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An effective method to calculate the composition-dependent interdiffusivity with one diffusion couple

Kaiming Cheng [a,*], Jixue Zhou [a], Huixia Xu [b], Shouqiu Tang [a], Yuansheng Yang [c]

[a] Shandong Key Laboratory for High Strength Lightweight Metallic Materials, Advanced Materials Institute, Shandong Academy of Sciences, Jinan 250014, China
[b] State Key Laboratory of Powder Metallurgy, Central South University, Changsha 410083, China
[c] Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, China

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ABSTRACT

Previous numerical inverse method to calculate composition-dependent interdiffusivity with one diffusion couple can encounter with low calculation efficiency due to the unavoidable diffusion simulation procedure. The present work applies the numerical inverse method to the integrated form of diffusion equation, degenerating the original inverse problem into a linear multi-objective optimization problem, which can be solved with dramatically increased calculation efficiency while maintaining the overall accuracy. The current method is verified in the fcc phase of the Al-Mg, Al-Mg-Zn, Al-Mg-Zn-Cu system as well as the intermetallic compounds of the Al-Mg system. The increment in computation efficiency is discussed.

1. Introduction

Composition-dependent interdiffusion coefficient is an indispensable parameter for quantitative description of amount of physical chemistry phenomena in materials science, such as alloy solidification, heat treatment, oxidation, bonding, coating and electric packaging. Owning to the extensive application, amount of continuous effort has been made to look for methods to extract interdiffusivity from the experimental results of diffusion couple. And the classical diffusion equation is often the basis of these methods to calculate interdiffusivity. Considering an alloy system of n species, there are $n-1$ simultaneous diffusion equations in one dimension when species n is selected as the solute [1–3].

$$\frac{\partial C_i}{\partial t} = \nabla\left(\sum_{j=1}^{n-1}\tilde{D}_{ij}^{n}\nabla C_j\right) \quad (i = 1 \ldots n-1) \tag{1}$$

where C_i is the composition of species i and $\tilde{D}_{ij}^{n}$ is the interdiffusivity matrix of $(n-1)\times(n-1)$ dimension changing with composition. To determine the interdiffusivity, one can follow the procedure of Boltzmann-Matano analysis [4,5] often used for binary system to obtain the integrated form of Eq. (1),

$$\frac{1}{2t}\int_{C_i^{-\infty}\ or\ C_i^{+\infty}}^{C_i}(x-x_0)dC_i = -\sum_{j=1}^{n-1}\tilde{D}_{ij}^{n}\nabla C_j \quad (i = 1 \ldots n-1) \tag{2}$$

where $C_i^{-\infty}$ and $C_i^{+\infty}$ are the initial terminal composition and x_0 is the Matano plane. The left side of Eq. (2) gives the formula to compute interdiffusion flux $\tilde{J}_i$, while the right side of Eq. (2) contains interdiffusivity $\tilde{D}_{ij}^{n}$ and composition gradient ∇C_j. It thusly relates the interdiffusivity to the properties that can be measured from the diffusion couple experiment and can be used to calculate interdiffusion coefficients.

When $n = 2$, i.e. in a binary system, Eq. (2) can be directly used to compute the single composition-dependent interdiffusion coefficient with one diffusion couple. In a ternary system, i.e. $n = 3$, solving the 2×2 interdiffusivity matrix requires four independent equations, but one diffusion couple can provide only two independent equations according to Eq. (2). The Kirkaldy-Matano analysis [3] can be performed to generate two more equations by providing an extra diffusion path have intersection composition point. Following this procedure, the composition-dependence of interdiffusivity can be studied by creating lots of diffusion paths to get enough intersections, but its efficiency is unsatisfactory. Situation becomes more difficult in multicomponent system, i.e. n > 3. Since one diffusion path provides only n-1 independent equations, it results in the problem of using an underdetermined equation set to solve the $(n-1)\times(n-1)$ interdiffusivity matrix. Following the procedure of the Kirkaldy-Matano analysis, one may create $n-2$ more diffusion paths with one common intersection to

* Corresponding author.
E-mail addresses: chengkaimingtry@gmail.com, chengkm@sdas.org (K. Cheng).

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provide extra equations, but this is an extremely strict condition for experimental sample preparation. And it hampers the determination of composition-dependent interdiffusivity in multicomponent systems.

To remedy such situation, several one-diffusion-couple methods based on Eq. (2) have been presented. Dayananda and Sohn [6] evaluated the averaged interdiffusion coefficients of ternary systems by integrating both sides of Eq. (2) on certain composition ranges along the diffusion path. Following this procedure, Cermak and Rothova [7] tried to compute the composition-dependent interdiffusivity by selecting infinitely small integration composition range, but this treatment can lead to the ill-conditioned problem [8]. The pseudobinary approach was recently presented by Paul [9], in which the compositions of the end members of a diffusion couple should be selected such that only two elements diffuse into the interdiffusion zone. The method can be very effective when the pseudobinary condition is experimentally fulfilled, but may encounter with limitation in the case of complex diffusion behavior among species in multicomponent system. Nevertheless, the advantage of these one-diffusion-couple methods based on Eq. (2) is the high calculation efficiency of solving the first-order linear equations set independent of time, and more study on obtaining the composition-dependent interdiffusivity within this frame of methodology is still needed.

In addition, there is another type of one-diffusion-couple method to determine the $\tilde{D}_{ij}^{n}$ matrix by solving the typical parabolic inverse (ill-posed) problem through numerical inverse method based on Eq. (1) [10]. The interdiffusivity can be defined as a function of composition, and the undetermined parameters in these functions can be adjusted by reproducing the composition profile in each iteration process using Eq. (1). When the error between calculated and experimental composition profile is within certain critical value, the composition-dependent interdiffusivity can be obtained. Bouchet and Mevrel [11] applied the numerical inverse method to calculate the ternary interdiffusion coefficient in solution phase, and the continuous function of interdiffusivity was defined in the form of polynomial,

$$\tilde{D}_{ij}^{n} = p_{ij0} + \sum_{k=1}^{n-1} p_{ijk} C_k + \sum_{l=n}^{2n-2} p_{ijl} (C_{l-n+1})^2 \tag{3}$$

where p_{ij} are the parameters to determine. The physical model of atomic mobility [12], which can describe the temperature and composition dependence of interdiffusivity, was then introduced by Chen et al. [13] to study the diffusion coefficient in the solution phase of multicomponent system,

$$\begin{aligned}\tilde{D}_{ij}^{n} &= RT\left(M_i\Phi_{ij}^{n} - C_i\sum_m M_m\Phi_{mj}^{n}\right)M_i \\ &= \frac{1}{\mathrm{RT}}\exp\left(\frac{\sum_{j=1}^{n} C_j\Delta G_i^{j} + \sum_j\sum_{k\neq j} C_jC_k\Delta G_i^{j,k} + \ldots}{\mathrm{RT}}\right)\end{aligned} \tag{4}$$

where Φ_{ij}^{n} is the thermodynamic factor and one may choose to set it to constant. ΔG_i^{j} and $\Delta G_i^{j,k}$ are the parameters to be determined in the numerical inverse way. In addition to the solution phase, Zhang and Zhao [14] presented a forward-simulation method for the cases of multi diffusion layers, which should be included in this frame of methodology. By solving Eq. (1) and the moving boundary problem,

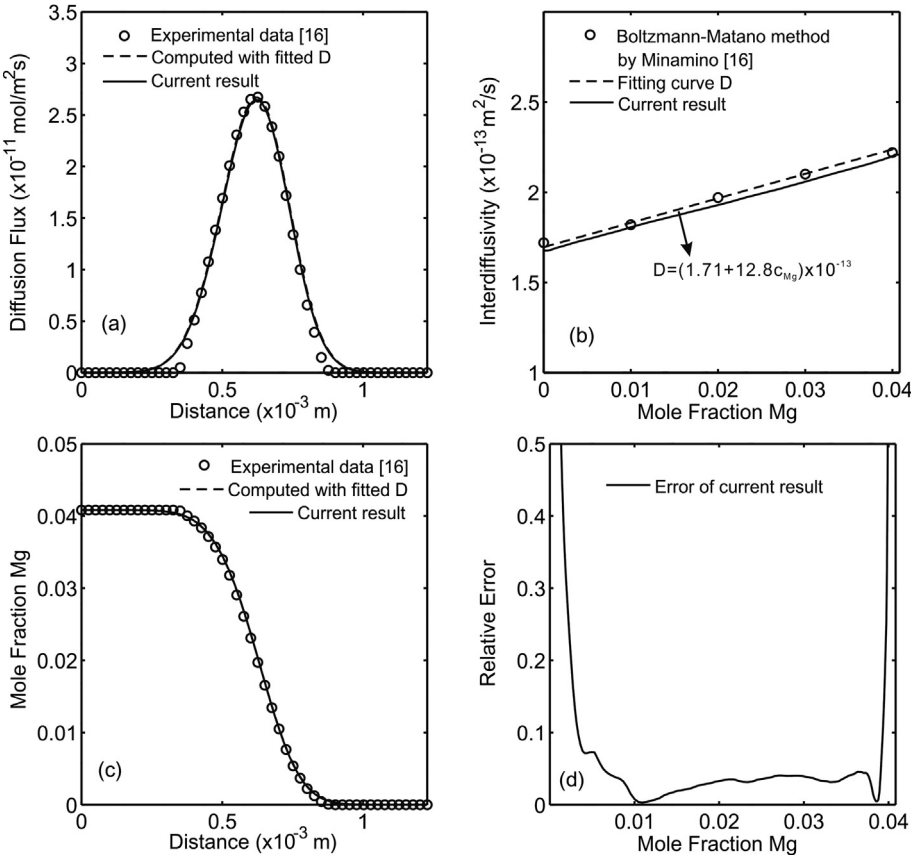

Fig. 1. The currently calculated (a) interdiffusion flux, (b) interdiffusivity, (c) composition profile and (d) relative error of interdiffusivity of the Al-Mg fcc single-phase diffusion couple at 781 K for 36,960 s compared with experimental data [16]. The previous interdiffusivity calculated *via* Boltzmann-Matano method by Minamino et al. [16] and the corresponding prediction curves are shown in dashed lines.