Full length article

# Model of diffusive interaction between two-phase alloys with explicit fine-tuning of the morphology evolution

Marek Danielewski [a,*], Andriy Gusak [b], Bogusław Bożek [c], Marek Zajusz [a]

[a] Department of Physical Chemistry and Modeling, AGH University of Science and Technology, 30-059 Cracow, Poland
[b] Physics Department, Cherkasy National University, 81 Shevchenko Blvd., 18031 Cherkasy, Ukraine
[c] Faculty of Applied Mathematics, AGH University of Science and Technology, 30-059 Cracow, Poland

## ABSTRACT

Interdiffusion between two-phase ternary alloys is described analytically and numerically with self-consistent account of thermodynamical constraints and of morphology evolution. At that, growth/shrinking of minority phase precipitates and their flow with parent phase lattices are taken into account. Description scheme is multiscale (actually − double-scaled): it uses both coarsened scale for overall concentrations and phases redistribution, and it uses fine-scale for description of growth or shrinking of each precipitate. Natural constraints on the effective interdiffusivity matrices in coarsened scale are formulated (zero determinant). We show characteristic zigzag-type diffusion paths, horn-like paths and additional regimes with single-phase sublayers. Model enables to trace the history of deviations from the Local Equilibrium condition in both matrix phases and enables to predict the redistribution of precipitates in both matrix phases.

## 1. Introduction

In high temperature coatings, welded parts and a range of other applications, components in the contact zone interdiffuse at elevated temperatures and may react to change the phase composition. In spite of the complexity of interdiffusion zone, it can be divided into regions separated by boundaries. The boundaries between the regions can be classified into types based on the number of phases that change on crossing the boundary [1,2]. Such a classification has been proven useful in analyzing and predicting complicated interdiffusion microstructures in multi-component and multiphase systems. The topic of boundary types and how they influence the diffusion path in three-component diffusion couples was recently reviewed [2,3]. In this work a more general topic, type 0 boundaries in *r*-component diffusion couples and evolution of the precipitates is considered.

Formation and growth of precipitates and interdiffusion in the two-phase zone of ternary alloy remains one of not well understood diffusion-controlled processes. One can show a vivid example demonstrating that, in general, the concentration gradients are not the true driving forces. Indeed, let the diffusion couple consists of the two-phase alloys (left and right) with average compositions corresponding to two points at the same conode. Contrary to typical expectations, no smoothing of concentration profiles will happen. The reason is obvious − each side of couple consists of the same phases (but with different volume fractions) which are in equilibrium with each other (as should be at the local equilibrium condition). Thus, in this case we have the huge gradient of overall concentrations but no gradient of chemical potentials of any component. Therefore no fluxes are expected (except those related to the coarsening of grains[1]). If both initial compositions are situated in the two-phase region of the phase diagram but at different conodes, the formation and evolution of two-phase zone becomes inevitable. Many authors [4–9] try to use the effective interdiffusivity 2 × 2 matrix $\tilde{D}_{ij}^{eff}$ for description of diffusion in the two-phase zone:

$$\frac{\partial N_1(t,x)}{\partial t} = \frac{\partial}{\partial x}\left(\tilde{D}_{11}^{eff}\frac{\partial N_1}{\partial x} + \tilde{D}_{12}^{eff}\frac{\partial N_2}{\partial x}\right),$$

$$\frac{\partial N_2(t,x)}{\partial t} = \frac{\partial}{\partial x}\left(\tilde{D}_{21}^{eff}\frac{\partial N_1}{\partial x} + \tilde{D}_{22}^{eff}\frac{\partial N_2}{\partial x}\right),$$

(1)

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\* Corresponding author.
  *E-mail address:* daniel@agh.edu.pl (M. Danielewski).

[1] It should be obvious that we neglect driving forces (factors) such as stress effects, surface tension etc.

where $N_i$ denotes atomic ratio of an $i$-component, termed here as concentration: $N_1 + N_2 + N_3 = 1$. The local values $N_i(t,x)$ are the result of averaging over "elementary" volume around point $\mathbf{x}$ (in coarsened scale) containing both phases of the two-phase mixture.

The main usual assumption in the two-phase zone is a local equilibrium between phases inside each physically small volume $dx$. Here $dx$ is considered as "physically small" elementary layer containing sufficient number of segments of both phases. In what follows $x$ will be called a coarsened scale. Overall concentrations in the two-phase zone are in fact the average concentrations

$$
\begin{aligned}
N_1(t,x) &= N_1^\alpha(K(t,x))\varphi^\alpha(t,x) + N_1^\beta(K(t,x))\varphi^\beta(t,x), \\
N_2(t,x) &= N_2^\alpha(K(t,x))\varphi^\alpha(t,x) + N_2^\beta(K(t,x))\varphi^\beta(t,x),
\end{aligned}
\tag{2}
$$

where $N_i^\alpha$, $N_i^\beta$ are concentration of $i$-th components in $\alpha$ and $\beta$ phase, $\varphi^\alpha(t,x)$, $\varphi^\beta(t,x)$ are the volume fractions of two phases, $\varphi^\alpha + \varphi^\beta = 1$, $K(t,x)$ is a so-called conode parameter, which varies from one conode to another and determines the compositions of both phases which are in local equilibrium between them. The equilibrium between two phases means equalizing three chemical potentials:

$$
\begin{aligned}
\mu_1^\alpha\left(N_1^\alpha, N_2^\alpha\right) &= \mu_1^\beta\left(N_1^\beta, N_2^\beta\right), \\
\mu_2^\alpha\left(N_1^\alpha, N_2^\alpha\right) &= \mu_2^\beta\left(N_1^\beta, N_2^\beta\right), \\
\mu_3^\alpha\left(N_1^\alpha, N_2^\alpha\right) &= \mu_3^\beta\left(N_1^\beta, N_2^\beta\right).
\end{aligned}
\tag{3}
$$

Above three equations are constraints for 4 unknowns: $N_1^\alpha, N_2^\alpha, N_1^\beta, N_2^\beta$, and imply only one free parameter (degree of freedom) that is a conode parameter $K(t,x)$, see Eq. (2).

One can demonstrate the conflict between usual simplified approach of using ideal solution approximation in multiphase systems, i.e., $\mu_i^j(t,x) = \mu_i^j(0) + RT \ln c_i^j(t,x)$ and thermodynamics. Let us treat both conode parameter and phase volume fraction as differentiable functions (which in fact may not be true for volume fraction), then the gradients of concentrations can be expressed in terms of gradients of $K$ and $\phi^\alpha$:

$$
\frac{\partial N_i(t,x)}{\partial x} = \left(\varphi^\alpha \frac{\partial N_i^\alpha}{\partial K} + \varphi^\beta \frac{\partial N_i^\beta}{\partial K}\right) \frac{\partial K}{\partial x} + \left(N_i^\alpha - N_i^\beta\right) \frac{\partial \varphi^\alpha}{\partial x}.
\tag{4}
$$

Following common approach, we consider the interdiffusivity matrix as some effective matrix with components depending on diffusivities in single phases and (what is key factor in this work) on morphology of the two-phase zone, in particular the local phase volume fraction, $\varphi^\alpha$. It is important to note that there exists a very strong constraint on such effective diffusivity matrix. Indeed, when we express fluxes using these effective diffusivities, e.g., upon combining Eqs. (1) and (2) we get:

where $\Omega \tilde{J}_i$ and $\Omega$ denote the overall volume flux and overall, composition invariant molar volume, respectively.

The last terms on the right hand side of Eqs. (5) and (6) visibly show (contrary to the phase rule) that in the case when terminal compositions are located on the same conode the diffusion may occur and phase fractions changes. It means that thermodynamics of two-phase regions should imply some constraints upon the interdiffusivity matrix inside two-phase zone. Thus important remark follows:

## 1.1. Remark 1

In case of arbitrary coefficients of the interdiffusivity matrix of the two-phase zone two compositions at the same conode do not warrant zero driving force and zero flux when thermodynamics of the ternary or multicomponent system is neglected. At the same conode volume fractions depend on initial composition distribution $(\partial \varphi^\alpha / \partial x \neq 0)$ and do not imply zero gradients. On the other hand, the flux between two regions with compositions at the same conode should be zero. For that reason, coefficients before the spatial derivatives of volume fractions should be zero:

$$
\begin{aligned}
\left(N_1^\alpha - N_1^\beta\right)\tilde{D}_{11}^{eff} + \left(N_2^\alpha - N_2^\beta\right)\tilde{D}_{12}^{eff} &= 0, \\
\left(N_1^\alpha - N_1^\beta\right)\tilde{D}_{21}^{eff} + \left(N_2^\alpha - N_2^\beta\right)\tilde{D}_{22}^{eff} &= 0.
\end{aligned}
\tag{7}
$$

This immediately gives us:

$$
\tilde{D}_{11}^{eff}\tilde{D}_{22}^{eff} - \tilde{D}_{12}^{eff}\tilde{D}_{21}^{eff} = 0, \det\tilde{D}^{eff} = 0.
\tag{8}
$$

Thus, effective interdiffusivity matrix describing quasi-equilibrium regime of diffusion in two-phase zone must be degenerate – one of its eigenvalues must be equal zero [6]. Otherwise, the "diffusion along conode" is implied by Eqs. (5) and (6) [7]. Mathematically, it became a reason for stochastization of diffusion path [7,10,11] or of zigzag-type path [12,13]. It means that the system admits possibility of "random walk" along conode that is consistent with conservation of matter.

More appropriate approach to diffusion in two-phase zone is based on Onsager approach, with the direct use of chemical potential gradients as the driving forces:

$$
\begin{aligned}
\frac{\partial N_1(t,x)}{\partial t} &= \frac{\partial}{\partial x}\left(\tilde{L}_{11}\frac{\partial \mu_1}{\partial x} + \tilde{L}_{12}\frac{\partial \mu_2}{\partial x}\right) = \frac{\partial}{\partial x}\left(\left(\tilde{L}_{11}\frac{d\mu_1}{dK} + \tilde{L}_{12}\frac{d\mu_2}{dK}\right)\frac{\partial K}{\partial x}\right), \\
\frac{\partial N_2(t,x)}{\partial t} &= \frac{\partial}{\partial x}\left(\tilde{L}_{21}\frac{\partial \mu_1}{\partial x} + \tilde{L}_{22}\frac{\partial \mu_2}{\partial x}\right) = \frac{\partial}{\partial x}\left(\left(\tilde{L}_{21}\frac{d\mu_1}{dK} + \tilde{L}_{22}\frac{d\mu_2}{dK}\right)\frac{\partial K}{\partial x}\right).
\end{aligned}
\tag{9}
$$

Effective Onsager coefficients $\tilde{L}_{ij}$ depend on diffusion mechanism, volume fractions of phases, on the morphology (parallel

$$
\begin{aligned}
-\Omega\tilde{J}_1 &= \tilde{D}_{11}^{eff}\frac{\partial N_1}{\partial x} + \tilde{D}_{12}^{eff}\frac{\partial N_2}{\partial x} = \tilde{D}_{11}^{eff}\left[\left(\varphi^\alpha\frac{\partial N_1^\alpha}{\partial K} + \varphi^\beta\frac{\partial N_1^\beta}{\partial K}\right)\frac{\partial K}{\partial x} + \left(N_1^\alpha - N_1^\beta\right)\frac{\partial \varphi^\alpha}{\partial x}\right] + \tilde{D}_{12}^{eff}\left[\left(\varphi^\alpha\frac{\partial N_2^\alpha}{\partial K} + \varphi^\beta\frac{\partial N_2^\beta}{\partial K}\right)\frac{\partial K}{\partial x} + \left(N_2^\alpha - N_2^\beta\right)\frac{\partial \varphi^\alpha}{\partial x}\right] = \\
&= \left[\tilde{D}_{11}^{eff}\left(\varphi^\alpha\frac{\partial N_1^\alpha}{\partial K} + \varphi^\beta\frac{\partial N_1^\beta}{\partial K}\right) + \tilde{D}_{12}^{eff}\left(\varphi^\alpha\frac{\partial N_2^\alpha}{\partial K} + \varphi^\beta\frac{\partial N_2^\beta}{\partial K}\right)\right]\frac{\partial K}{\partial x} + \left[\tilde{D}_{11}^{eff}\left(N_1^\alpha - N_1^\beta\right) + \tilde{D}_{12}^{eff}\left(N_2^\alpha - N_2^\beta\right)\right]\frac{\partial \varphi^\alpha}{\partial x},
\end{aligned}
\tag{5}
$$

$$
-\Omega\tilde{J}_2 = \tilde{D}_{21}^{eff}\frac{\partial N_1}{\partial x} + \tilde{D}_{22}^{eff}\frac{\partial N_2}{\partial x} = \left[\tilde{D}_{21}^{eff}\left(\varphi^\alpha\frac{\partial N_1^\alpha}{\partial K} + \varphi^\beta\frac{\partial N_1^\beta}{\partial K}\right) + \tilde{D}_{22}^{eff}\left(\varphi^\alpha\frac{\partial N_2^\alpha}{\partial K} + \varphi^\beta\frac{\partial N_2^\beta}{\partial K}\right)\right]\frac{\partial K}{\partial x} + \left[\tilde{D}_{21}^{eff}\left(N_1^\alpha - N_1^\beta\right) + \tilde{D}_{22}^{eff}\left(N_2^\alpha - N_2^\beta\right)\right]\frac{\partial \varphi^\alpha}{\partial x},
\tag{6}
$$