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Abstract

The study of concentration dependent diffusion is important in the field of alloys and semiconductors. It is a key issue to calculate accurate interdiffusion coefficients using experimentally obtained concentration profiles. The Boltzmann-Matano (BM) method is often used for determining diffusion coefficients. But this technique has some shortcomings in calculating an accurate interdiffusion coefficient. Because of this, the Sauer and Freise (SF) method (which is a clever modification of the BM method) is more useful for calculating the interdiffusion coefficient. The Hall Method (HM) was specifically designed for determining the interdiffusion coefficient at the low and high concentration limits. In the present study, concentration profiles have been numerically generated as a solution to the interdiffusion problem in a binary system when the interdiffusion coefficient is dependent on concentration. This has been done using an explicit finite difference method. A comparative study of the HM, BM and SF methods has been performed using the generated concentration profiles. This allows for a direct comparison between the SF, BM and HM techniques. Present results clearly indicate that the HM technique can only be applicable when the interdiffusion coefficient is constant (independent of concentration) or almost constant at the low concentration regions. In all other cases the SF method gives the best agreement with the input interdiffusion function.

Keywords: Diffusion Equation; Hall method; Sauer-Freise Method; Finite Difference Method
1. Introduction

The study of concentration dependent mass diffusion is important in the field of metals and semiconductors. There is considerable demand for information on accurate diffusion coefficients, including interdiffusion coefficients. When the diffusion coefficient is dependent on concentration, it is difficult to find a closed form solution. Kass and O’Keeffe [1] studied the numerical solution of the Diffusion Equation with concentration dependent diffusion coefficients. Mittemeijer and Rozendaal [2] applied a step method for numerical solution of the Diffusion Equation and developed an iterative procedure when the diffusion coefficient is concentration dependent. They proposed that their iterative method takes less calculation time than other procedures. Garcia et al. [3] studied a finite difference scheme to solve the one-dimensional in space Diffusion Equation with special investigation of the stability and convergence of the scheme.

An analytical method for calculating the diffusion coefficients was originally investigated by Boltzmann [4]. This method was first used by Matano [5] to analyze experimental interdiffusion concentration profiles. Nowadays, this method is known as the Boltzmann-Matano (BM) method. However, the solutions obtained by the BM method are valid only under some preconditions. This analysis was carried out for mathematical and educational purposes. The BM method, at first, was introduced as a graphical method to find the interdiffusion coefficient. But the graphical method has some disadvantages for calculating an accurate interdiffusion coefficient. For this reason, Sauer and Freise [6] proposed a new equation for calculating the interdiffusion coefficient which is a further modification of the BM method. Using this method, it is possible to find an accurate interdiffusion coefficient as a function of concentration, avoiding the calculation of the Matano-interface location. Den Broeder [7] proposed a general simplification and improvement of the BM method for calculating interdiffusion coefficients in binary systems. Wagner [8] suggested a simplified derivation of the Sauer and Freise (SF) equation for calculation of the interdiffusion coefficient as a function of concentration. Kailasam et al. [9] studied the BM, SF, Wagner and den Broeder methods for calculating the concentration dependent interdiffusion coefficient in binary systems. In addition, a finite difference method was investigated by Wei et al. [10] for determining the interdiffusion coefficient of an aluminide coating formed on a superalloy.

Appel [11] investigated a further development of the BM method analytically for a multiphase system. Hall [12] developed an analytical method which is called a further modification of the BM method and also suggested that the resulting method, now called the Hall Method (HM), gives an accurate determination of the diffusion coefficients near the high and low concentration limits. It was slightly modified by Crank [13] using the Boltzmann variable divided by two. Finally, the HM was extended by Sarafianos [14]. Okino et al. [15] studied an analytical solution of the Boltzmann transformation equation with no preconditions.

Stenlund [16] studied three methods (two methods for three-dimensional and a third one for the one-dimensional case) to calculate the interdiffusion coefficient from a concentration profile without any limitations by boundary conditions. But these methods are suitable for numerical calculation only when the concentration data and the time series are available. Zhang and Zhao [17] 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. [18] 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 Sauer and Freise method can be modified for the analysis of the combined tracer and interdiffusion experiment.

The primary aim of current study is to generate the numerical solution of the Diffusion Equation by using a finite difference method. We then investigate the analysis of the thus generated concentration profiles by means of the methods of BM, SF and Hall to find the interdiffusion coefficient.
2. Mathematical Formulation

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

\[
\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}
\]  
\[\text{(1)}\]

with the boundary conditions: \( C = 1, x = -\infty, t > 0 \) and \( C = 0, x = +\infty, t > 0 \). Here \( C \) is the concentration as a function of distance, \( x \) and time, \( t \), \( D \) is the diffusion coefficient. \( D \) could be a constant but in general it depends on concentration. Once the concentration profile \( C(x,t) \) is determined the BM method can be applied to determine the concentration dependent diffusion coefficient \( D(C) \) at time, \( t \), as:

\[
D(C^*) = \frac{1}{2t} \left[ \int_{0}^{x_M} (C^* - C) \, dC + \int_{x}^{+\infty} C \, dx \right]
\]  
\[\text{(2)}\]

where \( x_M \) is the position of the Matano plane. The location of the Matano plane is determined from the conservation condition \( \int_{x_M}^{x_M} (1 - C(x)) \, dx = \int_{-\infty}^{+\infty} C(x) \, dx \). A further development of BM method has been proposed by Eversole et al. [19] for dilute solutions. They evaluated the integration term by parts. Then from Eq. (2) the following expression is found:

\[
D(C^*) = \frac{1}{2t} \left[ \int_{0}^{x_M} (C^* - C) \, dC + \int_{x}^{+\infty} C \, dx \right]
\]  
\[\text{(3)}\]

According to the SF method the concentration dependent diffusion coefficient \( D(C) \) at time, \( t \), is given as:

\[
D(C^*) = \frac{1}{2t} \left[ \int_{-\infty}^{x_M} (C^* - C) \, dC + \left( 1 - C^* \right) \int_{x}^{+\infty} C \, dx \right]
\]  
\[\text{(4)}\]

In HM, the following transform is used:

\[
C = erfc(u)
\]  
\[\text{(5)}\]

where (as defined at the time by Hall) \( erfc(u) = \frac{1}{2} \left( 1 + erf(u) \right) \), \( u = h\lambda + k \) and \( \lambda = \frac{x - x_M}{\sqrt{t}} \). Hall evaluated the integration term of Eq. (2) by using Eq. (5).
3. Finite Difference Solution

To solve Eq. (1) we used the explicit finite difference method. In this case, the region along the space coordinate \( x \) is divided into equally spaced mesh points. It is assumed that the maximum length is \( x_{\text{max}} = 16 \) where \( x_{-\infty} = -8 \) and \( x_{+\infty} = 8 \) as corresponds to \( x \rightarrow -\infty \) and \( x \rightarrow +\infty \), i.e., \( x \) varies from \(-8\) to \( 8 \) and the number of grid spacings in the \( x \) direction is \( m = 200 \), hence the constant mesh size along \( x \) axis becomes \( h = 0.08 \), \( (-8 \leq x \leq 8) \) with a smaller time-step \( \Delta t = 0.0001 \) chosen in such a way that the stability condition is satisfied. Let \( C^n \) denote the value of \( C \) at the end of \( n \)th time-step.

Using the explicit finite difference approximation, the following finite difference equation is obtained:

\[
\frac{C_{i+1}^n - C_i^n}{\Delta t} = D^n \frac{C_{i+1}^n - 2C_i^n + C_{i-1}^n}{(\Delta x)^2} + \frac{\partial D^n}{\partial C} \left( \frac{C_{i+1}^n - C_{i-1}^n}{2\Delta x} \right)^2
\]

with the boundary conditions, \( C_{-\infty}^n = 1 \) and \( C_{+\infty}^n = 0 \).

In Eq. (6) 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 \( n = 0,1,2,\ldots \). The concentration \( C \) 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. [3,4])

\[
\max \left( \frac{D_i^n}{(\Delta x)^2} \right) \Delta t \leq \frac{1}{2}
\]

In this research, we studied the following test cases:

Case-1 (constant): \( D = 1 \).

Case-2 (linear concentration dependence): \( D = 0.5 + 0.5C \).

Case-3 (quadratic concentration dependence): \( D = 1 - 2C(1 - C) \).

Case-4 (quadratic concentration dependence): \( D = 2C(1 - C) + 0.5 \).

In the application of the BM and SF methods, the numerical values of integration terms are calculated by the Trapezoidal Rule. But for implementation of the HM we have used Eq. (5) to get numerical values of integration terms at each space/concentration point as:

\[
D(i) = \frac{1}{\Delta x} \left[ \frac{e^{\lambda(i+1)} - e^{\lambda(i-1)}}{k(i)} \right] I(i+1) - \frac{1}{\Delta x} \left[ \frac{e^{\lambda(i-1)} - e^{\lambda(i+1)}}{k(i)} \right] \lambda(i) I(i) - \frac{1}{\Delta x} \left[ \frac{k(i) - k(i-1)}{k(i)} \right] I(i) I(i-1)
\]
\[ C'(i) = 0.5(C(i) + C(i+1)), \quad u'(i) = 0.5(u(i) + u(i+1)), \quad \lambda'(i) = 0.5(\lambda(i) + \lambda(i+1)), \quad \mu'(i) = \frac{u(i+1) - u(i)}{\lambda(i+1) - \lambda(i)} \quad \text{and} \quad \kappa'(i) = \frac{\lambda(i+1)u(i) - \lambda(i)u(i+1)}{\lambda(i+1) - \lambda(i)}. \]

4. Results and Discussion

To obtain the finite difference solutions, the computations have been carried out for \( t = 0.40 \) time units. Then we calculated the interdiffusion coefficient making use of BM, SF and HM for all of the above test cases. The graphical representations of the resulting interdiffusion coefficients are given in Figs. 3-4.

In Fig. 3(a) it can be seen that both the BM method and SF method give the same results for Case-1. But the HM gives better results than the other two methods. This is particularly clear at and near the zero concentration limit, as expected. In Fig. 3(b) it can be seen that the SF method gives better results than the HM and BM method for the Case-2. At low concentrations the BM method and SF method both give the same results. But at high concentrations only the SF method gives good results. In Fig. 4(a) it can be seen that for Case-3 the BM and SF methods both give the same results. And HM gives comparable results to the other two methods. In Fig. 4(b) the same behavior of the SF and BM results for the Case-4 as for the Case-3 can be observed. But HM gives a much poorer result for this test. This trend is most obvious at and near to the low and high concentration limits.

5. Conclusions

In this study, the explicit finite difference solution of the Diffusion Equation for binary alloy systems with concentration dependent interdiffusion coefficients has been used to generate interdiffusion concentration profiles for several test cases. Three methods to obtain the interdiffusion coefficient as a function of concentration were investigated for those test cases. They were the Boltzmann-Matano, Sauer and Freise and Hall methods. It was
observed that the results of the SF method were generally the best compared with the results of the BM and Hall methods. Only for a constant interdiffusion coefficient did the Hall method give the best agreement with the required interdiffusion coefficient. Therefore it was concluded that for the determination of the interdiffusion coefficient at or near to the low and high concentration levels the Hall method should be applied with care.

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