

A Transfer-Matrix Method for Analysis of Multicomponent Diffusion with Any Number of Components

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A transfer-matrix method (TMM) is presented for the development of concentration and flux profiles in multicomponent diffusion involving any number n of components. From interdiffusion fluxes or concentration gradients available at an initial position x_s , the authors derive expressions for the transfer matrix and its integral so that the concentrations or interdiffusion fluxes of the components can be obtained at any coordinate x . The TMM requires data for interdiffusion coefficients, which are obtained as average values over selected regions by the method of moments developed by Dayananda. Expressions for the concentrations are also obtained from initial conditions on the fluxes or the concentration gradients. The method is also applicable to the case when all the concentrations are known at two ends of a region over which the diffusion coefficients are considered constant. The integration of the fluxes over time, or over the coordinate x , can be evaluated using the transfer-matrix approach, provided the value of the interdiffusion flux is given at a given coordinate. The TMM is applicable to any number of components and can be regarded as a compact generalization of the solutions available for ternary diffusion couples with constant interdiffusion coefficients. An application of the method is illustrated with the experimental data for a ternary Cu-Ni-Zn diffusion couple, and the results are compared with those based on the Fujita-Gosting solution.

Keywords modeling, multicomponent diffusion, transfer matrix

1. Introduction

An analysis of one-dimensional diffusion in n -component alloys is normally based on Onsager's^[1] formalism for Fick's law,^[2] where the interdiffusion flux $\tilde{J}_i(x)$ of component i is defined in terms of $(n - 1)$ independent concentration gradients by:

$$\tilde{J}_i(x) = - \sum_{j=1}^{n-1} \tilde{D}_{ij}^{(n)} \frac{\partial C_j(x)}{\partial x} \quad (i = 1, 2, \dots, n - 1) \quad (\text{Eq 1})$$

Here, $(n - 1)^2$ interdiffusion coefficients, $\tilde{D}_{ij}^{(n)}$, based on a laboratory-fixed frame are defined and the concentration C_n is treated as the dependent variable. The $n - 1$ equations in Eq 1 can be solved for the $(n - 1)^2$ interdiffusion coefficients

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coefficients $\tilde{D}_{ij}^{(n)}$, provided one can set up $(n - 1)$ diffusion couples, whose diffusion paths intersect at the same composition point of intersection.^[3] Such a requirement is very hard to realize experimentally for systems containing three or more components. Furthermore, the interdiffusion coefficients vary with composition over the diffusion path. Both these issues were considered by Dayananda and Sohn,^[4] who developed a procedure for evaluating interdiffusion coefficients as *averaged* constants over small, selected ranges of composition along the entire diffusion path of a single diffusion couple. Through the use of this analysis^[4-6] identified as Dayananda analysis, one can obtain interdiffusion coefficients over various selected composition regions within the diffusion zone from one diffusion couple. The use of this procedure has been recently tested^[7] with individual ternary diffusion couples and has been shown to yield ternary interdiffusion coefficients comparable to those determined by the conventional Boltzmann-Matano analysis at common compositions of intersecting diffusion paths.

In this context the authors have developed a free, downloadable software called "MultiDiFlux"^[8] to automate the analysis. This program employs cubic hermite interpolation polynomials for interpolation,^[9] and through a least-square fit^[10,11] of the experimental data the concentrations and their derivatives are evaluated at the interior element nodes. The program then evaluates the interdiffusion flux of each component directly from the experimental concentration profile $C_i(x)$ from the relation:^[5,12]

$$\tilde{J}_i(x) = \frac{1}{2t} \int_{C_i^-}^{C_i^+} (x - x_0) dC_i \quad (i = 1, 2, \dots, n) \quad (\text{Eq 2})$$

where t is the time of diffusion and x_0 is the location of the Matano plane^[13] for the couple. The concentrations are functions of the Boltzmann variable,^[14] $(x - x_0)/\sqrt{t}$. Here, it has been assumed that the variation of the molar volume within the diffusion zone is negligible. The program then evaluates low-order moments of both sides of Eq 1 over given x intervals. Treating the interdiffusion coefficients as average values over these small intervals, one can then generate sufficient sets of equations so that these coefficients can be determined^[4,7,11] and used to regenerate the initial input concentration curves.

Similar issues arise when the diffusion coefficients are already known and initial values of the concentrations or fluxes are given at a few sections, and one is required to predict the concentration profiles and fluxes over selected regions in the diffusion zone. The authors have recently examined such problems in multicomponent diffusion and have developed a transfer-matrix method (TMM)^[15] for their solutions. In this approach flux at any section x is represented in terms of the interdiffusion flux given at a section x_s employing a transfer matrix, where the matrix elements are Gaussian functions. Next, solutions are generated for the concentrations of the individual components at any section x in terms of the interdiffusion fluxes or concentration gradients given at a section x_s . In addition, solutions for concentrations at various x values are also developed in terms of the concentrations given at two ends of a region, utilizing another transfer matrix, where the matrix elements are error functions. The transfer-matrix approach is then used for the integration of the interdiffusion flux at a section x over time, as well as for the integration of flux over a finite region in the diffusion zone. The applicability of this method is also examined with the experimental profiles of a Cu-Ni-Zn ternary diffusion couple.^[16]

2. Transfer-Matrix Solution for Fluxes and Concentrations

2.1 Fluxes Generated at Any x in Terms of Their Initial Values at x_s

For an isothermal, solid-solid diffusion couple the diffusion zone extends over the coordinate range ($x_{(-)} = -\infty$, $x_{(+)} = +\infty$). Let the concentrations of the components $C_i(x, t)$ be identified by $C_i^{(-)}$ and $C_i^{(+)}$ in the terminal alloys of the couple. The entire diffusion zone can be divided into small regions with a region s ranging over $x_s \leq x \leq x_{s+1}$. From the equation of continuity $\partial \hat{J}_i(x, t) / \partial x = -\partial C_i(x, t) / \partial t$, one can show^[12] that at time t :

$$\frac{\partial \tilde{J}_i(x, t)}{\partial x} = \frac{(x - x_0)}{2t} \frac{\partial C_i(x, t)}{\partial x} \quad (\text{Eq 3})$$

where x_0 is the Matano plane and $(x - x_0)/2t$ refers to the velocity of propagation of a concentration level identified at C_i . Utilizing Eq 1, and the matrix notation, Eq 3 can be written^[15] as:

$$\frac{\partial}{\partial x} \tilde{\mathbf{J}}^{(n)}(x, t) = -\frac{(x - x_0)}{2t} (\tilde{\mathbf{D}}^{(n)})^{-1} \cdot \tilde{\mathbf{J}}^{(n)}(x, t) \quad (\text{Eq 4})$$

where the diffusion coefficient matrix is assumed to be invertible. These $(n - 1)$ coupled linear first-order differential equations in Eq 4 are solved for the interdiffusion fluxes in the range $x_s \leq x \leq x_{s+1}$ with the boundary conditions that $\tilde{J}_i(x_s)$ are given.

To decouple the equations, one first diagonalizes the matrix $\tilde{\mathbf{D}}^{(n)}$ using a similarity transformation \mathbf{P} such that

$$\mathbf{P}^{-1} \cdot \tilde{\mathbf{D}}^{(n)} \cdot \mathbf{P} = \Delta^{(n)} \quad (\text{Eq 5})$$

where $\Delta^{(n)}$ is a diagonal matrix with elements $\Delta_{ij}^{(n)} = d_i \delta_{ij}$ and δ_{ij} is the Kronecker tensor. The same transformation \mathbf{P} diagonalizes $(\tilde{\mathbf{D}}^{(n)})^{-1}$ so that $\mathbf{P}^{-1} \cdot (\tilde{\mathbf{D}}^{(n)})^{-1} \cdot \mathbf{P} = (\Delta^{(n)})^{-1}$.

The flux vector in the diagonal basis, $\hat{\mathbf{J}}(x, t)$ denoted with a carat, is defined to be:

$$\mathbf{P}^{-1} \cdot \tilde{\mathbf{J}}^{(n)}(x, t) = \hat{\mathbf{J}}^{(n)}(x, t) \quad (\text{Eq 6})$$

Multiplying Eq 4 from the left by \mathbf{P}^{-1} one obtains the $(n - 1)$ decoupled equations. In vector notation:

$$\frac{\partial}{\partial x} \hat{\mathbf{J}}^{(n)}(x, t) = -\frac{(x - x_0)}{2t} (\Delta^{(n)})^{-1} \cdot \hat{\mathbf{J}}^{(n)}(x, t) \quad (\text{Eq 4'})$$

To solve Eq 4' the Peano-Baker method^[17] is used with iterative nested integrations on each component. Integrating both sides component by component one obtains:

$$\begin{aligned} \hat{J}_i(x, t) &= \hat{J}_i(x_s, t) - \int_{x_s}^x dx' \frac{x' - x_0}{2t} (d_i^{-1}) \hat{J}_i(x', t) \\ &= \exp\left(-\frac{(x - x_0)^2 - (x_s - x_0)^2}{4t} (d_i^{-1})\right) \hat{J}_i(x_s, t) \end{aligned} \quad (\text{Eq 7})$$

Multiplying Eq 4' from the left by \mathbf{P} , the fluxes can be converted back into the original basis. In addition, on the basis of Eq 6 one has:

$$\begin{aligned} \mathbf{T}(x, x_s, t, \tilde{\mathbf{D}}^{(n)}) &\equiv \exp\left(-\frac{(x - x_0)^2 - (x_s - x_0)^2}{4t} (\tilde{\mathbf{D}}^{(n)})^{-1}\right) \\ &= \mathbf{P} \cdot \begin{bmatrix} \ddots & & & 0 \\ & \exp\left(-\frac{(x - x_0)^2 - (x_s - x_0)^2}{4t} (d_i^{-1})\right) & & \\ & & \ddots & \\ 0 & & & \ddots \end{bmatrix} \cdot \mathbf{P}^{-1} \end{aligned} \quad (\text{Eq 8})$$

The fluxes are now given by:

$$\tilde{\mathbf{J}}^{(n)}(x, t) = \mathbf{T}(x, x_s, t, \tilde{\mathbf{D}}^{(n)}) \cdot \tilde{\mathbf{J}}^{(n)}(x_s, t) \quad x_s \leq x \leq x_{s+1} \quad (\text{Eq 9})$$

The matrix $\mathbf{T}(x, x_s, t, \tilde{\mathbf{D}}^{(n)})$ called the *transfer matrix*,^[18,19] evolves the flux from its initial value $\tilde{\mathbf{J}}^{(n)}(x_s, t)$ at $x = x_s$ to its value at any x in the interval $x_s \leq x \leq x_{s+1}$.

The diagonal form of the transfer matrix on the right side of Eq 8 will be designated by τ , with:

$$\tau(x, x_s, t, \tilde{\mathbf{D}}^{(n)}) = \begin{bmatrix} \ddots & & & 0 \\ & \exp\left(-\frac{(x-x_0)^2 - (x_s-x_0)^2}{4t} (d_i^{-1})\right) & & \\ 0 & & & \ddots \end{bmatrix} = \frac{\exp\left(-\frac{(x-x_0)^2}{4t} (\Delta^{(n)})^{-1}\right)}{\exp\left(-\frac{(x_s-x_0)^2}{4t} (\Delta^{(n)})^{-1}\right)} \quad (\text{Eq 10})$$

so that Eq 8 takes the compact form $\mathbf{T} = \mathbf{P} \cdot \boldsymbol{\tau} \cdot \mathbf{P}^{-1}$. Note that the $(n - 1)$ -dimensional transfer matrix can be reexpressed in terms of $(n - 1)$ terms involving the powers $(0, 1, 2, \dots, n - 2)$ of the matrix $\tilde{\mathbf{D}}_{ij}^{(n)}$ by using the Cayley-Hamilton theorem.^[17,20] Also, the initial condition on the fluxes may be replaced by one on the concentration gradients with the help of Eq 1. Hence, on the basis of Eq 9, one gets:

$$\tilde{\mathbf{J}}^{(n)}(x, t) = -\mathbf{T}(x, x_s, t) \cdot \tilde{\mathbf{D}}^{(n)} \cdot \frac{\partial \mathbf{C}^{(n)}(x_s, t)}{\partial x} \quad (\text{Eq 11})$$

It is shown here that the interdiffusion fluxes of all components can be determined in each segment of the diffusion zone once the initial values of either the fluxes or the concentration gradients at x_s are given. The evolution can be forward ($x > x_s$) or backward ($x < x_s$) by choosing the corresponding value of x and x_s in the transfer matrix.

2.2 Concentration Profiles from the Initial Fluxes at x_s

Once the interdiffusion fluxes are determined everywhere in the diffusion zone, one can determine the concentrations in that region through Eq 1:

$$\frac{\partial}{\partial x} \mathbf{C}^{(n)}(x, t) = -(\tilde{\mathbf{D}}^{(n)})^{-1} \cdot \tilde{\mathbf{J}}^{(n)}(x, t) \quad (\text{Eq 12})$$

On integrating both sides one has:

$$\mathbf{C}^{(n)}(x, t) = \mathbf{C}^{(n)}(x_s, t) - (\tilde{\mathbf{D}}^{(n)})^{-1} \left[\int_{x_s}^x dx' \mathbf{T}(x', x_s, t, \tilde{\mathbf{D}}^{(n)}) \right] \tilde{\mathbf{J}}^{(n)}(x_s, t) = \mathbf{C}^{(n)}(x_s, t) - (\tilde{\mathbf{D}}^{(n)})^{-1} \left[\int_{x_s}^x dx' \exp\left(-\frac{(x-x_0)^2 - (x_s-x_0)^2}{4t} (\tilde{\mathbf{D}}^{(n)})^{-1}\right) \right] \tilde{\mathbf{J}}^{(n)}(x_s, t) \quad (\text{Eq 13})$$

The integral can be performed in the diagonal basis. Alternatively, the integral over the transfer matrix is simply the integral of each matrix element in \mathbf{T} performed independently. Again, as in Eq 9, the initial condition, $\tilde{\mathbf{J}}^{(n)}(x_s, t)$, in Eq 13 can be replaced by:

$$-\tilde{\mathbf{D}}^{(n)} \cdot \left(\frac{\partial \mathbf{C}^{(n)}(x, t)}{\partial x} \right)_{x=x_s}$$

These integrals are treated in detail in the next section.

2.3 Concentration Profiles from the Initial and Final Concentrations $\mathbf{C}_i(x_s)$ and $\mathbf{C}_i(x_{s+1})$

Some notation is set up first to simplify later derivations. The integral of the transfer matrix in the diagonal representation is defined to be $\boldsymbol{\epsilon}$, with:

$$\boldsymbol{\epsilon}(x, x_s, t, \Delta^{(n)}) = \int_{x_s}^x dx' \begin{bmatrix} \ddots & & & 0 \\ & \exp\left(-\frac{(x-x_0)^2 - (x_s-x_0)^2}{4t d_i}\right) & & \\ 0 & & & \ddots \end{bmatrix} = \begin{bmatrix} \ddots & & & 0 \\ & \sqrt{\pi t d_i} \left(\text{erf}\left(\frac{x-x_0}{2\sqrt{t d_i}}\right) - \text{erf}\left(\frac{x_s-x_0}{2\sqrt{t d_i}}\right) \right) & & \\ 0 & & & \ddots \end{bmatrix} \cdot \begin{bmatrix} \ddots & & & 0 \\ & \exp\left(\frac{(x_s-x_0)^2}{4t d_i}\right) & & \\ 0 & & & \ddots \end{bmatrix} \quad (\text{Eq 14})$$

One can see that the diagonal elements are the usual error functions that appear in the expressions for the composition. Here the usual definition of the error function $\text{erf}(x) = (2/\sqrt{\pi}) \int_0^x d\xi \exp(-\xi^2)$ is used. The final expressions in Eq 14 have been factorized as the product of two diagonal matrices for convenience in representing the result.

Equation 14 can be recast in matrix form:

$$\boldsymbol{\epsilon}(x, x_s, t, \Delta^{(n)}) = \sqrt{\pi t} (\Delta^{(n)})^{1/2} \cdot \left(\mathbf{erf}\left(\frac{x-x_0}{2\sqrt{t d_i}}\right) - \mathbf{erf}\left(\frac{x_s-x_0}{2\sqrt{t d_i}}\right) \right) \cdot \exp\left(\frac{(x_s-x_0)^2}{4t d_i}\right) \quad (\text{Eq 15})$$

where the diagonal matrices \mathbf{erf} contain the error-function terms along the diagonal as shown in Eq 14, and $(\Delta^{(n)})^{1/2}$ is the square root of the diagonal diffusion coefficient matrix $\Delta^{(n)}$, with square roots of the eigenvalues d_i occurring along the diagonal.

The integral of the transfer matrix \mathbf{T} , which is designated by \mathbf{E} in the standard basis, is then given by:

$$\mathbf{E}(x, x_s, t, \mathbf{D}^{(n)}) = \mathbf{P} \cdot (\boldsymbol{\epsilon}(x, x_s, t, \Delta^{(n)})) \cdot \mathbf{P}^{-1} \quad (\text{Eq 16})$$

Both $\boldsymbol{\epsilon}$ and \mathbf{E} are $(n - 1) \times (n - 1)$ matrices and can be inverted as long as the diffusion matrix has nonzero eigenvalues.

Since the error function can be expanded in a power series, one can transform it back to the original basis term-by-term by suitably inserting $\mathbf{P} \cdot \mathbf{P}^{-1} = 1$. One can therefore write:

$$\begin{aligned}
 E(x, x_s, t, \mathbf{D}^{(n)}) &= \mathbf{P} \cdot \boldsymbol{\varepsilon}(x, x_s, t, \Delta^{(n)}) \cdot \mathbf{P}^{-1} \\
 &= \sqrt{\pi t} (\mathbf{D}^{(n)})^{1/2} \cdot \left[\mathbf{ERF} \left(\frac{x - x_0}{2\sqrt{t}} (\mathbf{D}^{(n)})^{-1/2} \right) \right. \\
 &\quad \left. - \mathbf{ERF} \left(\frac{x_s - x_0}{2\sqrt{t}} (\mathbf{D}^{(n)})^{-1/2} \right) \right] \\
 &\quad \times \exp \left(\frac{(x_s - x_0)^2}{4t} (\mathbf{D}^{(n)})^{-1} \right) \quad (\text{Eq 17})
 \end{aligned}$$

The matrix function **ERF** is introduced for convenience in expressing the integrated fluxes in the following.

Returning to the concentration profiles in the interval $[x_s, x_{s+1}]$, one sees that they can be obtained in terms of the initial and final values of the concentrations $C_i(x_s, t)$ and $C_i(x_{s+1}, t)$ in the interval. First, one writes $C_i(x_{s+1}, t)$, Eq 13, in terms of the initial fluxes $\tilde{\mathbf{J}}^{(n)}(x_s, t)$. This provides a set of equations that can be inverted for the initial fluxes in terms of $C_i(x_{s+1}, t)$ and then substituted back into the expression for the concentrations at x in the range $x_s \leq x \leq x_{s+1}$. Equation 17 is used to write Eq 16 in the form:

$$\begin{aligned}
 \mathbf{C}^{(n)}(x, t) &= \mathbf{C}^{(n)}(x_s, t) - (\tilde{\mathbf{D}}^{(n)})^{-1} \cdot \mathbf{E}(x, x_s, t, \tilde{\mathbf{D}}^{(n)}) \cdot \tilde{\mathbf{J}}^{(n)}(x_s, t) \\
 &= \mathbf{C}^{(n)}(x_s, t) - \sqrt{\pi t} (\mathbf{D}^{(n)})^{-1/2} \\
 &\quad \times \left[\mathbf{ERF} \left(\frac{x - x_0}{2\sqrt{t}} (\mathbf{D}^{(n)})^{-1/2} \right) \right. \\
 &\quad \left. - \mathbf{ERF} \left(\frac{x_s - x_0}{2\sqrt{t}} (\mathbf{D}^{(n)})^{-1/2} \right) \right] \\
 &\quad \times \exp \left(\frac{(x_s - x_0)^2}{4t} (\mathbf{D}^{(n)})^{-1} \right) \cdot \tilde{\mathbf{J}}^{(n)}(x_s, t) \quad (\text{Eq 18})
 \end{aligned}$$

Rewriting the first equation of Eq 18 for $x = x_{s+1}$ allows us to identify the fluxes at x_s in terms of the concentrations at the two end points of the subregion as:

$$\tilde{\mathbf{J}}^{(n)}(x_s, t) = -(\mathbf{E}(x_{s+1}, x_s, t, \tilde{\mathbf{D}}^{(n)}))^{-1} \cdot \tilde{\mathbf{D}}^{(n)} \cdot [\mathbf{C}^{(n)}(x_{s+1}, t) - \mathbf{C}^{(n)}(x_s, t)] \quad (\text{Eq 19})$$

We then have:

$$\begin{aligned}
 \mathbf{C}^{(n)}(x, t) &= \mathbf{C}^{(n)}(x_s, t) + (\tilde{\mathbf{D}}^{(n)})^{-1} \cdot \mathbf{E}(x, x_s, t, \tilde{\mathbf{D}}^{(n)}) \\
 &\quad \times (\mathbf{E}(x_{s+1}, x_s, t, \tilde{\mathbf{D}}^{(n)}))^{-1} \cdot \tilde{\mathbf{D}}^{(n)} \cdot [\mathbf{C}^{(n)}(x_{s+1}, t) - \mathbf{C}^{(n)}(x_s, t)] \quad (\text{Eq 20})
 \end{aligned}$$

The above relation, Eq 20, can be simplified considerably by using the diagonal representations of $\mathbf{D}^{(n)}$, $(\mathbf{D}^{(n)})^{-1}$ and the \mathbf{E} matrix (Eq 17). Noting that the product of diagonal matrices is also a diagonal matrix one obtains:

$$\begin{aligned}
 \mathbf{C}^{(n)}(x, t) &= \mathbf{C}^{(n)}(x_s, t) + \mathbf{P} \cdot \begin{bmatrix} \ddots & 0 \\ & \phi_i \\ & & \ddots \end{bmatrix} \cdot \mathbf{P}^{-1} \cdot (\mathbf{C}^{(n)}(x_{s+1}, t) - \mathbf{C}^{(n)}(x_s, t)) \\
 &= \mathbf{C}^{(n)}(x_s, t) + \mathbf{P} \cdot \boldsymbol{\Phi}(x, x_s, x_{s+1}, x_0, t, \Delta^{(n)}) \cdot \mathbf{P}^{-1} \cdot (\mathbf{C}^{(n)}(x_{s+1}, t) - \mathbf{C}^{(n)}(x_s, t)) \quad (\text{Eq 21})
 \end{aligned}$$

where ϕ_i are given by:

$$\phi_i(x, x_s, x_{s+1}, x_0, t, d_i^{(n)}) = \frac{\left[\text{erf} \left(\frac{x - x_0}{2\sqrt{t d_i}} \right) - \text{erf} \left(\frac{x_s - x_0}{2\sqrt{t d_i}} \right) \right]}{\left[\text{erf} \left(\frac{x_{s+1} - x_0}{2\sqrt{t d_i}} \right) - \text{erf} \left(\frac{x_s - x_0}{2\sqrt{t d_i}} \right) \right]} \quad (\text{Eq 22})$$

Fujita and Gosting^[21] derived expressions for the concentration profiles of ternary diffusion couples in terms of error functions. Equations 21 and 22 generalize their results to arbitrary number of concentration components. The use of TMM is illustrated for ternary diffusion^[15] to derive error-function solutions for concentrations over selected regions in the diffusion zone and to compare them with those of Fujita and Gosting. An example of such a comparison is presented in Section 3.

2.4 The Integrated Fluxes

Equation 2 for the interdiffusion flux $\tilde{J}_i(x)$ can be written with the integrands expressed in terms of the Boltzmann parameter $(x - x_0)/\sqrt{t}$. Then the fluxes are given by:^[22]

$$\begin{aligned}
 \tilde{J}_i(x, t) 2\sqrt{t} &= \int_{C_i^{(+)}}^{C_i(\lambda)} (\lambda' + \lambda) dC_i(\lambda') \equiv K_i(\lambda), \\
 (i = 1, 2, \dots, n) \quad (\text{Eq 23})
 \end{aligned}$$

where $K_i(\lambda)$ is the specific value of the integral and depends on the given $\lambda = (x - x_0)/\sqrt{t}$. Thus, for fixed λ one has the total interdiffusion flux $\mathbf{S}^{(n)}$:

$$\mathbf{S}^{(n)} = \int_0^t \tilde{\mathbf{J}}^{(n)}(x, t) dt = \mathbf{K}(\lambda) \sqrt{t} = 2t \tilde{\mathbf{J}}(x, t) \quad (\text{Eq 24})$$

over the time interval $(0, t)$ again related to the flux at that coordinate x at time t . Note that while $K_i(\lambda)$ depends on λ , for a given λ it is independent of t . If the interdiffusion fluxes are known at a specific coordinate, say the Matano coordinate, the interdiffusion fluxes on the right side of Eq 24 can be expressed in terms of $\tilde{\mathbf{J}}^{(n)}(x_0, t)$ using Eq 11 with x_s replaced by x_0 . Thus, in terms of the transfer matrix \mathbf{T} one has:

$$\mathbf{S}^{(n)} = 2t \mathbf{T}(x, x_0, t, \tilde{\mathbf{D}}^{(n)}) \cdot \tilde{\mathbf{J}}^{(n)}(x_0, t) \quad (\text{Eq 25})$$

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In a similar fashion, the flux can be integrated over a coordinate range x_s to x . One obtains:

$$\int_{x_s}^x dx' \tilde{J}^{(n)}(x', t) = \int_{x_s}^x dx' T(x, x_s, t, \tilde{D}^{(n)}) \cdot \tilde{J}^{(n)}(x_s, t) \quad (\text{Eq 26})$$

As in Eq 17, the integral can be rewritten over the transfer matrix T associated with the fluxes in terms of the transfer matrix E associated with the concentrations, so that:

$$\begin{aligned} \int_{x_s}^x dx' \tilde{J}^{(n)}(x', t) &= E(x, x_s, t, D^{(n)}) \cdot \tilde{J}^{(n)}(x_s, t) \\ &= P \cdot [\epsilon(x, x_s, t, \Delta^{(n)})] \cdot P^{-1} \cdot \tilde{J}^{(n)}(x_s, t) \end{aligned} \quad (\text{Eq 27})$$

In the limit $x \rightarrow \infty$, the error function reaches its asymptotic value of unity, and Eq 27 reduces to:

$$\begin{aligned} \lim_{x \rightarrow \infty} \int_{x_s}^x dx' \tilde{J}^{(n)}(x', t) &= \lim_{x \rightarrow \infty} E(x, x_s, t, D^{(n)}) \cdot \tilde{J}^{(n)}(x_s, t) = \sqrt{\pi t} (D^{(n)})^{1/2} \\ &\cdot \left[1 - \text{ERF} \left(\frac{x_s - x_0}{2\sqrt{t}} (D^{(n)})^{-1/2} \right) \right] \\ &\times \exp \left(\frac{(x_s - x_0)^2}{4t} (D^{(n)})^{-1} \right) \cdot \tilde{J}^{(n)}(x_s, t) \end{aligned} \quad (\text{Eq 28})$$

In the diagonal basis, instead of Eq 28, one obtains the relation:

$$\begin{aligned} (P^{-1} \cdot \lim_{x \rightarrow \infty} \int_{x_s}^x ds' \tilde{J}^{(n)}(x', t)) &= \epsilon(x = \infty, x_s, t, \Delta^{(n)}) \cdot (P^{-1} \cdot \tilde{J}^{(n)}(x_s, t)) \\ &= \sqrt{\pi t} (\Delta^{(n)})^{1/2} \cdot \left(1 - \text{erf} \left(\frac{x_s - x_0}{2\sqrt{t} d_i} \right) \right) \\ &\cdot \exp \left(\frac{(x_s - x_0)^2}{4t d_i} \right) \cdot (P^{-1} \cdot \tilde{J}^{(n)}(x_s, t)) \end{aligned} \quad (\text{Eq 29})$$

For $x_s = x_0$, the **erf** matrix reduces to zero and the matrix **exp** becomes a unit diagonal on the right side of Eq 29, so that:

$$(P^{-1} \cdot \lim_{x \rightarrow \infty} \int_{x_0}^{\infty} dx' \tilde{J}^{(n)}(x', t)) = \sqrt{\pi t} (\Delta^{(n)})^{1/2} \cdot (P^{-1} \cdot \tilde{J}^{(n)}(x_0, t)), \quad (\text{Eq 30})$$

in conformity with earlier derivations.^[23,24]

3. Comparison with Experimental Data and Concluding Remarks

An application of TMM has been carried out with the experimental concentration profiles of a single-phase (fcc) ternary Cu-Ni-Zn diffusion couple. The couple was assembled with alloys α_2 (73.8Cu-9.5Ni-16.7Zn) and α_7 (55.5Cu-44.5Ni) and annealed for 48 h at 775 °C.^[16] The experimental data for concentration profiles for the couple are presented in Fig. 1. Superimposed on the data are the concentration profiles fitted with Hermite interpolation

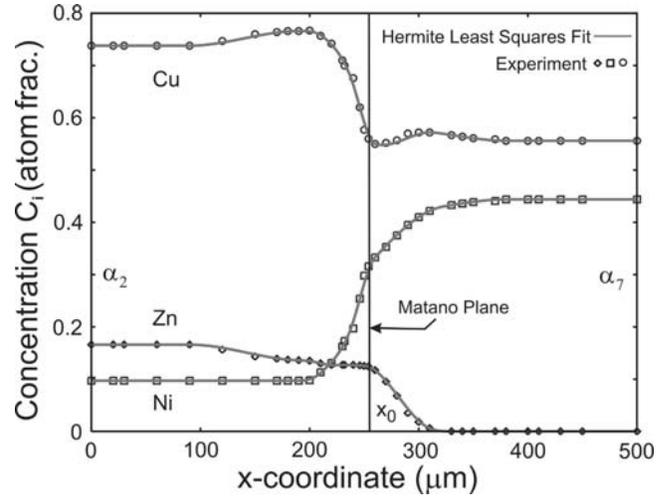


Fig. 1 Experimental data for the concentration profiles of the Cu-Ni-Zn couple, α_2 versus α_7 , annealed at 775 °C for 2 days, and the fitted profiles employing cubic Hermite interpolation polynomials.

Table 1 Regions and elements used for fitting with cubic Hermite interpolation polynomials the experimental data for the α_2 versus α_7 Cu-Ni-Zn ternary diffusion couple annealed at 775 °C for 2 days

Range of region, μm	Number of elements
0-90	1
90-190	1
190-260	3
260-310	1
310-330	1
330-380	1
380-500	1

Table 2 Ternary interdiffusion coefficients $\tilde{D}_{ij}^{(3)}$ ($i, j = 1, 2$) calculated for two selected regions in the diffusion zone of the α_2 versus α_7 couple with the aid of *MultiDiFlux* software

Range of regions, μm	$\tilde{D}_{11}^{(3)}$, m^2/s	$\tilde{D}_{12}^{(3)}$, m^2/s	$\tilde{D}_{21}^{(3)}$, m^2/s	$\tilde{D}_{22}^{(3)}$, m^2/s
[0, 255]	$+1.63 \times 10^{-14}$	-2.26×10^{-15}	-8.93×10^{-17}	$+1.59 \times 10^{-15}$
[255, 500]	$+6.76 \times 10^{-15}$	$+3.38 \times 10^{-15}$	$+1.17 \times 10^{-15}$	$+6.07 \times 10^{-15}$

polynomials with the aid of *MultiDiFlux* software employing seven selected regions in the diffusion zone, as identified in Table 1.

The fitted profiles were analyzed by Dayananda analysis using the zeroth and first moments of concentration gradients and interdiffusion fluxes. Interdiffusion coefficients were determined as average values over three selected regions, as shown in Table 2. With these constant diffusion coefficients as input one obtains the transfer-matrix solutions to the concentrations in each of the regions. These

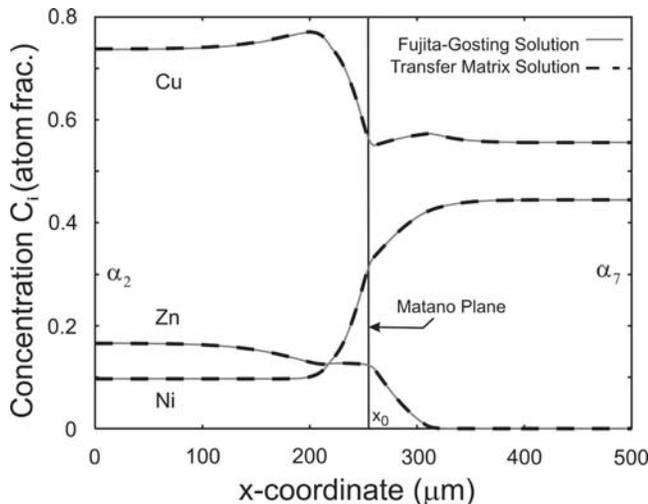


Fig. 2 A comparison of the Fujita-Gosting solution for the concentration profiles of the α_2 versus α_7 couple with those generated by using the transfer-matrix method and the ternary interdiffusion coefficients determined for two regions in the diffusion zone.

solutions are compared with the concentration profiles obtained from the Fujita-Gosting ternary solutions in Fig. 2. One can see that the profiles generated by the TMM are identical to the error-function solutions of Fujita and Gosting. The equivalence of the solutions by the two methods has been discussed in an earlier paper.^[15]

The authors have shown that the TMM provides an efficient approach to the calculation of fluxes and concentrations in multicomponent diffusion couples. If the concentrations are known at the two ends of a subregion, one can also construct the concentration profile within the subregion in a manner similar to the work of Fujita and Gosting for ternary systems. In addition, the use of TMM becomes particularly attractive for analyzing systems with more than three components, since detailed analytical solutions containing error functions can be circumvented. The transfer-matrix representations can also be used when the fluxes are integrated over time or over a region within the diffusion zone. Furthermore, as the TMM is a matrix approach for the analysis of diffusion couples with *any number of components*, one can express solutions in a compact form convenient for computational simulations. The TMM has now been incorporated in the current version of the *MultiDiFlux* program.

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