CrossMark

Comparison of the Sauer-Freise and Hall Methods for Obtaining Interdiffusion Coefficients in Binary Alloys

T. Ahmed, I.V. Belova, A.V. Evteev, E.V. Levchenko, and G.E. Murch

In the present paper (1) the Hall method (HM) (specifically designed for determining the interdiffusion coefficient at the low and high composition limits of the corresponding interdiffusion composition profile) is further developed in order to be applied to the whole composition profile resulting in the Extended Hall method (EHM); (2) A comparative study of the HM, EHM, Boltzmann-Matano (BM) and Sauer and Freise (SF) methods is performed using composition profiles generated by computer simulation. The results clearly indicate that the HM/EHM technique is only applicable when the interdiffusion coefficient is constant (i.e. independent of composition) or almost constant at the low composition regions. In all other cases, the BM and SF methods give the best agreement with the input interdiffusion function even at the ends of the composition profiles.

1. Introduction

The study of the composition dependence of mass diffusion is important in the field of metals and semiconductors. There is also considerable demand for information on accurate diffusion coefficients, including interdiffusion coefficients. For a comprehensive older compilation of experimental interdiffusion studies see Ref. 1. Recently, numerous experimental studies have been conducted on binary systems, such as Pd-Pt, Cu-Pt, Ni-Pt, Co-Pt, Ni-Al, Ti-Al, dilute Cu(Sn), Ni-Nb, Mo-Si, Nb-Si, V-Si, Co-Ni, Fe-Nb, Ni-Mo, Mg-Al, Mg-Zn, U-Fe, U-Mo, Mo-Zr and Zr-Al.[2–25]

Usually, the experimental data for the single-phase binary interdiffusion couples are processed using the standard analytical technique, Sauer and Freise (SF) or Boltzmann-Matano (BM). There are cases when the experimental data were also processed using the Hall method (HM) technique. This latter method was designed to be applicable at the dilute ends of the composition profiles. While the SF and BM techniques usually agree with each other, the results of the HM analysis can be quite different.[26–29] In the present paper, using numerically simulated interdiffusion profiles we will test the validity of these three methods at the dilute ends and along the bulk of the composition profiles.

Historically, the first analytical method for calculating the diffusion coefficients was developed by Boltzmann.[30] This method was then used by Matano[31] to analyze experimental interdiffusion composition profiles. Matano also extended Boltzmann's[30] method by introducing the new concept of a 'special' plane. This plane was later named after Matano. In[31] Matano proposed that the location of the Matano plane be determined from the condition of mass conservation. Nowadays, this method is known generally as the BM method. The BM method, at first, was introduced as a graphical method to find the interdiffusion coefficient. But a graphical method has some disadvantages for calculating an accurate interdiffusion coefficient. For this reason, Sauer and Freise[32] proposed a new equation for calculating the interdiffusion coefficient which is, in fact, a elegant modification of the BM method. With this method, it is possible to find an accurate interdiffusion coefficient as a function of composition, thereby avoiding the calculation of the Matano plane location. Den Broeder[33] proposed a general simplification and improvement of the BM method for calculating interdiffusion coefficients in binary systems. Wagner[34] suggested a simplified derivation of the SF equation for calculation of the interdiffusion coefficient as a function of composition. Kailasam et al.[35] studied the BM, SF, Wagner and den Broeder methods for calculating the composition-dependent interdiffusion coefficient in binary systems. Appel[36] investigated a further development of the BM method analytically for a multiphase system. Hall[26] developed an analytical method which is, in fact, a further modification of the BM method. Hall also suggested that the resulting method, (called the HM), gives an accurate estimation of the diffusion coefficients near the high and low composition limits. It was slightly modified by Crank[37] using the Boltzmann variable divided by two. Finally, the HM was extended by Sarafianos.[38] Okino et al.[39] studied an analytical solution of the Boltzmann transformation equation with non-linear interdiffusion coefficients.

T. Ahmed, I.V. Belova, A.V. Evteev, E.V. Levchenko, and G.E. Murch, Centre for Mass and Thermal Transport in Engineering Materials, School of Engineering, The University of Newcastle, Callaghan, NSW 2308, Australia. Contact e-mail: Irina.Belova@newcastle.edu.au.

Stenlund[40] studied three methods (two methods for three-dimensional and a third one for the one-dimensional case) to calculate the interdiffusion coefficient from a composition profile without any limitations on the boundary conditions. These methods are suitable for numerical analysis only because there is no closed form solution. Zhang and Zhao[41] developed a MATLAB-based program to calculate the interdiffusion coefficients for binary diffusion couples using traditional methods i.e. BM method, SF method, the HM, and the Wagner method and a forward-simulation method. Recently, Belova et al.[42] derived a novel way of measuring interdiffusion and tracer diffusion coefficients in one experiment with an analysis based on the application of linear response theory. They showed that the SF method can be modified for the analysis of the combined tracer and interdiffusion experiment. Kass and O'Keeffe[43] studied the numerical solution of the Diffusion Equation with composition-dependent diffusion coefficients. This method is applicable to two different types of boundary condition corresponding to physical situations. Mittemeijer and Rozendaal[44] applied a step method for numerical solution of the Diffusion Equation and developed an iterative procedure when the diffusion coefficient is composition-dependent. They proposed that their iterative method takes less calculation time than other procedures. Garcia et al.[45] studied a finite difference scheme to solve the one-dimensional Diffusion Equation with special focus on the stability and convergence of the scheme. They outlined the better numerical methodology and its applicability for a metal-metal system. In addition, a finite difference method was used by Wei et al.[46] for determining the interdiffusion coefficient of an aluminide coating formed on a superalloy.

The principal aim of the present study is to investigate the applicability of the HM for the analysis of interdiffusion composition profiles in comparison with the BM and SF methods. Originally the HM was developed for application only at the dilute ends of the profile. We will extend this method for application to the whole profile. The Extended Hall method (EHM) will be compared with the original HM and with the BM and SF methods as well. In order to perform this investigation we will first generate the numerical solution of the Diffusion Equation by using an explicit finite difference method. Then we will investigate the analysis of the thus generated composition profiles by means of the BM, SF, HM and EHM techniques to find the interdiffusion coefficient and compare them with the input one. Note that for the implementation of the HM, EHM and BM method we will need to numerically determine the location of the Matano plane as accurately as possible.

In choosing this strategy of investigation we reasonably assume that if the HM does not perform well when the 'smooth' profiles are used (simulated using numerical methods as in the present study) then it will never perform better on the 'less smooth' profiles (as in the real experiments). Furthermore, the well-known high sensitivity of the interdiffusion profiles (the small differences in the profiles usually produce large differences in the corresponding interdiffusion coefficients) dictates the use of very accurately simulated profiles.

2. Mathematical Formulation

The governing equation of the standard interdiffusion process in a binary alloy is the one-dimensional Diffusion Equation:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial C}{\partial x}\right) \qquad \text{(Eq 1)}$$

where C is the (composition) mole fraction of one of the diffusing atomic components, C is a function of distance, x and time, t, D is the interdiffusion coefficient. It could be a constant but, in general, it depends on composition. In writing Eq 1 we assume that in the diffusion process the molar volume does not change. The Diffusion Equation 1 is to be solved subject to the following boundary conditions for all $t > 0$:

$C = 1.0, x = -\infty$, and $C = 0.0, x = +\infty$ and initial conditions: $C = 1.0, x < 0$ and $C = 0.0, x \geq 0$.

We should emphasise here that the analysis of this study can easily be applied to a general case when $C = C^{-\infty}$ at $x = -\infty$, and $C = C^{+\infty}$ at $x = \infty$. Then C should be replaced with a normalised composition as:

$$Y = \frac{C - C^{+\infty}}{C^{-\infty} - C^{+\infty}}. \qquad \text{(Eq 2)}$$

In the interdiffusion experiment the composition depth profile is measured as a function of distance. Then using one of the appropriate analytical methods, the interdiffusion coefficient is obtained. As was mentioned above there are three main methods to use: the BM, SF and HMs. The latter was designed especially to deal with the experimental uncertainties at the dilute ends of the composition profile in order to improve the accuracy of the interdiffusion coefficient. The purpose of the present analysis is to test these three methods using numerical techniques to simulate the interdiffusion composition profiles and to make conclusions about the applicability of all methods.

2.1 BM Method

With the known composition profile $C(x, t)$ the BM method can be applied to determine the composition-dependent diffusion coefficient $D(C)$ as:

$$D(C^*) = -\frac{1}{2t}\frac{\int_0^{C^*}(x - x_M)dC}{\left(\frac{dC}{dx}\right)_{C^*}}, \qquad \text{(Eq 3)}$$

where x_M is the position of the Matano plane. The location of the Matano plane is determined from the following (flux) conservation condition:

$$\int_{-\infty}^{x_M}(1 - C(x))dx = \int_{x_M}^{+\infty}C(x)dx. \qquad \text{(Eq 4)}$$

A further development of the BM method has been proposed by Eversole et al.[47] for dilute solutions. They simply evaluated the integral term in Eq 3 by parts. Then the following expression was found:

$$D(C^*) = -\frac{1}{2t} \frac{(x^* - x_M)C^* + \int\limits_{x^*}^{+\infty} Cdx}{\left(\frac{dC}{dx}\right)_{C^*}}$$

(Eq 5)

Moreover, it is easy to show that the position of the Matano plane, x_M is given exactly by the following integral relations:

$$x_M = \int_0^1 xdC = \int_{-\infty}^0 (1 - C(x))dx + \int_0^{+\infty} C(x)dx.$$

(Eq 6)

2.2 SF Method

According to the SF method, the interdiffusion coefficient $D(C)$ is given as:

$$D(C^*) = -\frac{1}{2t}\left(\frac{dx}{dC}\right)_{C^*} \left[C^* \int\limits_{-\infty}^{x^*} (1 - C)dx + (1 - C^*) \int\limits_{x^*}^{+\infty} Cdx \right]$$

(Eq 7)

In the derivation of the SF method the BM expression Eq 3 was combined with the expression for the Matano plane Eq 4. As a result, SF method does not require x_M explicitly and therefore is more convenient from an experimental perspective.

Wagner[34] provided a simplified derivation of the SF relation (Eq 7) for the calculation of the interdiffusion coefficient. However the main significance of his paper is in developing the SF relation further to apply to the interdiffusion profiles with multiple phases. In[34] it was shown that in multiphase systems with intermediate compounds which have a narrow composition range, it is possible to calculate the values of the integral $\int DdC$, extended over the composition range of the compounds. These values then serve as the integrated (or average) interdiffusion coefficients. In the present paper, we will restrict our study only to the case of a single phase in the diffusion zone.

2.3 Hall Method (HM)

The main requirement for the HM is that one of the diffusion couple sides should have a zero composition. Then in the HM, the following supplementary transform is used for the dilute tail in the composition profile:

$$C = erfc(u),$$

(Eq 8)

where (as defined at the time by Hall) $erfc(u) \equiv \frac{1}{2}(1 + erf(u))$, $u = h\lambda + k$ and $\lambda = \frac{x - x_M}{\sqrt{t}}$, and it is assumed that the dilute end/tail of the profile has a characteristic linear behaviour. Hall evaluated the derivative and integral

terms in Eq 3 by using the following relations (for the derivation, see Ref. 26):

$$\frac{dC}{dx} = \frac{1}{\sqrt{t}}\frac{dC}{d\lambda} = \frac{1}{\sqrt{t}}\frac{h}{\sqrt{\pi}}\exp(-u^2)$$

(Eq 9)

$$\int_0^{C^*} (x - x_M)dC = \sqrt{t}\int_0^{C^*} \lambda dC = -\sqrt{t}\left(\frac{1}{2h\sqrt{\pi}}\exp(-u^2) + \frac{kC}{h}\right)$$

(Eq 10)

Combining these relations together with Eq 3 we have the final expression for the HM:

$$D(C) = \frac{1}{4h^2} + \frac{k\sqrt{\pi}}{2h^2}C\exp(u^2).$$

(Eq 11)

2.4 Extended Hall Method (EHM)

The HM was originally described[26] for implementation only at that end of the composition profile where the composition is approaching zero in a linear fashion when presented on a probability plot. Here we develop this approach in such a way that the whole composition profile can be analysed. The starting point should still be chosen at the zero composition end. The new development of HM can be readily obtained when the basic integration and differentiation steps and the combination of them into the interdiffusion coefficient (Eq 9-11 above) are performed in a piece-wise fashion at every two neighbouring composition points. Then the new set of composition points C' and corresponding sets of u' and λ' can be simply defined as:

$$C'(i) = 0.5(C(i) + C(i + 1)), u'(i) = 0.5(u(i) + u(i + 1)),$$
$$\lambda'(i) = 0.5(\lambda(i) + \lambda(i + 1)),$$

(Eq 12)

and the coefficients for the piece-wise linear fits $u' = h'\lambda' + k'$ are:

$$h'(i) = \frac{u(i + 1) - u(i)}{\lambda(i + 1) - \lambda(i)},$$

(Eq 13)

and

$$k'(i) = \frac{\lambda(i + 1)u(i) - \lambda(i)u(i + 1)}{\lambda(i + 1) - \lambda(i)}$$

(Eq 14)

for all i points. This procedure should be performed consecutively, starting with the very first point at the chosen side of the diffusion profile. Then it is easy to show that the final iterative expression for the interdiffusion coefficient is as follows:

$$D(C'(i)) = D(i) = -\frac{1}{2}\frac{\sqrt{\pi}}{h'(i)}e^{\{u'(i)\}^2}I(i + 1),$$

(Eq 15)

where

$$I(i) = I(i-1) + II(i-1) + III(i-1) \qquad \text{(Eq 16)}$$

and

$$I(1) = -\frac{1}{2h'(1)\sqrt{\pi}} e^{\{-u'(1)^2\}} - \frac{k'(1)C'(1)}{h'(1)}, \qquad \text{(Eq 17)}$$

$$II(1) = 0, \; III(1) = 0,$$

$$
\begin{aligned}
II(i) = &-\frac{1}{2h'(i-1)\sqrt{\pi}} \left[e^{\{-u(i)^2\}} - e^{\{-u'(i-1)^2\}} \right] \\
&- \frac{k'(i-1)}{h'(i-1)} (C(i) - C'(i-1)),
\end{aligned}
$$
$$\text{(Eq 18)}$$

$$
\begin{aligned}
III(i) = &-\frac{1}{2h'(i)\sqrt{\pi}} \left[e^{\{-u'(i)^2\}} - e^{\{-u(i)^2\}} \right] \\
&- \frac{k'(i)}{h'(i)} (C'(i) - C(i))
\end{aligned}
$$
$$\text{(Eq 19)}$$

for all i points. The choice of the starting point should be done in such a way that $C'(i)$ is as close to zero as possible.
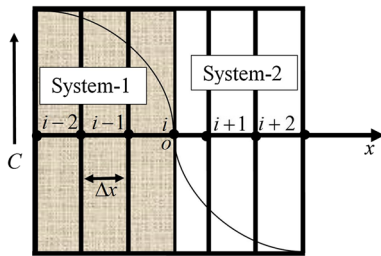

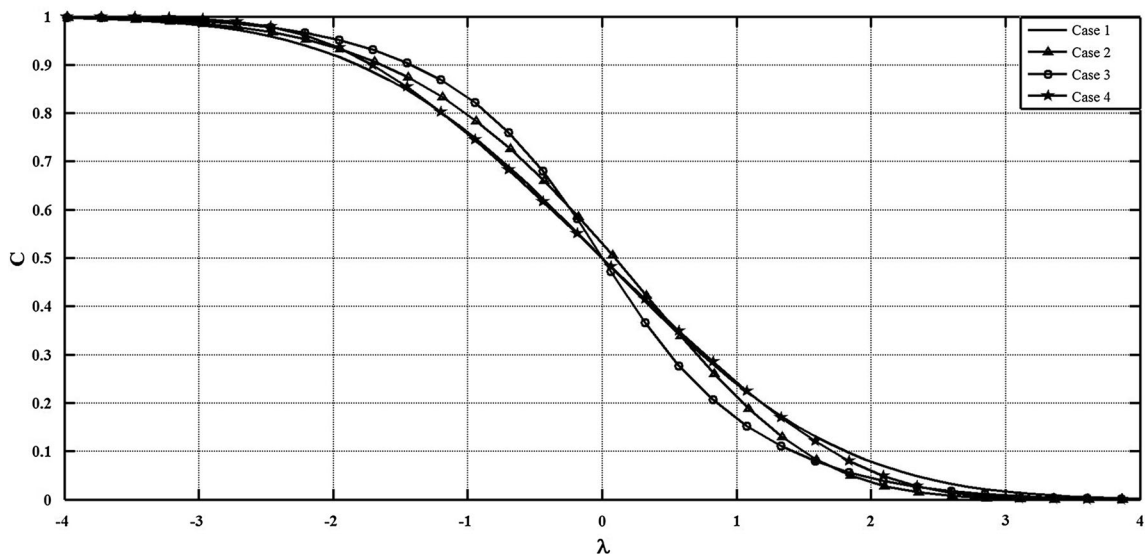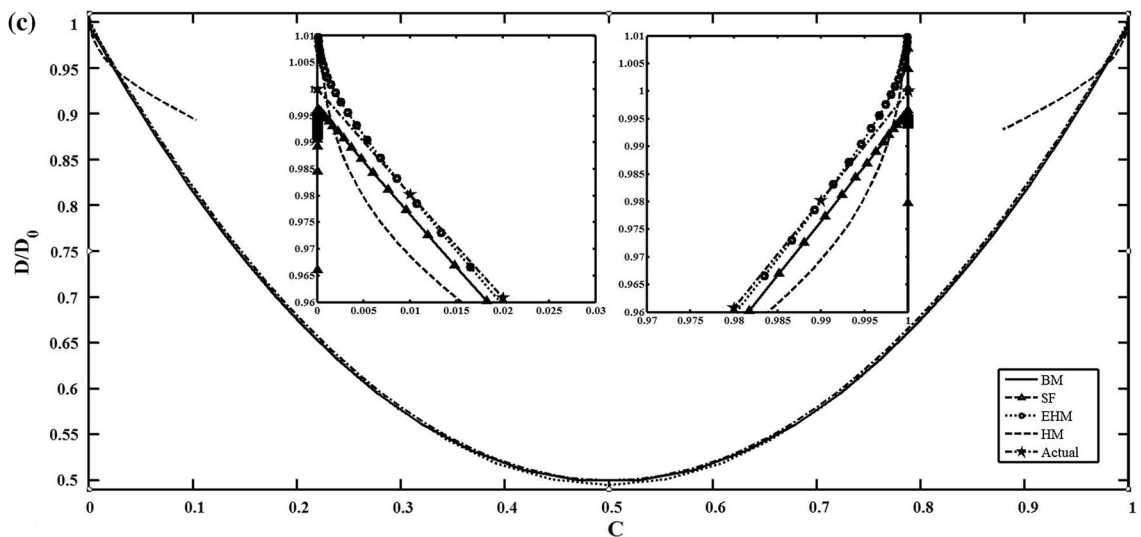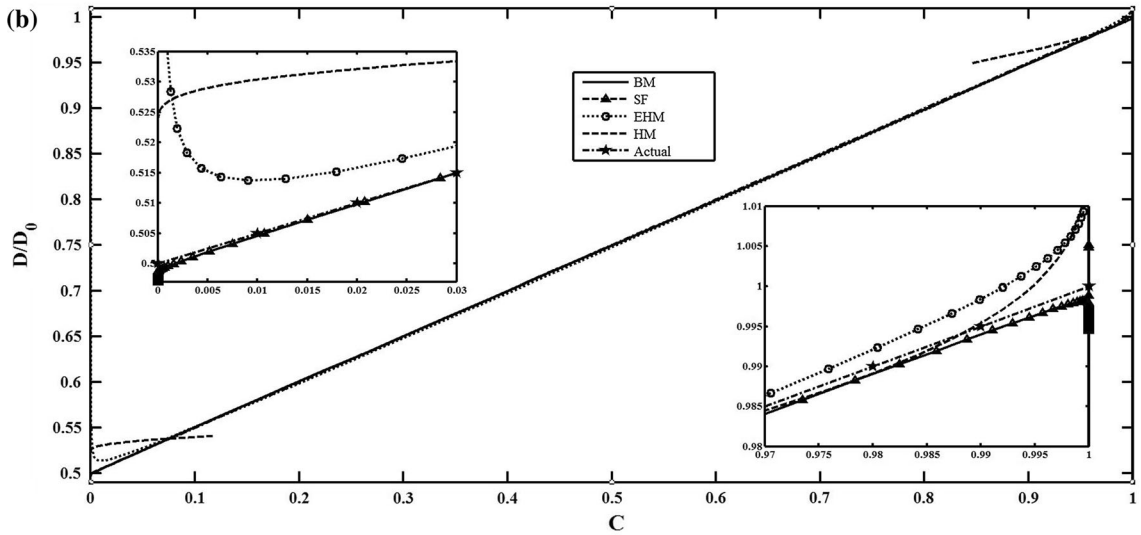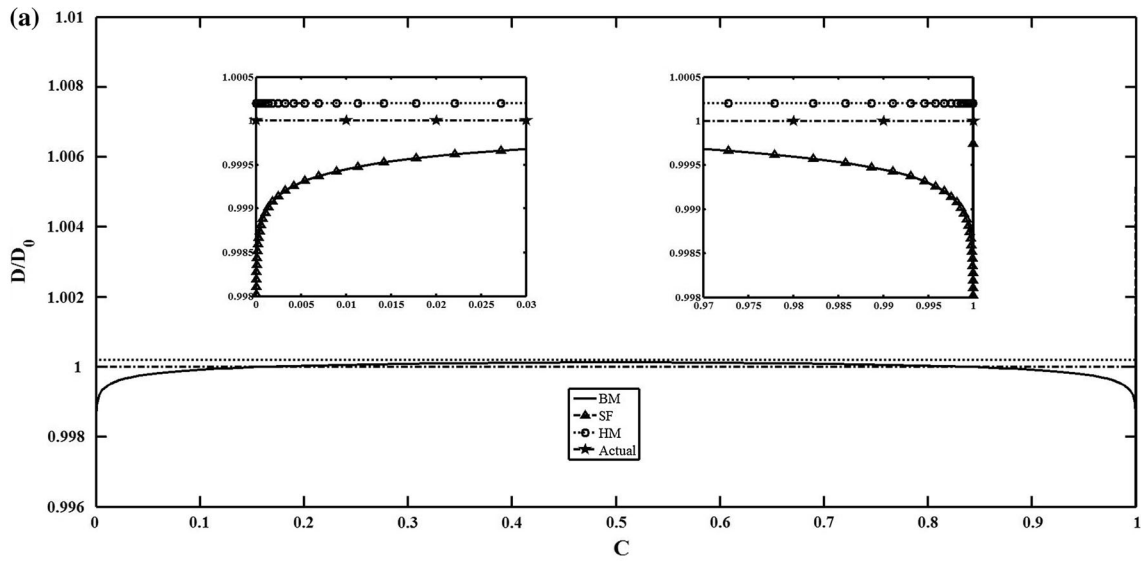**Fig. 1** Finite difference system mesh for the binary system

3. Numerical Solution for Composition Profiles

In this section we solve numerically the Diffusion Equation (Eq 1), with the associated initial and boundary conditions. The explicit finite difference method is used. The present problem requires a finite difference mesh. The region along the coordinate x is divided into equally spaced $m + 1$ mesh points (see Fig. 1). The maximum length (dimensionless) was chosen $x_{\max} = 16$, with $x_{-\infty} = -8$ and $x_{+\infty} = 8$ and these points correspond to $x \to -\infty$ and $x \to -\infty$. The number of mesh spacings in the x direction was chosen as $m = 200$, hence the constant mesh size along x axis becomes $\Delta x = 0.08$, $(-8 \leq x \leq 8)$ with a small enough time-step $\Delta t = 0.0001$ that was chosen in such a way that the stability condition (see further) is satisfied.

Let C^n denote the value of C at the end of the nth time-step. Using the explicit finite difference approximation, the following finite difference equation is obtained:

$$\frac{C_i^{n+1} - C_i^n}{\Delta t} = D_i^n \frac{C_{i+1}^n - 2C_i^n + C_{i-1}^n}{(\Delta x)^2} + \left.\frac{\partial D}{\partial C}\right|_i^n \left(\frac{C_{i+1}^n - C_{i-1}^n}{2\Delta x} \right)^2$$
$$\text{(Eq 20)}$$

with the boundary conditions, $C_{-\infty}^n = 1$ and $C_{+\infty}^n = 0$. (Note that these conditions were used only for monitoring, not assigning, the C values at the ends of the calculation region. In other words, at each time step we monitor that the initial values 1 and 0 were not changed at the boundary points $i = 1, 2$ and $i = m, m + 1$. If they were changed (from 1 and
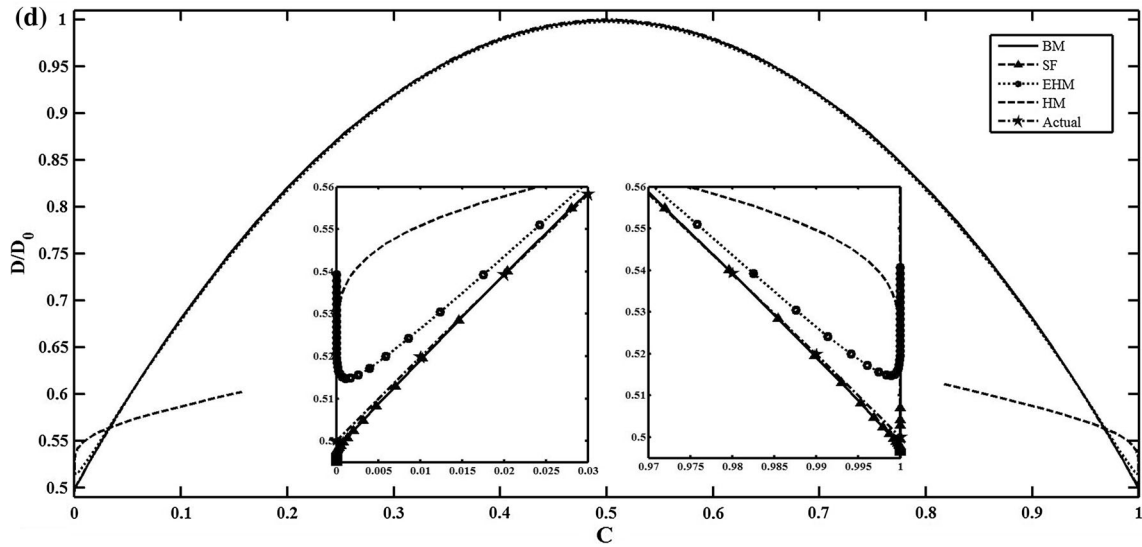

Fig. 2 Composition profiles for the different cases (1-4). Total computational diffusion time $t = 0.40$

Fig. 3 continued

0 respectively) then the calculations would have to be stopped with the appropriate warning message and the numerical interval would have to be extended. Descriptions of this procedure can be found in standard handbooks on finite difference methods.[48,49] In our simulations for a chosen maximum time t these conditions were always satisfied.

As usual, in Eq 20 the subscript i denotes the grid points along the x coordinate and the superscript n denotes a step in time, $t = n\Delta t$ where $n = 0, 1, 2, \ldots$ with $\Delta t = 0.0001$. The composition C at all interior mesh points is computed by successive applications of the above finite difference equations. The stability condition and convergence criterion for the finite difference solution is given by (e.g.[45,46]) $\frac{\max(D_i^n)\Delta t}{(\Delta x)^2} \leq \frac{1}{2}$. For all cases that were considered in the present paper this parameter was < 0.02.

In this paper, we studied the following four test cases:

Case-1 (constant interdiffusion coefficient): $D = D_0$.
Case-2 (linear composition dependence): $D = (0.5 + 0.5C)D_0$.
Case-3 (quadratic composition dependence): $D = (1 - 2C(1 - C))D_0$.
Case-4 (quadratic composition dependence): $D = (2C(1 - C) + 0.5)D_0$.

D_0 is a constant with units of diffusion coefficient. In Fig. 2 we show the profiles generated for all studied cases as functions of $= (x - x_M)/\sqrt{t}$. Total computational diffusion time is 0.4 in arbitrary time units that are consistent with chosen units of diffusion coefficient and the x-axis. If, as a practical example, $D_0 = 0.1$ μm^2/s and the unit distance in the x-direction is equal to 100 μm then the total diffusion time will be 4×10^4 s $= 11.1$ h and in Fig. 2 the unit of λ is equal to 0.316 μm/s$^{1/2}$.

4. Mass Conservation

The Law of Mass Conservation states that mixtures can be made or separated, but the total amount of mass must be constant for all times. It is easy to show that for the considered diffusion processes in the binary systems the total amount of mass is proportional to the integral $M(t) = \int_{-8}^{8} C(t)dx$. The mass conservation tests for all the composition profiles and all times returned near constant values that remain within the $O(\Delta x^2)$ error term and this is in agreement with the specified error/tolerance for the chosen finite difference scheme. Therefore we can safely conclude that all our simulated systems obey the Mass Conservation law.

5. Results and Discussion

To obtain the finite difference solutions, the computations have been carried out for $t = 0.4$ (arbitrary units). Then we calculated the interdiffusion coefficient making use of the BM, SF, and original HM for all of the above test cases. In application of the BM and SF methods, the integration terms were calculated by the Trapezoidal Rule and the derivative was calculated using the central difference scheme, both of the second order of accuracy. The newly developed EHM was applied to the Cases 2-4. For Case 1 there was obviously no need for the use of the EHM. The original HM was applied to Case 1 from each dilute end up to the middle point and, as a result, covered the whole composition range. For Cases 2-4 the original HM technique was only applied at the dilute ends. For implementation of the BM and both HM and EHM methods we calculated the Matano plane numerically and obtained the following values: Case 1: $x_M = -0.0400$; Case 2: $x_M = -0.0467$; Case 3: $x_M =$

−0.0400; Case 4: $x_M = -0.0400$. Graphical representations of the resulting interdiffusion coefficients for Cases 1-4 are given in Fig. 3(a)-(d) respectively. (It was found that the accuracy of x_M has a profound effect on the resulting diffusion coefficient.) In each figure we presented the overall results to cover a 0-100% composition range together with two inserts to cover the first and the last 3% of composition with magnifications of up to factor of 10. In the inserts we have used lines with symbols for the results of the SF, HM and for the original input D function whereas for the overall results we used the same type of lines but without symbols to avoid cluttering the figures.

We would like to point out that a similar strategy was used in[35,50] where the authors used the closed form solutions for generation of the discretized composition profiles followed by application of the inverse analysis using SF and BM methods. The closed form solution exists only for the constant interdiffusion coefficient and some transcendental functions.[35,50] In our study we choose to investigate three basic functional dependencies: constant, linear and quadratic.

In Fig. 3(a) we plot the actual (input) interdiffusion coefficient and results of application of BM, SF and original HM techniques to the profiles generated for the constant interdiffusion coefficient, according to the Case-1 study. In this case, it was possible to apply the original HM to the whole composition profile. It can be seen that both the BM method and SF methods give the same results for this case (see inserts and the overall coverage). But the (original) HM gives better results than the other two methods at the initial and final 3% of the composition range. For the remaining part of the composition range all three methods give comparable results.

Here we would like to point out that results of this case, namely application SF and BM methods, can be directly compared with the results of application of these inverse methods in[35,50] to the same constant interdiffusion case. It is clear that the accuracy is higher in our application and this can be linked directly to the accuracy of the chosen numerical integration and differentiation as parts of the implementation of the SF and BM methods.

In Fig. 3(b) we plot the actual (input) interdiffusion coefficient and results of application of the considered techniques to the profiles generated for the interdiffusion coefficient that is linearly dependent on composition, according to the Case-2 study. The original HM was applied only at the ends of the profile. It can be seen that in this case the BM and SF methods give better results than the EHM at the ends of the composition range (see inserts). And the EHM gives better results than the original HM. This makes the original HM technique the worst for this case. For the remaining internal part of the composition range all three methods again give comparable results.

In Fig. 3(c) we plot the actual (input) interdiffusion coefficient together with the results of application of the considered techniques to the profiles generated for the interdiffusion coefficient that is a concave quadratic function of composition, according to the Case-3 study. It can be seen that for this case, at the ends of the composition range (see insets) again the BM and SF methods give the same

results that are comparable with the results of the EHM technique. The original HM again gives the worst agreement with the input interdiffusion coefficient. For the remaining internal part of the composition range all three methods again give comparable results.

In Fig. 3(d) we plot the actual (input) interdiffusion coefficient together with the results of application of the considered techniques to the profiles generated for the interdiffusion coefficient that is a convex quadratic function of composition, according to the Case-4 study. In this case, the same behaviour of the SF and BM results as for Case 3 can be observed. But at the ends of the composition range the EHM technique gives a much poorer result for this test. And again application of the original HM at the ends of the composition range gives the worst agreement with the input interdiffusion coefficient. As for the other cases for the remaining internal part of the composition range all three methods again give comparable results.

It is obvious that apart from the case of a constant interdiffusion coefficient (Fig. 3a)) the EHM and especially the HM do not in fact do well at the dilute ends of the composition profile where $C \approx 0.0$ or $C \approx 1.0$. This result contradicts the original claim[26] that HM should give a superior accuracy at these limits. It seems that the reason for this effect is that together with magnification of the composition profile the probability plot magnifies the errors (of the applied computational techniques for differentiation and integration in Eq 9, 10) at the composition profile ends as well. Even application of the EHM does not bring the accuracy of the resulting interdiffusion coefficient to the level of SF/BM accuracy. Therefore, we must make the unavoidable conclusion that the improvements of the interdiffusion coefficients found in, for example,[26] and in[27] for the Cu-Ni system are not in fact real improvements and the standard SF/BM analysis gives the correct results.

On the other hand, from the analysis of the Fig. 3(a) it is clear that the SF and BM methods do not do well at the first and the last 10% of composition range for the Case 1 of the constant interdiffusion coefficient. In fact, the HM (and EHM) give much better results there. Therefore we can make the following suggestion for the improved analysis of experimentally obtained interdiffusion composition profiles. We suggest that the EHM is applied (separately from the left side to the center and from the right side to the center) together with the SF/BM techniques. If at the first 5-10% the EHM gives a clear constant interdiffusion coefficient this must be accepted as the correct one; otherwise the results of the SF/BM techniques should be treated as the correct ones. A similar strategy should be applied for the last 5-10% of the composition range.

6. Conclusions

In this research, the explicit finite difference numerical solution of the Diffusion Equation for binary alloy systems with composition-dependent interdiffusion coefficients has been used to generate interdiffusion composition profiles for

several test cases. Three methods, BM, SF and Hall (original (HM) and a newly developed extended (EHM)) methods, were used to obtain the interdiffusion coefficient as a function of composition for those test cases. With the Matano plane calculated numerically, it was found that the results of the BM method and SF method were generally the best compared with the results of the HM and EHM especially at the dilute ends of the profile where the HM was originally[26] designed to improve the accuracy. Only for a constant interdiffusion coefficient did the HM (EHM was not needed for this case) give the best agreement with the required interdiffusion coefficient. Apart from the case of a constant interdiffusion coefficient, results of the EHM method were usually in a better agreement with the input data than the original HM. Therefore it was concluded that for the determination of the interdiffusion coefficient at or near to the low and high composition levels the HM should only be used with considerable care.

Acknowledgments

References

1. G.E. Murch and C.M. Bruff, Chemical Diffusion in Inhomogeneous Binary Alloys Diffusion in Solid Metals and Alloys, *Landolt-Börnstein—Group III Condensed Matter*, H. Mehrer, Ed., Vol 26, Springer, Berlin, 1990, p 279-371
2. V.A. Baheti, R. Ravi, and A. Paul, Interdiffusion Study in the Pd-Pt System, *J. Mater. Sci. Mater. Electron.*, 2013, **24**, p 2833-2838
3. B. Mishra, P. Kiruthika, and A. Paul, Interdiffusion in the Cu-Pt System, *J. Mater. Sci. Mater. Electron.*, 2014, **25**, p 1778-1782
4. A. Paul, A.A. Kodentsov, and F.J.J. van Loo, On Diffusion in the β-NiAl Phase, *J. Alloys Compd.*, 2005, **403**(1-2), p 147-153
5. V.D. Divya, U. Ramamurty, and A. Paul, Interdiffusion and the Vacancy Wind Effect in Ni-Pt and Co-Pt Systems, *J. Mater. Res.*, 2011, **26**(18), p 2384-2394
6. S. Santra and A. Paul, Vacancy Wind Effect on Interdiffusion in a Dilute Cu(Sn) Solid Solution, *Philos. Mag. Lett.*, 2012, **92**(8), p 373-383
7. S.S.K. Balam, H.Q. Dong, T. Laurila, V. Vuorinen, and A. Paul, Diffusion and Growth of the μ Phase (Ni$_6$Nb$_7$) in the Ni-Nb System, *Metall. Mater. Trans.*, 2011, **42**(7), p 1727-1731
8. C. Cserháti, A. Paul, A.A. Kodentsov, M.J.H. van Dal, and F.J.J. van Loo, Intrinsic Diffusion in Ni$_3$Al System, *Intermetallics*, 2003, **11**(4), p 291-297
9. S. Prasad and A. Paul, Growth Mechanism of Phases by Interdiffusion and Atomic Mechanism of Diffusion in the Molybdenum-Silicon System, *Intermetallics*, 2011, **19**(8), p 1191-1200
10. S. Prasad and A. Paul, Diffusion Mechanism in XSi$_2$ and X$_5$Si$_3$ (X = Nb, Mo, V) Phases, *Defect Diffus. Forum*, 2012, **323-325**, p 459-464
11. S. Prasad and A. Paul, An Overview of the Diffusion Studies in the V-Si System, *Defect Diffus. Forum*, 2011, **312-315**, p 731-736
12. S. Prasad and A. Paul, Growth Mechanism of Phases by Interdiffusion and Diffusion of Species in the Niobium-Silicon System, *Acta Mater.*, 2011, **59**(4), p 1577-1585
13. S.S.K. Balam and A. Paul, Study of Interdiffusion and Growth of Topologically Closed Packed Phases in the Co-Nb System, *J. Mater. Sci.*, 2011, **46**, p 889-895
14. S.S.K. Balam and A. Paul, Interdiffusion Study in the Fe-Nb System, *Metall. Mater. Trans. A*, 2010, **41**(9), p 2175-2179
15. V.D. Divya, U. Ramamurty, and A. Paul, Diffusion in Co-Ni System Studied by Multifoil Technique, *Defect Diffus. Forum*, 2011, **312-315**, p 466
16. T. Ikeda, A. Almazouzi, H. Numakura, M. Koiwa, W. Sprengel, and H. Nakajima, Single-Phase Interdiffusion in Ni$_3$Al, *Acta Mater.*, 1998, **46**(15), p 5369-5376
17. M. Watanabe, Z. Horita, and M. Nemoto, Measurements of Interdiffusion Coefficients in Ni-Al System, *Defect Diffus. Forum*, 1996, **143-147**, p 345-350
18. Y. Mishin and C. Herzig, Diffusion in the Ti-Al System, *Acta Mater.*, 2000, **48**(3), p 589-623
19. V.D. Divya, S.S.K. Balam, U. Ramamurty, and A. Paul, Interdiffusion in the Ni-Mo system, *Scripta Mater.*, 2010, **62**(8), p 621-624
20. E. Perez, T. Patterson, and Y.H. Sohn, Interdiffusion Analysis for NiAl Vs. Superalloys Diffusion Couples, *J. Phase Equilib. Diffus.*, 2006, **27**, p 659-664
21. S. Brennan, K. Bermudez, N. Kulkarni, and Y.H. Sohn, Interdiffusion and Intrinsic Diffusion in β-Mg$_2$Al$_2$ System, *Met. Mater. Trans. A*, 2012, **43**(11), p 4043-4052
22. K. Huang, Y. Park, A. Ewh, B.H. Sencer, J.R. Kennedy, Jr., and Y.H. Sohn, Interdiffusion and Reaction Between Uranium and Iron, *J. Nucl. Mater.*, 2012, **424**(1-3), p 82-88
23. K. Huang, D.D. Keiser, Jr., and Y.H. Sohn, Interdiffusion, Intrinsic Diffusion, Atomic Mobility, and Vacancy Wind Effects in (bcc) Uranium-Molybdenum Alloy, *Met. Mater. Trans. A*, 2013, **44**(2), p 738-746
24. A. Paz y Puente, J. Dickson, D.D. Keiser, Jr., and Y.H. Sohn, Investigation of Interdiffusion Behavior in the Mo-Zr Binary System via Diffusion Couple Studies, *J. Refract. Met. Hard Mater.*, 2014, **43**, p 317-321
25. J. Dickson, L. Zhou, A. Paz y Puente, M. Fu, D.D. Keiser, Jr., and Y.H. Sohn, Interdiffusion and Reaction Between Zr and Al Alloys from 450° to 625°C, *Intermetallics*, 2014, **49**, p 154-162
26. L.D. Hall, An Analytical Method of Calculating Variable Diffusion Coefficients, *J Chem Phys*, 1953, **21**, p 87-89
27. I.D. Marchukova and M.I. Miroshkina, Diffusion in the System Copper-Nickel, *Fiz. Met. Metalloved.*, 1971, **32**(6), p 1254-1269
28. C. Kammerer, Thesis Master of Science, 2013, UCF, FL, USA
29. C. Kammerer, N. Kulkarni, B. Warmack, and Y.H. Sohn, Interdiffusion and Impurity Diffusion in Polycrystalline Mg Solid Solution with Al or Zn, *J. Alloys Compd.*, 2014, **617**, p 968-974
30. L. Boltzmann, Zur Integration der Diffusionsgleichung bei variabeln Diffusionscoefficienten, *Ann. Phys.*, 1894, **53**, p 959-964, in German
31. C. Matano, On the Relation Between the Diffusion-Coefficients and Compositions of Solid Metals (The Nickel-Copper System), *Jpn. J. Phys.*, 1933, **8**, p 109-113
32. F. Sauer and V. Freise, Diffusion in binären Gemischen mit Volumenänderung, *Z. Elektrochem.*, 1962, **66**, p 353-362, in German
33. F.J.A. den Broeder, A General Simplification and Improvement of the Matano-Boltzmann Method in the Determination

of the Interdiffusion Coefficients in Binary Systems, *Scripta Metall.*, 1969, **3**, p 321-325

34. C. Wagner, The Evaluation of Data Obtained with Diffusion Couples of Binary Single-Phase and Multiphase Systems, *Acta Metall.*, 1969, **17**, p 99-107
35. S. Kailasam, J. Lacombe, and M. Glicksman, Evaluation of the Methods for Calculating the Composition-Dependent Diffusivity in Binary Systems, *Met. Mater. Trans. A*, 1999, **30**, p 2605
36. M. Appel, Solution for Fick's 2nd Law with Variable Diffusivity in a Multi-phase system, *Scripta Metall.*, 1968, **2**, p 217-221
37. J. Crank, *The Mathematics of Diffusion*, Oxford University Press, London, 1979
38. N. Sarafianos, An Analytical Method of Calculating Variable Diffusion Coefficients, *J. Mater. Sci.*, 1986, **21**, p 2283-2288
39. T. Okino, T. Shimozaki, R. Fukuda, and H. Cho, Analytical Solutions of the Boltzmann Transformation Equation, *Defect Diffus. Forum*, 2012, **322**, p 11-31
40. H. Stenlund, *Three Methods for Solution of Composition Dependent Diffusion Coefficient.* Tech. Rep., Visilab Signal Technologies Oy, Mäntsälä, 2011
41. Q. Zhang and J.C. Zhao, Extracting Interdiffusion Coefficients from Binary Diffusion Couples Using Traditional Methods and a Forward-Simulation Method, *Intermetallics*, 2013, **34**, p 132-141
42. I.V. Belova, N.S. Kulkarni, Y.H. Sohn, and G.E. Murch, Simultaneous Measurement of Tracer and Interdiffusion Coefficients: An Isotopic Phenomenological Diffusion Formalism for the Binary Alloy, *Philos. Mag.*, 2013, **93**, p 3515
43. W. Kass and M. O'Keeffe, Numerical Solution of Fick's Equation with Composition-Dependent Diffusion Coefficients, *J. Appl. Phys.*, 1966, **37**, p 2377-2379
44. E.J. Mittemeijer and H.C.F. Rozendaal, A Rapid Method for Numerical Solution of Fick's Second Law Where the Diffusion Coefficient is Composition Dependent, *Scripta Metall.*, 1976, **10**, p 941-943
45. V. Garcia, P. Mors, and C. Scherer, Kinetics of Phase Formation in Binary Thin Films: The Ni/Al Case, *Acta Mater.*, 2000, **48**, p 1201-1206
46. H. Wei, X. Sun, Q. Zheng, G. Hou, H. Guan, and Z. Hu, A Finite Difference Method for Determining Interdiffusivity of Aluminide Coating Formed on Superalloy, *J. Mater. Sci. Technol.*, 2004, **20**, p 595-598
47. W. Eversole, J.D. Peterson, and H. Kindsvater, Diffusion Coefficients in Solution. An Improved Method for Calculating D as a Function of Composition, *J. Phys. Chem.*, 1941, **45**, p 1398-1403
48. J.H. Mathews, *Numerical Methods for Mathematics, Science, and Engineering*, Prentice Hall, Englewood Cliffs, 1992
49. G.D. Smith, *Numerical Solution of Partial Differential Equations: Finite Difference Methods*, 3rd ed., Oxford University Press, Oxford, 1985
50. M.E. Glicksman, *Diffusion in Solids*, Wiley, New York, 2000, p 180-185