JPEDAV (2005) 26:441-446
DOI: 10.1361/154770305X66493
1547-7037/$19.00 ©ASM International

Analysis of Multicomponent Diffusion Couples for Interdiffusion Fluxes and Interdiffusion Coefficients

Mysore A. Dayananda

(Submitted July 18, 2005)

A procedure for the analysis of an isothermal, multicomponent, solid-solid diffusion couple is presented for the direct determination of interdiffusion fluxes of all components over the entire diffusion zone and for the evaluation of main and cross interdiffusion coefficients over regions selected in the diffusion zone. The average effective interdiffusion coefficients for the individual components are also determined over the selected compositional ranges. A user-friendly computer program called *Multi*DiFlux has been developed to carry out all of the analysis and calculations. With the aid of this program, selected diffusion couples in the ternary Cu-Ni-Zn system were analyzed for interdiffusion fluxes and ternary interdiffusion coefficients, and were assessed for up-hill diffusion, zero-flux plane development, and diffusional interactions among components. The interdiffusion coefficients determined over various regions of the diffusion zone are used by the program to regenerate the concentration profiles of the couple.

1. Introduction

The phenomenon of interdiffusion in an n-component system can be described with the aid of $(n-1)^2$ interdiffusion coefficients,[1] which are determined as functions of composition. The determination of such coefficients requires $(n-1)$ independent, isothermal diffusion couples with their diffusion paths intersecting at a common composition. Hence, for a ternary system a pair of experiments needs to be carried out with two diffusion couples with intersecting diffusion paths, and the four ternary interdiffusion coefficients are evaluated only at the common composition of the couple pair.[1] To circumvent such experimental challenges, an alternative method was developed by Dayananda and Sohn[2] in which a single, solid-solid ternary diffusion couple can be analyzed for the four ternary interdiffusion coefficients over various composition ranges that are selected along the diffusion path. In this method, the four evaluated coefficients represent average values over the selected concentration ranges within the diffusion zone.

The purpose of this article is to present and discuss the analysis of individual multicomponent diffusion couples for the direct determination of interdiffusion fluxes and interdiffusion coefficients for all components. A user-friendly computer program called *Multi*DiFlux has been developed by Dayananda and Ram-Mohan[3] to carry out such calculations from experimental data on concentration profiles of solid-solid diffusion couples. The interdiffusion coefficients calculated by the program over selected regions of the diffusion zone can be used to reproduce the concentration profiles of the individual components on the basis of error functions. This program has been applied for the analysis of selected Cu-Ni-Zn couples, and the details of such analysis are presented and discussed in this article. The program can be downloaded freely from the Web site: https://engineering.purdue.edu/MSE/Fac_Staff/Faculty/dayananda.wshtml.[3]

This article is a revised version of the paper printed in the *Proceedings of the First International Conference on Diffusion in Solids and Liquids—DSL-2005*, Aveiro, Portugal, July 6-8, 2005, Andreas Öchsner, José Grácio and Frédéric Barlat, eds., University of Aveiro, 2005.

Mysore A. Dayananda, School of Materials Engineering, Purdue University, 501 Northwestern Avenue, West Lafayette, IN 47907-2044. Contact e-mail: dayanand@ecn.purdue.edu.

2. Diffusion Analysis

The various key steps in the analysis of experimental data on concentration profiles of multicomponent diffusion couples are identified and described in this section.

2.1 Calculation of Interdiffusion Fluxes

Dayananda and Kim[4] and Dayananda[5] showed that the concentration profiles of an isothermal, n-component diffusion couple can be analyzed directly for the interdiffusion fluxes of all components without a prior knowledge of the interdiffusion coefficients. For a solid-solid couple characterized by terminal alloys of concentrations, C_i^- and C_i^+, the interdiffusion flux $\tilde{J}_i(x)$ of component i at any section x is calculated by[4]:

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

where x_o refers to the location of the Matano plane, and t is the diffusion time. An alternative equation bypassing the step of determining the Matano plane and including information on changes in molar volume variation with x is given by[5]:

$$\tilde{J}_i(x) = \frac{(C_i^- - C_i^+)}{2t}\left[Y_i \int_{-\infty}^{x} \frac{(1 - Y_i)}{V_m}\, dx + (1 - Y_i) \int_{x}^{+\infty} \frac{Y_i}{V_m}\, dx \right] \quad \text{(Eq 2)}$$

This equation may also be used for the direct calculation of the interdiffusion fluxes and is more appropriate particularly for cases in which the assumption of constant molar volume within the diffusion zone is not appropriate and the variation in molar volume needs to be included in the analysis.

2.2 Calculation of Interdiffusion Coefficients

In ternary systems, the interdiffusion flux $\tilde{J}_i$ of component i is related[6] to two independent concentration gradients by:

$$\tilde{J}_i = -\tilde{D}_{i1}^3 \frac{\partial C_1}{\partial x} - \tilde{D}_{i2}^3 \frac{\partial C_2}{\partial x} \quad (i = 1,2) \quad \text{(Eq 3)}$$

where $\tilde{D}_{i1}^3$ and $\tilde{D}_{i2}^3$ refer to the main and cross interdiffusion coefficients, respectively. An integration of interdiffusion fluxes over any selected region between C_i (x_1) and C_i (x_2) in the diffusion zone may be carried out on the basis of the equation given by[2]:

$$\int_{x_1}^{x_2} \tilde{J}_i (x - x_0)^n\, dx = -\bar{\tilde{D}}_{i1}^3 \int_{C_1(x_1)}^{C_1(x_2)} (x - x_0)^n\, dC_1 - \bar{\tilde{D}}_{i2}^3 \int_{C_2(x_1)}^{C_2(x_2)} (x - x_0)^n\, dC_2 \quad (i - 1,2) \quad \text{(Eq 4)}$$

where $\bar{\tilde{D}}_{i1}^3$ and $\bar{\tilde{D}}_{i2}^3$ correspond to the average values of the main and cross interdiffusion coefficients, respectively, over a selected composition range between x_1 and x_2, and n is an integer. For n values of 0 and 1, Eq 4 yields, respectively:

$$\int_{x_1}^{x_2} \tilde{J}_i dx = \bar{\tilde{D}}_{i1}^3 [C_1(x_1) - C_1(x_2)] + \bar{\tilde{D}}_{i2}^3 [C_2(x_1) - C_2(x_2)] \quad (i = 1,2) \quad \text{(Eq 5)}$$

and

$$\int_{x_1}^{x_2} \tilde{J}_i (x - x_0)\, dx = 2t \left\{ \begin{matrix} \bar{\tilde{D}}_{i1}^3 [\tilde{J}_1(x_1) - \tilde{J}_1(x_2)] \\ + \bar{\tilde{D}}_{i2}^3 [\tilde{J}_2(x_1) - \tilde{J}_2(x_2)] \end{matrix} \right\} \quad (i = 1,2) \quad \text{(Eq 6)}$$

With components 1 and 2 considered independent components for the ternary couple, Eq 5 and 6 are set up and solved simultaneously for the four $\bar{\tilde{D}}_{ij}^3$ coefficients over various regions selected in the diffusion zone.

2.3 Regeneration of the Concentration Profiles

The $\bar{\tilde{D}}_{ij}^3$ sets of interdiffusion coefficients determined for various contiguous regions selected within the diffusion zone can then be used[2] for the regeneration of concentration profiles over any selected region between x_I and x_{II} with appropriate error function solutions. These solutions are given by:

$$C_1 = K_1 \left[\frac{\operatorname{erf}\left(\frac{x - x_0}{2\sqrt{u.t}}\right) - \operatorname{erf}\left(\frac{x_I - x_0}{2\sqrt{u.t}}\right)}{\operatorname{erf}\left(\frac{x_{II} - x_0}{2\sqrt{u.t}}\right) - \operatorname{erf}\left(\frac{x_I - x_0}{2\sqrt{u.t}}\right)} \right] + K_2 \left[\frac{\operatorname{erf}\left(\frac{x - x_0}{2\sqrt{v.t.}}\right) - \operatorname{erf}\left(\frac{x_I - x_0}{2\sqrt{v.t.}}\right)}{\operatorname{erf}\left(\frac{x_{II} - x_0}{2\sqrt{v.t.}}\right) - \operatorname{erf}\left(\frac{x_I - x_0}{2\sqrt{v.t.}}\right)} \right] + C_{1I} \quad \text{(Eq 7)}$$

$$C_2 = K_3 \left[\frac{\operatorname{erf}\left(\frac{x - x_0}{2\sqrt{u.t}}\right) - \operatorname{erf}\left(\frac{x_I - x_0}{2\sqrt{u.t}}\right)}{\operatorname{erf}\left(\frac{x_{II} - x_0}{2\sqrt{u.t}}\right) - \operatorname{erf}\left(\frac{x_I - x_0}{2\sqrt{u.t}}\right)} \right] + K_4 \left[\frac{\operatorname{erf}\left(\frac{x - x_0}{2\sqrt{v.t}}\right) - \operatorname{erf}\left(\frac{x_I - x_0}{2\sqrt{v.t}}\right)}{\operatorname{erf}\left(\frac{x_{II} - x_0}{2\sqrt{v.t}}\right) - \operatorname{erf}\left(\frac{x_I - x_0}{2\sqrt{v.t}}\right)} \right] + C_{2I} \quad \text{(Eq 8)}$$

where

$$K_1 = \frac{1}{\tilde{D}} \left[[\bar{\tilde{D}}_{12}^3 (C_{2II} - C_{2I})] - (\bar{\tilde{D}}_{22}^3 - \bar{\tilde{D}}_{11}^3 - \tilde{D}) \left[\frac{C_{1II} - C_{1I}}{2} \right] \right] \quad \text{(Eq 9)}$$

$$K_2 = \frac{1}{\tilde{D}} \left[[\bar{\tilde{D}}_{12}^3 (C_{2I} - C_{2II})] - (\bar{\tilde{D}}_{22}^3 - \bar{\tilde{D}}_{11}^3 + \tilde{D}) \left[\frac{C_{1I} - C_{1III}}{2} \right] \right] \quad \text{(Eq 10)}$$

$$K_3 = \frac{1}{\tilde{D}} \left[[\bar{\tilde{D}}_{21}^3 (C_{1II} - C_{1I})] - (\bar{\tilde{D}}_{11}^3 - \bar{\tilde{D}}_{22}^3 - \tilde{D}) \left[\frac{C_{2II} - C_{2I}}{2} \right] \right] \quad \text{(Eq 11)}$$

$$K_4 = \frac{1}{\tilde{D}} \left[[\bar{\tilde{D}}_{21}^3 (C_{1I} - C_{1II})] - (\bar{\tilde{D}}_{11}^3 - \bar{\tilde{D}}_{22}^3 + \tilde{D}) \left[\frac{C_{2I} - C_{2II}}{2} \right] \right] \quad \text{(Eq 12)}$$

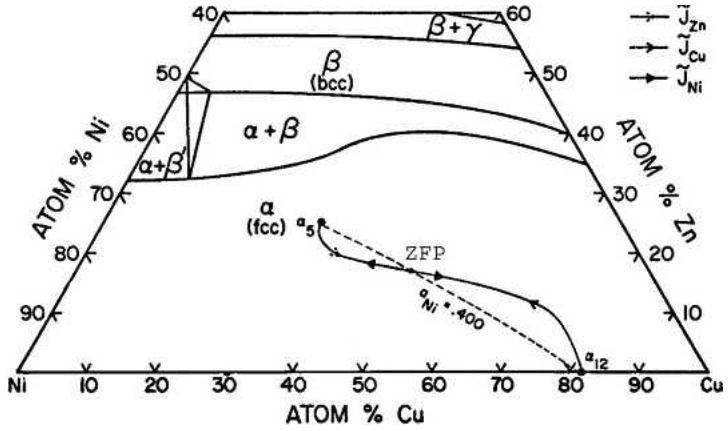

Fig. 1 Diffusion path for the Ni-isoactivity couple, α_5 versus α_{12}, diffusion annealed at 775 °C for two days

$$u = \bar{\bar{D}}^3_{11} + 0.5\,(\bar{\bar{D}}^3_{22} - \bar{\bar{D}}^3_{11} + \tilde{D}) \quad \text{(Eq 13)}$$

$$v = \bar{\bar{D}}^3_{22} + 0.5\,(\bar{\bar{D}}^3_{11} - \bar{\bar{D}}^3_{22} - \tilde{D}) \quad \text{(Eq 14)}$$

$$\tilde{D} = \sqrt{(\bar{\bar{D}}^3_{11} - \bar{\bar{D}}^3_{22})^2 + 4\bar{\bar{D}}^3_{12}\,\bar{\bar{D}}^3_{21}} \quad \text{(Eq 15)}$$

2.4 Determination of Average Effective Interdiffusion Coefficients

For an *n*-component system, the average effective interdiffusion coefficients over a range between x_1 and x_2 can be defined by[7]:

$$\tilde{D}^{\text{eff}}_{i\Delta C} = \frac{\int_{x_1}^{x_2} \tilde{J}_i(x)dx}{[C_i(x_1) - C_i(x_2)]} \quad (i = 1,2,\ldots,n-1) \quad \text{(Eq 16)}$$

alternatively,

$$\tilde{D}^{\text{eff}}_{i,\Delta C} = \frac{\sum_{j=1}^{n-1} \bar{\bar{D}}^n_{ij}[C_j(x_1) - C_j(x_2)]}{[C_i(x_1) - C_i(x_2)]} \quad \text{(Eq 17)}$$

Hence, $\tilde{D}^{\text{eff}}_{i,\Delta C}$ can also be calculated from fluxes or $\bar{\bar{D}}^3_{ij}$ coefficients. Such coefficients would include the diffusional interactions among the components and may be used for a simpler representation of multicomponent diffusion.[7]

3. Sequence of Calculations by the *Multi*DiFlux Program

The experimental data on concentration profiles (C_i versus x) of a ternary couple constitute the input file for the *Multi*DiFlux program. As the first step, the program interpolates these data over the diffusion zone, which is divided into a number of regions based on the user's choice. Over each region, the experimental data are fitted by cubic Hermite interpolation polynomials by employing the method of the general linear least-squares fitting developed by Ram-Mohan.[8] In the second step, the Matano plane is calculated from the fitted concentration profile for each component from mass balance. In the third step interdiffusion fluxes of all components are calculated as functions of x on the basis of Eq 2. The fourth step involves an integration of the fluxes for setting up Eq 5 and 6 over selected regions within the diffusion zone and simultaneously solving them for the determination of a set of average, ternary interdiffusion coefficients for each region. In the fifth step, these sets of interdiffusion coefficients are used by the program for the recalculation of the individual concentration profiles on the basis of error function solutions given by Eq 7 and 8.

4. Selected Applications of the *Multi*DiFlux Program

The application of the *Multi*DiFlux program is illustrated with two selected Cu-Ni-Zn diffusion couples assembled with α (face-centered cubic) Cu-Ni-Zn alloys and annealed at 775 °C for 2 days. One of the couples identified as α_5 (32Cu-44Ni-24Zn) versus α_{12} (83Cu-17Ni) corresponded to a Ni-isoactivity couple, because the compositions of their terminal alloys lie on a Ni-isoactivity line, as shown in Fig. 1. Such Ni-isoactivity couples have been shown to develop zero-flux planes (ZFPs)[4,5,9] for Ni within the diffusion zone. At a ZFP for a component *i*, the interdiffusion flux of *i* goes to 0 and exhibits a change of sign from one side of the ZFP to the other.

The experimental data points for the concentration profiles for the α_5 versus α_{12} couple are shown in Fig. 2(a). Also shown in Fig. 2(a) are the concentration profiles fitted by the *Multi*DiFlux program with cubic Hermite interpolation polynomials. The interdiffusion flux profiles calculated by the program from Eq 2 are shown in Fig. 2(b). Ni develops a ZFP[4,5] within the diffusion zone on the α_5 side of the couple.

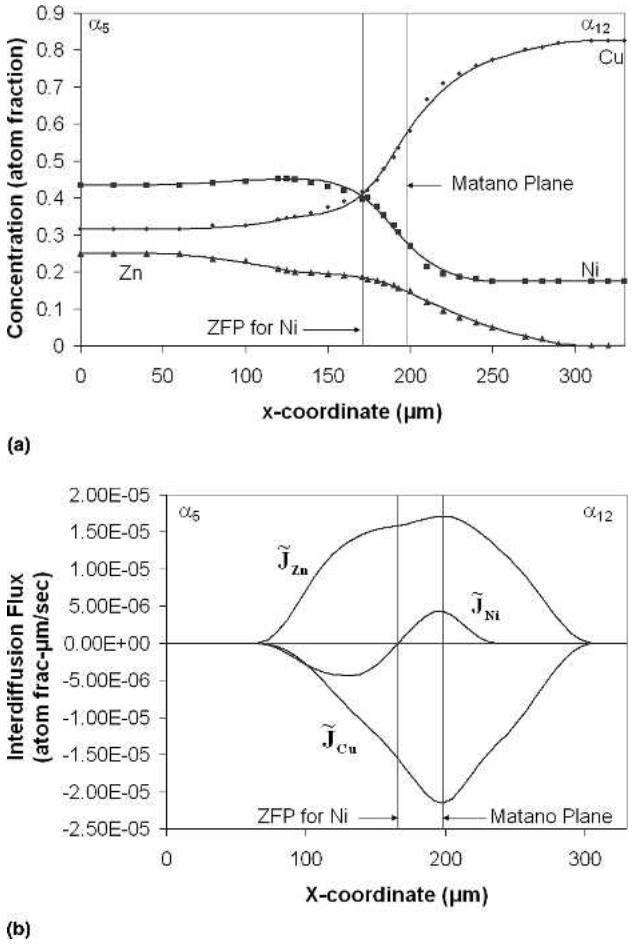

Fig. 2 (a) Concentration profile data fitted with cubic Hermite polynomials shown by continuous lines. (b) Profiles of fluxes calculated from the concentration profiles from Eq 1. Note that a ZFP is developed for Ni.

Table 1 Ternary interdiffusion coefficients calculated for ranges on either side of the Matano plane for the α_5 versus α_{12} couple diffusion annealed at 775 °C for two days

	$\tilde{D}^3_{ij}$, m²/s × 10¹⁵			
x coordinate μm	$\tilde{D}^3_{11}$	$\tilde{D}^3_{12}$	$\tilde{D}^3_{21}$	$\tilde{D}^3_{22}$
$-\infty$ to x_o	14.6	1.5	−5.7	1.6
x_o to $+\infty$	5.6	2.4	0	1.2

From the fitted profiles, a set of four ternary interdiffusion coefficients, $\bar{\tilde{D}}^3_{ij}$ (i = 1,2), was calculated on the basis of Eq 7 and 8 for the two regions, one on either side of the Matano plane. These calculated interdiffusion coefficients are presented in Table 1. These sets of interdiffusion coefficients were then used by the *Multi*DiFlux program to back-calculate the concentration profiles of the individual components on the basis of Eq 7 and 8. These calculated profiles are presented in Fig. 3.

The calculated profiles for the α_5 versus α_{12} couple

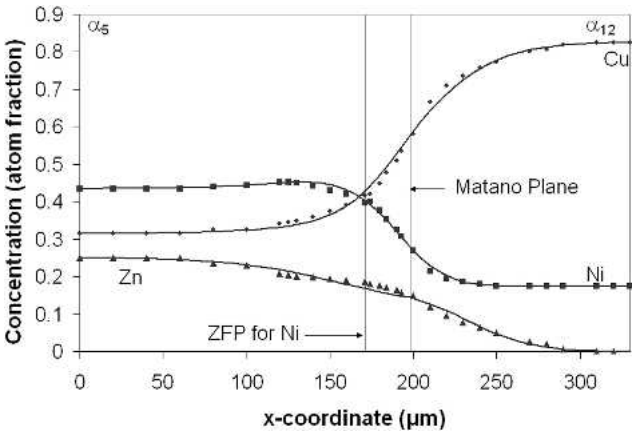

Fig. 3 Concentration profiles generated for the α_5 versus α_{12} couple from the calculated interdiffusion coefficients on the basis of Eq 7 and 8

shown in Fig. 3 clearly indicate that the two sets of ternary interdiffusion coefficients, one set determined on either side of the Matano plane, adequately regenerate the profiles within the diffusion zone on the basis of error function solutions. If the regenerated profiles were to be unsatisfactory, one could choose several smaller regions within the diffusion zone for the evaluation of several sets of interdiffusion coefficients $\bar{\tilde{D}}^3_{ij}$ (i = 1,2) and for the subsequent back-calculation of the concentration profiles. The variation of the interdiffusion coefficients with composition along the diffusion path dictates the number of regions over the diffusion zone one needs to evaluate individual sets of interdiffusion coefficients for the satisfactory generation of the concentration profiles. A minimum number of regions in the diffusion zone may initially be explored but can be gradually increased, as needed, for the adequate representation and reproduction of the profiles by the *Multi*DiFlux program, as illustrated below with another couple.

A second Cu-Ni-Zn couple characterized by terminal alloy compositions lying on a Cu-isoactivity line, as shown in Fig. 4(a), was also analyzed by the program. The couple corresponds to α_2 (73.8Cu-9.5Ni-16.7Zn) versus α_7 (55.5Cu-44.5Ni), and its diffusion path is also presented in Fig. 4(a). The interpolated concentration profiles obtained from the experimental data are shown in Fig. 4(b), and the profiles of interdiffusion fluxes calculated from them are presented in Fig. 4(c). The couple developed a ZFP for Cu as identified on the profiles of concentrations and fluxes, which are shown in Fig. 4(b) and (c), respectively. The Cu concentration profile shows two maxima, one on either side of the Matano plane and a relative minimum in the vicinity of the Matano plane.

From Fig. 4(b) and (c), one can easily see that Cu exhibits uphill diffusion against its own concentration gradient over regions to the right of the Matano plane and to the left of the Cu ZFP. The Zn profile becomes flatter in the midsection of the diffusion zone; this observation suggests higher values for the interdiffusion coefficients for Zn in that region.

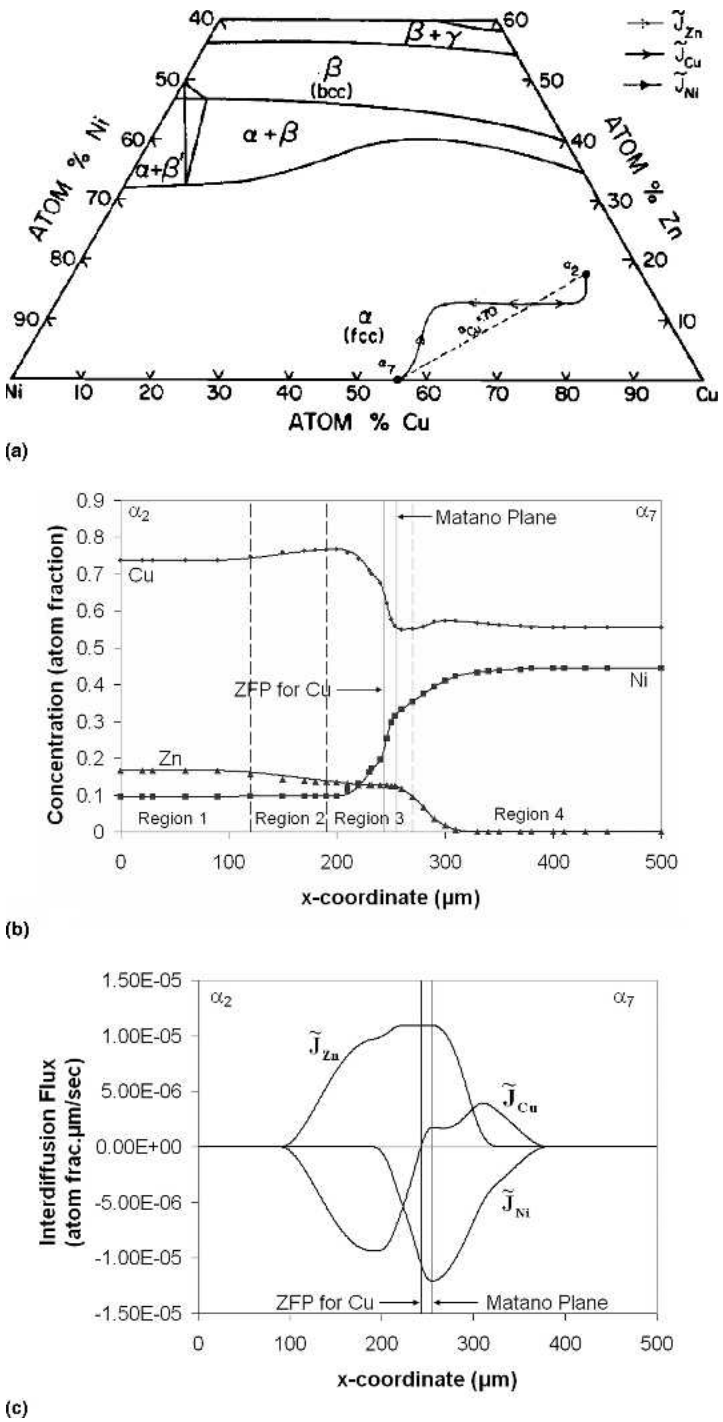

Fig. 4 (a) Diffusion path for the Cu-isoactivity couple, α_2 versus α_7, annealed at 775 °C for two days. (b) Interpolated concentration profiles (lines) from the experimental concentration data points for the couple. (c) Profiles of interdiffusion fluxes calculated from the concentration profiles. Cu exhibits a ZFP in the diffusion zone.

For the purpose of calculation of the ternary interdiffusion coefficients, the diffusion zone of the α_2 versus α_7 couple was divided into four regions, as indicated by the vertical dashed lines in Fig. 4(b). In addition, region 3 was further divided into 10 equal subregions. The various values of interdiffusion coefficients calculated by the *Multi*DiFlux program over these various regions and subregions are plotted in Fig. 5(a). These coefficients were used by the program for the regeneration of concentration profiles on the basis of Eq 7 and 8, and the regenerated profiles are presented in Fig. 5(b). Region 3 in Fig. 5(a) indicates a variation in the values of the interdiffusion coefficients, and the

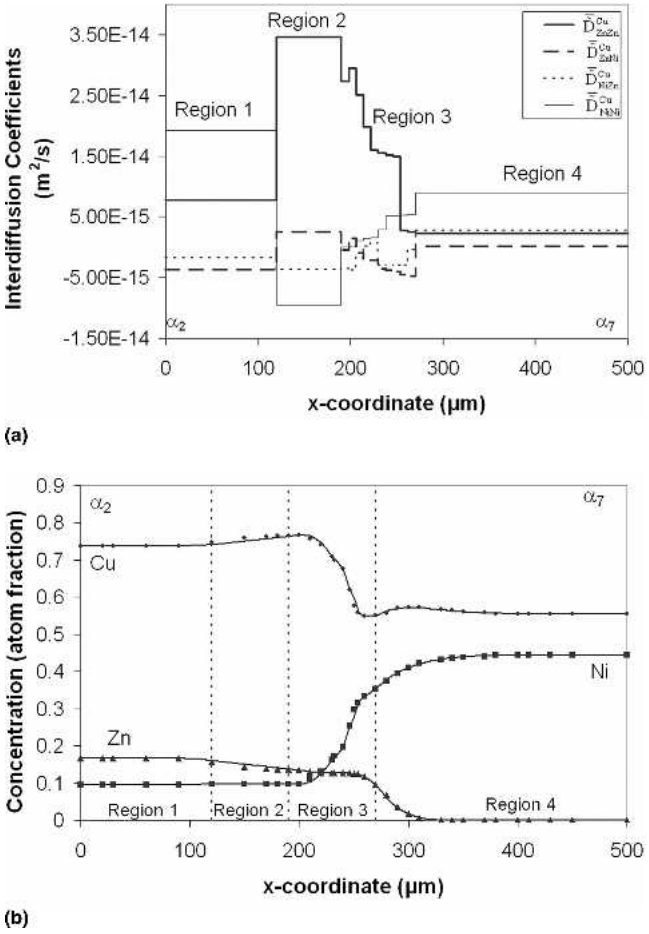

Fig. 5 (a) Ternary interdiffusion coefficients calculated over various regions and subregions in the diffusion zone. (b) Concentration profiles generated on the basis of these coefficients from Eq 7 and 8

use of the *Multi*DiFlux program can bring out such variations. Also, the program can regenerate the concentration profiles for the couple on the basis of these coefficients very satisfactorily, as can be seen in Fig. 5(b).

In summary, the *Multi*DiFlux program is a user-friendly code that was developed as a teaching and research tool for the analysis of multicomponent diffusion couples. It can be downloaded freely at a Purdue University website,[3] and can be used for the calculation of interdiffusion fluxes and interdiffusion coefficients and the generation of profiles in binary and multicomponent systems.

Acknowledgment

This work was supported by the National Science Foundation under grant No. DMR-0304777.

References

1. J.S. Kirkaldy and D.J. Young, *Diffusion in the Condensed State,* The Institute of Metals, London, 1987, p 226-272
2. M.A. Dayananda and Y.H. Sohn, A New Analysis for the Determination of Ternary Interdiffusion Coefficients from a Single Diffusion Couple, *Metall. Mater. Trans. A,* Vol 30, 1999, p 535-543
3. M.A. Dayananda and L.R. Ram-Mohan, "*Multi*DiFlux" website, https://engineering.purdue.edu/MSE/Fac Staff/Faculty/dayananda.wshtml
4. M.A. Dayananda and C.W. Kim, Zero-Flux Planes and Flux Reversals in Cu-Ni-Zn Diffusion Couples, *Metall. Mater. Trans. A,* Vol 10, 1979, p 1333-1339
5. M.A. Dayananda, An Analysis of Concentration Profiles for Fluxes, Diffusion Depths and Zero-Flux Planes in Multicomponent Diffusion, *Metall. Mater. Trans. A,* Vol 14, 1983, p 1851-1858
6. L. Onsager, Theories and Problems of Liquid Diffusion, *Ann. N. Y. Acad. Sci.,* Vol 46, 1945, p 241-265
7. M.A. Dayananda, Average Effective Interdiffusion Coefficients and the Matano Plane Composition, *Metall. Mater. Trans. A,* Vol 27, 1996, p 2504-2509
8. L.R. Ram-Mohan, *Finite Element and Boundary Element Applications to Quantum Mechanics,* Oxford University Press, Oxford, UK, 2002, p 63-81
9. C.W. Kim and M.A. Dayananda, Identification of Zero-Flux Planes and Flux Reversals in Several Studies of Ternary Diffusion, *Metall. Mater. Trans. A,* Vol 14, 1983, p 857-864