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Determination of eigenvalues, eigenvectors, and interdiffusion coefficients in ternary diffusion from diffusional constraints at the Matano plane

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ABSTRACT

New diffusional constraints interlinking interdiffusion fluxes, concentration gradients and concentrations of the components at the Matano plane are derived for an isothermal, solid-solid ternary diffusion couple. The derivations are based on the diagonalization of the interdiffusion coefficient matrices employed for the description of selected regions of the diffusion zone and on the integration of the decoupled concentration gradients and interdiffusion fluxes over those regions. By selecting two diffusion regions, one on either side of the Matano plane, the diffusional constraints are employed for the direct determination of eigenvalues, eigenvector parameters and a matched pair of interdiffusion coefficient matrices for the generation of concentration profiles over the two regions. For a diffusion couple assembly, the input data needed for the calculations are the concentration gradients, interdiffusion fluxes and composition developed at the Matano plane at a given time. The diffusion parameters determined by the new analysis help ensure that the calculated concentration profiles, interdiffusion fluxes and concentration gradients of the components are continuous everywhere including the Matano plane. The application of the analysis is illustrated and discussed with selected experimental diffusion couples investigated in the Cu-Ni-Zn ternary system.

1. Introduction

By employing a transfer matrix methodology (TMM), Ram-Mohan and Dayananda [1] developed an analysis of multicomponent diffusion with any number of components for the determination of interdiffusion fluxes and concentrations at any section in the diffusion zone from those given at another section. This analysis employed interdiffusion coefficients determined as average values over selected regions by the method of Dayananda and Sohn [2]. The TMM enabled the generation of concentration profiles over any selected region of the diffusion zone and generalized the analytical solutions of Fujita and Gosting [3] developed for ternary diffusion. The TMM has been further developed by Ram-Mohan and Dayananda [4] to describe slopes of diffusion paths directly in terms of eigenvalues and eigenvectors obtained by diagonalizing the diffusion coefficient matrices. New relations between eigenvalues and concentration gradients of individual components have also been derived as constraints at selected sections in the diffusion zone. Relations between the composition developed at the Matano plane [5] of a multicomponent diffusion couple and effective interdiffusion coefficients of the individual components on the two sides of the Matano plane have also been developed [6] by the author.

One of the objectives of this paper is to derive diffusional constraints that interlink interdiffusion fluxes, concentrations, and concentration gradients of the components at the Matano plane (x_o) of an isothermally annealed ternary diffusion couple. A second objective is to present a novel approach to utilize such diffusional constraints for the direct determination of eigenvalues, eigenvector parameters and a matched pair of $\tilde{\boldsymbol{D}}^{(3)}$ interdiffusion coefficient matrices for the description of two diffusion regions, one on either side of x_o. Concepts of decoupled interdiffusion fluxes, concentrations and their gradients on the diagonal basis obtained by diagonalizing the $\tilde{\boldsymbol{D}}^{(3)}$ matrices [1,4] are utilized along with new expressions obtained from an integration of the decoupled concentration gradients and interdiffusion fluxes over the selected regions. New relations are presented to relate interdiffusion fluxes, concentrations, and concentration gradients of the components at the Matano plane with terminal alloy compositions and eigenvalue and eigenvector parameters for the two diffusion regions. The

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application of the analysis for the determination of the various diffusion parameters on the two sides of the Matano plane from diffusional information available just at x_o is illustrated and discussed with selected Cu-Ni-Zn diffusion couples [7] investigated at 775 °C.

2. Relations among fluxes, concentrations and their gradients

Fick's law extended to interdiffusion in ternary systems is expressed by Ref. [8].

$$\tilde{\boldsymbol{J}}^{(3)}(x,t) = -\tilde{\boldsymbol{D}}^{(3)} \cdot \frac{\partial \boldsymbol{C}^{(3)}(x,t)}{\partial x} \tag{1}$$

where the bold-faced symbols $\tilde{\boldsymbol{J}}^{(3)}$ and $\boldsymbol{C}^{(3)}$ represent, respectively, vectors of interdiffusion fluxes $\{\tilde{J}_1, \tilde{J}_2\}$ and concentrations $\{C_1, C_2\}$ of independent components 1 and 2, and $\tilde{\boldsymbol{D}}^{(3)}$ is the matrix of four ternary interdiffusion coefficients with component 3 taken as the dependent variable. If these coefficients are considered constant over a selected region, $x_s \le x \le x_{s+1}$ in the diffusion zone of a diffusion couple, $\tilde{\boldsymbol{D}}^{(3)}$ can be diagonalized [1,4] through the relation

$$\boldsymbol{P}^{-1} \cdot \tilde{\boldsymbol{D}}^{(3)} \cdot \boldsymbol{P} = \boldsymbol{\Delta}^{(3)}, \tag{2}$$

where $\boldsymbol{P}$ is the matrix of eigenvectors and $\boldsymbol{\Delta^{(3)}}$ is the matrix of eigenvalues. $\boldsymbol{P}$ and $\boldsymbol{\Delta^{(3)}}$ matrices are described by Ref. [1].

$$\boldsymbol{P} = \begin{pmatrix} 1 & \alpha_2 \\ \beta_1 & 1 \end{pmatrix} \tag{3}$$

and

$$\Delta^{(3)} = \begin{pmatrix} d_1 & 0 \\ 0 & d_2 \end{pmatrix} \tag{4}$$

where β_1 and α_2 are the parameters for the major eigenvector and minor eigenvector, respectively, and d_1 and d_2 are the major eigenvalue and minor eigenvalue, respectively.

The decoupled interdiffusion fluxes denoted by $\widehat{J}_i(x,t)$ in the diagonal basis are given by Refs. [1,4].

$$\widehat{J}_i(x,t) = -d_i \cdot \frac{\partial \widehat{C}_i(x,t)}{\partial x} \quad (i = 1,\ 2) \tag{5}$$

where

$$\widehat{J}_1 = \frac{\left(\tilde{J}_1 - \alpha_2 \tilde{J}_2\right)}{(1 - \alpha_2\beta_1)}, \tag{6}$$

$$\widehat{J}_2 = \frac{\left(-\beta_1 \tilde{J}_1 + \tilde{J}_2\right)}{(1 - \alpha_2\beta_1)}, \tag{7}$$

$$\widehat{C}_1(x,t) = \frac{C_1 - \alpha_2 C_2}{(1 - \alpha_2\beta_1)}, \tag{8}$$

and

$$\widehat{C}_2(x,t) = \frac{(-\beta_1 C_1 + C_2)}{(1 - \alpha_2\beta_1)}. \tag{9}$$

In terms of interdiffusion fluxes $\tilde{J}_i(x,t)$ and concentration gradients, $\partial C_i/\partial x$, Eq. (5) yields two important relations given by Refs. [1,4,9].

$$\tilde{J}_1 - \alpha_2 \tilde{J}_2 = -d_1 \left(\frac{\partial C_1}{\partial x} - \alpha_2 \frac{\partial C_2}{\partial x}\right) \tag{10}$$

and

$$-\beta_1 \tilde{J}_1 + \tilde{J}_2 = -d_2 \left(-\beta_1 \frac{\partial C_1}{\partial x} + \frac{\partial C_2}{\partial x}\right) \tag{11}$$

Also, it has been shown that the decoupled interdiffusion flux $\widehat{J}_i(x,t)$ at any x in the range $x_s \le x \le x_{s+1}$ can be expressed by Ref. [1].

$$\widehat{J}_i(x,t) = \exp\left[-\frac{\left\{\left(x - x_{0)}\right)^2 - (x_s - x_0)^2\right\}}{4t \cdot d_i}\right] \widehat{J}_i(x_s,t) \quad (i = 1,\ 2) \tag{12}$$

where $\widehat{J}_i(x_s,t)$ refers to the decoupled interdiffusion flux at x_s. From Eqs. (5) and (12), one can also get

$$\frac{\partial \widehat{C}_i(x,t)}{\partial x} = -\frac{1}{d_i} \cdot \exp\left[-\frac{(x - x_o)^2 - (x_s - x_o)^2}{4t \cdot d_i}\right] \cdot \widehat{J}_i(x_s,t) \quad (i = 1,\ 2) \tag{13}$$

Integrating Eq. (13) between the limits, x_s and x, we get

$$\widehat{C}_i(x,t) = \widehat{C}_i(x_s,t) - \sqrt{\frac{\pi t}{d_i}} \cdot \left[erf\left(\frac{(x - x_o)}{2\sqrt{t \cdot d_i}}\right) - erf\left(\frac{(x_s - x_o)}{2\sqrt{t \cdot d_i}}\right)\right] \cdot \exp\left(\frac{(x_s - x_o)^2}{4t \cdot d_i}\right) \cdot \widehat{J}_i(x_s,t) \quad (i = 1,\ 2) \tag{14}$$

For $x = x_{s+1}$, Eq. (14) yields:

$$\widehat{J}_i(x_s,t) = \frac{-\left[\widehat{C}_i(x_{s+1}, t) - \widehat{C}_i(x_s,t)\right]}{\sqrt{\frac{\pi t}{d_i}} \cdot \left[erf\left(\frac{x_{s+1} - x_o}{2\sqrt{t \cdot d_i}}\right) - erf\left(\frac{x_s - x_o}{2\sqrt{t \cdot d_i}}\right)\right] \cdot \exp\left(\frac{(x_s - x_o)^2}{4t \cdot d_i}\right)} \quad (i = 1,\ 2) \tag{15}$$