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A pragmatic method to determine the composition-dependent interdiffusivities in ternary systems by using a single diffusion couple

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A pragmatic method for determining the composition-dependent interdiffusivities in ternary systems by means of a single diffusion couple was developed and realized via a homemade code. Its reliability was further validated in a series of Co-based diffusion couples annealed at 1373 K by comparing with the results via the traditional Matano–Kirkaldy method. In addition, various diffusion properties were predicated, and comprehensively compared with the experimental data.

Keywords: Diffusion; Alloys; Ternary system; Diffusion couple

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The single-phase diffusion couple technique is frequently employed to determine the interdiffusivities of the target phase. In a binary system, only one independent interdiffusivity exists. Thus one single-phase diffusion couple, together with, for example, the Boltzmann–Matano method, results in the composition-dependent interdiffusivities in a binary system. In a ternary system, however, the situation becomes dramatically complex because four independent interdiffusivities (two main and two cross ones) need to be determined. The first feasible method to determine the interdiffusivities in a ternary system was carried out by Kirkaldy and Young [1], who employed two diffusion couples with a common intersection point along their diffusion paths coupled with the extended Boltzmann–Matano method. With the well-known Matano–Kirkaldy method [1] or its variance [2], the four independent interdiffusivities at the intersection point can be obtained for a ternary system. Though the Matano–Kirkaldy method has been widely used in the materials community, its low efficiency cannot meet the requirement of abundant experimental data in the MGI (Materials Genome Initiative [3,4]) and/or ICME (Integrated Computational Materials Engineering [5]) projects nowadays. In addition, if one uses such a set of interdiffusivities to predict composition profiles of the ternary diffusion couple by means of simple error functions or even complex numerical simulation tools like DICTRA (DIffusion Controlled TRAnsformation) [6] and the phase-field method [7], the abnormal compositions like the "negative" composition [8] may occur in error function solutions or numerical simulations.

To remedy such a situation, several methods for evaluating the average interdiffusivity in ternary systems by using a single diffusion couple have been developed by Dayananda and Sohn [9], Zhang et al. [10], Jaques and LaCombe [11] and Paul [12]. Though more than one group of ternary interdiffusivities can be determined, the reliability of the determined average interdiffusivities depends largely on their variation within the specified composition range. Very recently, the present authors [13] verified that the interdiffusivities evaluated on the basis of the Cermak–Rothova method [14] are still the average ones, but not the truly composition-dependent values. In order to determine the truly composition-dependent interdiffusivities in a ternary system with one diffusion couple, Bouchet and Mevrel [15] developed a purely mathematical method for evaluating the composition-dependent interdiffusivities in ternary

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systems based on the determined composition profiles and Fick's second law. However, their method is extremely time-consuming [15], and all their determined cross-interdiffusivities in the ternary Ni–Al–Pt system are "unreasonable" zero [16], which largely hampers its wide acceptance in the materials community.

Consequently, there is an urgent need to develop an effective method to determine the composition-dependent interdiffusivities in ternary systems by using a single diffusion couple, which is the main target in the present work.

Assuming in a hypothetical A–B–C ternary system (C is chosen as the solvent here), the evolution of concentration for component i ($i = A$ or B) is governed by Fick's second law:

$$\frac{\partial c_i}{\partial t} = \frac{\partial}{\partial x}\left(\tilde{D}_{iA}^{C}\frac{\partial c_A}{\partial x} + \tilde{D}_{iB}^{C}\frac{\partial c_B}{\partial x}\right)(i = A \text{ or } B) \tag{1}$$

where c_i is concentration of component i, x is diffusion distance, t is diffusion time, $\tilde{D}_{AA}^{C}$ and $\tilde{D}_{BB}^{C}$ are the main interdiffusivities and $\tilde{D}_{AB}^{C}$ and $\tilde{D}_{BA}^{C}$ are the cross ones. According to Manning's random alloy model [17], the interdiffusivities $\tilde{D}_{ij}^{C}$ ($i, j = A$ or B) and the mobility M_i are related by:

$$\begin{aligned}\tilde{D}_{ij}^{C} &= RT\left[M_i\Phi_{ij}^{C} - c_i\left(M_A\Phi_{Aj}^{C} + M_B\Phi_{Bj}^{C} + M_C\Phi_{Cj}^{C}\right)\right]\\ &\quad + s\left[(M_i - c_AM_A - c_BM_B - c_CM_C)\frac{2c_iRT\sum_m(M_m\Phi_{mj}^{C})}{A_0\sum_m(c_mM_m)}\right]\end{aligned} \tag{2}$$

where R is the gas constant and T is temperature. And the thermodynamic factor Φ_{ij}^{C} is expressed by:

$$\Phi_{ij}^{C} = \frac{c_i}{RT}\cdot\left(\frac{\partial\mu_i}{\partial c_j} - \frac{\partial\mu_i}{\partial c_C}\right) \tag{3}$$

where μ_i is the chemical potential of component i, and can be obtained from the corresponding thermodynamic descriptions, which are usually available for most alloy systems nowadays [18]. The second term on the right-hand side of Eq. (2) denotes the vacancy-wind effect, which considers the contribution of the vacancy flux. The vacancy-wind effect will be considered if s equals 1, while not if s equals 0. The parameter A_0 is a factor depending only on crystal structure, and here equals to 7.15 for face centered cubic (fcc) crystals [17]. In principle, the mobility can be represented by different functions, but they should be generally concentration- and temperature-dependent. In order to assign more physical meanings to the present method, the one developed by Andersson and Ågren [19] and incorporated in DICTRA software was employed in the present work to express the atomic mobility for element i:

$$M_i = \frac{1}{RT}\exp\left(\frac{\Delta G_i}{RT}\right) \tag{4}$$

where ΔG_i can be expanded by the Redlich–Kister polynomial:

$$\begin{aligned}\Delta G_i &= c_A\Delta G_i^{A} + c_B\Delta G_i^{B} + c_C\Delta G_i^{C} + c_Ac_B\Delta G_i^{A,B}\\ &\quad + c_Ac_C\Delta G_i^{A,C} + c_Bc_C\Delta G_i^{B,C} + c_Ac_Bc_C\Delta G_i^{A,B,C}\end{aligned} \tag{5}$$

In DICTRA notation, ΔG_i^{A}, ΔG_i^{B} and ΔG_i^{C} are the end-members for diffusion of element i in element A, B and C, while $\Delta G_i^{A,B}$, $\Delta G_i^{A,C}$, $\Delta G_i^{B,C}$ and $\Delta G_i^{A,B,C}$ are the interaction parameters for the mobility of element i in the A–B, A–C, B–C and A–B–C systems, respectively. Most of those parameters are temperature-dependent, and in principle they are critically assessed based on the corresponding experimental diffusivities in a typical DICTRA-type assessment. However, in the present work, all these coefficients in Eq. (5) are treated as adjustable parameters, which can be evaluated on the basis of one or several sets of composition profiles. Considering the fact that too many adjustable parameters are available in Eq. (5) for a ternary system, ΔG_i^{A}, ΔG_i^{B} and ΔG_i^{C} are first fixed because these parameters corresponding to self and impurity diffusivities can be easily obtained from the experimental data, first-principles calculations, molecular dynamic simulation or some semi-empirical relations nowadays. Moreover, for the other adjustable parameters, such as $\Delta G_i^{A,B}$, $\Delta G_i^{A,C}$, $\Delta G_i^{B,C}$ and $\Delta G_i^{A,B,C}$, only one or two of them are needed to be evaluated in most cases for one diffusion couple. Therefore, by combining Eqs. (1)–(5), one can evaluate the concentration-dependent interdiffusivities based on the measured concentration profiles together with the available thermodynamic description.

Following the above strategy, a C++ program was compiled to determine the concentration-dependent interdiffusivities from a single diffusion couple. This C++ program consists of three modules, i.e., "read-in", "fitting-check" and "write-out". In the "read-in" module, all the experimental information for the target single diffusion couple including the measured concentration profiles, annealing temperature, diffusion time, nominal concentration, the thermodynamic description of the target phase as well as the Arrhenius expressions of self- and impurity diffusion for the pure elements, are first read in. In the "fitting-check" module, an optimal set of adjustable parameters such as $\Delta G_i^{A,B}$, $\Delta G_i^{A,C}$, $\Delta G_i^{B,C}$ and $\Delta G_i^{A,B,C}$ were carefully chosen by iterative fitting until the minimization of the error between the measured and calculated concentration profiles is achieved:

$$\min < error >= \min < \frac{1}{N}\sum_{i=A,B}\sum_{j=1}^{N}\left(|c_{ij}^{\mathrm{cal}} - c_{ij}^{\mathrm{exp}}|\right) > \tag{6}$$

where c_{ij}^{cal} and c_{ij}^{exp} are the calculated and experimental concentrations of component i at the jth point, respectively, and N is the number of the experimental data. With the optimal set of fitting parameters, the concentration-dependent interdiffusivities in the target ternary system can be computed via Eq. (2). All the obtained interdiffusivities were then subject to be examined by the following thermodynamically stable constraints [1]:

$$\tilde{D}_{AA}^{C} + \tilde{D}_{BB}^{C} > 0 \tag{7}$$

$$\tilde{D}_{AA}^{C}\tilde{D}_{BB}^{C} - \tilde{D}_{AB}^{C}\tilde{D}_{BA}^{C} \geqslant 0 \tag{8}$$

$$(\tilde{D}_{AA}^{C} - \tilde{D}_{BB}^{C})^2 + 4\tilde{D}_{AB}^{C}\tilde{D}_{BA}^{C} \geqslant 0 \tag{9}$$