J. Phase Equilib. Diffus. (2019) 40:522–531
https://doi.org/10.1007/s11669-019-00740-0

Interdiffusion Analysis in Ternary Systems to Process Composition Profiles and Obtain Constant Interdiffusion Coefficients Using One Compact Diffusion Couple

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Submitted: 13 December 2018 / in revised form: 21 June 2019 / Published online: 26 July 2019

Abstract The interdiffusion process in a three-component alloy system has been studied by means of numerical analysis. The composition profiles for a ternary system were generated making use of the closed-form solution with a constant interdiffusion matrix with the accompanying analysis of the diffusion paths. Two methods [the Fitting Method and the modified square root diffusivity (MSQRD) method] have been considered to investigate the inverse interdiffusion problem for application to a single interdiffusion couple measurement. The Fitting Method simultaneously fits the required functional form into the data obtained for two composition profiles. Such fitted parameters are used to determine the constant interdiffusion matrix. The MSQRD method has been applied to the generated composition profiles and performs very well for all the cases considered. It was found that the errors of the MSQRD method are, in general, lower than in the use of the Fitting Method even without imposing artificial noise on the composition profiles to mimic the experimental data. In addition, it has been shown that the back-tests of the composition profiles must not be used as the only proof of the reliability of the methods used.

Keywords compact diffusion couple · error-function solution · interdiffusion · modified square root diffusivity method · ternary alloys

1 Introduction

Interdiffusion problems are central to the processing and in-service behaviour of materials. Initially, Boltzmann[1] introduced an exact method for the calculation of the single interdiffusion coefficient analytically from the composition interdiffusion profile for a binary alloy. Following this, a number of studies, e.g., Ref 2-5 were published where the same interdiffusion problem in binary alloys was analysed in several different ways. In, Ref 2 the important concept of the Matano plane (a plane across which equal amounts of mass diffuse to the left and the right sides) was introduced and basic relationships were derived from it. In, Ref 3 this method was further advanced using the interrelationships between the atomic fluxes in such a way that the exact position of the Matano plane was not needed. In, Ref 4 a further modification of the basic relationships was introduced for application to the dilute ends of the composition profiles. In, Ref 5 it was shown that the method in Ref 4 can only be applied (in the dilute regions) if the interdiffusion coefficient is constant, and that, in the general case of a composition-dependent interdiffusion coefficient, the original methods[2,3] should be used.

This invited article is part of a special issue of the *Journal of Phase Equilibria and Diffusion* in honour of the 2018 J. Willard Gibbs Phase Equilibria Award winner, Dr. John Morral. The award was presented to Dr. Morral during MS&T'18, October 14-18, 2018, in Columbus, Ohio, "for fundamental and applied research on topology of phase diagrams and theory of phase equilibria resulting in major advances in the calculation and interpretation of phase equilibria and diffusion."

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However, technologically important metallic alloys are often comprised of three or more components. Indeed, ternary diffusion is central in most commercial materials systems employed in high-temperature as well as nuclear reactor environments, where interdiffusion processes play a vital role. Fujita and Gosting[6,7] investigated diffusion in both binary and ternary systems. In the binary case, they described a general theoretical foundation for interpreting diffusion data. In the ternary case, they described an exact (error function-based) solution of two simultaneous differential diffusion equations in terms of the four interdiffusion coefficients. Following that, they developed a new procedure[8] for solving the inverse interdiffusion problem in the ternary system – calculating the four diffusion coefficients of three-component systems from Gouy diffusiometer data. They showed that they obtained more accurate results than in previous studies. In, Ref 9, 10 the authors mainly focused on different methods for determining the diffusion coefficients in ternary alloys. In, Ref 9 a full description of available methods was given. In, Ref 10 a variation on the fitting method was used and favourably compared with the other available methods. Dayananda and Grace[11] worked on ternary diffusion in Cu-Zn-Mn alloys and showed that a vapour-solid diffusion pair can effectively be used in ternary diffusion studies. Ternary diffusion in Cu-Ag-Au metallic alloys is discussed in. Ref 12 There, the author systematically studied the diffusion behaviour over the entire, two-dimensional composition domain. Vrentas and Vrentas[13] developed some theoretical aspects of ternary diffusion problems. In the general case of a multi-component system, the composition profiles cannot be accurately calculated by means of a binary analysis. Therefore, a different approach for solving the (inverse) multicomponent diffusion equations must be used. (It should be noted that recently a good experimental interdiffusion study in a quinary alloy by means of the quasi-binary interdiffusion analysis has been reported,[14,15] although the study has attracted some scepticism[16]).

Dayananda and Sohn[17] defined a new method for the determination of *constant* ternary interdiffusion coefficients using experimental composition profiles. In, Ref 17 the interdiffusion coefficients in ternary alloys were calculated over composition points on either side of the Matano plane for selected diffusion couples, Cu-Ni-Zn, Fe-Ni-Al, and Ni-Cr-Al. Here, average interdiffusion coefficients were used to manipulate the composition profiles. Next et al.[18] analysed different properties of ternary metallic systems directly from the composition profiles. The MultiDiFlux software was developed for calculating ternary interdiffusion coefficients from the composition profiles (Cu-Ni-Zn couples were used as an example).[18] More recently, Dayananda[19] investigated interdiffusion coefficients in ternary diffusion from diffusion constraints at the Matano plane. The diffusion constraints interlink the compositions, composition gradients and interdiffusion fluxes at the Matano plane in a ternary diffusion couple. In addition, in, Ref 19 composition-dependent interdiffusion coefficients were calculated from composition profiles in a ternary alloy system using several techniques.

The square root diffusivity (SQRD) method[20] can be directly applied to multicomponent (ternary and higher systems) inverse interdiffusion problems. We will call the application of this method for the case of a single diffusion couple as the modified square root diffusivity (MSQRD) method. This is to be distinguished from the application of this method to two or more diffusion couples. Thompson et al.[21] investigated applications of square root diffusivity for ternary (Ni-Al-Cr) alloys using two couples. Jaques and LaCombe[22] studied the MSQRD method equations for determining ternary diffusivities from a single couple. Multicomponent diffusivities using one diffusion couple or two diffusion couples were analysed in Ref 23, 24 on the basis of the estimated uncertainties. In this case, the SQRD method predicted errors that were approximately equal to the experimental error, while the MSQRD method had much larger errors that could not be predicted without a prior knowledge of the interdiffusivity, especially for diffusion couples with certain composition differences. In, Ref 25 the SQRD method was used to measure diffusivities in Ni-Cr-Al-Mo alloys. In, Ref 26, the use of the SQRD method for five and six component alloys is also discussed. In, Ref 27-30 the different available methods were applied for solution of the inverse interdiffusion problem in ternary systems. There, the composition profiles were analysed by employing several programs such as MultiDiFlux, VisiMat and a graphical user interface.

The scheme of the present computational study on the ternary interdiffusion problem is first to produce discretised composition profiles (without superimposing artificial noise that is usually used to simulate experimentally obtained profiles). This is followed by investigating the inverse interdiffusion problem using the MSQRD method and the Fitting Method. The Fitting Method simultaneously fits the required functional form into the data obtained for two composition profiles. Such obtained fitted parameters are used then to determine the constant interdiffusion matrix.

2 Theory and Analysis

The governing equations for diffusion in the ternary system can be written as[7]:

$$\frac{\partial C_1}{\partial t} = \widetilde{D}_{11}\frac{\partial^2 C_1}{\partial x^2} + \widetilde{D}_{12}\frac{\partial^2 C_2}{\partial x^2} \qquad \text{(Eq 1)}$$

$$\frac{\partial C_2}{\partial t} = \widetilde{D}_{21}\frac{\partial^2 C_1}{\partial x^2} + \widetilde{D}_{22}\frac{\partial^2 C_2}{\partial x^2} \qquad \text{(Eq 2)}$$

where C_1 and C_2 are compositions that can be functions of distance x and time t and $C_3 = 1 - C_1 - C_2$. $\widetilde{D}_{11}$, $\widetilde{D}_{12}$, $\widetilde{D}_{21}$ and $\widetilde{D}_{22}$ are the four interdiffusion coefficients and they are assumed to be constant, independent of composition. It is assumed that the reference atomic component is C_3. The initial conditions are:

$$C_I = \bar{C}_I + \frac{\Delta C_I}{2}; \quad \text{for } x > 0,\ t = 0 \qquad \text{(Eq 3)}$$

$$C_I = \bar{C}_I - \frac{\Delta C_I}{2}; \quad \text{for } x < 0, t = 0 \qquad \text{(Eq 4)}$$

in which ΔC_I is a function of distance and time. The boundary conditions are:

$$C_I \to \bar{C}_I + \frac{\Delta C_I^0}{2}; \quad \text{for } x \to \infty, t > 0 \qquad \text{(Eq 5)}$$

$$C_I \to \bar{C}_I - \frac{\Delta C_I^0}{2}; \quad \text{for } x \to -\infty, t > 0 \qquad \text{(Eq 6)}$$

where

$$\bar{C}_I = \left[(C_I)_{-\infty} + (C_I)_{\infty}\right]/2 \qquad \text{(Eq 7)}$$

$$\Delta C_I^0 = (C_I)_{\infty} - (C_I)_{-\infty} \qquad \text{(Eq 8)}$$

In Eq 7 and 8, $(C_I)_{-\infty} = C_I(x \to -\infty)$ and $(C_I)_{\infty} = C_I(x \to \infty)$ are the two end (terminal) compositions of component I. According to the definition of the composition vector (see Ref 31) $[\Delta C]$ is then defined as $[\Delta C] = \left[\Delta C_1^0, \Delta C_2^0\right]$.

The diffusion Eq 1 and 2 are to be solved with the initial and boundary conditions presented in Eq 3-8.

The exact solution for the compositions C_1 and C_2 can be presented in the following closed form7:

$$C_1 = \overline{C_1} + K_1^{+}\Phi(\sqrt{\sigma_1}x) + K_1^{-}\Phi(\sqrt{\sigma_2}x) \qquad \text{(Eq 9)}$$

$$C_2 = \overline{C_2} + K_2^{+}\Phi(\sqrt{\sigma_1}x) + K_2^{-}\Phi(\sqrt{\sigma_2}x) \qquad \text{(Eq 10)}$$

in which the error function Φ is given by:

$$\Phi(q) = \frac{2}{\sqrt{\pi}}\int_0^q e^{-q^2}\,\mathrm{d}q \qquad \text{(Eq 11)}$$

and

$$K_1^{+} = \frac{(\sigma_1 - E)\Delta C_1^0 - F\Delta C_2^0}{2(\sigma_1 - \sigma_2)} \qquad \text{(Eq 12)}$$

$$K_1^{-} = \frac{(\sigma_2 - E)\Delta C_1^0 - F\Delta C_2^0}{2(\sigma_2 - \sigma_1)} \qquad \text{(Eq 13)}$$

$$K_2^{+} = \frac{(\sigma_1 - H)\Delta C_2^0 - G\Delta C_1^0}{2(\sigma_1 - \sigma_2)} \qquad \text{(Eq 14)}$$

$$K_2^{-} = \frac{(\sigma_2 - H)\Delta C_2^0 - G\Delta C_1^0}{2(\sigma_2 - \sigma_1)} \qquad \text{(Eq 15)}$$

and

$$E = \frac{\widetilde{D}_{11}}{\left|\widetilde{D}_{ij}\right|},\ F = \frac{\widetilde{D}_{12}}{\left|\widetilde{D}_{ij}\right|},\ G = \frac{\widetilde{D}_{21}}{\left|\widetilde{D}_{ij}\right|},\ H = \frac{\widetilde{D}_{22}}{\left|\widetilde{D}_{ij}\right|} \qquad \text{(Eq 16)}$$

$$\sigma_1 = \frac{1}{2}\left\{H + E + \left[(H - E)^2 + 4FG\right]^{\frac{1}{2}}\right\} \qquad \text{(Eq 17)}$$

$$\sigma_2 = \frac{1}{2}\left\{H + E - \left[(H - E)^2 + 4FG\right]^{\frac{1}{2}}\right\} \qquad \text{(Eq 18)}$$

For the inverse part of the problem, the fitting functions for the two compositions are:

$$C_1 = \overline{C_1} + a_{11}\Phi(a(x)) + \left(\frac{\Delta C_1^0}{2} - a_{11}\right)\Phi(b(x)) \qquad \text{(Eq 19)}$$

$$C_2 = \overline{C_2} + \left(\frac{\Delta C_2^0}{2} - a_{22}\right)\Phi(a(x)) + a_{22}\Phi(b(x)) \qquad \text{(Eq 20)}$$

Here, a_{11}, a_{22}, a and b are fitting parameters.

It is known (see, for example, 32) that when the composition vector $[\Delta C]$ is aligned with the direction of an eigenvector of the interdiffusion matrix, the coefficients of one error function in Eq 19 and 20 will be zero. In the plane (C_1, C_2) the angle ϕ_c of the composition vector is defined as $\tan\phi_c = \Delta C_2^0/\Delta C_1^0$.[31] The corresponding angles of the major and minor eigenvectors, ϕ_1 and ϕ_2, can then be defined as $\tan\phi_1 = (\sigma_1 - E)/F$ and $\tan\phi_2 = (\sigma_2 - E)/F$.[31]

For the generation of the composition profiles for each test simulations, we have used the closed form solution given by Eq 9-20. Following that, the profiles were discretised at the grid in the x-direction containing 200 points. The choice of time and the total width of the diffusion zone in this procedure was consistent with the standard resolution of the experimental measurements of the interdiffusion profiles of 2-3 μm.

2.1 Calculation to Recover $\widetilde{D}_{ij}$ Using the Fitting Method

To calculate the interdiffusion matrix, the first step is to calculate the inverse interdiffusion matrix $\{E, F; G, H\}$. Once $\{E, F; G, H\}$ is recovered, one then calculates $\frac{1}{EH-FG} = \det\left[\widetilde{D}\right]$ and the matrix $\{\widetilde{D}_{11}, \widetilde{D}_{12}, \widetilde{D}_{21}, \widetilde{D}_{22}\}$ can be found by multiplying $\{H, -F; -G, E\}$ by $\det\left[\widetilde{D}\right]$. The components of the matrix $\{E, F; G, H\}$ can be calculated as follows:

$$E = \left(s_1\left(\Delta C_1^0 - 2a_{11}\right)\left(\Delta C_2^0 - 2a_{22}\right) - 4s_2a_{11}a_{22}\right)/ \left(-2\Delta C_2^0 a_{11} + \Delta C_1^0\left(\Delta C_2^0 - 2a_{22}\right)\right) \quad \text{(Eq 21)}$$

$$H = s_1 + s_2 - E \quad \text{(Eq 22)}$$

$$F = 6a_{11}(s_1 - s_2) - s_1 + E \quad \text{(Eq 23)}$$

$$G = 6a_{22}(s_1 - s_2) + s_1 - E \quad \text{(Eq 24)}$$

Here, s_1 and s_2 are related to the fitting parameters a, b and time t as:

$$s_1 = 4ta^2 \text{ and } s_2 = 4tb^2 \quad \text{(Eq 25)}$$

2.2 Calculation to Recover $\widetilde{D}_{ij}$ Using the MSQRD Method

In this method, the diffusivity $\left[\widetilde{D}\right]$ is replaced by the matrix of the square root diffusivity $[r]$ in an obvious way [20,33]:

$$\left[\widetilde{D}\right] = [r][r] \quad \text{(Eq 26)}$$

The amount of atoms I that is passing through the Matano plane at $x = 0$ in time t can be calculated as:

$$S_I = \int_0^{+\infty} \left(C_I - (C_I)_\infty\right)\mathrm{d}x \quad \text{(Eq 27)}$$

The square root diffusivity analysis for the ternary systems is based on the solution to a system of linear equations. The first two of them have the following form:

$$S_I = -\sqrt{\frac{t}{\pi}}\left(r_{i1}\Delta C_1^0 + r_{i2}\Delta C_2^0\right) \quad \text{(Eq 28)}$$

where r_{ij} is an element of $[r]$.

In matrix notation, Eq 28 can be written as:

$$[S] = -\sqrt{\frac{t}{\pi}}[r][\Delta C] \quad \text{(Eq 29)}$$

When two compact diffusion couples (i.e., diffusion couples with a nearly constant diffusivity) are prepared that have diffusion paths that cross at $x = 0$, Eq 28 provides four equations to calculate the four elements of $[r]$. This is the SQRD method. Another two equations can be derived from the ternary generalization of the Boltzmann–Matano analysis as [20]:

$$\int_{(C_I)_\infty}^{C_I(x')} x dC_I = -2t\sum_{j=1}^{2}\widetilde{D}\left.\frac{\partial C_j}{\partial x}\right|_{x'} \quad \text{(Eq 30)}$$

Evaluating Eq 30 at $x' = 0$, the equation is reduced to:

$$S_I = -2t\sum_{j=1}^{2}\widetilde{D}\nabla C_j^0 \quad \text{(Eq 31)}$$

or

$$[S] = -2t\left[\widetilde{D}\right]\left[\nabla C^0\right] \quad \text{(Eq 32)}$$

where ∇C^0 is treated as the composition gradient of component j at $x = 0$. Combining Eq 26, 29 and 30 to extract $[S]$ and $\left[\widetilde{D}\right]$ gives:

$$\frac{[\Delta C]}{2\sqrt{\pi t}} = [r]\left[\nabla C^0\right] \quad \text{(Eq 33)}$$

Equation 33 give another two linear equations at $x = 0$. When Eq 33 is applied to two diffusion couples that have a crossing diffusion path at $x = 0$, there are now four linear equations to find the four components of the matrix $[r]$. This is an alternate form of the SQRD method. The preferred method depends on whether S_I or ∇C_I^0 has the lowest experimental error.

The MSQRD method combines Eq 28 from the SQRD method with a similar equation from the alternate method that involves ΔC_I^0 and ∇C_I^0. That provides four equations to calculate the four elements of $[r]$ from one diffusion couple. Therefore, the MSQRD method requires the composition vector, concentration gradients, and atoms that have crossed the Matano plane, whereas the Fitting Methods require both the composition vector and the end compositions.

3 Analysis of Diffusion Paths in the Ternary Diagram

Analysing the diffusion path is one of the standard steps in the computation of the interdiffusion in a three (or more) component alloy system. The information on the end compositions of the couples together with the composition vectors is given in Table 1.

In our investigation, we have chosen four different interdiffusion matrices with the same diagonal terms and different off-diagonal ones. The four interdiffusion matrices (scaled to the highest component $\widetilde{D}_{11}$) are given in Table 2 together with their eigenvalues $\{\lambda_1, \lambda_2\}$ and eigenvectors $[v_1]$ and $[v_2]$.

In Fig. 1a and d, we present the minor and major eigenvector directions together with three composition vector directions for the Cases-i–iv. It is clear that for Case-i the composition vector of the BC-1 is near the directions of the minor eigenvector; and for Case-ii and Case-iv the composition vector of the BC-2 is near the directions of the minor eigenvectors.

Diffusion paths for the couples are presented in the ternary diagram in Fig. 2, from which it is clear that, in general, as it should be, the diffusion paths are not straight. The shape is determined by the interdiffusion matrix and the composition vector.[31] In agreement with the

Table 1 The end compositions (in molar fractions) and corresponding composition vectors for three chosen diffusion couples

Diffusion couple	$(C_1)_{+\infty}$	$(C_2)_{+\infty}$	$(C_1)_{-\infty}$	$(C_2)_{-\infty}$	$[\Delta C]$
BC-1	0.50	0.0	0.33	0.33	[0.18, − 0.33]
BC-2	0.50	0.17	0.25	0.08	[0.25, − 0.08]

Table 2 Interdiffusion matrices, their eigenvalues and corresponding eigenvectors for four considered cases

Case	$\widetilde{D}^{(3)}/\widetilde{D}^{(3)}_{11}$	$\{\lambda_1 \lambda_2\}$	$[v_1]$	$[v_2]$
Case-I	$\begin{bmatrix} 1.0 & 0.5 \\ 0.1 & 0.5 \end{bmatrix}$	$\{1.08, 0.41\}$	$[0.98, 0.17]$	$[-0.65, 0.76]$
Case-ii	$\begin{bmatrix} 1.0 & -0.1 \\ 0.1 & 0.5 \end{bmatrix}$	$\{0.98, 0.52\}$	$[0.98, 0.20]$	$[0.20, 0.98]$
Case-iii	$\begin{bmatrix} 1.0 & 0.5 \\ -0.1 & 0.5 \end{bmatrix}$	$\{0.86, 0.64\}$	$[0.96, -0.27]$	$[-0.81, 0.59]$
Case-iv	$\begin{bmatrix} 1.0 & -0.1 \\ -0.1 & 0.5 \end{bmatrix}$	$\{1.02, 0.48\}$	$[-0.98, 0.19]$	$[-0.19, -0.98]$

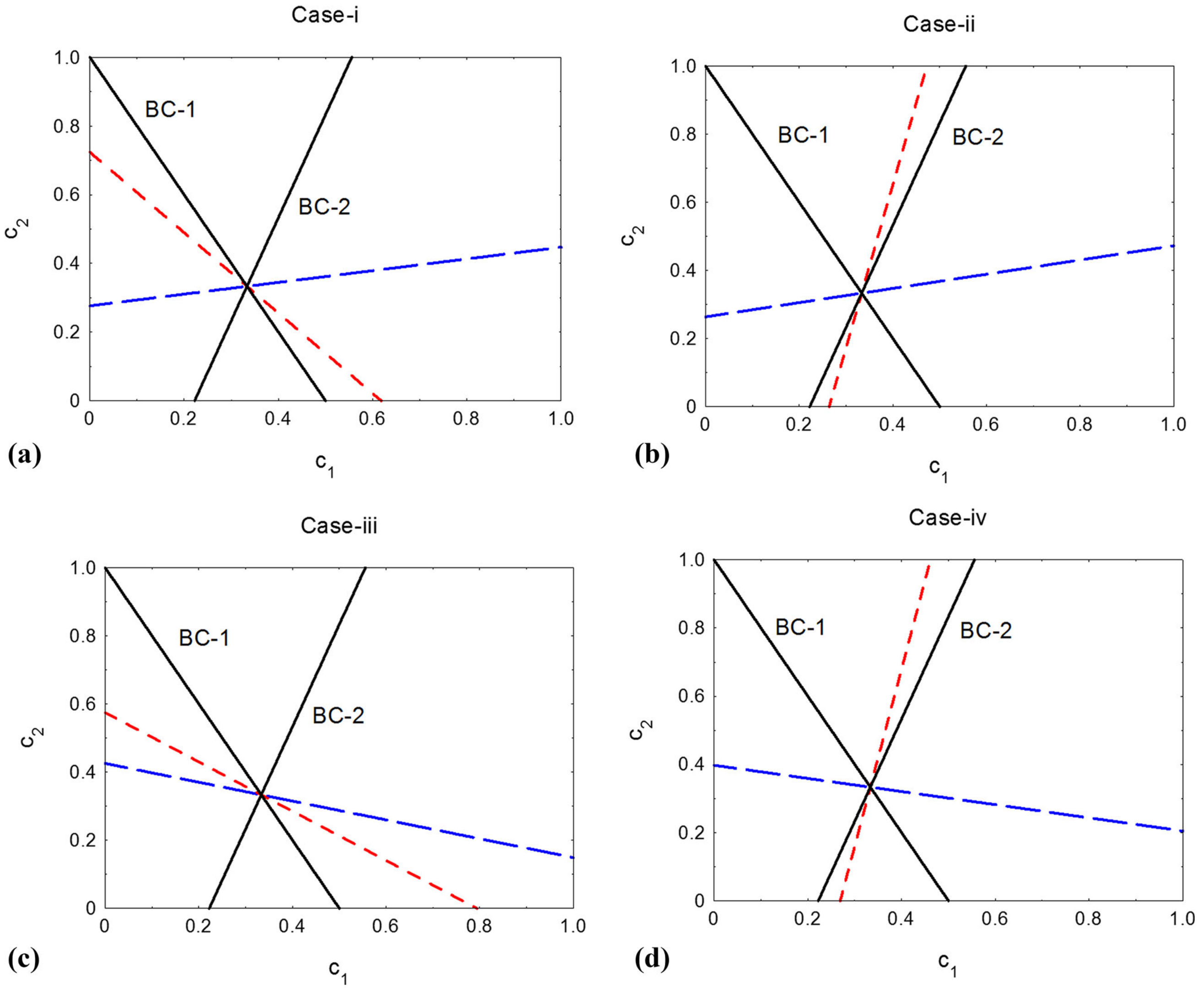

Fig. 1 Major (short-dashed red lines) and minor (long-dashed blue lines) eigenvectors shown together with two composition vectors (solid black lines) for the diffusion couples BC-1 and BC-2 for (a) Case-i; (b) Case-ii; (c) Case-iii; (d) Case-iv

conclusions in [31] it can be seen that, for the BC-1 couple, the shape of the diffusion paths are nearly straight lines for the diffusion matrices in Case-i and Case-iii (directions of the composition vectors are reasonably close to the minor eigenvalue directions). In addition, it is interesting to see that the diffusion path in the BC-2 couple does follow somewhat nearly (but not exactly!) a straight line for all four matrices, despite the fact that the BC-2 composition vector is closed to the minor eigenvector only for Case-ii and Case-iv. This is, of course, not in contradiction with the prediction in [31] because each composition vector must have the maximum deviation from the straight diffusion path (for a given interdiffusion matrix). For BC-2, this maximum deviation is clearly very small.

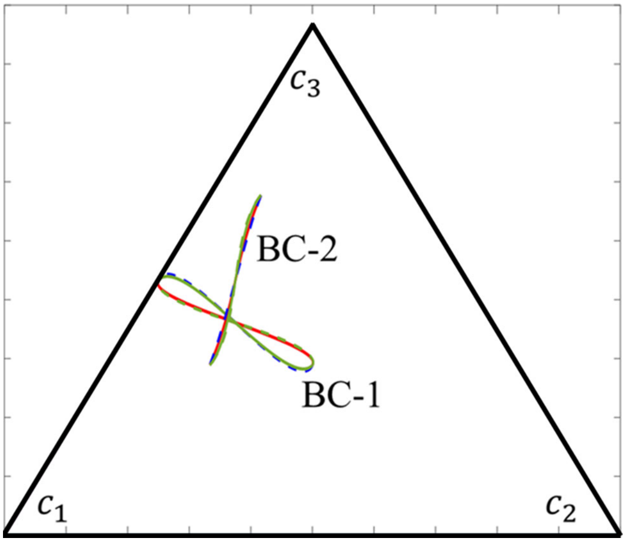

Fig. 2 Comparison of diffusion paths for BC-1 and BC-2. Cases-i and -iii are represented by and solid red dashed green lines whereas the dashed blue and solid green lines represent Cases-ii and -iv, respectively (Color figure online)

4 Investigating the Interdiffusion Matrix

The present analysis was carried out for the purposes of comparing two methods for solving an inverse interdiffusion problem. Another purpose was to determine whether or not the use of one compact diffusion couple can give reliable results for [D] if its eigenvectors are not known before doing the experiments. As was described above, for the testing calculations, we have chosen four different interdiffusion matrices and two diffusion couples with different boundary conditions. For analysis of the Fitting Method and the MSQRD method (as discussed above), the composition profiles were computed using a closed form solution and then they were discretised at a convenient step

Table 3 Interdiffusion coefficients calculated using several approaches from the original profiles obtained from closed form solution with the couple BC-1

Case-i	$\widetilde{D}_{11}/\widetilde{D}_{11}$ 1.0	$\widetilde{D}_{12}/\widetilde{D}_{11}$ 0.5	$\widetilde{D}_{21}/\widetilde{D}_{11}$ 0.1	$\widetilde{D}_{22}/\widetilde{D}_{11}$ 0.5
Cftool	1.0525 (5.2)	0.4949 (1.0)	0.0532 (46.8)	0.4753 (4.9)
Origin	0.9435 (5.6)	0.4314 (13.7)	0.0494 (50.6)	0.4718 (5.6)
MSQRD method	0.9401 (6.0)	0.4605 (7.9)	0.1101 (10.1)	0.5001 (0.0)
Case-ii	$\widetilde{D}_{11}/\widetilde{D}_{11}$ 1.0	$\widetilde{D}_{12}/\widetilde{D}_{11}$ − 0.1	$\widetilde{D}_{21}/\widetilde{D}_{11}$ 0.1	$\widetilde{D}_{22}/\widetilde{D}_{11}$ 0.5
Cftool	1.0104 (1.0)	− 0.0903 (9.7)	0.0524 (47.6)	0.5069 (1.4)
Origin	1.0066 (0.6)	− 0.0913 (8.7)	0.0505 (49.5)	0.5055 (1.1)
MSQRD method	0.9949 (0.5)	− 0.1014 (1.4)	0.0830 (17)	0.4937 (1.3)
Case-iii	$\widetilde{D}_{11}/\widetilde{D}_{11}$ 1.0	$\widetilde{D}_{12}/\widetilde{D}_{11}$ 0.5	$\widetilde{D}_{21}/\widetilde{D}_{11}$ − 0.1	$\widetilde{D}_{22}/\widetilde{D}_{11}$ 0.5
Cftool	1.1709 (17)	0.6496 (30)	− 0.0434 (56.6)	0.5302 (6.0)
Origin	1.1933 (19)	0.6744 (25)	− 0.0201 (79.9)	0.5302 (6.0)
MSQRD method	0.9805 (1.9)	0.4903 (1.9)	− 0.1000 (0.0)	0.5000 (0.0)
Case-iv	$\widetilde{D}_{11}/\widetilde{D}_{11}$ 1.0	$\widetilde{D}_{12}/\widetilde{D}_{11}$ − 0.1	$\widetilde{D}_{21}/\widetilde{D}_{11}$ − 0.1	$\widetilde{D}_{22}/\widetilde{D}_{11}$ 0.5
Cftool	0.9730 (3.9)	0.1609 (!)	− 0.0487 (51.3)	0.4818 (3.6)
Origin	0.9613 (4.9)	0.1513 (!)	− 0.0483 (51.7)	0.4823 (3.5)
MSQRD method	0.9938 (0.6)	− 0.1017 (1.7)	− 0.1059 (5.9)	0.4977 (0.5)

The percentage of the relative error is given in parentheses next to each number. An exclamation sign is used if the sign was not correctly reproduced (relative error is then over 100%)

in space that corresponds to a standard experimental resolution of 2-3 μm. The Fitting Method is then used for the recovery of the matrix of interdiffusion coefficients. For the application of the Fitting Method, there are two main procedures available: first, using specialized software, e.g. Origin-17, a simultaneous fitting of two related functions into two sets of data can be obtained; second, the manual iterative manipulation of the fitting functions can be performed using conventional software (e.g. Cftool from MATLAB). The results of these two approaches of the Fitting Method will be called Origin and Cftool, respectively. The obtained fitted parameters permit the immediate determination of the ternary interdiffusion matrix .

Application of the MSQRD method involves the calculations of the Matano plane, the gradient of compositions at this plane, ∇C_i^0, and the integrated atomic fluxes, S_i, passing through the Matano plane. Usually, the location of the Matano plane is calculated on the basis of the mass equilibrium for individual atomic components using the trapezoidal method and is determined from the conservation condition:

$$\int_{-\infty}^{x_M} (1 - C(x))\mathrm{d}x = \int_{x_M}^{+\infty} C(x)\mathrm{d}x, \qquad \text{(Eq 34)}$$

where x_M is the position of the Matano plane. For the closed form solution given by Eq 19 and 20, the Matano plane must be located at the average composition point, x_A where $C_1(x_A) = \overline{C_1}$, $C_2(x_A) = \overline{C_2}, C_3(x_A) = \overline{C_3}$. The (possible) deviation of x_M from x_A can then be treated as the indication of the accuracy of the constant interdiffusion matrix approximation. In the present study, for the simulated composition profiles, this deviation is of the order of the computational error (14 decimal places as a default in Matlab) and can be neglected. The composition gradients at the Matano plane are calculated by using the fourth order finite difference approximation.

The calculated inverse interdiffusion coefficients are shown in Table 3 for the diffusion couple BC-1 for the application of Cftool and Origin and the MSQRD methods. In this couple, in all four Cases, it is clear that the MSQRD method gives the best agreement with the input interdiffusion matrix for the diagonal and off-diagonal terms with a maximum of 6 and 10% relative errors, respectively.

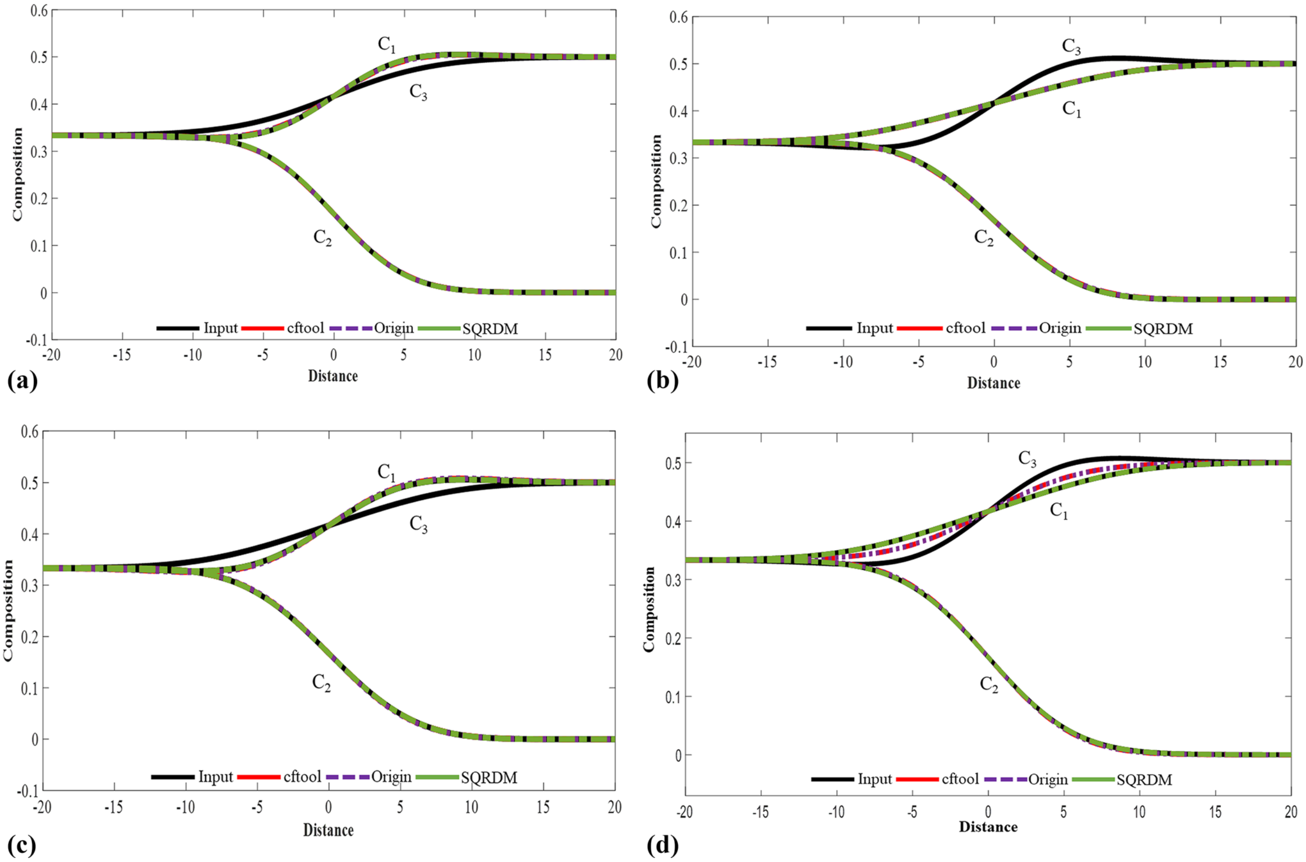

Fig. 3 Comparison of composition profiles for the couple BC-1 using a different set of interdiffusion matrices obtained from the Cftool, Origin and MSQRD methods with original profiles: (a) Case-i, (b) Case-ii, (c) Case-iii, (d) Case-iv. The composition profile for C_3 is shown for completeness

Results for the two Fitting Methods (both implementations) is much worse than for the MSQRD method, especially when the off-diagonal terms are considered, with a relative error of up to 80%. (In Case-iv, the Fitting Methods result in the wrong sign for the one off-diagonal term.) In these cases, the Origin implementation of the Fitting Methods gives the highest maximum of the relative errors for the diagonal terms (up to 19%). The Cftool implementation of the Fitting Methods gives somewhat better results than the Origin implementation.

In Fig. 3, comparisons of composition profiles for the diffusion couple BC-1 for the four cases are presented. The matrices obtained using the Fitting Methods and the MSQRD method have been used for generating the back-test composition profiles that were plotted along with the initial set of profiles. It can be seen that the composition profiles obtained using all different interdiffusion matrices are almost the same as the initial composition profiles. In this case, the big differences are present only for the off-diagonal coefficients of the interdiffusion matrices (up to a factor of 2 when the sign is correct). It is indirect evidence that accurate estimation of the off-diagonal (and the diagonal!) interdiffusion coefficients using a single diffusion couple experiment is very difficult and would require a very high accuracy in the measurement of the composition profiles.

Next, the analysis of the diffusion couples using the Fitting Methods and the MSQRD method is investigated using another standard ternary couple BC-2. Results of this analysis are presented in Table 4.

Analysis of this couple shows that for all the Cases, the results of the MSQRD method are the most accurate for the diagonal (up to 7.5%) and off-diagonal (up to 19%) terms. Both implementations of the Fitting Methods give the least accurate results for all cases, especially for the off-diagonal terms. This effect can be attributed to the fact that the diffusion paths for this couple are all almost straight (see Fig. 2). As a result, the composition profiles follow an effective single error function and fitting them into a two error functions form becomes very difficult.

Both the Origin and Cftool implementation of the Fitting Methods fail to reproduce the sign of some of the off-diagonal terms (for all the Cases). The MSQRD method always gives the correct sign of the off-diagonal terms. The conclusion can be drawn that the MSQRD method is the preferred method for the analysis of a single diffusion couple. In addition, to ensure reliability of this method, the accuracy of the experimentally obtained profiles should be as high as possible.

In Fig. 4, the comparison of the composition profiles for the couple BC-2 for all the Cases are presented. The back-test

Table 4 Interdiffusion coefficients calculated using several approaches from the original profiles obtained from the closed form solution with the couple BC-2

	$\widetilde{D}_{11}/\widetilde{D}_{11}$	$\widetilde{D}_{12}/\widetilde{D}_{11}$	$\widetilde{D}_{21}/\widetilde{D}_{11}$	$\widetilde{D}_{22}/\widetilde{D}_{11}$
Case-i	1.0	0.5	0.1	0.5
Cftool	0.8658 (13.4)	− 0.1215 (!)	0.1537 (53.7)	0.4282 (14.5)
Origin	0.8539 (14.6)	− 0.1250 (!)	0.1556 (55.6)	0.4266 (14.7)
MSQRD method	0.9992 (0.1)	0.4979 (0.4)	0.1189 (19.0)	0.4626 (7.5)
	$\widetilde{D}_{11}/\widetilde{D}_{11}$	$\widetilde{D}_{12}/\widetilde{D}_{11}$	$\widetilde{D}_{21}/\widetilde{D}_{11}$	$\widetilde{D}_{22}/\widetilde{D}_{11}$
Case-ii	1.0	− 0.1	0.1	0.5
Cftool	1.0224 (2.2)	0.0306 (!)	0.0503 (49.7)	0.5117 (2.3)
Origin	1.0226 (2.3)	0.0308 (!)	0.0500 (50.0)	0.5116 (2.3)
MSQRD method	0.9934 (0.7)	− 0.0893 (16.1)	− 0.1017 (1.7)	0. 5043 (0.9)
	$\widetilde{D}_{11}/\widetilde{D}_{11}$	$\widetilde{D}_{12}/\widetilde{D}_{11}$	$\widetilde{D}_{21}/\widetilde{D}_{11}$	$\widetilde{D}_{22}/\widetilde{D}_{11}$
Case-iii	1.0	0.5	− 0.1	0.5
Cftool	0.9071 (9.3)	0.0940 (80.6)	0.0228 (!)	0.4524 (9.5)
Origin	0.9061 (9.4)	0.0942 (80.6)	0.0287 (!)	0.4526 (9.5)
MSQRD method	0.9939 (0.4)	0.5117 (2.4)	− 0.0966 (3.4)	0.4934 (1.3)
	$\widetilde{D}_{11}/\widetilde{D}_{11}$	$\widetilde{D}_{12}/\widetilde{D}_{11}$	$\widetilde{D}_{21}/\widetilde{D}_{11}$	$\widetilde{D}_{22}/\widetilde{D}_{11}$
Case-iv	1.0	− 0.1	− 0.1	0.5
Cftool	0.9787 (2.1)	0.0198 (!)	− 0.0497 (50.2)	0.4887 (2.3)
Origin	0.9780 (2.2)	0.0197 (!)	− 0.0498 (50.2)	0.4889 (2.2)
MSQRD method	0.9947 (0.5)	− 0.0893 (10.7)	− 0.1017 (1.7)	0.5043 (0.9)

The percentage of the relative error is given in the parentheses next to each number. The exclamation sign is used if the sign was not correctly reproduced (relative error is then over 100%)

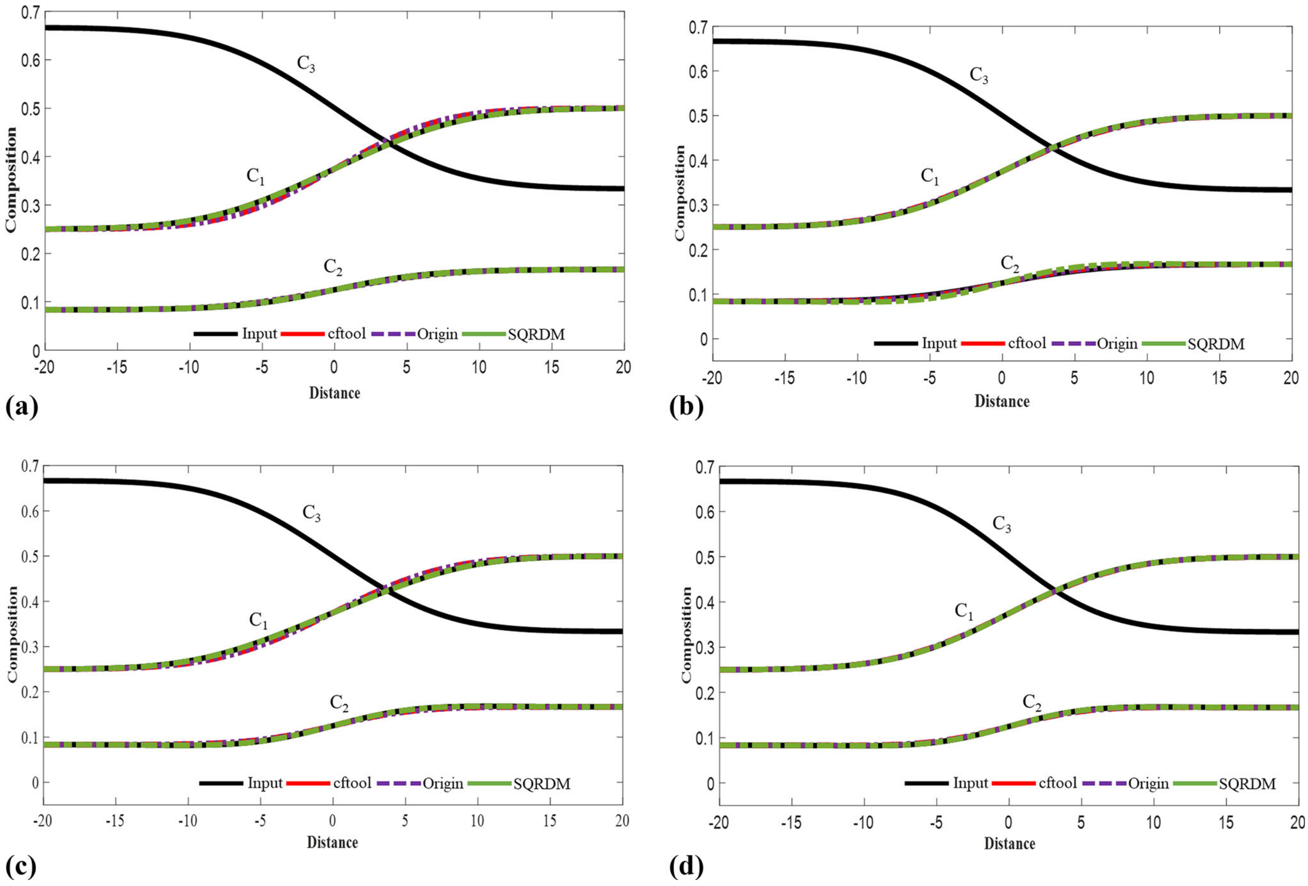

Fig. 4 Comparison of composition profiles for the couple BC-2 using a different set of interdiffusion matrices obtained from the Cftool, Origin and MSQRD methods with original profiles: (a) Case-i, (b) Case-ii, ©) Case-iii, (d) Case-iv

profiles obtained using the MSQRD method (as well as the Fitting Methods!) gives very good agreement with the initial profiles. This again is indirect evidence that the use of a single diffusion couple for the analysis of the full interdiffusion matrix is difficult. Another important conclusion is that the back-tests of the composition profiles must not be used as the only proof of the reliability of the methods used.

From Fig. 3 and 4, it is clear that, despite some large differences in the matrices (especially in the off-diagonal terms), the back-tests of the composition profiles are all surprisingly close to the original ones. The maximum deviations are for the C_1 profiles, and only up to 0.009 atomic fractions. In, Ref 10 a different Fitting Method was found to give a consistently good accuracy for a similar single diffusion couple applications. There, the accuracy of the fitting procedure was set to an exceptionally high level, up to 10^{-14} order. Together with our results, this provides strong evidence that, to be able to use a single diffusion couple for a reliable interdiffusion analysis, the experimental data must be obtained with a very high level of accuracy (which is, of course, impossible in a real experiment). The use of two diffusion couples should be treated as the best option for the application of the SQRD method[23,24] to the experimental data.

Nonetheless, it is highly recommended that the MSQRD method (with increased accuracy in numerical differentiation and integration) is used for the interdiffusion analysis using one compact couple.

5 Conclusions

The Fitting (into a closed form error-function solution) Method and the MSQRD method were used for the analysis of the inverse interdiffusion problem in a ternary alloy (using one diffusion couple) with a constant interdiffusion matrix. The interdiffusion coefficients have been determined from the initially generated composition profiles obtained from the closed form solution.

In all the diffusion couples, the MSQRD method gives, on average, the best agreement with the initial matrices and profiles. The MSQRD method gives an error up to only 2% for the diagonal terms for most cases. With respect to the off-diagonal terms, it was shown that, for the cases considered, the MSQRD method always accurately reproduced the sign of the terms. This is not the case for the two Fitting Methods. The accuracy of the MSQRD method could, in principle, be increased by making use of the higher-order accuracy finite difference approximations to the composition gradients.

In addition, strong evidence has been presented that the back-tests of the composition profiles must not be used as the only proof of the reliability of the methods used.

Acknowledgment The research was supported under the Australian Research Council Discovery Project funding scheme (Project Number: DP 170101812).

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