Available online at www.sciencedirect.com

ScienceDirect

Scripta Materialia 76 (2014) 5–8

Scripta MATERIALIA

www.elsevier.com/locate/scriptamat

Comments and Reply

Analysis of the Cermak–Rothova method for determining the concentration dependence of ternary interdiffusion coefficients with a single diffusion couple

K. Cheng,[a,1] W. Chen,[a,1] D. Liu,[a,b,1] L. Zhang[a,*] and Y. Du[a]

[a] *State Key Laboratory of Powder Metallurgy, Central South University, Changsha, Hunan 410083, China*
[b] *School of Materials Science and Engineering, Central South University, Changsha, Hunan 410083, China*

Received 8 November 2013; revised 29 November 2013; accepted 29 November 2013
Available online 10 December 2013

Dayananda's method for calculating the average ternary interdiffusion coefficient ($\tilde{\tilde{D}}^3_{ij}$) using a single diffusion couple has recently been extended by Cermak and Rothova to determine the composition-dependent interdiffusion coefficients ($\tilde{D}^3_{ij}$) in ternary systems based on the limitation of $\lim_{x_1 \to x_2} \tilde{\tilde{D}}^3_{ij} = \tilde{D}^3_{ij}$ in the distance interval $<x_1, x_2>$. In the present paper, the authors argue that such a limitation is not applicable, and the so-called Cermak–Rothova approach cannot be used to obtain the "truly" composition-dependent interdiffusion coefficients.

Keywords: Diffusion; Alloys; Diffusion couple; Ternary system

Reliable diffusion coefficients, especially composition-dependent diffusion coefficients, are of great importance for quantitative description of phase transformation processes via various computational techniques based on the extension of Fick's laws [1,2]. Among different diffusion coefficients, the interdiffusion coefficient represents an important type. Experimental measurement of composition-dependent interdiffusion coefficients in binary systems can easily be realized by, for example, a combination of the diffusion couple technique and the Boltzmann–Matano method [3,4], since there is only one independent interdiffusion coefficient in a binary phase, while in ternary systems, the situation becomes extremely complex owing to the existence of four independent interdiffusion coefficients (two main and two cross) [5]. Assuming a fictitious 1–2–3 ternary system (here, 3 is chosen as the solvent component), the interdiffusion flux of solute component i ($i = 1$ or 2), $\tilde{J}_i$, according to Onsager's formalism [6] can be expressed as

$$\tilde{J}_i = -\tilde{D}^3_{i1}\frac{dc_1}{dx} - \tilde{D}^3_{i2}\frac{dc_2}{dx} \quad (i = 1,\ 2) \tag{1}$$

In the present paper, only diffusion in one dimension is considered. In Eq. (1), c_i is the concentration of component i, x is distance, while $\tilde{D}^3_{i1}$ and $\tilde{D}^3_{i2}$ stand for the interdiffusion coefficients. The slopes of concentration profiles, dc_1/dx and dc_2/dx, can be directly calculated from the smoothed and fitted functions for concentration profiles, while the interdiffusion flux $\tilde{J}_i$ at any position x^* can be calculated from the Boltzmann–Matano method:

$$\tilde{J}_i(x^*) = \frac{1}{2t}\int_{c_i^+ \text{ or } c_i^-}^{c_i(x^*)} (x - x_0)dc_i \quad (i = 1,\ 2) \tag{2}$$

where c_i^+ and c_i^- are the terminal compositions, and x_0 denotes the position of the Matano plane, which is defined as

$$\int_{c_i^-}^{c_i^+} (x - x_0)dc_i = 0 \quad (i = 1,\ 2) \tag{3}$$

With one diffusion couple, one can only have two equations like Eq. (1). In order to obtain the four independent interdiffusion coefficients in one ternary system, two additional equations are needed.

* Corresponding author. Tel.: +86 731 88877963; fax: +86 731 88710855; e-mail addresses: xueyun168@gmail.com; lijun.zhang@csu.edu.cn

[1] These authors contributed equally to the work.

1359-6462/$ - see front matter © 2013 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.scriptamat.2013.11.033

The first attempt to calculate the four interdiffusion coefficients in a ternary system was from Kirkaldy [7,8] by employing two diffusion couples, of which the diffusion paths intersect at one common point. By solving four equations similar to Eq. (1), the four interdiffusion coefficients at the intersection point can be obtained. Considering its simplicity, the Kirkaldy method is widely used even now to determine the interdiffusion coefficients in ternary systems. However, since the interdiffusion coefficients can be obtained only at the intersection point when a pair of diffusion couples are used, the Kirkaldy method is time consuming, especially if the composition-dependent diffusion coefficients are needed.

Therefore, Dayananda and Sohn [9] developed a method for determining the average ternary interdiffusion coefficients over a selected composition range on the basis of a single diffusion couple. By assuming that the interdiffusion coefficients are constant over the selected composition range $<c_i(x_1), c_i(x_2)>$, Eq. (1) leads to the following equation via the integration on both sides

$$\begin{aligned}\int_{x_1}^{x_2}\tilde{J}_i dx &= -\int_{c_1(x_1)}^{c_1(x_2)}\tilde{D}_{i1}^3 dc_1 - \int_{c_2(x_1)}^{c_2(x_2)}\tilde{D}_{i2}^3 dc_2 \\ &= \bar{\tilde{D}}_{i1}^3[c_1(x_1)-c_1(x_2)] + \bar{\tilde{D}}_{i2}^3[c_2(x_1)-c_2(x_2)]\end{aligned} \quad (i=1,2) \tag{4}$$

Here, the average interdiffusion coefficients over the selected composition range $<c_i(x_1), c_i(x_2)>$ are defined as

$$\bar{\tilde{D}}_{ij}^3 = \frac{\int_{c_j(x_1)}^{c_j(x_2)}\tilde{D}_{ij}^3 dc_j}{\int_{c_j(x_1)}^{c_j(x_2)} dc_j} (i,j=1,\ 2) \tag{5}$$

By further multiplying $(x - x_0)$ on both sides of Eq. (1), and coupling with Eq. (2), a new equation can be obtained

$$\begin{aligned}\int_{x_1}^{x_2}\tilde{J}_i(x-x_0)dx &= -\bar{\tilde{D}}_{i1}^3\int_{c_1(x_1)}^{c_1(x_2)}(x-x_0)dc_1 \\ &\quad -\bar{\tilde{D}}_{i2}^3\int_{c_2(x_1)}^{c_2(x_2)}(x-x_0)dc_2 \\ &= 2t\cdot\{\bar{\tilde{D}}_{i1}^3[\tilde{J}_1(x_1)-\tilde{J}_1(x_2)] \\ &\quad +\bar{\tilde{D}}_{i2}^3[\tilde{J}_2(x_1)-\tilde{J}_2(x_2)]\}\end{aligned} \quad (i=1,2) \tag{6}$$

Then, by combining Eqs. (4) and (6), the four average interdiffusion coefficients over the selected composition range can be obtained. The method from Dayananda and Sohn [9] provides an approach to obtain the ternary interdiffusion coefficients using a single diffusion couple, which definitely increases the computation efficiency. However, only limited average interdiffusion coefficients can be determined, and their reliability depends largely on its variation within the specified composition range.

In order to determine the "truly" composition-dependent interdiffusion coefficients in a ternary system with only one diffusion couple, Cermak and Rothova [10] extended the method proposed by Dayananda and Sohn [9] by making the interval between x_1 and x_2 sufficiently small. With a sufficiently small interval $<x_1,\ x_2>$, the average interdiffusion coefficients can approach the true values with an arbitrary required accuracy [10]

$$\lim_{x_1\to x_2}\bar{\tilde{D}}_{ij}^3 = \tilde{D}_{ij}^3 \tag{7}$$

Based on the following simplifications and abbreviations in the chosen interval $<x_m,\ x_n>$

$$\Delta J_i = \tilde{J}_i(x_m) - \tilde{J}_i(x_n) \tag{8}$$

$$\Delta c_i = c_i(x_m) - c_i(x_n) \tag{9}$$

$$\Delta x = x_m - x_n \tag{10}$$

$$\bar{J}_i = \frac{1}{2}[\tilde{J}_i(x_m) + \tilde{J}_i(x_n)] \tag{11}$$

$$\bar{c}_i = \frac{1}{2}[c_i(x_m) + c_i(x_n)] \tag{12}$$

$$\bar{x} = \frac{1}{2}(x_m + x_n) \tag{13}$$

Eqs. (4) and (6) can be modified as [10]

$$\bar{J}_i\Delta x = -\bar{\tilde{D}}_{i1}^3\Delta c_1 - \bar{\tilde{D}}_{i2}^3\Delta c_2\ (i=1,\ 2) \tag{14}$$

$$\bar{J}_i(\bar{x}-x_0)\Delta x = 2t\cdot(-\bar{\tilde{D}}_{i1}^3\Delta J_1 - \bar{\tilde{D}}_{i2}^3\Delta J_2)\ (i=1,\ 2) \tag{15}$$

With the above two equations, the average interdiffusion coefficients over the small interval $<x_m,\ x_n>$ can be expressed by

$$\bar{\tilde{D}}_{ij}^3 = \frac{K_1\Delta J_1 + K_2\Delta J_2 - \frac{(\bar{x}-x_0)}{2t}(K_1\Delta c_1 + K_2\Delta c_2)}{\Delta c_2\Delta J_1 - \Delta c_1\Delta J_2}\bar{J}_i\Delta x \quad (i,\ j=1,\ 2) \tag{16}$$

using combinations of Kronecker's symbols

$$K_1 = \delta_{ij}\delta_{i1} - \delta_{ij}\delta_{i2} - \delta_{i1} \tag{17}$$

$$K_2 = \delta_{ij}\delta_{i1} - \delta_{ij}\delta_{i2} + \delta_{i2} \tag{18}$$

As claimed by Cermak and Rothova [10], when the small interval $<x_m,\ x_n>$ approaches 0, $\bar{\tilde{D}}_{ij}^3$ calculated from Eq. (16) should approach the true composition-dependent interdiffusion coefficients. The Cermak–Rothova method was first used by themselves in the Al–(Cr, Fe, Nb, Ti)–Ni systems [10], and then by Yao et al. [11] in the Nb–Mo–Si system as well as Wei et al. [12] in the Ni–Al–Mo system.

When the Cermak–Rothova method came to the present authors' attention, it seemed to be a great idea. However, the results from Cermak and Rothova [10] and Wei et al. [12] cannot be reproduced by the present authors. By eliminating the effect of the singularity point (i.e. when the denominator in Eq. (16) equals 0) as done in Ref. [10], the situation still cannot be improved. Furthermore, the calculated interdiffusion coefficients change a lot with the decrease in the interval $<x_1,\ x_2>$. Therefore, there is an urgent need to check whether the Cermak–Rothova method is theoretically correct for determining the composition-dependent interdiffusion coefficients in ternary systems.

First, the four interdiffusion coefficients from Eq. (16) due to the Cermak–Rothova approach result in an interesting relation