D_{ij}, $i \neq j$,

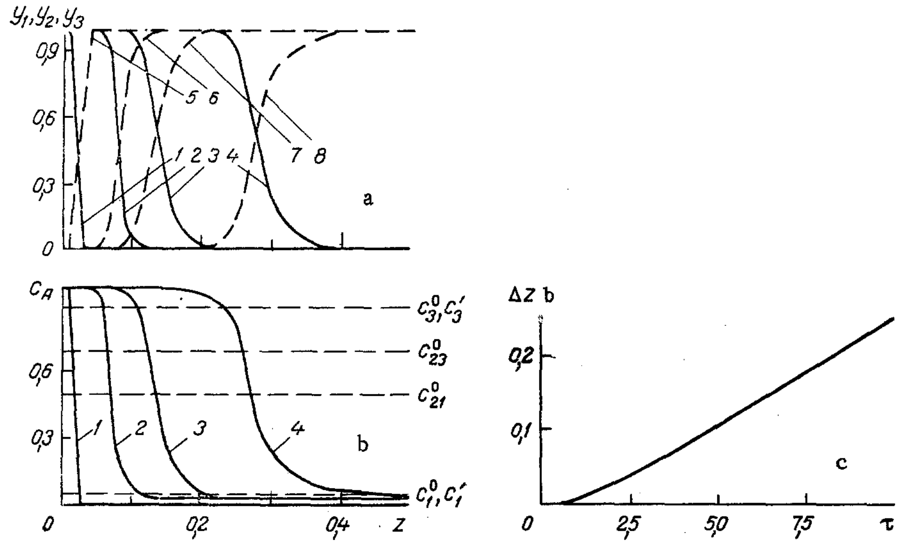

Fig. 4. Suppression of new phase formation during saturation from the external medium: a) bulk fraction of phases 1 and 3 [1-4) y_3; 5-8) y_1; 1-5) $\tau = 0$; 2, 6) 3.0; 3, 7) 5.0; 4, 8) 10.0]; b) content of the element A [1) $\tau = 0$; 2) 3.0; 3) 5.0; 4) 10.0]; c) growth of the phase 3.

of the matrix of the mutual diffusion coefficients D characterize the influence of the concentration gradient of the element A in the j-th phase on the flux in the i-th phase because of the elastic connection of the crystalline lattices of these phases during oriented (epitaxial) growth that is observed experimentally in a number of binary systems [1-3]. The formulas for the mutual diffusion coefficients for a coherent connection of the crystalline lattices are presented in [14]. In the absence of an elastic connection, the nondiagonal elements $D_{ij} = 0$, $i \neq j$ while the diagonal elements are determined by the Darken formula. The system (4) describes phase transformation front motion while (5) is the change in composition of the three phases.

If there is no phase 3 ($y_3(x) = 0$, $\partial y_3/\partial x = 0$) or phase 1 ($y_1(x) = 0$, $\partial y_1/\partial x = 0$) in the diffusion zone, then the components containing q_{12} and q_{32} vanish and the systems (4) and (5) reduce to the problem formulated in [14]. In the case when phases 3 and 1 are separated by a continuous layer of intermetallide 2, the systems (4) and (5) dissociate into two problems for two phases. For growth limited by diffusion, the equations reduce to a problem of Stefan type [10, 11], and in cases when the limiting stage is the atom transition through the interphasal boundary ($s_{ij} \ll p_{ij}$) and phase transformation ($p_{ij} \ll s_{ij}$), to the models [12] and [13], respectively [14].

Seed formation of the new intermetallide 2 on the boundary of phases 1 and 3 is possible because of rebuilding of the crystalline lattice of phase 1 if the concentration of the element A therein is greater than equilibrium $c_1 > c_{12}^0$, or of phase 3 for $c_3 < c_{32}^0$ (Fig. 1c). The seed formation rates can be determined by formulas used in chemical macrokinetics

$$q_{12} = \begin{cases} Q_{12}(c_1 - c_{12}^0)^{n_{12}} & \text{for} \quad c_1 > c_{12}^0, \\ 0 \quad \text{for} \quad c_1 \leqslant c_{12}^0, \end{cases} \qquad q_{32} = \begin{cases} Q_{32}(c_{32}^0 - c_3)^{n_{32}} & \text{for} \quad c_3 < c_{32}^0, \\ 0 \quad \text{for} \quad c_3 \geqslant c_{32}^0, \end{cases} \tag{6}$$

where Q_{12}, Q_{32}, n_{12}, n_{32} are constants for a given temperature. For the metastable equilibrium of the phases 1 and 3 $\mu_A^{(1)}[c_1'] = \mu_A^{(3)}[c_3']$, $\mu_B^{(1)}[1 - c_1'] = \mu_B^{(3)}[1 - c_3']$ (Fig. 1d). Rebuilding of the crystalline lattice 1 → 3 or vice versa occurs upon deviation of the phase compositions beyond the limits c_1', c_3'

$$p_{13} = \begin{cases} M_{13}(c_1 - c_1')^{m_{13}} & \text{for} \quad c_1 > c_1', \\ 0 \quad \text{for} \quad c_1 \leqslant c_1', \end{cases} \qquad p_{31} = \begin{cases} M_{31}(c_3' - c_3)^{m_{31}} & \text{for} \quad c_3 < c_3', \\ 0 \quad \text{for} \quad c_3 \geqslant c_3', \end{cases} \tag{7}$$

where M_{13}, M_{31}, m_{13}, m_{31} are constants. Since $c_1' \gtrsim c_{12}^0$, $c_3' \lesssim c_{32}^0$ (Fig. 1d), a larger deviation of the boundary concentration from the equilibrium is required for the transformation of phases 1 and 3 or vice versa, than for seed formation for the new phase 2. Phase 1 is stable for $c_1 \leq c_{12}^0$, 2 for $c_{21}^0 \leq c_2 \leq c_{23}^0$, and 3 for $c_3 > c_{32}^0$ (Fig. 1c). Consequently, the quantities p_{12}, p_{21}, p_{23}, p_{32} are determined by formulas of the type (7) in which the equilibrium concentrations c_{21}^0, c_{21}^0, c_{23}^0, c_{32}^0 replace c_1' and c_3'.

There are no macroscopic boundary fluxes of the atoms A, $f_{21} = c_2 s_{21} - c_1 s_{12} = 0$, $f_{32} = c_3 s_{32} - c_2 s_{23} = 0$, $f_{31} = c_3 s_{31} - c_1 s_{13} = 0$ for equilibrium of phases 1 and 2 ($c_1(x) = c_{12}^0$, $c_2(x) = c_{21}^0$), 2 and 3 ($c_2(x) = c_{23}^0$, $c_3(x) = c_{32}^0$) and 1 and 3 ($c_1(x) = c_1'$, $c_3(x) = c_3'$), from which

$$s_{12}/s_{21} = c_{21}^0/c_{12}^0, \quad s_{23}/s_{32} = c_{32}^0/c_{23}^0, \quad s_{13}/s_{31} = c_3'/c_1' \,. \tag{8}$$

The quantities s_{ij} are independent of the concentration of the element A for small deviations of the boundary compositions of the phases from the equilibrium values.

Let us examine contact of the intermetallide 3 with the solid solution 1 in the absence of phase 2. The systems (1) and (2) for $y_2 = 0$, $\partial y_2/\partial x = 0$ take the form

$$\frac{\partial y_1}{\partial t} + (p_{13} - p_{31} + q_{12})\,\frac{\partial y_1}{\partial x} = 0, \quad \frac{\partial y_3}{\partial t} + (p_{31} - p_{13} + q_{32})\,\frac{\partial y_3}{\partial x} = 0,$$

$$\frac{\partial y_1 c_1}{\partial t} = -\frac{1}{n_1^0}\,\frac{\partial y_1 J_1}{\partial x} + \frac{\partial y_1}{\partial x}\;[c_3(p_{31} + s_{31}) - c_1(p_{13} + s_{13} + q_{12})],$$

$$\frac{\partial y_3 c_3}{\partial t} = -\frac{1}{n_3^0}\,\frac{\partial y_3 J_3}{\partial x} + \frac{\partial y_3}{\partial x}\;[c_1(p_{13} + s_{13}) - c_3(p_{31} + s_{31} + q_{32})].$$

Since $c_1' \gtrsim c_{12}^0$, $c_3' \lesssim c_{32}^0$, the seed formation rates q_{12}, q_{32} are determined by the coefficients Q_{12}, Q_{32} (see (6)), which can depend strongly on the temperature in a number of systems. Seed formation of the new intermetallide 2 is suppressed at low temperatures, $q_{12} = 0$, $q_{32} = 0$ and phase 3 grows because of the solid solution 1. In the absence of a supply of atoms A from the external medium and low specimen thickness the concentrations along the 0x axis rapidly equilibrate and $J_1 = J_3 = 0$. A metastable equilibrium is set up between phases 1 and 3, thus $c_1(x) = c_1'$, $c_3(x) = c_3'$, $f_{31} = c_3 s_{31} - c_1 s_{13} = 0$. Then $p_{13} = 0$, $p_{31} = 0$, $\partial y_1/\partial t = -\partial y_3/\partial t = 0$ and the equations (9) vanish identically. Such a situation is observed in the thin-film diffusion pair Pd—Si: after formation of Pd_2Si and exhaustion of the palladium layer during further annealing at 200-300°C, the Pd_2Si phase is found in metastable equilibrium with the silicon. The phase PdSi [5] occurs at the Pd_2Si—Si boundary only at 810°C.

The ratio of the rates of direct (3 → 2) and reverse (2 → 3) rebuilding of the crystal lattices $p_{32}/p_{23} \sim \exp[-\Delta G_{32}/(RT)]$ is associated with a change in the Gibbs potential ΔG_{32}. For formation of seeds of the new intermetallide 2 from the phase 3 an isobaric—isothermal potential $\Delta G_{32}'$, which differs from ΔG_{32} by the magnitude of the surface energy W $\Delta G_{32}' = \Delta G_{32} + W$, associated with the occurrence of a new interphasal boundary enters the ratio $q_{32}/p_{32} \sim \exp[-\Delta G'_{32}/(RT)]$. Since the seeds of the new phase have the shape of thin discs of radius r [15], $W \approx \pi r^2(\gamma_{21} + \gamma_{32} - \gamma_{31})$, where γ_{ij} is the surface energy per unit area of the boundary of the phases i and j.

The problem (4) and (5) was solved numerically on an electronic computer by using finite difference methods. The equations were made dimensionless by $z = x/L$, $\tau = t/T_0$, $\bar{s}_{ij} = s_{ij}/s_0$, $\bar{p}_{ij} = p_{ij}/p_0$, $\bar{D} = D/D_0$, $\bar{q}_{12} = q_{12}/p_0$, $\bar{q}_{32} = q_{32}/p_0$, where L is the dimension of the computation domain, T_0 is the annealing time scale ($T_0 \sim 1$ hr), s_0, p_0, D_0 are characteristic values of the appropriate quantities. The parameters $\bar{p}_{ij}$, $\bar{q}_{12}$, $\bar{q}_{32}$ were calculated by formulas (6) and (7), $\bar{s}_{12}$, $\bar{s}_{13}$, $\bar{s}_{23}$ are given, and $\bar{s}_{21}$, $\bar{s}_{31}$, $\bar{s}_{32}$ are determined by using (8). For the annealing of the diffusion pair the boundary of phases 1 and 3 was placed at the middle of the specimen and $y_2(z, \tau = 0) = 0$ was assumed. Content of element A in intermetallide 3 corresponding to its stoichiometry was taken as one. For commensurate seed formation rates and growth of the intermetallide 2 because of the initial phases ($Q_{32}/p_0 = 1$, $\bar{q}_{12} = 0$, $M_{32}/p_0 = 1.5$, $M_{23}/p_0 = 1$, $M_{12}/p_0 = 0.5$, $M_{21}/p_0 = 0.3$, $\bar{p}_{13} = p_{31} = 0$, $m_{12} = m_{21} = m_{23} = m_{32} = 1.1$), the values $\bar{s}_{12} = 0.2$, $\bar{s}_{13} = 1$, $\bar{s}_{23} = 0.5$, $D_0/L:p_0:s_0 = 0.2:6:1$, the formation of phase 2 is initially limited by the transition of the atoms A through the boundary of phases 1 and 3. Later, rebuilding of the crystalline lattices becomes the limiting stage. A continuous layer of intermetallide 2 is rapidly formed on the initial-phase boundary and grows according to a linear dependence on the time because of phase 3 and partially the solid solution 1 (Fig. 2a and 2d, curve 1). For large time the process is limited by diffusion and the growth law is approximately parabolic. The step corresponding to the composition of phase 2 appears on the curve of the dependence of the content of the element A $c_A = \Sigma y_i c_i$ on the coordinate z for sufficiently large thickness of this phase (Fig. 2b). If seed formation occurs more slowly than their growth because of phase 3 ($Q_{32}/p_0 = 0.4$, $\bar{q}_{12} = 0$, $M_{32}/p_0 = 2$, $M_{23}/p_0 = 1$, $M_{12}/p_0 = 0.1$, $M_{21}/p_0 = 0.1$, $\bar{p}_{13} = \bar{p}_{31} = 0$, $\bar{s}_{12} = 0.5$, $\bar{s}_{13} = 1$, $\bar{s}_{23} = 0.5$, $D_0/L:p_0:s_0 = 0.2:6:1$), phase 2 is formed in the form of a layer of inhomogeneous thickness (Fig. 2c). This is related to the fact that the seeds of the new phase 2 originating on the boundary of the initial phases 1 and 3 grow rapidly along the 0z axis. The results of a computation are in qualitative agreement with experimental data on the formation of PdSi in the thin-film pair Pd_2Si—Si [1, 5], $HfSi_2$ in the pair HfSi—Si [8]. Limiting stage is seed formation. Therefore, features of intermetallide formation in the diffusion zone are governed by the relationship of the seed formation rate and the growth rate of the new phase because of the originals.

It was assumed when modelling diffusion saturation from an external medium (Figs. 3 and 4) that for $\tau = 0$ there is thin layer of intermetallide 3 on the surface of phase 1 and a boundary condition of the third kind was posed

$$\frac{T_0}{L}\, J_3|_{z=0} = \bar{H}_3 (c_3^{\mathrm{p}} - c_3|_{z=0}), \tag{10}$$

where $\bar{H}_3$ is the dimensionless mass transfer coefficient for phase 3 ($\bar{H}_3 = H_3 T_0/L$) and c_3^p is the concentration that would be built up for equilibrium with the external medium. When the rate of seed formation for the intermetallide 2 is commensurate with the rate of growth of the phase 3 ($Q_{12}/p_0 = 0.25$, $\bar{q}_{32} = 0$, $M_{12}/p_0 = 1$, $M_{21}/p_0 = 0.2$, $M_{23}/p_0 = 0.05$, $M_{32}/p_0 = 0.1$, $M_{13}/p_0 = 2$, $M_{31}/p_0 = 1$, $\bar{s}_{12} = 1$, $\bar{s}_{13} = 2$, $\bar{s}_{23} = 1$, $D_0/L:p_0:s_0 = 0.2:6:2$, $\bar{H}_3 = 10$, $c_3^p = 1$), after a brief "incubation" period a layer of new phase occurs on the boundary of phases 1 and 3. The boundaries of the phases 3-2 and 2-1 move according to a linear law (Figs. 3a and c). Such a situation is qualitatively close to that observable in a thin-film pair Co—Si at 500°C [17]. First Co_2Si occurs, and then CoSi, and later both silicides in the system Co—Co_2Si—CoSi—Si grow in proportion to the time. Phases 2 and 3 near the boundary are supersaturated by the element A, $c_3 \gg c_{32}^0$, $c_2 > c_{23}^0$ (Fig. 3b), which is associated with a high mass transfer coefficient $\bar{H}_3 = 10$ and a low rate of phase 2 transformation into phase 3 $M_{23}/p_0 << M_{12}/p_0$. For a smaller value $\bar{H}_3 = 6$ and the value $M_{23}/p_0 = 0.1$ supersaturation on the boundary of phases 2 and 3 diminishes and it moves more rapidly (Fig. 3c), but qualitatively the nature of the process does not change. If the rate of seed formation is significantly less than the rate of phase 3 growth because of phase 1 ($Q_{12}/p_0 = 0.05$, $M_{13}/p_0 = 2$, $M_{23}/p_0 = 1$, the rest of the parameters as before), then the new intermetallide is not formed (Fig. 4a) despite supersaturation of phase 1 (Fig. 4b). Its formation is suppressed by the rapid growth of phase 3. Motion of the 3-1 phase boundary is limited initially by redistribution of the atoms A and then by rebuilding of the crystalline 3-1 lattice (Fig. 4c). Such a case corresponds to growth of WSi_2, $MoSi_2$, $NbSi_2$ according to a linear law in the absence of the remaining equilibrium phases during silicidation of infusible metals [7]. Therefore, formation of intermetallides is governed by the relationship between the rate of seed formation of a new compound and the growth rate of one original phase because of the other. For commensurate values the phase composition of the diffusion zone corresponds, and for a low rate of seed formation does not correspond, to the equilibrium diagram.

The results of modeling the kinetics of VSi_2 growth in a thin-film diffusion pair V—Si for parameter values L = 1600 nm, $T_0 = 0.4$ h; $D_0 = 2.5 \cdot 10^{-3}$ cm²/sec, $D_0/L:p_0:s_0 = 1:1:1$ agree with the data [2] for 600°C (see Fig. 2e, curves 2 and 3).

NOTATION

J_i, diffusion flux of atoms A; n_i^0, number or crystalline lattice sites per unit volume; a, interatomic spacing; h_{cr}, critical seed thickness; x, z, dimensional and dimensionless space coordinate; t, τ, dimensional and dimensionless time; c_i, concentration of the element A; y_i, bulk fraction of the phase in a section perpendicular to the 0x axis; c_{12}^0, c_{21}^0, c_{23}^0, c_{32}^0, equilibrium concentrations; p_{ij}, rate of crystalline lattice rebuilding from the phase i to the phase j; q_{12}, q_{32}, rates of formation of seeds of phase 2 from phases 1 and 3; s_{ij}, rate of atom A transition from the phase i to the phase j; α_{ij}, contact probability for the phases i and j; $\mu_A^{(i)}$, $\mu_B^{(i)}$, chemical potentials of the elements A and B in the phase i; T, temperature; R, gas constant; L, characteristic dimension of the diffusion zone; T_0, time scale of diffusion annealing; D_0, p_0, s_0, characteristic values of the diffusion coefficient, the phase transformation and the atom transition rates through the interphasal boundaries; H_3 is the mass transfer coefficient on the surface of phase 3. Subscripts i and j are the phase numbers.

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