The choice of reaction path during ternary diffusion process

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Abstract. The complete understanding of the phenomenological process related to the evolution of the ternary multiphase system is still lacking. In this paper the ternary interdiffusion process in multiphase system is discussed by means of numerical modeling. The entropy production principle is proposed to chose the proper diffusion path during the process (e.g. internal oxidation). The bi-velocity method of the three-component multi-phase system is presented. The simulations show the local entropy production curve that determines the thickness of the two-phase zone.

1. Introduction

Many materials are multicomponent alloys and consist of several grains and phases. Their macroscopic properties and reliability highly depend on the microstructure and its evolution in time. It has been shown extensively that the phase field technique is capable of dealing in a phenomenological and also quantitative way with the complex processes and morphologies involved in microstructure evolution [1, 2, 3, 4, 5, 6, 7].

As it is well known, the second law of thermodynamics indicates only the general direction of the evolution of the system, the tendency of a closed system’s entropy to reach the maximum, the tendency of free energy to be minimum at fixed volume and temperature, and the tendency of Gibbs’s potential to reach minimum at fixed temperature and pressure [8, 9]. In this paper we will try to answer the fundamental question: how is the choice made, if more than one diffusion path to relaxation is possible?

The interplay between inter-diffusion in the multi-phase system involves thermodynamics as well as kinetic considerations [10]. It follows that the knowledge of the thermodynamics in the ternary system preferably in the form of a ternary phase diagram is a necessity [11]. On the ternary A–B–C system with a miscibility gap, the diffusion effects can be graphically represented at the concentration triangle as a diffusion path. The diffusion path can go across single and two-phase regions in the ternary diagram. When the diffusion path crosses the tie lines, 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.

In this paper the bi-velocity model is proposed to calculate the time evolution of the reactive diffusion in multi-phase system. The bi-velocity model allow to calculate the local entropy production...
[12] and Kirkendall effect [13] during the diffusion process. The local entropy production is the missing element in proper choice of diffusion path. It will be presented, that the maxims on the local entropy production curve corresponds to the intersection points between the diffusion path and phase boundaries.

2. Model.
To calculate the ternary diffusion in multiphase system the bi-velocity method [14, 15, 16] will be used. It is applicable in multicomponent - multiphase systems but we will further consider the three-component system in which \( m \) layers, separated by the interfaces of finite thicknesses, can grow. The main equation describing the concentration (in this case the average concentration) is mass conservation law for each component and for each phase.

\[
\frac{\partial \overline{c}_i}{\partial t} + \frac{\partial}{\partial x} (\overline{c}_i \overline{v}_i) = 0, \quad i = 1, 2, 3
\]  

(1)

where: \( \overline{c}_i \) and \( \overline{v}_i \) denote an average concentration and velocity of the i-th component, respectively.

The schematic picture representing the diffusion between two phases \( \alpha \) and \( \beta \) with two phase zone formation \( \alpha + \beta \) is presented on figure 1. The straight lines represent the boundaries between the phase and two phase zone. The dotted lines shows the conodes (tie lines), note that on one conode the chemical potentials are equal. The conodes are evenly distributed over the boundaries. The average concentration is defined inside two phase region. The average concentration can be estimated from the composition triangle:

\[
\overline{c}_i = f_\alpha c_{i,\alpha} + (1 - f_\alpha) c_{i,\beta}, \quad i = 1, 2, 3.
\]  

(2)

where \( f_\alpha \) denote the volume fraction in a two-phase region between \( \alpha \) and \( \beta \) phase, \( c_{i,j} \) denote the concentration of the \( i \)-th component in \( j \)-th phase. In the two-phase system the following relation holds:

\[
f_\alpha + f_\beta = 1, \quad 0 < f_\alpha \leq 1.
\]  

(3)

Let: \( f_\alpha = f \) and \( f_\beta = 1 - f \), then \( f \) equals 1 in \( \alpha \) phase region \( (\overline{c}_i = c_{i,\alpha}) \) and 0 within \( \beta \) phase region \( (\overline{c}_i = c_{i,\beta}) \). In \( \alpha + \beta \) phase zone: \( 0 < f < 1 \).

Following the Darken, the average flux \( \overline{c}_i \overline{v}_i \) is divided into two parts, i.e. the diffusion, \( \overline{c}_i \overline{v}_i^d \), and drift, \( \overline{c}_i \overline{v}_i^{\text{drift}} \):

\[
\overline{c}_i \overline{v}_i = \overline{c}_i \overline{v}_i^d + \overline{c}_i \overline{v}_i^{\text{drift}}, \quad i = 1, 2, 3
\]  

(4)

The diffusion flux is expressed by 2-nd fick law:

\[
\overline{c}_i \overline{v}_i^d = -D_i \frac{\partial \overline{c}_i}{\partial x}, \quad i = 1, 2, 3
\]  

(5)

Finally, the drift velocity can be defined by volume continuity equation [14] as:

\[
\overline{v}_i^{\text{drift}} = \sum_{j=1}^{3} D_i \frac{\partial \overline{N}_i}{\partial x}, \quad i = 1, 2, 3
\]  

(6)

where \( \overline{N}_i = \overline{c}_i / \sum_{j=1}^{3} \overline{c}_j \).

The average entropy production rate in case of isothermal process (i.e. the temperature gradient, pressure are negligible) is define as [17]:

\[
A^\prime = R \sum_{i} \left( \frac{\overline{c}_i \overline{v}_i^{\text{drift}}}{\overline{c}_i D_i} \right)^2
\]  

(7)
where \( R \) denote the gas constant and the average diffusion coefficient [18] equal
\[
\bar{D}_i = D_{i,\alpha} \frac{\partial c_{i,\alpha}}{\partial \bar{c}_i} + D_{i,\beta} \frac{\partial c_{i,\beta}}{\partial \bar{c}_i}, \quad i = 1, 2, 3
\] (8)

The final form of the proposed model describe the following set of the equations (average mass conservation for each component and entropy density equation):
\[
\frac{\partial \bar{c}_i}{\partial t} + \frac{\partial}{\partial x} \left( -D_{i,\alpha} \frac{\partial c_{i,\alpha}}{\partial \bar{c}_i} + D_{i,\beta} \frac{\partial c_{i,\beta}}{\partial \bar{c}_i} \right) = 0, \quad i = 1, 2, 3
\] (9)

and
\[
A' = -R \sum_{i=1}^{3} \left( \frac{\partial c_{i,\alpha}}{\partial \bar{c}_i} + \frac{\partial c_{i,\beta}}{\partial \bar{c}_i} \right)^2
\] (10)

Finally the two-phase zone in bi-velocity phase field method can be approximated by the gradients of concentrations in \( \alpha \) and \( \beta \) phase:
\[
\frac{\partial \bar{c}_i}{\partial t} + \frac{\partial}{\partial x} \left( -D_{i,\alpha} \frac{\partial c_{i,\alpha}}{\partial \bar{c}_i} + D_{i,\beta} \frac{\partial c_{i,\beta}}{\partial \bar{c}_i} + \bar{N} \sum_{i=1}^{3} \left( D_{i,\alpha} \frac{\partial c_{k,\alpha}}{\partial \bar{c}_k} + D_{i,\beta} \frac{\partial c_{k,\beta}}{\partial \bar{c}_k} \right) \right) = 0, \quad i = 1, 2, 3
\] (11)

and
\[
A' = -R \sum_{i=1}^{3} \left( \frac{\partial c_{i,\alpha}}{\partial \bar{c}_i} + \frac{\partial c_{i,\beta}}{\partial \bar{c}_i} \right)^2
\] (12)

The component mass conservations law Eq. (11) can be rearranged to:
\[
\frac{\partial \bar{c}_i}{\partial t} + \frac{\partial}{\partial x} \left( -D_{i,\alpha} \frac{\partial c_{i,\alpha}}{\partial \bar{c}_i} + \bar{N} \sum_{i=1}^{3} D_{i,\alpha} \frac{\partial c_{i,\alpha}}{\partial \bar{c}_i} - D_{i,\beta} \frac{\partial c_{i,\beta}}{\partial \bar{c}_i} + \bar{N} \sum_{i=1}^{3} D_{i,\beta} \frac{\partial c_{i,\beta}}{\partial \bar{c}_i} \right) = 0, \quad i = 1, 2, 3
\] (13)

Then using the definition describing the average concentration, Eq. (2):
\[
\frac{\partial}{\partial t} \left( f_a c_{i,\alpha} + (1-f_a) c_{i,\beta} \right) + \frac{\partial}{\partial x} \left( -D_{i,\alpha} \frac{\partial c_{i,\alpha}}{\partial \bar{c}_i} + \left( f_a N_{i,\alpha} + (1-f_a) N_{i,\beta} \right) \sum_{i=1}^{3} D_{i,\alpha} \frac{\partial c_{k,\alpha}}{\partial \bar{c}_k} \right) = 0,
\] (14)

By simple algebraic rearranging above expression can be rewritten as follow:
Finally, assuming that the mass conservation law holds for each phase separately the following expressions are valid:

\[
(c_{i,\alpha} - c_{i,\beta}) \frac{\partial f_{i,\alpha}}{\partial t} + f_{i,\alpha} \frac{\partial c_{i,\alpha}}{\partial t} + (1 - f_{i,\alpha}) \frac{\partial c_{i,\beta}}{\partial t} - D_{i,\alpha} \frac{\partial^2 c_{i,\alpha}}{\partial x^2} + \frac{\partial}{\partial x} \left( f_{i,\alpha} N_{i,\alpha} \sum_{k=1}^{3} D_{k,\alpha} \frac{\partial c_{k,\alpha}}{\partial x} \right) + \frac{\partial}{\partial x} \left( (1 - f_{i,\alpha}) N_{i,\beta} \sum_{i=1}^{3} D_{i,\beta} \frac{\partial c_{k,\beta}}{\partial x} \right) - \right.
\]

\[
= 0, \quad i = 1, 2, 3
\]

(15)

and

\[
\frac{\partial c_{i,\beta}}{\partial t} + \frac{\partial}{\partial x} \left( -D_{i,\beta} \frac{\partial c_{i,\beta}}{\partial x} + N_{i,\beta} \sum_{k=1}^{3} D_{k,\beta} \frac{\partial c_{k,\beta}}{\partial x} \right) = 0, \quad i = 1, 2, 3
\]

(16)

thus, Eqs. (15) can be rewritten in form:

\[
0 = \left( c_{i,\alpha} - c_{i,\beta} \right) \frac{\partial f_{i,\alpha}}{\partial t} + \left( N_{i,\alpha} \sum_{k=1}^{3} D_{k,\alpha} \frac{\partial c_{k,\alpha}}{\partial x} - D_{i,\alpha} \frac{\partial c_{i,\alpha}}{\partial x} - N_{i,\beta} \sum_{i=1}^{3} D_{i,\beta} \frac{\partial c_{k,\beta}}{\partial x} + D_{i,\beta} \frac{\partial c_{i,\beta}}{\partial x} \right) \frac{\partial f_{i,\alpha}}{\partial x}
\]

\[
+ \frac{\partial}{\partial x} \left( (1 - f_{i,\alpha}) \left[ -D_{i,\alpha} \frac{\partial c_{i,\alpha}}{\partial x} + N_{i,\alpha} \sum_{k=1}^{3} D_{k,\alpha} \frac{\partial c_{k,\alpha}}{\partial x} \right] - f_{i,\alpha} \left[ -D_{i,\beta} \frac{\partial c_{i,\beta}}{\partial x} + N_{i,\beta} \sum_{i=1}^{3} D_{i,\beta} \frac{\partial c_{k,\beta}}{\partial x} \right] \right), \quad i = 1, 2, 3
\]

(18)

Equation (18) shows that the two-phase zone can be described by the derivative of the phase fraction in time. Note, that the two-phase zone formation near the \( \alpha \) phase boundary \( (f_{i,\alpha} \approx 1) \) depend mainly on the gradient of concentration of components from \( \beta \) phase, thus two-phase zone will grow:

\[
0 = -D_{i,\beta} \frac{\partial c_{i,\beta}}{\partial x} + N_{i,\alpha} \sum_{k=1}^{3} D_{k,\beta} \frac{\partial c_{k,\beta}}{\partial x}
\]

(19)

analogous situation can be shown near the \( \beta \) phase boundary.

2.1. The calculations performed at each time step:

To solve above equations the following steps should be accomplished:

- Solve diffusion flux equations (for each component), Eq. (5), volume continuity equation, Eq. (6) and the equation for local entropy production, Eq. (7). Calculate diffusion velocities, \( \hat{\nu}_i \), \( i = 1, 2, 3 \), drift velocity, \( \hat{D}^{\alpha/\beta} \) and local entropy production rate, \( A' \). The interphase boundaries are identified with the two maxims of the local entropy-production rate where the driving force for the irreversible mass transport is highest.

- Solve the conservation laws, Eqs. (1). Calculate concentrations, \( \bar{c}_i \), \( i = 1, 2, 3 \) for advancement \( t_k \rightarrow t_{k+1} \). Determine the conode which cross the \( \bar{c}_i \), \( i = 1, 2, 3 \) in the two-phase region. The conodes are evenly distributed over the boundaries;

- Compute the intersection points of the conodes with the boundaries. These intersections determine the concentrations of the components in each phase, \( c_{i,\alpha} \), \( c_{i,\beta} \) for \( i = 1, 2, 3 \);

- Calculate the volume fractions of each phase, \( f_{\alpha} \) and \( f_{\beta} \), Eq. (3);
2.2. The initial steps:
- Determine the boundaries of the two phase region and represent them by the polynomials dependent on the mole fractions of two from the three components;
- define the conodes (tie lines), $k$, which are evenly distributed along the boundaries

The remaining initial data necessary in the calculations include: terminal composition of the diffusion couple (representing the terminal points of the diffusion path), diffusion coefficients and molar volumes of the components in all phases, processing time and temperature (results section).

2.3. Numerical method [19]
The numerical treatment of the bi-velocity method comes down to solving a set of ordinary differential equations $\frac{dy}{dt} = f(y,t)$, where $f : R^n \rightarrow R^n$, $y = y(t) \in R^n$. To solve the ODEs e.g. the explicit Euler method can be used. In this method the passage from time $t_k$ to $t_{k+1} = t_k + \Delta t$ was carried out by one-step evaluation. The advancement $t_k \rightarrow t_{k+1}$ was executed in which $y_{k+1} = y_k + \Delta t \cdot f(y_k,t_k)$ with $f(y,t)$ evaluated for $t = t_k$ and $y = y_k$ [19].

In the present calculations, the method of lines to solve numerically the ODEs system resulting from the space discretization of the bi-velocity set of equations was used [20]. The uniform grid, contained 100 mesh points, was used and the concentrations and pressure were defined at points $x_k$. The applied discretization led to the system of ordinary differential equations (ODEs) in time variable. For example, the equations for diffusion flux (Eq. (5)) of all three components were transposed by finite difference approximation in one dimensional space, as follows:

$$ \frac{k}{\Delta k} \bar{J}_i^d(t) := J_i^d(x_k,t) = -\frac{\partial C_i}{\partial x}(x_k,t) \approx -\frac{C_i(x_{k+1}) - C_i(x_{k-1})}{x_{k+1} - x_{k-1}}, \quad i = 1, 2, 3 \quad (20) $$

For boundary nodes the one-sided uniform finite differences were used:

$$ ^0 \bar{J}_i^d(t) \approx -\bar{D}_i(x_0,t) \frac{C_i - 0 C_i}{x_1 - x_0}, \quad i = 1, 2, 3 \quad \text{and} \quad (21) $$

$$ ^n \bar{J}_i^d(t) \approx -\bar{D}_i(x_n,t) \frac{n C_i - C_i}{x_n - x_{n-1}}, \quad i = 1, 2, 3 \quad (22) $$

where: $\frac{k}{\Delta k} C_i = C_i(x_k,t)$.

The space derivatives in the above equations were approximated by two point (first derivative) and three point (second derivative) uniform finite differences:

$$ \frac{\partial \Phi}{\partial x}(x_k,t) \approx \frac{k+1 \Phi - k-1 \Phi}{x_{k+1} - x_{k-1}} \quad (23) $$

and

$$ \frac{\partial^2 \Phi}{\partial x^2}(x_k,t) \approx \frac{k+1 \Phi(x_k - x_{k-1}) + k-1 \Phi(x_{k+1} - x_{k}) - k \Phi(x_{k+1} - x_{k-1})}{0.5(x_{k+1} - x_{k-1})(x_{k+1} - x_k)(x_k - x_{k-1})} \quad (24) $$

Both were calculated from Taylor expansion.

The obtained discretization formulae (Eqs. (20)-(24)) are sufficient to implement the computations, but to solve the ODEs a time integrator is needed. The time integrator, used in the present computations, was based on Runge-Kutta method. Exactly, the adaptive step size Runge-Kutta-Fehlberg modification was used. The six evaluations of the functions from the fifth-order Runge-Kutta algorithm were used to make the another combinations implemented in the fourth-order Runge-Kutta method. A difference between these two estimates served as an estimate of the truncation error. Hence, the step size was adjusted [21].
2.4. Computer implementations.
In particular, the phase boundaries, which are margins for the single-phase and multi-phase regions, must be known, fig. 1.

![Figure 1](image)

**Figure 1.** The schematic view of the concentration triangle. The straight lines denotes the boundaries between phases \((\alpha, \beta, \gamma, \text{ and } \varepsilon)\). The dashed lines represent the tie lines connecting the phases.

They provide the boundary conditions for the solution of equations governing diffusion. During calculations (in each time step) the concentration profiles for the three components are calculated. Hence diffusion path and other properties can be determined.

3. Results.
In order to calculate the diffusion between \(\alpha\) and \(\beta\) phase three possible diffusion path was assumed and calculated: \(\alpha \rightarrow \gamma \rightarrow \beta\), \(\alpha \rightarrow \varepsilon \rightarrow \beta\). The kinetic data used in simulations are presented in Table 1.

| Table 1. The diffusion coefficients, \(D_{i,j}[cm^2s^{-1}]\), and initial concentrations, at. %, used in simulations of reactive diffusion in two-phase system. |
|---|---|---|---|
| Diffusion coefficient | Component | 1 | 2 | 3 |
| \(D_{\alpha}\) | 1.0 \(10^{-8}\) | 5.0 \(10^{-8}\) | 3.0 \(10^{-8}\) |
| \(D_{\gamma}\) | 1.0 \(10^{-9}\) | 5.0 \(10^{-9}\) | 3.0 \(10^{-9}\) |
| \(D_{\beta}\) | 1.0 \(10^{-8}\) | 5.0 \(10^{-8}\) | 3.0 \(10^{-8}\) |
| \(D_{\varepsilon}\) | 1.0 \(10^{-7}\) | 5.0 \(10^{-7}\) | 3.0 \(10^{-7}\) |
| Phase | Terminal composition, at. % |
| \(\alpha\) | 13 | 78 | 9 |
| \(\gamma\) | 7 | 50 | 43 |
| \(\beta\) | 20 | 3 | 77 |
| \(\varepsilon\) | 53 | 35 | 12 |
3.1. Diffusion path $\alpha \rightarrow \gamma \rightarrow \beta$.

On figures 2 and 3 the time evolution of the concentration profile and corresponding evolution of the local entropy production is shown. The presented data describes the changes of the average composition of the system parallel to the mass transport direction, as it results from the concentration profiles. It is seen that the diffusion path passes the $\alpha + \gamma$ and $\gamma + \beta$ two-phase regions. The thickness of the two-phase zones can be determined from the local average entropy production, Fig. 3. The maxims on the local entropy production curve are correlated with the points where the diffusion path cross the interphase boundaries. It is evident that the entropy produced at the heat and mass diffusion does not depend on the frame of reference and it can serve additional parameter characterizing the formation of the diffusion zone in two-phase system.

![Figure 2](image-url)

**Figure 2.** The concentration profile of the arbitrary three-phase system between $\alpha \rightarrow \gamma \rightarrow \beta$ phases after 1h of reactive diffusion process. The vertical lines denotes the phase boundaries.

![Figure 3](image-url)

**Figure 3.** The local entropy production profile of the arbitrary three-phase system between $\alpha \rightarrow \gamma \rightarrow \beta$ phases after 1h of reactive diffusion process. The vertical lines denotes the phase boundaries.

3.2. Diffusion path $\alpha \rightarrow \varepsilon \rightarrow \beta$.

On figures 4 and 5 the time evolution of the concentration profile and corresponding evolution of the local entropy production is shown. The presented data describes the changes of the average composition of the system parallel to the mass transport direction, as it results from the concentration profiles. It is seen that the diffusion path passes the $\alpha + \varepsilon$ and $\varepsilon + \beta$ two-phase regions. The diffusion coefficients in $\varepsilon$ phase are grater than in $\gamma$ phase, thus the thickness of the $\varepsilon$ phase is larger.

![Figure 4](image-url)

**Figure 4.** The concentration profile of the arbitrary three-phase system between $\alpha \rightarrow \varepsilon \rightarrow \beta$ phases after 1h of reactive diffusion process. The vertical lines denotes the phase boundaries.

![Figure 5](image-url)

**Figure 5.** The local entropy production profile of the arbitrary three-phase system between $\alpha \rightarrow \varepsilon \rightarrow \beta$ phases after 1h of reactive diffusion process. The vertical lines denotes the phase boundaries.
4. Conclusions.
The bi-velocity concept of calculating the evolution of the concentration profile and entropy production was presented. It was shown that the entropy production curve can be used to estimate the thickness of the formed two-phase zones (the maxims on the curve correspond to the boundaries of the phases). The method can be further generalized to calculate the kinetic of the diffusion reaction processes in multiphase systems, e.g. internal oxidation or aluminization processes.

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