Extracting interdiffusion coefficients from binary diffusion couples using traditional methods and a forward-simulation method

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A B S T R A C T

A MatLab program is developed to allow effective extraction of both interdiffusion coefficients and impurity diffusivities from concentration profiles of binary diffusion couples. In addition to implementing the Boltzmann–Matano method, the Sauer–Freise method, the Hall method, and the Wagner method, a forward-simulation method was developed and implemented in the program. Eight binary systems (Fe–Ni, Co–Ni, Nb–W, Ni–W, Ni–Mo, Co–Mo, Fe–Nb and Ni–Nb) were used to test the program and to evaluate the advantages and disadvantages of the various methods. The forward-simulation method shows advantages including the ability to extract the impurity diffusion coefficients. Valuable impurity diffusivities and interdiffusion coefficients data at 1100 °C for the eight binary systems are obtained and they are in good agreements with available literature data. The successful diffusivity extraction from several complicated composition profiles with several intermetallic compounds demonstrates the reliability and robustness of the program.

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1. Introduction

A diffusion multiple is an assembly of several metal blocks arranged in a pre-designed geometry to allow many diffusion couples and triples to be assembled in a single sample [1–3]. It has been applied to effective determination of phase diagrams by taking advantage of the local equilibrium at the phase interfaces and to rapid measurements of composition-dependent properties using micron-scale resolution materials property measurement techniques [4]. Since diffusion coefficients are essential kinetic parameters for the simulation of homogenization, phase transformations, and materials properties (such as creep-rupture), it is highly desirable to develop an automated program to extract interdiffusion coefficients from the large amounts of binary diffusion profiles that are obtained from diffusion-multiple samples. Since most profiles consist of more than one phase, the program needs to effectively handle multi-phase cases including the capability of obtaining effective interdiffusion coefficients for intermetallic phases with a very narrow stoichiometry range.

A MatLab code is developed to test several existing methods such as the Boltzmann–Matano method [5,6], the Sauer–Freise method [7], the Hall method [8], and the Wagner method [9]. Using diffusion profiles of several binary systems obtained from diffusion multiples, the interdiffusion coefficient data extracted using these methods are obtained and compared. A novel forward-simulation method for extracting interdiffusion coefficients is then developed; and its advantage in smoothing out irregularities in the extracted diffusion coefficients is demonstrated. The results also show that the forward-simulation method can obtain the impurity diffusion coefficients reliably from even pure metal to pure metal diffusion couples.

This article will start with a brief introduction to various methods for extracting interdiffusion coefficients of binary systems, followed by a description of the forward-simulation method. The algorithm to implement the methods will then be described, followed by the Results and Discussion Section which will show several examples for comparison of the results. A conclusion at the end summarizes the results from this work.

2. Methods

2.1. Boltzmann–Matano method

The Boltzmann–Matano (B–M) [5,6] analysis is widely used to extract concentration dependent interdiffusion coefficients $\tilde{D}(C)$ from experimental concentration profiles obtained from diffusion couples as following.

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$$\tilde{D}(C') = \left(-\frac{1}{2t}\frac{dx}{dC} \right)\Big|_{C'} \int_{C_L}^{C'} (x - x_M)dC \tag{1}$$

Here, C is concentration and C' is the concentration at a specific location x', x is the distance coordinate, and t is time. Position of the Matano plane x_M can be determined by Equation (2) based on mass balance.

$$\int_{-\infty}^{x_M} [C(x) - C_L]dx = \int_{x_M}^{+\infty} [C_R - C(x)]dx \tag{2}$$

In Equations (1) and (2), the C_L and C_R represent the concentration at the far left end and far right end of the diffusion couple. The Matano analysis is applicable for both single phase and multi-phase diffusion couples since the assumption for B–M analysis is valid even when the concentration profile is discontinuous [10].

Since errors can be introduced during the process of evaluating the position of the Matano plane as well as in determining the concentration gradient near phase interface/boundary areas and at the far ends of the diffusion zone [6], several modified methods such as the Sauer–Freise method [7] and the Hall method [8] have been developed to reduce these errors.

2.2. Sauer–Freise method

To eliminate the need of evaluating the Matano plane position x_M, Sauer and Freise [6,7] defined a concentration ratio Y via Equation (3):

$$Y(x) = \frac{C(x) - C_L}{C_R - C_L} \tag{3}$$

An equation for interdiffusivity $\tilde{D}$ can be derived as following.

$$\tilde{D}(C') = \frac{1}{2t(dY/dx)|_{x'}}\left\{ [1 - Y(x')] \int_{-\infty}^{x'} Y(x)dx \right. \\ \left. + Y(x') \int_{x'}^{+\infty} [1 - Y(x)]dx \right\} \tag{4}$$

where $Y(x')$ is the concentration ratio value at point x'. This method was further discussed by Wagner [9] and later derived by Broeder [11] again with simpler derivations.

2.3. Wagner method

Wagner [9] considered the variation of molar volume V_m with composition and derived the diffusivity extraction equation with a similar equation as the Sauer–Freise method.

$$\tilde{D}(C') = \frac{V_m(C')}{2t(dY/dx)|_{x'}}\left\{ [1 - Y(x')] \int_{-\infty}^{x'} \frac{Y(x)}{V_m(C)}dx \right. \\ \left. + Y(x') \int_{x'}^{+\infty} \frac{1 - Y(x)}{V_m(C)}dx \right\} \tag{5}$$

An average diffusion coefficient in an intermetallic compound with a narrow concentration range (i.e., the lowest and highest compositions c_1 and c_2 of an intermediate phase are very close) was also defined to avoid the large uncertainty in computing the concentration gradient within the phase [9].

$$\int_{C_{i,i-1}}^{C_{i,i+1}} \tilde{D}dC = (C_R - C_L)\left\{ Y^{(i)}\left(1 - Y^{(i)}\right)\frac{(\Delta x_i)^2}{2t} \right. \\ + \frac{\Delta x_i V_m^{(i)}}{2t}\left[\left(1 - Y^{(i)}\right) \int_{-\infty}^{x_{i,i-1}} \frac{Y(x)}{V_m(C)}dx + Y^{(i)} \right. \\ \left. \left. \times \int_{x_{i,i+1}}^{+\infty} \frac{1 - Y(x)}{V_m(C)}dx \right] \right\} \tag{6}$$

$$\overline{\overline{D}} = \frac{1}{C_2 - C_1} \int_{C_1}^{C_2} \tilde{D}(C)dC \tag{7}$$

Here C_1 and C_2 are the compositions at both low and high end of the phase region with $x_{i,i-1}$ and $x_{i,i+1}$ being the locations of the left edge and right edge of this intermetallic phase, and Δx_i is the thickness of this phase. $V_m^{(i)}$ and $Y^{(i)}$ are the average values of molar volume V_m and concentration ratio Y in the phase i. $\overline{\overline{D}}$ is the calculated average diffusion coefficient in the phase with a narrow stoichiometric range.

2.4. Hall method

Another uncertainty of the B–M analysis is associated with the evaluation of concentration gradients at the two far ends of the diffusion profiles where the concentrations are almost constant and equal to the two alloy compositions that the diffusion couple was made up of. Hall [8] constructed an alternative way to evaluate the diffusion coefficients of the compositions near the far ends by analyzing the profile of u vs λ with a linear fit $u = h\lambda + k$. Here u and λ are defined as:

$$Y \equiv \frac{c - c_L}{c - c_R} = \frac{1}{2}[1 + erfc(u)] \tag{8}$$

$$\lambda = x/\sqrt{t} \tag{9}$$

The diffusion coefficients near the left composition C_L and right composition C_R can be estimated by Equations (10.1) and (10.2), respectively, with knowing the linear fit coefficients h_1, k_1 for left side and h_2, k_2 for the right side of the diffusion couple.

$$\tilde{D}(C') = \frac{1}{4h_1^2}\left[1 + \frac{2k_1}{\sqrt{\pi}}\exp\left(u^2\right) \times Y(C') \right] \tag{10.1}$$

$$\tilde{D}(C') = \frac{1}{4h_2^2}\left\{ 1 - \frac{2k_2}{\sqrt{\pi}}\exp\left(u^2\right)[1 - Y(C')] \right\} \tag{10.2}$$

2.5. Forward-simulation method

A MatLab program was developed to use the above-mentioned methods to extract interdiffusion coefficients of binary systems, especially multi-phase binary systems. The results to be presented subsequently will show that the obtained diffusion coefficients have large uncertainty/scatter due to both the scatter in the experimental data and the artifacts introduced by the smoothing scheme. During data smoothing there is a constant battle between the number of points to be averaged and the granularity of the experimental data. When too few data points are used in the moving average, the scatter in the experimental data cannot be smoothed out. On the contrary, when too many data points are used in the averaging process, the real local composition gradients