Modeling of Kinetics of Diffusive Phase Transformation in Binary Systems with Multiple Stoichiometric Phases

J. Svoboda, E. Gamsjäger, F.D. Fischer, and E. Kozeschnik

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The thermodynamic extremal principle is used for the treatment of the evolution of a binary system under the assumption that all phases in the system are nearly stoichiometric with no sources and sinks for vacancies in the bulk. The interfaces between the individual phases are assumed to act as ideal sources and sinks for vacancies, and to have an infinite mobility. Furthermore, it is assumed that several phases are nucleated in the contact plane of the diffusion couple at the beginning of the computer experiment. Then, it is shown that the number of newly nucleated phases determines the maximum number of polyfurcations (i.e., branching of a single configuration into several distinct configurations) of the initial contact (Kirkendall) plane. The model is demonstrated on a hypothetical binary system with four stoichiometric phases. The inverse problem, namely, the determination of the tracer diffusion coefficients in newly nucleated phases from the thicknesses of new phases and the positions of polyfurcated Kirkendall planes, is treated too.

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1. Introduction

Kirkendall experiments seem to be very significant for understanding the mechanism of diffusion; see the report on Kirkendall's seminal work, now more than 50 years later, by Nakajima.[1] Such experiments have been performed also on systems forming manifold, nearly stoichiometric phases with the surprising result that the original single Kirkendall plane splits into several planes. This effect is called a "polyfurcation" of the Kirkendall plane. The Kirkendall plane is a plane in the diffusion zone that is delineated by inert markers. The initial position of this plane is located at the contact plane of the diffusion couple. Paul et al.[2] have

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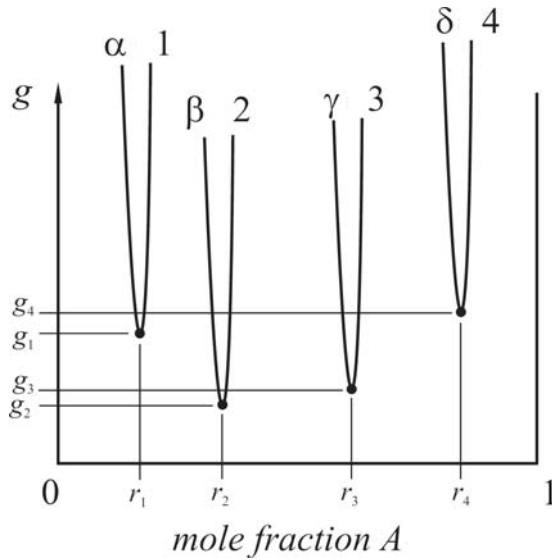
treated the problem by a physicochemical approach, based on the theory of reactive diffusion,[3-8] for one, two, and three newly nucleated phases. This approach utilizes the kinetic parameters in the newly nucleated phases like the integrated interdiffusion coefficient and the ratio of intrinsic fluxes.

It is necessary to note that the theory of reactive diffusion more or less tacitly assumes ideal sources and sinks for vacancies at the interfaces as well as at the infinite interface mobility. This seems to be a realistic assumption for incoherent interfaces. Moreover, the analysis[2] assumes inactive sources and sinks for vacancies in the bulk of the newly nucleated phases and their stoichiometricity.

The aim of this article is to present an alternative model to that of Paul et al.[2] for the diffusive phase transformation in binary systems with multiple stoichiometric phases. This new model is based on a purely thermodynamic treatment. It is more general, allows for an arbitrary number of newly nucleated phases, and utilizes thermodynamic data as the tracer diffusion coefficients, molar Gibbs energies, and molar volumes in the stoichiometric phases. It is also shown that the present treatment enables the solution of the inverse problem, namely, the determination of tracer diffusion coefficients of components in the newly nucleated phases. The model is demonstrated on a hypothetical binary system forming four nearly stoichiometric phases. The behavior of the Kirkendall plane is calculated with dependence on the values of the tracer diffusion coefficients in the newly nucleated phases.

2. The Model

Let us assume a binary system of components, A and B, forming n stable stoichiometric phases $A_{r_i}B_{1-r_i}$, with r_i being the mole fraction of the component A in the phase i, $0 \le r_i \le 1$, $i = 1, \ldots, n$, and r_i increasing with i (Fig. 1).
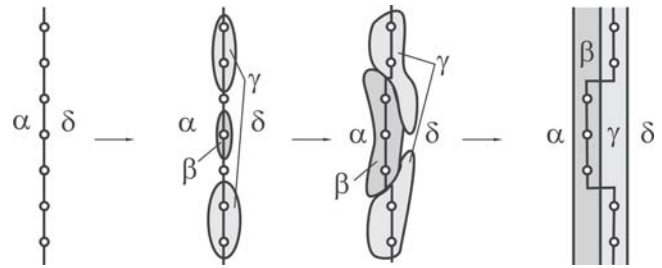
Fig. 1 Gibbs energy diagram for binary *AB* system with four stoichiometric phases

Fig. 2 Schematic plot of nucleation stages at the interface with deposited markers

Fig. 3 Definition of the kinetic parameters and of the system geometry

The molar Gibbs energies of the phases (in their minima) are denoted by g_i, $i = 1, \ldots, n$. If the partial molar volumes of components A and B in individual phases i, Ω_{Ai}, and Ω_{Bi} are known, the molar volume Ω_i of the phase i is given by:

$$\Omega_i = r_i \Omega_{Ai} + (1 - r_i)\Omega_{Bi} \qquad \text{(Eq 1)}$$

As a starting configuration, the authors assume a diffusion couple of unit cross section consisting of the phases A_{r_1} B_{1-r_1} at the left side and $A_{r_n} B_{1-r_n}$ at the right side of the interface with inert markers on it. It is assumed that during a negligible time interval very small nuclei of all other phases are built at the original interface and they grow into a sequence of phases, as schematically depicted in Fig. 2. All newly nucleated phases contain some of the markers. All phases are considered as single crystals without defects available for sources and sinks for vacancies in the bulk. The assumption of stoichiometricity guarantees a constant chemical composition and a constant molar volume in each phase. Because no sources and sinks for vacancies are assumed in the bulk of each phase, this implies that both diffusive fluxes, j_{Ai} and j_{Bi}, as well as the material velocity must be constant in each region occupied by an individual phase. The reason for the existence of fluxes is the fact that a very small alteration of the mole fraction in each phase causes large changes in the chemical potentials of both components. The interfaces between the phases are considered as incoherent, being freely mobile and acting as ideal sources and sinks for vacancies.

Let us analyze the behavior of an interface between the phases i and $i + 1$ where the diffusive fluxes j_{Ai}, j_{Bi} and j_{Ai+1}, j_{Bi+1} occur. Figure 3 shows an advanced stage of the system. The balance between the fluxes at each interface is coupled with both the interface migration and the thickening or thinning (i.e., deposition or removal of new atomic layers) at the interface. The second effect causes a motion of the lattices of the individual phases relative to each other.
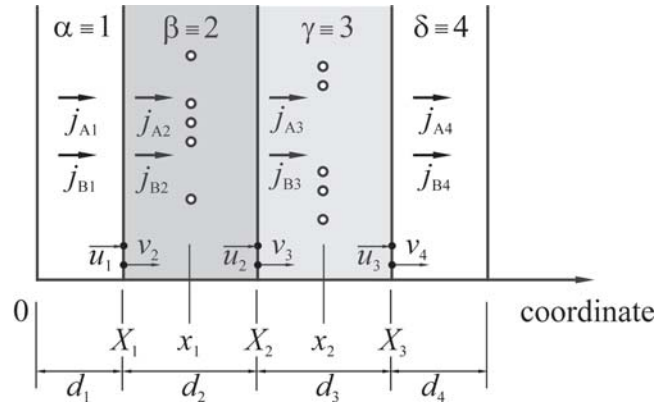
Let u_i be the velocity of the interface between the phases i and $i + 1$ relative to the lattice of the phase i, and let v_{i+1} be the velocity of the interface relative to the lattice of the phase $i + 1$. The mass conservation for both the A and B components leads to the equations (see section 3 in the article by Fischer and Simha[9]):

$$\frac{u_i r_i}{\Omega_i} - \frac{v_{i+1} r_{i+1}}{\Omega_{i+1}} = j_{Ai} - j_{Ai+1}, \quad i = 1, \ldots, n - 1 \qquad \text{(Eq 2)}$$

$$\frac{u_i(1 - r_i)}{\Omega_i} - \frac{v_{i+1}(1 - r_{i+1})}{\Omega_{i+1}} = j_{Bi} - j_{Bi+1}, \quad i = 1, \ldots, n - 1$$
$$\text{(Eq 3)}$$

The velocities u_i and v_i can be calculated from Eq 2 and 3 as:

$$u_i = \frac{\Omega_i}{r_i - r_{i+1}} [(j_{Ai} - j_{Ai+1})(1 - r_{i+1}) - (j_{Bi} - j_{Bi+1})r_{i+1}]$$
$$i = 1, \ldots, n - 1 \qquad \text{(Eq 4)}$$

$$v_{i+1} = \frac{\Omega_{i+1}}{r_i - r_{i+1}} [(j_{Ai} - j_{Ai+1})(1 - r_i) - (j_{Bi} - j_{Bi+1})r_i]$$
$$i = 1, \ldots, n - 1 \qquad \text{(Eq 5)}$$

We consider a closed system with no deposition of matter at the surface of the system yielding the boundary conditions:

$$j_{A1} = 0, \; j_{B1} = 0, \; j_{An} = 0, \; j_{Bn} = 0, \; v_1 = 0 \text{ and } u_n = 0 \quad \text{(Eq 6)}$$

Then the rate of change of the thickness $\dot{d}_i$ of the region of phase i (Fig. 3) is given by:

$$\dot{d}_i = u_i - v_i, \qquad i = 1, \ldots, n \tag{Eq 7}$$

With Eq 4 to 6, $\dot{d}_i$ can be expressed by means of the independent fluxes j_{Ai} and j_{Bi}, $i = 2, \ldots, n - 1$.

If it is assumed that the left end of the specimen is fixed and situated in the origin of a spatially fixed coordinate system, one can determine the velocity w_i of the lattice of the phase i from:

$$w_{i+1} = w_i + u_i - v_{i+1}, \qquad i = 1, \ldots, n - 1 \tag{Eq 8}$$

and with $w_1 = 0$ as:

$$w_{i+1} = \sum_{k=1}^{i}(u_k - v_{k+1}), \qquad i = 1, \ldots, n - 1 \tag{Eq 9}$$

Using Eq 1, 4, and 5 in Eq 9, one obtains, after some algebra:

$$w_i = -\Omega_{Ai} j_{Ai} - \Omega_{Bi} j_{Bi}, \qquad i = 2, \ldots, n - 1 \tag{Eq 10}$$

which is a commonly used equation. If, however, the partial molar volumes of components A and B in the individual phases i, Ω_{Ai}, and Ω_{Bi} are not known explicitly (which may be the case for stoichiometric phases) and only the molar volumes Ω_i are known, these quantities are sufficient to determine the velocity w_i by using Eq 4 and 5 in Eq 9 by a more complicated expression.

The velocity V_i of the interface i between the phases i and $i + 1$ can be calculated from:

$$V_i = \sum_{k=1}^{i} \dot{d}_k = \sum_{k=1}^{i}(u_k - v_k), \qquad i = 1, \ldots, n - 1 \tag{Eq 11}$$

The position X_i of the interface i at time t is given by the integration of Eq 11 with respect to time as:

$$X_i = X_{0i} + \int_0^t V_i dt, \qquad i = 1, \ldots, n - 1 \tag{Eq 12}$$

where X_{0i} is the position of the interface at time $t = 0$.

In some experimental studies of the Kirkendall effect in multiphase systems,[10,11] the polyfurcation of the Kirkendall plane is evident. After a certain time of annealing, the inert markers, which were originally positioned at the contact plane of the two alloys welded together, are found at different positions in the new phases nucleated at the contact plane and grown during annealing. Thus, one may assume that a new phase i nucleates at the contact region, and its lattice carries some of the markers with the velocity w_i. This is given by Eq 9 or 10. However, one cannot exclude that a specific interface crosses the Kirkendall plane by migration, and then the Kirkendall plane with markers that was originally positioned in a newly nucleated phase i is later embedded in another phase or remains fixed at the migrating interface. This makes the treatment of the calculation of the positions of the multiple Kirkendall planes slightly more complicated. The authors do not assume any drag of the markers by moving with an interface or any pinning effect.

The actual positions X_i of the interfaces i are given by Eq 12, which can always be determined independently of the positions of the Kirkendall planes. Let us assume that at time $t = 0$ the position x_{0k} of the Kirkendall plane k and its actual correspondence to a phase l are known. Then, the actual velocity of the Kirkendall plane k is w_i, and the position of the Kirkendall plane k at time t is given by:

$$x_k = x_{0k} + \int_0^t w_l dt \tag{Eq 13}$$

The corresponding phase index l must be determined at any time from the actual positions of the interfaces X_i and the actual position of the Kirkendall plane x_k. In the multiphase Kirkendall experiments,[2] starting with a diffusion couple, all of the positions x_{0k} and X_{0i} coincide and are equal to the original position of the contact plane with markers. After the two parts of the diffusion couple are brought into contact and heated, nucleation of the new phases begins. During this process, it is assumed that each individual marker becomes captured in the bulk of one of the new phases. This scenario of nucleation is schematically depicted in Fig. 2. This situation represents the starting condition in the modeling with an already split Kirkendall plane and no singularity.

The kinetics of the system is now unambiguously determined by the independent diffusive fluxes j_{Ai} and j_{Bi}, with $i = 2, \ldots, n - 1$ being the free kinetic parameters of the system. The actual values of the fluxes j_{Ai} and j_{Bi}, $i = 2, \ldots, n - 1$, can be determined by the application of the thermodynamic extremal principle, which has been worked out in detail by Svoboda et al.[12] and is based on Onsager's work on the maximum dissipation rate in a diffusive process.[13]

2.1 Total Gibbs Energy and Its Rate of Change

The total Gibbs energy G of the system is given by

$$G = \sum_{i=1}^{n} \frac{g_i}{\Omega_i} d_i \tag{Eq 14}$$

The molar Gibbs energies g_i and the molar volumes Ω_i are supposed to be known and fixed quantities at a given temperature. Then, the rate of change of the total Gibbs energy can be calculated by using Eq 4 to 7 as:

$$\dot{G} = \sum_{i=1}^{n} g_i \left\{ (j_{Ai} - j_{Ai+1}) \frac{1 - r_{i+1}}{r_i - r_{i+1}} - (j_{Bi} - j_{Bi+1}) \frac{r_{i+1}}{r_i - r_{i+1}} \right.$$
$$\left. - (j_{Ai-1} - j_{Ai}) \frac{1 - r_{i-1}}{r_{i-1} - r_i} + (j_{Bi-1} - j_{Bi}) \frac{r_{i-1}}{r_{i-1} - r_i} \right\} \tag{Eq 15}$$

The partial derivatives with respect to diffusive fluxes are given by:

$$\frac{\partial \dot{G}}{\partial j_{Ai}} = g_i \left(\frac{1 - r_{i+1}}{r_i - r_{i+1}} + \frac{1 - r_{i-1}}{r_{i-1} - r_i} \right) - g_{i-1} \frac{\Omega_{i-1}}{\Omega_i} \frac{1 - r_i}{r_{i-1} - r_i}$$

$$- g_{i+1} \frac{\Omega_{i+1}}{\Omega_i} \frac{1 - r_i}{r_i - r_{i+1}} = -F_{Ai}, \qquad i = 2, \ldots, n-1$$

(Eq 16)

$$\frac{\partial \dot{G}}{\partial j_{Bi}} = -g_i \left(\frac{r_{i+1}}{r_i - r_{i+1}} + \frac{r_{i-1}}{r_{i-1} - r_i} \right) + g_{i-1} \frac{\Omega_{i-1}}{\Omega_i} \frac{r_i}{r_{i-1} - r_i}$$

$$+ g_{i+1} \frac{\Omega_{i+1}}{\Omega_i} \frac{r_i}{r_i - r_{i+1}} = -F_{Bi}, \qquad i = 2, \ldots, n-1$$

(Eq 17)

The quantities F_{Ai} and F_{Bi} can be understood as the driving forces at a given temperature conjugated to the fluxes j_{Ai} and j_{Bi}.

2.2 Total Gibbs Energy Dissipation

The Gibbs energy is assumed to dissipate only by bulk diffusion. The migration of interfaces and thickening or thinning are considered to not be connected with dissipation. Then the total dissipation in the system is given by Svoboda et al.[12] as:

$$Q = \sum_{i=2}^{n-1} R_g T \Omega_i d_i \left(\frac{j_{Ai}^2}{r_i D_{Ai}^*} + \frac{j_{Bi}^2}{(1 - r_i) D_{Bi}^*} \right)$$

(Eq 18)

where R_g is the gas constant, T is the absolute temperature, and D_{Ai}^* and D_{Bi}^* are the tracer diffusion coefficients of components A and B, respectively, in the phase i.

The partial derivatives of Q with respect to the independent fluxes are given by:

$$\frac{\partial Q}{\partial j_{Ai}} = \frac{2 R_g T \Omega_i d_i j_{Ai}}{r_i D_{Ai}^*}, \qquad i = 2, \ldots, n-1$$

(Eq 19)

$$\frac{\partial Q}{\partial j_{Bi}} = \frac{2 R_g T \Omega_i d_i j_{Bi}}{(1 - r_i) D_{Bi}^*}, \qquad i = 2, \ldots, n-1$$

(Eq 20)

2.3 Kinetic Equations

The independent diffusive fluxes j_{Ai} and j_{Bi}, $i = 2, \ldots, n-1$ can be determined by application of the thermodynamic extremal principle,[12] which leads to a set of linear algebraic equations in the fluxes:

$$\frac{\partial \dot{G}}{\partial j_{Ai}} = \frac{1}{2} \frac{\partial Q}{\partial j_{Ai}} \quad \text{and} \quad -\frac{\partial \dot{G}}{\partial j_{Bi}} = \frac{1}{2} \frac{\partial Q}{\partial j_{Bi}}, \quad i = 2, \ldots, n-1 \quad \text{(Eq 21)}$$

The matrix of the set of linear equations is diagonal, and the solution of the problem can be performed easily as:

$$j_{Ai} = F_{Ai} \frac{r_i D_{Ai}^*}{R_g T \Omega_i d_i} \text{ and } j_{Bi} = F_{Bi} \frac{(1 - r_i) D_{Bi}^*}{R_g T \Omega_i d_i}, \quad i = 2, \ldots, n-1$$

(Eq 22)

If one supposes that the values of d_i, $i = 2, \ldots, n-1$, are practically zero at the time $t = 0$, then the integration of the system of differential equations in Eq 7 yields, after the insertion of Eq 4, 5, and 22, a solution of the so-called parabolic type:

$$d_i = \tilde{d}_i \sqrt{t} \text{ and } \dot{d}_i = \tilde{d}_i / (2\sqrt{t}) \rightarrow \dot{d}_i = d_i / (2t)$$

$$i = 2, \ldots, n-1$$

(Eq 23)

with $\tilde{d}_i$ being parameters independent of time. Putting Eq 4, 5, 7, 22, and 23 together, one can eliminate the time, and the problem is reduced to a set of nonlinear equations for $\tilde{d}_i$, $i = 2, \ldots, n-1$. Then, it is easy to also show that all other kinetic parameters j_{Ai}, j_{Bi}, u_i, v_i, w_i, and V_i are proportional to $1/\sqrt{t}$. Furthermore, the changes of the position of each interface $X_i - X_{0i}$, $i = 1, \ldots, n-1$, (Eq 12) are proportional to $\sqrt{t}$, and this holds also for the changes of the positions of the Kirkendall planes $x_k - x_{0k}$, if the Kirkendall plane k remains always in the same phase. Then the velocities V_i are given by:

$$V_i = (X_i - X_{0i}) / (2t), \qquad i = 1, \ldots, n-1$$

(Eq 24)

Moreover, if the Kirkendall plane k always remains in the same phase i, then the velocity w_i can be calculated as:

$$w_i = (x_k - x_{0k}) / (2t)$$

(Eq 25)

2.4 Inverse Problem: Determination of Diffusion Coefficients $D_{Ai}^\star$ and $D_{Bi}^\star$

Let us assume that all values of g_i, r_i, and Ω_i, $i = 1, \ldots, n$ are available for the n-phase system, and the tracer diffusion coefficients D_{Ai}^* and D_{Bi}^*, $i = 2, \ldots, n-1$, (altogether $2n - 4$ diffusion coefficients) have to be determined from one Kirkendall experiment. In the ideal case, if Kirkendall planes always remain in the same nucleated phase, one has at disposal $2n - 3$ independent kinetic parameters (e.g., V_i, $i = 1, \ldots, n-1$, and w_i, $i = 2, \ldots, n-1$), which are given by Eq 24 and 25. Thus, if no or only one of the Kirkendall planes leaves its original phase, the geometric data measured on the specimen are still sufficient for the determination of the tracer diffusion coefficients D_{Ai}^* and D_{Bi}^*, $i = 2, \ldots, n-1$. By using $2n - 4$ independent kinetic parameters from the sets d_i, $i = 2, \ldots, n-1$, V_i, $i = 1, \ldots, n-1$ and w_i, $i = 2, \ldots, n-1$, given by Eq 23 to 25, the diffusive fluxes j_{Ai} and j_{Bi}, $i = 2, \ldots, n-1$, can be calculated by means of Eq 4 to 7 and 9. If d_i, $i = 2, \ldots, n-1$ and w_i, $i = 2, \ldots, n-1$, are chosen as the independent kinetic parameters, then the solution of the set of $4n$ linear equations $\mathbf{H} \cdot \mathbf{y} = \mathbf{z}$ provides the diffusive fluxes j_{Ai} and j_{Bi}, $i = 2, \ldots, n-1$. The vector $\mathbf{y}$ of unknowns is given by:

$$y_i = j_{Ai}, \; y_{n+i} = j_{Bi}, \; y_{2n+i} = u_i, \; y_{3n+i} = v_i, \quad i = 1, \ldots, n$$

(Eq 26)

The matrix $\mathbf{H}$ and the right-hand side vector $\mathbf{z}$ are given in the Appendix.
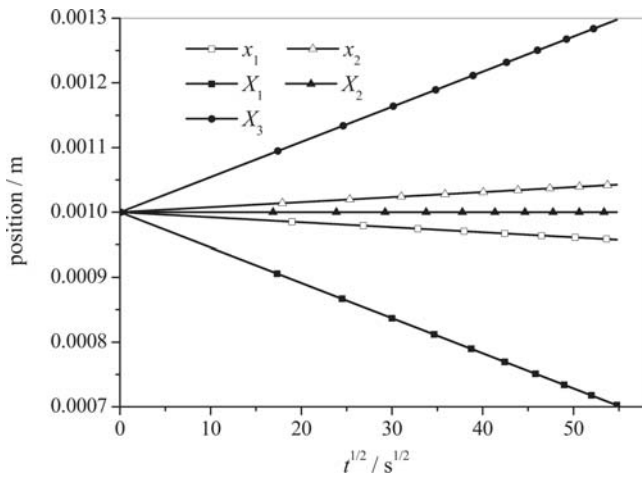
Fig. 4 Evolution of the positions of the interfaces and of the Kirkendall planes for $D_A^0 = (10^{-5}, 10^{-5}, 2 \cdot 10^{-5}, 10^{-5})$ and $D_B^0 = (10^{-5}, 2 \cdot 10^{-5}, 10^{-5}, 10^{-5})$

Fig. 5 Evolution of the positions of the interfaces and of the Kirkendall planes for $D_A^0 = (10^{-5}, 10^{-5}, 3 \cdot 10^{-5}, 10^{-5})$ and $D_B^0 = (10^{-5}, 2 \cdot 10^{-5}, 10^{-5}, 10^{-5})$

An analogous set of equations can also be obtained if one of the w_i value is replaced by one of the v_i values.

After determination of the diffusive fluxes j_{Ai} and j_{Bi}, $i = 2, \ldots, n - 1$, Eq 22 together with Eq 16 and 17 can be used for the evaluation of the tracer diffusion coefficients D_{Ai}^* and D_{Bi}^*, $i = 2, \ldots, n - 1$. The whole procedure outlined in this paragraph is applied to the results of the simulations presented in the following paragraph and leads to a perfect reproduction of the diffusion coefficients.

3. Results of Simulations and Discussion

To demonstrate the model, $n = 4$ is chosen, and Eq 12 and 13 are integrated in time numerically. The molar volumes of all phases are chosen to be the same, namely, $\Omega_i = 7 \times 10^{-6}$ m^3 mol^{-1}. The activation energies of all tracer diffusion coefficients are $E_{Ai} = E_{Bi} = 1.5 \times 10^5$ Jmol^{-1}, $(D_{ki}^* = D_{ki}^0 \exp[-E_{ki}/(R_g T)]$, $k = A,B$. The temperature T is chosen as $T = 1000$ K. The vector of the values of g_i is chosen as $g = (10^5,0,0,10^5)$Jmol^{-1}, the vector of the values of r_i as $r = (0.2,0.4,0.6,0.8)$, and the initial values of d_i as $d_0 = (10^{-3},10^{-8},10^{-8},10^{-3})$m. The initial positions of the Kirkendall planes are chosen in the center of phases 2 and 3. Then the only parameters kept free are the vectors D_A^0 and D_B^0 of the preexponential factors D_{Ai}^0, and D_{Bi}^0 of the tracer diffusion coefficients.

The first simulation is performed for a "symmetric" case, $D_A^0 = (10^{-5}, 10^{-5}, 2 \cdot 10^{-5}, 10^{-5})$ and $D_B^0 = (10^{-5}, 2 \cdot 10^{-5}, 10^{-5}, 10^{-5})$, which is depicted in Fig. 4. From Fig. 4 as well as from the following figures it is evident that the parabolic law holds. The selected diffusion coefficients ensure the deposition of atoms at the central interface, and, thus, symmetric bifurcation of the Kirkendall plane occurs. If the symmetry of the problem is destroyed by choosing $D_A^0 = (10^{-5}, 10^{-5}, 3 \cdot 10^{-5}, 10^{-5})$ and $D_B^0 = (10^{-5}, 2 \cdot 10^{-5}, 10^{-5}, 10^{-5})$ (by increasing the value of D_{A3}^0), the results remain qualitatively the same (compare Fig. 4 and 5). A further increase of D_{A3}^0 ($D_A^0 = (10^{-5}, 10^{-5}, 5 \cdot 10^{-5}, 10^{-5})$ and
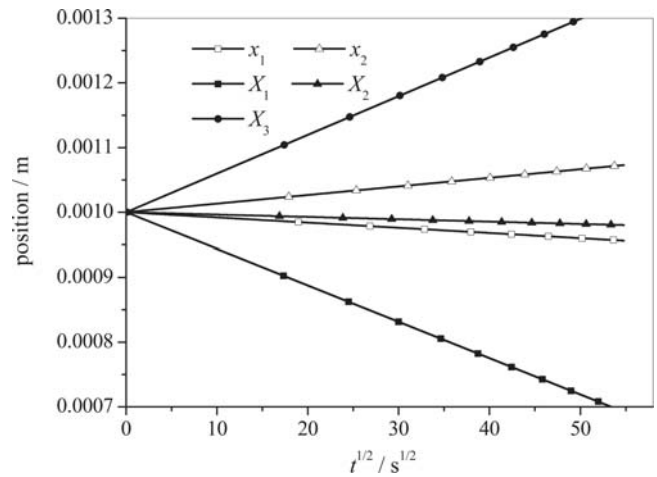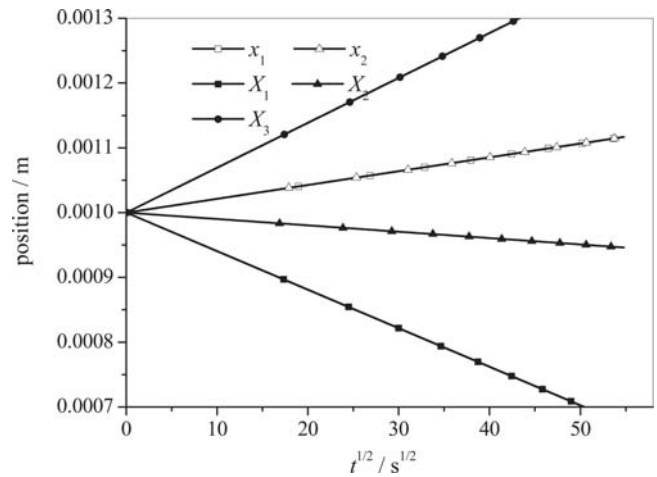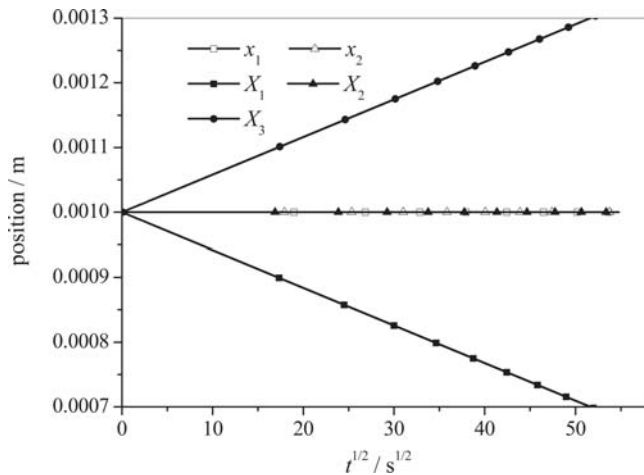

Fig. 6 Evolution of the positions of the interfaces and of the Kirkendall planes for $D_A^0 = (10^{-5}, 10^{-5}, 5 \cdot 10^{-5}, 10^{-5})$ and $D_B^0 = (10^{-5}, 2 \cdot 10^{-5}, 10^{-5}, 10^{-5})$

$D_B^0 = (10^{-5}, 2 \cdot 10^{-5}, 10^{-5}, 10^{-5})$, however, causes the Kirkendall plane, originally positioned in phase 3, to be very quickly absorbed by phase 2 and both, practically unseparated Kirkendall planes remain in the bulk of phase 2 (Fig. 6).

For the values of vectors $D_A^0 = (10^{-5}, 2 \cdot 10^{-5}, 10^{-5}, 10^{-5})$ and $D_B^0 = (10^{-5}, 10^{-5}, 2 \cdot 10^{-5}, 10^{-5})$, there is a collection of atoms at the central interface, and both, originally slightly separated Kirkendall planes get together and are fixed at the central interface (Fig. 7). The situation remains qualitatively unchanged, if D_{A2}^0 is increased (Fig. 8).

From the simulations, it is evident that the number of Kirkendall planes cannot increase during the computer experiment. This implies that if no markers are present in one of the newly nucleated phases at the beginning of the simulation, then the phase remains free of markers during the whole simulation unless a distinct Kirkendall plane moves into the phase from another phase. A new phase can nucle-

Fig. 7 Evolution of the positions of the interfaces and of the Kirkendall planes for $D_A^0 = (10^{-5}, 2 \cdot 10^{-5}, 10^{-5}, 10^{-5})$ and $D_B^0 = (10^{-5}, 10^{-5}, 2 \cdot 10^{-5}, 10^{-5})$
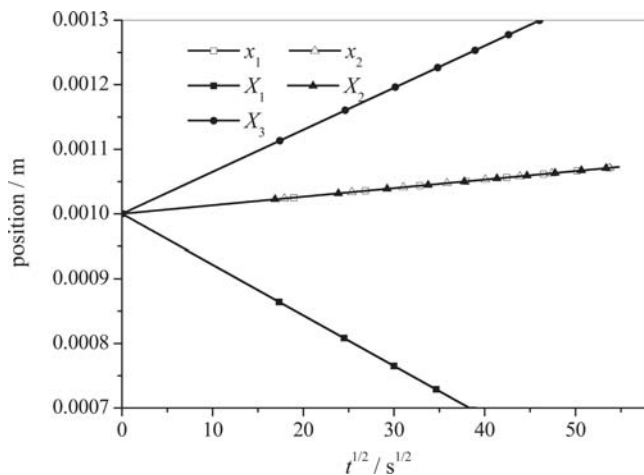
Fig. 8 Evolution of the positions of the interfaces and of the Kirkendall planes for $D_A^0 = (10^{-5}, 5 \cdot 10^{-5}, 10^{-5}, 10^{-5})$ and $D_B^0 = (10^{-5}, 10^{-5}, 2 \cdot 10^{-5}, 10^{-5})$

ate without markers if it nucleates a little bit later at an already newly created marker-free interface. In other words, splitting of the Kirkendall plane does not occur unless the nucleation process of the new phases ensures an initial redistribution of the markers into at least two new phases (e.g., according to the scenario depicted in Fig. 2). Such a nucleation process is obviously tacitly assumed also in the model by Paul et al.[2]: the nucleation process automatically redistributes the markers into all newly nucleated phases, and the phases with no markers are those that lose the markers during their growth. On this point, the model of Paul et al.[2] and the present model are in accordance.

The mechanism of splitting of the Kirkendall plane that is depicted in Fig. 2 is supported by the extensive work by Loo,[14] who used thin tungsten wires instead of thoria particles as markers. The wires were ruptured, and their fragments were present in all newly nucleated phases after the annealing. Moreover, Loo[14] also used square microinden-

tations at the specimen surface and observed their splitting in two halves accompanied by different shifts of the halves. The behavior of the microindentations can also be explained by the present model.

4. Summary

A new model for the phase transformations in binary systems forming stoichiometric phases is developed by means of the thermodynamic extremal principle. No sources and sinks for vacancies are assumed in the bulk of the phases. The interfaces are assumed to possess an infinite mobility and to act as ideal sources and sinks for vacancies. The model predicts the time evolution of positions of the interfaces as well as of the polyfurcated Kirkendall plane. The parabolic law for the positions of interfaces and Kirkendall planes is confirmed by the model. The problem formulation can be inverted, and the tracer diffusion coefficients of both components in the newly nucleated phases can be calculated from the positions of interfaces and Kirkendall planes. The behavior of the Kirkendall planes depending of the tracer diffusion coefficients of both components in the newly nucleated phases is simulated and discussed. It is also shown that the redistribution of the markers into newly nucleated phases at the original interface of the diffusive couple (e.g., according to the scenario depicted in Fig. 2) is the necessary condition for the polyfurcation of the Kirkendall plane.

Acknowledgments

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Appendix

In the case, that the values of the independent kinetic parameters $\dot{d}_i$, $i = 2, \ldots, n-1$, and w_i, $i = 2, \ldots, n-1$, are known, linear relations for the kinetic parameters j_{Ai}, j_{Bi}, u_i and v_i, $i = 1, \ldots, n$, can be obtained by considering the mass balance in the system expressed by Eq 4 to 9. A set of linear equations can be written as

$$\mathbf{H}\mathbf{y} = \mathbf{z} \qquad \text{(Eq A1)}$$

with the coefficient matrix $\mathbf{H}$ of the rank $4n$ and the solution vector $\mathbf{y}^{\mathbf{T}} = (j_{Ai}, j_{Bi}, u_i, v_i)$ consisting of $4n$ unknowns. The components of the coefficient matrix $\mathbf{H}$ and that of the right-hand side vector $\mathbf{z}$ write as following:

The first $n - 1$ equations follow from Eq 4 as:

$$H_{i,i} = \frac{\Omega_i \cdot (1 - r_{i+1})}{r_i - r_{i+1}}, \qquad H_{i,i+1} = -H_{i,i} \qquad H_{i,n+i} = -\frac{\Omega_i \cdot r_{i+1}}{r_i - r_{i+1}}$$

$$H_{i,n+i+1} = -H_{i,n+i} \qquad H_{i,2n+i} = -1 \qquad z_i = 0 \qquad i = 1, \ldots, n-1$$

$$\text{(Eq A2)}$$

As the n-th and $(n+1)$-th equations the boundary conditions $u_n = 0$ and $v_1 = 0$ (Eq 6) are chosen yielding

$$H_{n,3n} = 1, \qquad z_n = 0 \quad \text{and} \quad H_{n+1,3n+1} = 1 \qquad z_{n+1} = 0$$

$$\text{(Eq A3)}$$

Next $n - 1$ equations follow from Eq 5 as:

$$H_{n+i+1,i} = \frac{\Omega_{i+1} \cdot (1 - r_i)}{r_i - r_{i+1}}, \qquad H_{n+i+1,i+1} = -H_{n+i+1,i} \qquad H_{n+i+1,n+i}$$

$$= -\frac{\Omega_{i+1} \cdot r_i}{r_i - r_{i+1}}, \qquad H_{n+i+1,n+i+1} = -H_{n+i+1,n+i} \qquad H_{n+i+1,3n+i+1}$$

$$= -1, z_{n+i+1} = 0, \quad i = 1, \ldots, n-1 \qquad \text{(Eq A4)}$$

The boundary condition $j_{B1} = 0$ from Eq 6 represents the $(2n + 1)$-th equation as:

$$H_{2n+1,n+1} = 1, \qquad z_{2n+1} = 0 \qquad \text{(Eq A5)}$$

Equation 7 provide the next n-2 equations with the labels ranging from $2n + 2$ to $3n - 1$ as:

$$H_{2n+i,2n+i} = 1, \qquad H_{2n+i,3n+i} = -1 \qquad z_{2n+i} = \dot{d}_i \qquad i = 2, \ldots, n-1$$

$$\text{(Eq A6)}$$

The $3n$-th equation is given by the boundary condition $j_{A1} = 0$, (Eq 6), as:

$$H_{3n,1} = 1, \qquad z_{3n} = 0 \qquad \text{(Eq A7)}$$

The next n-2 linear relations $3n + 1$ to $4n - 2$ follow from Eq 9 as:

$$H_{3n+i,2n+k} = 1, \qquad H_{3n+i,3n+k+1} = -1 \quad \text{and} \quad z_{3n+i} = w_{i+1}$$

$$i = 1, \ldots, n-2 \qquad k = 1, \ldots, i \qquad \text{(Eq A8)}$$

The last two equations with the labels $4n - 1$ and $4n$ represent the boundary conditions $j_{An} = 0$ and $j_{Bn} = 0$, (Eq 6), yielding:

$$H_{4n-1,n} = 1, \qquad z_{4n-1} = 0 \quad \text{and} \quad H_{4n,2n} = 1 \qquad z_{4n} = 0$$

$$\text{(Eq A9)}$$