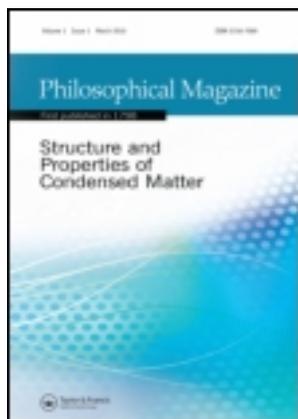


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Bi-velocity model of mass transport in two-phase zone of ternary system

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Bi-velocity model of mass transport in two-phase zone of ternary system

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Bi-velocity (Darken) method, which includes material drift and diffusion fluxes, is for the first time applied to describe mass transport in multiphase materials. The respective model is formulated in details and then applied for a ternary diffusion couple in which a two-phase zone can grow during isothermal diffusion. Thanks to the use of a phase-field order parameter, identified here with volume fraction of a chosen phase, the mass transport throughout both phases within a two-phase zone can be considered. The model allows smooth crossing of the type 1 boundary, which makes the mass transport equations valid in both single- and two-phase regions. The solution obtained for 1D geometry provides: (1) a diffusion path in the concentration triangle, (2) element-concentration profiles, (3) volume fractions of the phases in the two-phase zone and (4) drift-velocity distribution along x axis parallel to the mass transport. As an example, the interdiffusion in the $(\alpha + \beta)|(\alpha + \beta)$ diffusion couple of Type 0 boundary is modelled. The zigzag diffusion path is predicted and the profiles of the element concentrations are simulated. For the first time, the drift velocity for the diffusion in two-phase system is determined and correlated with the changes in volume fractions of the phases.

Keywords: bi-velocity method; multiphase system; diffusion path; interdiffusion; drift velocity

1. Introduction

Interdiffusion in a multicomponent-multiphase material, with associated evolving morphology, presents a considerable problem in many applications, like coatings, brazing, diffusion bonding, soldering and oxidation – just to name a few. In binary systems, a formation of sequential layers of solid solutions and intermediate phases by isothermal–isobaric diffusion is predicted. This is in agreement with Gibbs’ phase rule which provides one degree of freedom for single stable phase and zero degrees of freedom at the two-phase isothermal equilibrium. Thus, when the two-component diffusion couple, type $\alpha|\beta$, $\alpha|(\alpha + \beta)$ or $(\alpha + \beta)|(\alpha + \beta)$, is considered, the following can take place:

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- (1) The sequential layers of single-phase solid solutions and intermediate phases can grow;
- (2) In $\alpha|(\alpha + \beta)$ system, as long as α single phase is not saturated the two-phase zone may dissolve. A jump in the composition at the $\alpha|(\alpha + \beta)$ interphase boundary occurs.

In ternary systems, the situation is more complex. There is one degree of freedom in the two phase region (when $T, p = \text{const}$) and chemical potential gradients are possible. The diffusion forced by chemical potential gradients can lead to the formation of the spatial two-phase zone of complex morphology. A type of the final morphology depends on the initial conditions, that is, terminal compositions of the diffusion couple and diffusivities of the components. For the $\alpha|\beta$ diffusion couple, possible consequences of the mass transport include [1]:

- (1) Migration of the $\alpha|\beta$ interphase boundary in either direction and a jump in the concentration at it;
- (2) Growth of the two-phase zone, $(\alpha + \beta)$, and vanishing of the $\alpha|\beta$ interphase boundary, with or without jump in volume fractions of the phases;
- (3) Formation of the precipitate zone and the interphase boundary migration;
- (4) Growth of sequential single-phase and two-phase layers of various morphologies.

Note that three-phase zones cannot grow in the ternary system by isothermal diffusion (zero degrees of freedom). If the three-phase sample was coupled with unsaturated α -, β - or $(\alpha + \beta)$ - phase material then one of the phases would dissolve.

The diffusion effects in the ternary system can be graphically represented at the concentration triangle (precisely at the isothermal section of the equilibrium phase diagram) as a diffusion path. It is a curve which connects terminal compositions of the diffusion couple and traces the changes in average composition of the diffusion zone perpendicular to the initial interphase boundary. The diffusion path can go across single- and two-phase regions (just as through the three-phase region) in the ternary diagram but not all phases which stability is predicted by the phase diagram can grow in real space (in the specimen). In the two-phase region, the direction of the diffusion path with respect to the conodes is critical. When the diffusion path enters the two-phase field at the ends of the same conode, the two-phase zone does not grow. In the spatial region, the interphase boundary between the two phases at the equilibrium (of the compositions indicated by the conode ends) occurs. When the diffusion path crosses the conodes, the two-phase zone can grow. The points of the intersection of the diffusion path with the phase boundaries in the phase diagram serve as a basis to identify the sequential single- and two-phase layers present in the diffusion zone.

The diffusion path is very useful in the predicting and explaining morphology of the diffusion zone but it says nothing about the thicknesses of the sequential layers. It is often time invariant which means that its shape does not change with processing time, on condition the terminal concentrations are constant. In order to predict the thickness of the sequential layers in the real space, one has to compute the element distribution profiles in the spatial diffusion region and compare them with the diffusion path shape.

All this means that the studies on the diffusion in ternary (and generally in multi-phase) systems, and in particular the diffusion throughout the two phase zone,

Table 1. The progress and key differences between method presented in this work and previous approaches.

	Darken 1948	1992–2000 Danielewski, Holly et al	2008-Danielewski and Wierzba	This work
Number of components	$r=2$	Nonlimited	Nonlimited	$r=3$
Number of phases	One	One	One	Two phases and two-phase zone
Molar volumes	Equal and constant: $\Omega = \Omega_1 = \Omega_2 = \text{const}$	Equal and constant: $\Omega = \Omega_1 = \Omega_2 = \dots = \Omega_r = \text{const}$	Differ and constant: $\Omega(N_1, N_2, \dots, N_{r-1}) \neq \text{const}$	
Equation of state	$\Omega = 1/c = \text{const}$	$\Omega = 1/c = \text{const}$	$\text{div}(\sum_i J_i^d) = \text{div}(\sum_i \Omega_i J_i) = 0$	
Diffusivities	Constant & thermodynamic term	Constant	Concentration dependent	
Constitutive flux formula:	Fick: $J_i^d = D_i \text{grad} c_i$	Planck: $J_i^d = B_i c_i \text{grad}(\mu_i^{ch})$	Planck: $J_i^d = B_i c_i \text{grad}(\mu_i^{ch})$	
Geometry	R1	R1	R1 and R2	
Boundaries	Closed, semi-infinite: $\infty < x < \infty$	Open bounded: $a < x < b$	Open bounded: $a < x < b$	
References	[6]	[7, 8]	[9, 10]	

present a true modelling challenge. In the known approaches, the mass transport in the two-phase zone is described with neglecting the diffusion through the phase of lower fraction. The presence of this phase in the diffusion zone is included by introducing average Fickian fluxes of the components in the other, high fraction, phase. In such a case, the mass conservation law for average concentrations reduces to the diffusion equation which can be solved using known methods (for example see Ref. [2–5]). Some of the known solutions will be outlined in the next part of this work.

In this paper, we present a consistent model of mass transport in three-component, two-phase system which expands the previous approaches, Table 1. A main idea of the model is to describe the mass transport with the use of bi-velocity (generalized Darken) and to include the diffusion and drift fluxes in all phases present in the system. Such approach is presented for the first time. In the present model, a phase-field order parameter, identified with phase fraction of one of the phases, is introduced. It has simple physical meaning and can be used in the discussion concerning a phase composition and microstructure of the diffusion zone.

2. Diffusion in two-phase region

In the modelling of the interdiffusion in ternary systems, it is common to classify various types of the interphase boundaries, according to a change in the number of the phases when such interphase is crossed [11]. In most models, formulated for diffusion couples, the boundaries Type 0, $(\alpha + \beta)|(\alpha + \beta)$, with a characteristic discontinuity in the α - and β -phases volume fractions, or Type 1, $\alpha|(\alpha + \beta)$, with a change in the number of the phases at the initial contact are considered. In the first case, a diffusion leading to the growth of the two-phase zone is mainly predicted but the emergence of the single-phase layer cannot be excluded. For the diffusion in the couple with the boundary Type 0, both the diffusion in the single phase and the diffusion across the two-phase region must be included. The diffusion in single phase (say α) is treated in the usual manner in which the diffusion fluxes of two from the three components are considered:

$$(J_\alpha) = -[D_\alpha] \frac{\partial(c_\alpha)}{\partial x} \quad (1)$$

where $(J_\alpha)_{2 \times 1}$ is a one-column flux matrix, $[D_\alpha]_{2 \times 2}$ is 2×2 diffusivity matrix and $(c_\alpha)_{2 \times 1} = (c_\alpha(x, t))_{2 \times 1}$ is a one-column concentration matrix. Equation (1) treats the present system as one-dimensional, pseudobinary one in which the concentration of the third component can be calculated.

The mass conservation and the assumption of constant diffusivity further give:

$$\frac{\partial(c_\alpha)}{\partial t} = [D_\alpha] \frac{\partial^2(c_\alpha)}{\partial x^2} \quad (2)$$

A common computational method used to describe mass transport in the two-phase zone (treated as the two-phase mixture, say $\alpha + \beta$) is provided by transport equations expressed in the terms of overall (average) composition of the system. The average concentrations of the i th components (\bar{c}_i for $i = 1, 2, 3$) are determined from a mass

balance, as phase-fraction-weighted sums of the concentrations of this component in both phases [2,12,13].

At the phase diagram, the overall concentration lies on the conode and the opposite ends of this conode represent the compositions of the phases at the equilibrium. Thus, the relation between the average concentration of the i th component in the two-phase region and the concentrations of this component in α and β phases can be defined [14]:

$$\bar{c}_i = f(c_{i,\alpha}, c_{i,\beta}), \quad i = 1, 2 \quad (3)$$

The mass conservation gives [14]:

$$\frac{\partial(\bar{c})}{\partial t} = \frac{\partial}{\partial x} \left\{ [D^{eff}] \frac{\partial(\bar{c})}{\partial x} \right\} \quad (4)$$

where $\bar{c} = ((\bar{c})_{1 \times 2})$ is a one-column average concentration matrix.

The effective diffusivity, $[D^{eff}]$, is a product of diffusivity in the α phase (the diffusion through β phase is neglected); and transformation matrix, $[c^{TM}]$ [14]:

$$c_{ik}^{TM} = \frac{\partial c_{i,\alpha}}{\partial \bar{c}_k}, \quad i, k = 1, 2 \quad (5)$$

The above derivatives can be calculated from Equation (3). Each of them describes a change of the composition of the i th component with regard to the change of the average concentration of the k th component in the two-phase mixture.

For constant $[D^{eff}] = [D_x]$, the explicit form of (4) is [14]:

$$\begin{aligned} \frac{\partial \bar{c}_1}{\partial t} &= \left(D_{11,\alpha} \frac{\partial c_{1,\alpha}}{\partial \bar{c}_1} + D_{12,\alpha} \frac{\partial c_{2,\alpha}}{\partial \bar{c}_1} \right) \frac{\partial^2 \bar{c}_1}{\partial x^2} + \left(D_{11,\alpha} \frac{\partial c_{1,\alpha}}{\partial \bar{c}_2} + D_{12,\alpha} \frac{\partial c_{2,\alpha}}{\partial \bar{c}_2} \right) \frac{\partial^2 \bar{c}_2}{\partial x^2} \\ \frac{\partial \bar{c}_2}{\partial t} &= \left(D_{21,\alpha} \frac{\partial c_{1,\alpha}}{\partial \bar{c}_1} + D_{22,\alpha} \frac{\partial c_{2,\alpha}}{\partial \bar{c}_1} \right) \frac{\partial^2 \bar{c}_1}{\partial x^2} + \left(D_{21,\alpha} \frac{\partial c_{1,\alpha}}{\partial \bar{c}_2} + D_{22,\alpha} \frac{\partial c_{2,\alpha}}{\partial \bar{c}_2} \right) \frac{\partial^2 \bar{c}_2}{\partial x^2} \end{aligned} \quad (6)$$

Solutions of the above equations describe the diffusion in the two-phase zone. The diffusion in the single-phase zone follows from the solutions of Equation (2).

In the model presented by Wu, Morral, Wang [15], both phases and interfaces are considered simultaneously. The results show that there is significant difference between the diffusion path when the mass transport through both phases is considered and the diffusion path when the precipitates are neglected. The simulation of the microstructure shows the migration of the precipitates and Type 0 boundary due to Kirkendall effect.

The model proposed herewith is a next step of such treatment. It not only considers the simultaneous diffusion through both phases present in the phase zone but also includes drift next to diffusion flux – following with bi-velocity method.

3. Drift and diffusion in two-phase region

We will further consider a closed ternary system, at constant temperature, that is represented by the one-dimensional diffusion couple, of Type 0 boundary (i.e. α/β or

$(\alpha + \beta)|(\alpha + \beta)$) or Type 1 (i.e. $\alpha|(\alpha + \beta)$ or $\beta|(\alpha + \beta)$). In such system, a two-phase zone can grow by diffusion and we assume that the mass transport takes place through the both phases. It is also assumed that the mass transport through the external boundaries of the diffusion couple does not occur, thus the diffusion fluxes of the components vanish at the boundaries. The mass flux includes two contributions: drift and diffusion fluxes – as follows from the bi-velocity method [6,9,16,17]. In particular, the flux of the i th component ($i = 1, 2, 3$) in the j phase $j = \alpha, \beta$ equals:

$$J_{i,j} = J_{i,j}^d + J_{i,j}^{drift}, \tag{7}$$

The diffusion flux in (7), $J_{i,j}^d$, is given by a proper constitutive formula. In this work, we define it using the Nernst–Planck equation or by the first Fick’s law, when simplified with a substitution of the concentration instead of activity $a_{i,j} = c_{i,j}$:

$$J_{i,j}^d = -B_{i,j}c_{i,j} \frac{\partial \mu_{i,j}}{\partial x} = -D_{i,j} \frac{\partial c_{i,j}}{\partial x} \tag{8}$$

where $B_{i,j}$ and $\mu_{i,j}$ are mobility and diffusion potential of the i th component in the j phase.

The overall (average) flux of the i th component will be further represented as:

$$\bar{J}_i = \sum_{j=\alpha,\beta} \varphi_j J_{i,j}^d + \bar{J}_i^{drift} \tag{9}$$

where \bar{J}_i^{drift} is the average drift flux of the i th component.

In the single-phase region, the first sum in the above equation reduces to one contribution, either for α or for β phase. In the two-phase region, it includes two contributions, for the diffusion in α and in β phases.

We further assume that the diffusion flux in the two-phase region satisfies ‘the rule of mixtures’ and we identify φ_α and φ_β with the respective phase volume fractions satisfying the mass balance. In this case:

$$\phi_\alpha + \phi_\beta = 1 \tag{10}$$

$$\text{or } \varphi_\alpha = \varphi \text{ and } \varphi_\beta = 1 - \varphi, \quad 0 \leq \varphi \leq 1$$

It means that ϕ can be interpreted as the order parameter and the set of its values over the whole system defines the phase field. The continuous variation of the order parameter correlates with the changes of the phase composition across the diffusion zone. The parameter ϕ can assume values from [0,1] range: 1 within the region where only one chosen phase exists (say α), 0 when the other phase is stable (the phase β), and it is between 0 and 1 within the two-phase spatial region. The average composition of the system in the spatial region is a weighted average of the compositions of the phases in the equilibrium, that is, the compositions described by the conode ends (the points where the conode meets the margins of the single-phase regions). The mass balance expressed for each component says:

$$\bar{c}_i = \varphi c_{i,\alpha} + (1 - \varphi) c_{i,\beta}, \quad i = 1, 2, 3 \tag{11}$$

In the one-phase region there is simply:

$$\bar{c}_i = c_{i,\alpha} \quad \text{or} \quad \bar{c}_i = c_{i,\beta} \quad (12)$$

depending on the phase.

The mass conservation applied to Equation (9) results in:

$$\frac{\partial \bar{c}_i}{\partial t} = -\frac{\partial \bar{J}_i}{\partial x}, \quad i = 1, 2, 3 \quad (13)$$

regardless whether the mass transport is in single phase or in the two-phase zone.

Assuming that

$$\bar{J}_i^{drift} = \bar{c}_i \bar{v}^{drift} \quad (14)$$

and introducing it together with (8) into (13), one obtains:

$$\frac{\partial \bar{c}_i}{\partial t} = \frac{\partial}{\partial x} \left(\bar{D}_i \frac{\partial \bar{c}_i}{\partial x} - \bar{c}_i \bar{v}^{drift} \right), \quad i = 1, 2, 3 \quad (15)$$

where:

$$\bar{D}_i = \left(D_{i,\alpha} \frac{\bar{c}_i - c_{i,\beta}}{c_{i,\alpha} - c_{i,\beta}} + D_{i,\beta} \frac{c_{i,\alpha} - \bar{c}_i}{c_{i,\alpha} - c_{i,\beta}} \frac{\partial c_{i,\beta}}{\partial c_{i,\alpha}} \right) \frac{\partial c_{i,\alpha}}{\partial \bar{c}_i} \quad (16)$$

The drift flux is generated by non-compensated diffusion fluxes and its velocity in (14) and (15) can be calculated as

$$\bar{v}^{drift} = - \sum_{j=\alpha,\beta} \sum_{i=1,2,3} \phi_j \Omega_{i,j} J_{i,j}^d \quad (17)$$

or for the single phase region

$$\bar{v}^{drift} = v_j^{drift} = - \sum_{i=1,2,3} \Omega_{i,j} J_{i,j}^d, \quad j = \alpha, \beta \quad (18)$$

where $\Omega_{i,j}$ is a molar volume of the i th component in the j phase.

The set of Equations (15), together with (11), (16) and (17), can be solved when initial conditions and thermodynamics of the system are known. It is enough to have the isothermal section of the phase diagram for a given constant temperature, that is, the margins of the single and two-phase regions (phase boundaries) and the conodes in the two phase-region (tie-lines connecting the compositions of α and β at the equilibrium). Moreover, the diffusion coefficients of the components and their partial molar volumes must be specified.

The solution of Equation (15) gives time - spatial dependence of the average concentration of each component, $\bar{c}_i(x, t)$, $i = 1, 2, 3$, and the drift velocity in the

diffusion zone \bar{v}^{drift} . For the defined processing time, it gives spatial distribution of the elements and drift velocity along x -axis parallel to the mass transport direction. Obviously, spatial changes of the order parameter, here volume fraction of one of the phases, can be also calculated. When the spatial variable is treated like a hidden variable and the successive \bar{c}_i are drawn on the composition triangle, one obtains the diffusion path.

Equations (16) have been solved numerically. The respective procedure has been implemented into CADiff2p software [18]. The differential equation solver is based on the Runge-Kutta-Fehlberg (RKF) method with adaptive step-size control.

4. Diffusion path in $(\alpha+\beta)|(\alpha+\beta)$ diffusion couple

A model ternary diffusion couple has been considered as an example to illustrate the present method. In calculations, the interdiffusion in the $(\alpha+\beta)|(\alpha+\beta)$ diffusion couple has been modelled. It is assumed that equilibrium conditions for the system at constant temperature $T = T_0$ are known and represented by the isothermal section of the phase diagram in the rectangular, molar-fraction dependent, form, that is, N_2 vs. N_1 , $\sum_{i=1,2,3} N_{i,j} = 1$ for $j = \alpha, \beta$ (Figure 1). Thus, the phase boundaries, $g_\alpha(N_1, N_2)$ and $g_\beta(N_1, N_2)$, and the set of conodes $g_{\alpha\beta}(N_1, N_2)$ are specified. In calculations, the partial molar volumes of all three components are the same, and consistently the volume occupied by the diffusion couple is time invariant. The diffusion coefficients of two of the three components (here 1 and 2) are the same in the same phase but vary between the phases: $D_{1,\alpha} = D_{2,\alpha} \neq D_{1,\beta} = D_{2,\beta}$. The third component has the diffusion coefficient different: $D_{3,\alpha} \neq D_{3,\beta}$ and $D_{3,\alpha} \neq D_{1,\alpha}$, $D_{3,\beta} \neq D_{1,\beta}$. The terminal concentrations of the diffusion couple have been taken arbitrarily and are given in Table 2 next to other data. The processing time is 100 h.

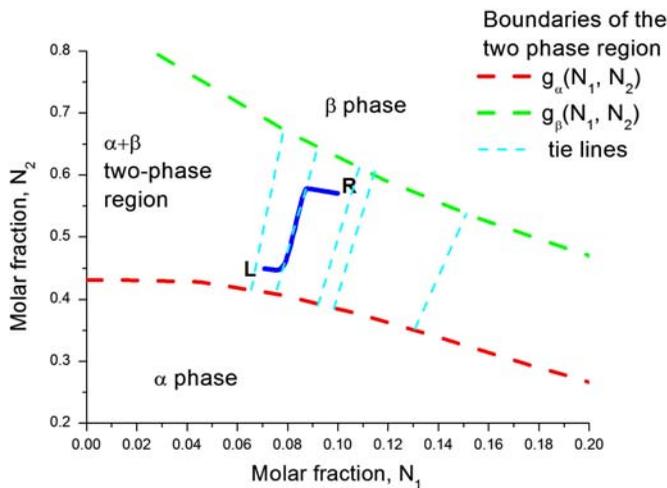


Figure 1. (colour online) Isothermal section of the ternary phase diagram with the diffusion path calculated in this work (solid line). The data used in the calculations are shown in Table 2. L and R refer to the left and right terminal compositions.

The results of the calculations performed with CADiff2p software [18] are presented in Figures 1–4. A characteristic zig-zag diffusion path composed of three segments and connecting initial compositions of the diffusion couple (L-left and R-right) is a key result [14]. Small deviation from the ideal zig-zag can be seen which appears as a single inward horn between the first zig-zag segment (adjacent to the L end) and directed from the α to β phase. [15,19]. We allow the diffusion in both phases present in the system, whilst, in earlier works, only the mass transport in the matrix phase has been considered.

The shape of the diffusion path correlates with the spatial variations of the volume fractions of the phases (Figure 2). In the neighbour of the initial contact (0.05 cm), a

Table 2. The data used to simulate interdiffusion in the $(\alpha + \beta)|(\alpha + \beta)$ ternary diffusion couple.

Component, i	1	2	3
Phase, j		Diffusion coefficients, cm^2/s	
α	10^{-9}	10^{-9}	$5 \cdot 10^{-9}$
β	10^{-10}	10^{-10}	$5 \cdot 10^{-10}$
		Molar volume, cm^3/mole	
α, β	10	10	10
Ends		Terminal compositions, at.%	
Left	7	45	48
Right	10	57	33
	Other data		
Time, h		100	
Sample thickness, cm		0.1	
Initial contact, cm		0.05	

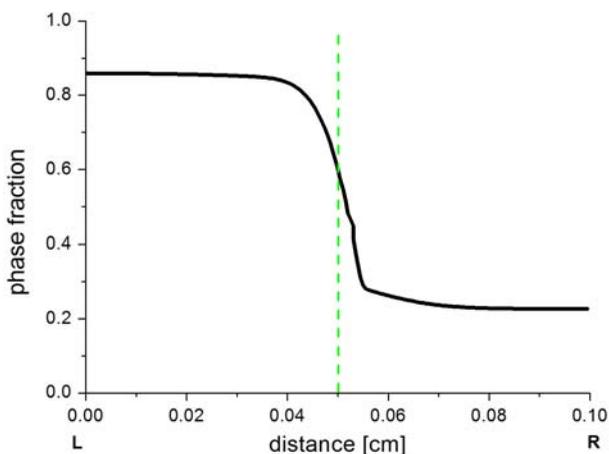


Figure 2. (colour online) Spatial changes of the α -phase volume fraction in the $(\alpha + \beta)|(\alpha + \beta)$ ternary diffusion couple. Initial contact is drawn with dotted line.

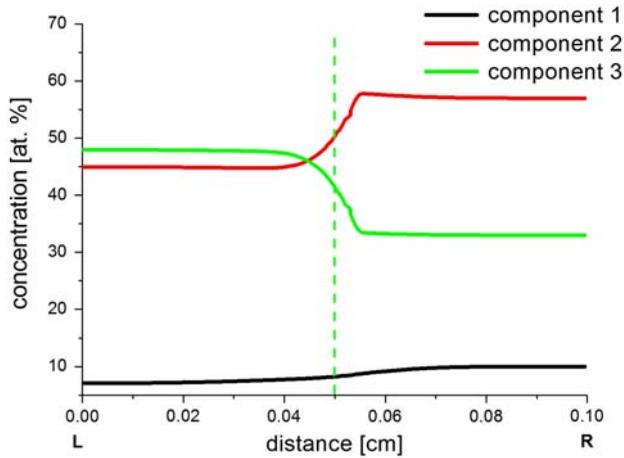


Figure 3. (colour online) Concentration profiles along mass transport direction in the $(\alpha + \beta)|(\alpha + \beta)$ ternary diffusion couple. Initial contact is drawn with dotted line.

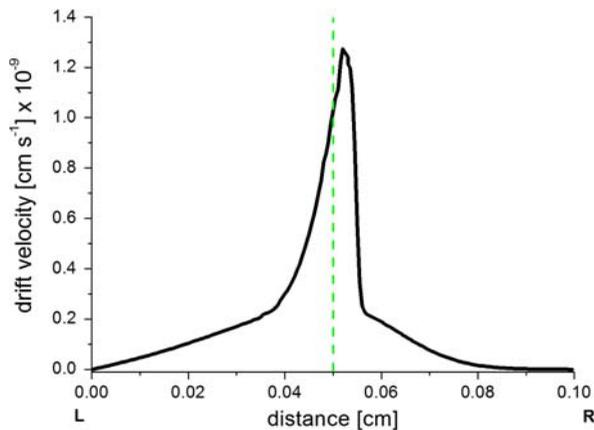


Figure 4. (colour online) Drift-velocity spatial changes along mass transport direction in the $(\alpha + \beta)|(\alpha + \beta)$ ternary diffusion couple. Initial contact is drawn with dotted line.

rapid change is seen. This should be related to the middle diffusion path segment which goes along the conode. Note, that the volume fraction of α phase goes down from 0.85 at the left end of the diffusion couple to 0.2 – at the right end. Respectively, the β -phase volume fraction increases from 0.15 to 0.8. The effects for the microstructure are obvious and can be described with a use of percolation theory. It predicts that critical concentration for bonds in 3D system for random close packing equals 0.27. When packing density is close to 100% then, for volume fraction of minor phase exceeding 0.27, both phases should be continuous. This means that, in the modelled system, only within the internal region, 0.01 cm thick (from 0.045 to 0.055 cm in Figure 2), both phases are continuous. In the outer regions, either β or α phase is dispersed. The other phase forms a matrix.

In Figure 3, the spatial distributions of the three components are shown. A sharp change of the composition falls next to the initial contact, similarly as the volume fraction changes. A small uphill diffusion effect is observed for the component 2, at the right side of the initial contact, which is compensated by shallow minimum of the concentration at the other side.

More attention needs to be paid to the drift velocity and its spatial distribution (Figure 4). It is positive along the entire sample which means the vacancy movement from right to the left. The drift velocity reaches maximum slightly shifted to the right side and vanished at the sample ends. A characteristic asymmetry is seen due to various diffusion coefficients of the components.

5. Summary

Interdiffusion in multicomponent systems leads to the formation of the diffusion zone of complex morphology that comprises both intermediate phases and multiphase regions. The problem has considerable meaning in many applications, like coatings and gradient materials design, welding, brazing or studies on material degradation by internal oxidation. That is why an intensive effort has been made to understand and model diffusion in such systems. Most of them reduce the problem and consider the diffusion throughout one phase of higher volume fraction. The unsolved issue concerns the modelling of mass transport throughout the whole diffusion zone, in particular across both phases being in equilibrium in the two-phase region. In this work, we have presented an approach which fulfils this requirement. The theoretical basis of the proposed method has been embedded within bi-velocity method, in which the mass conservation equation takes into account drift and diffusion fluxes. Thanks to the application of the phase-field parameter (here volume fraction) a smooth transition from one to two-phase field, without separate treating of these two cases, is possible, and all presented equations are valid throughout all concentration triangle. The derived set of equations allows calculating the average concentrations of the elements in the system as well as composition of the phases. In 1D geometry, the respective solutions are generally time-spatial dependent $\bar{c}_i(x;t)_{i=1,2,3}$. For constant time, they represent the element distribution profiles $\bar{c}_i(x)_{i=1,2,3,t=const}$. When x is a hidden variable, then the average concentrations, $\bar{c}_i|_{i=1,2,3,t=const}$, describe the diffusion path. The method also allows computing drift velocity across the whole diffusion zone which is of considerable interest in predicting the Kirkendall effect.

The diffusion path calculated for the interdiffusion in the model three-component two-phase diffusion couple, $(\alpha + \beta)|(\alpha + \beta)$ lies entirely within the two-phase region. It does not cross the phase boundary, thus a formation of single-phase layer in the studied diffusion couple is not confirmed. It is not, however, well understood what is an origin of some singularities in the diffusion path appearing as single inward horn. Some further studies are needed.

The exemplary results that have been obtained for a facultative $(\alpha + \beta)|(\alpha + \beta)$ diffusion couple can be easily applied to the real systems. In particular, a dependence of the intrinsic diffusivities on the chemical compositions can be included. The present method can be also generalized to the 3D geometry.

List of symbols

(c_α)	–	one-column concentration matrix in α phase, i.e. $\begin{bmatrix} c_{1,\alpha} \\ c_{2,\alpha} \end{bmatrix}$
$c_{i,\alpha}$	–	concentration of the i th component in α phase
$c_{i,\beta}$	–	concentration of the i th component in β phase
(\bar{c})	–	one-column average concentration matrix, i.e. $\begin{bmatrix} \bar{c}_1 \\ \bar{c}_2 \end{bmatrix}$
\bar{c}_i	–	average concentration of the i th component
$[c^{TM}]$	–	2×2 transformation matrix, i.e. $\begin{bmatrix} c_{11}^{TM} & c_{12}^{TM} \\ c_{21}^{TM} & c_{22}^{TM} \end{bmatrix}$ where $c_{ik}^{TM} = \frac{\partial c_{i,\alpha}}{\partial \bar{c}_k}$
(J_α)	–	one-column flux matrix in α phase, i.e. $\begin{bmatrix} J_{1,\alpha} \\ J_{2,\alpha} \end{bmatrix}$
$J_{i,j}$	–	flux of the i th component in j phase
$J_{i,j}^d$	–	diffusional flux of the i th component in j phase
$J_{i,j}^{drift}$	–	drift flux of the i th component in the j th phase
\bar{J}_i	–	average overall flux of the i th component
\bar{J}_i^{drift}	–	average drift flux of the i th component
$[D_\alpha]$	–	2×2 diffusivity matrix in α phase, i.e. $\begin{bmatrix} D_{11,\alpha} & D_{12,\alpha} \\ D_{21,\alpha} & D_{22,\alpha} \end{bmatrix}$
$D_{i,j}$	–	diffusivity of the i th component in the j th phase
\bar{D}_i	–	average diffusivity of the i th component
$[D^{eff}]$	–	2×2 effective diffusivity matrix, i.e. $\begin{bmatrix} D_{11}^{eff} & D_{12}^{eff} \\ D_{21}^{eff} & D_{22}^{eff} \end{bmatrix}$
\bar{v}^{drift}	–	average drift velocity of the i th component
$B_{i,j}$	–	mobility of the i th component in the j th phase
$\mu_{i,j}$	–	diffusion potential of the i th component in the j th phase
ϕ_j	–	volume fraction of the j th phase at local equilibrium
$\Omega_{i,j}$	–	molar volume of the i th component in j phase

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