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**ZERO-FLUX PLANES, FLUX REVERSALS AND DIFFUSION PATHS
IN TERNARY AND QUATERNARY DIFFUSION**

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DOE/ER/10814--12

DE86 011456

During isothermal multicomponent diffusion, interdiffusion fluxes of individual components can go to zero at zero-flux planes (ZFP) and exhibit flux reversals from one side to the other of such planes. Interdiffusion fluxes as well as the locations and compositions of ZFPs for components are determined directly from the concentration profiles of diffusion couples without the need for prior knowledge of interdiffusion coefficients. The development and identification of ZFPs is reviewed with the aid of single phase and two-phase diffusion couples investigated in the Cu-Ni-Zn system at 775°C. ZFP locations in the diffusion zone nearly correspond to sections where the activity of a component is the same as its activity in either of the terminal alloys of a couple. Path slopes at ZFPs are uniquely dictated by the atomic mobility and thermodynamic data for the components. Discontinuous flux reversals for the components can also occur at interfaces in multiphase couples. Identification of ZFPs is also presented for diffusion in the Cu-Ni-Zn-Mn quaternary system. Analytical representation of diffusion paths for both ternary and quaternary diffusion couples is presented with the aid of characteristic path parameters.

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1. Introduction

The phenomenon of diffusion in multicomponent alloy systems is of great interest to materials scientists and engineers both from theoretical and practical points of view. Since commercially important metallurgical systems normally contain more than two components, it is essential to develop a theoretical understanding of the interactions among the various components from diffusional as well as thermodynamic considerations. From a practical viewpoint, diffusion often plays a major role in most of the metallurgical processes involving phase changes, precipitation, oxidation, corrosion, etc. Also, the development and stability of diffusion structures in multicomponent, multiphase assemblies is of great practical relevance in processes such as carburizing, aluminizing, diffusion bonding and cladding.

The phenomenological description of multicomponent diffusion has been based on the Onsager's formalism [1,2] of Fick's law extended to multicomponent systems. The simplest of multicomponent systems is a ternary system. There exist in literature several experimental studies of diffusion in ternary systems. These include those that deal with the determination of diffusion data, such as interdiffusion coefficients [3-19], intrinsic diffusion coefficients [4,6,9,12,17,20] atomic mobilities [21-25] and vacancy wind effects [23,24]. Most of these studies have employed pairs of independent ternary diffusion couples with intersecting diffusion paths for the determination of either intrinsic or interdiffusion data at the common composition of the couples. For an n -component system such a procedure requires the use of $(n-1)$ independent diffusion couples for the determination of $(n-1)^2$ concentration-dependent interdiffusion coefficients at one composition. Hence, the determination of diffusion data in multicomponent systems is rather involved and difficult.

An alternative approach [26,27] in the study of isothermal diffusion in multicomponent systems is to analyze the concentration profiles of couples directly for interdiffusion fluxes of all components without invoking Fick's law. Such an analysis for the interdiffusion fluxes by-passes the need for $(n-1)^2$ interdiffusion coefficients and provides a direct insight into the directions as well as magnitudes of the fluxes at any section within the diffusion zone. An initial application of this flux analysis to ternary diffusion couples in the Cu-Ni-Zn system helped identify zero-flux planes (ZFP) and flux reversals for the individual components [26]. At a ZFP the interdiffusion flux of a component goes to zero and normally exhibits a change in direction from one side of the plane to the other. The development of ZFPs has also been identified for ternary diffusion couples in several systems [28] including Cu-Ag-Au, Cu-Zn-Sn, Fe-Ni-Al and Co-Ni-Cr. The ZFP development is dictated by the terminal alloys of a diffusion couple and can occur in both single phase and multiphase assemblies. In addition, discontinuous flux reversals of a component can also occur at an interface in a multiphase system.

One of the objectives of this paper is to review the flux analysis of concentration profiles and the method of identification of ZFPs in isothermal multicomponent

diffusion couples. In this analysis, concentrations are expressed as relative concentration variables, which help identify a common cross-over composition for an infinite couple and check the internal consistency among the concentration profiles of the various components. The identification of ZFPs and flux reversals is illustrated with the aid of couples selected from ternary diffusion studies (29) in the Cu-Ni-Zn system at 775°C. The couples examined include both single phase and multi-phase solid-solid diffusion couples. Observations of ZFP development in systems with more than three components are also presented for a single phase couple in the Cu-Ni-Zn-Mn quaternary system at 775°C [30].

Another important aspect of isothermal multicomponent diffusion relates to the development and representation of diffusion paths. The diffusion path corresponds to the sequence of compositions developed within the diffusion zone of a couple. For a single phase, solid-solid ternary diffusion couple, the diffusion path is a time-invariant S-shaped curve, when plotted on a ternary isotherm. Ternary diffusion paths cannot be easily predicted, since diffusion equations with four concentration dependent interdiffusion coefficients are not easily solvable and the solutions available in literature [31-34] include those that assume constant diagonal and cross coefficients or constant diagonal but variable cross coefficients. Simpler models [35] based on concepts of penetration tendencies for the individual components are inadequate for the description of experimental diffusion paths. However, an alternative approach for the analytical representation of paths for single phase ternary diffusion couples has been proposed [36] on the basis of two characteristic path parameters. The details of this procedure and its application to the representation of paths for several diffusion couples in the Cu-Ni-Zn systems are also presented in this paper. In addition, the procedure is extended for the analytical as well as geometric representation of diffusion paths for single phase quaternary diffusion couples. The extended method is applied to describe the diffusion path for a Cu-Ni-Zn-Mn diffusion couple.

2. Analysis of Concentration Profiles for Interdiffusion Fluxes.

Consider an n-component solid-solid diffusion couple assembled with disks of two terminal alloys I and II with respective concentrations, C_i^- and C_i^+ , for component i, as shown schematically in Fig. 1. On a laboratory frame of reference fixed at a section far from the diffusion zone, x_0 refers to the location of the initial plane of contact between the disks or the Matano plane. During isothermal diffusion, the concentration profile develops parabolically with time t and the concentration C_i at any section x in the diffusion zone is a function [37,4,29] of the Boltzmann parameter λ given by

$$\lambda = \frac{(x - x_0)}{\sqrt{t}} \quad (1)$$

At time t the effective diffusion zone for the couple may be considered to be within L^- to L^+ on the distance scale. The molar volume variation with composition in

Fig. 1. Schematic concentration profile of component i for an infinite diffusion couple.

the diffusion zone is assumed negligible. A relative concentration variable $Y_i(x, t)$ for component i can be defined by:

$$Y_i(x, t) = \frac{[C_i(x, t) - C_i^+]}{[C_i^- - C_i^+]} \quad (i=1, 2, \dots, n) \quad (2)$$

On the basis of a distance coordinate referred to as the Matano coordinate, whose origin is selected at x_0 , the boundary conditions for the couple in Fig. 1 are:

$$Y_i(-\infty, t) = 1; Y_i(+\infty, t) = 0$$

$$Y_i(x, 0) = 0 \text{ for } x > x_0$$

$$Y_i(x, 0) = 1 \text{ for } x < x_0 \quad (3)$$

Interdiffusion fluxes, $\tilde{J}_i$, referred to the Matano coordinate can be evaluated [26,27] at any section x directly from the concentration profiles. The continuity equation is given by:

$$\left(\frac{\partial \tilde{J}_i}{\partial x} \right)_t = - \left(\frac{\partial C_i}{\partial t} \right)_x \quad (i=1,2,\dots,n) \quad (4)$$

But,

$$\begin{aligned} \left(\frac{\partial C_i}{\partial t} \right)_x &= - \left(\frac{\partial x}{\partial t} \right)_{C_i} \left(\frac{\partial C_i}{\partial x} \right)_t \\ &= - v(C_i) \left(\frac{\partial C_i}{\partial x} \right)_t \end{aligned} \quad (5)$$

where $v(C_i)$ refers to the velocity of propagation of a concentration level identified at C_i in the diffusion zone. Hence, Eq. (4) becomes:

$$\frac{\partial \tilde{J}_i}{\partial x} = v(C_i) \frac{\partial C_i}{\partial x} \quad (6)$$

Since C_i is a function of λ ,

$$v(C_i) = \left(\frac{\partial x}{\partial t} \right)_{C_i} = \frac{1}{2} \frac{\lambda}{\sqrt{t}} \quad (7)$$

Substitution of Eq. (7) in Eq. (6) and integration with respect to x at constant t yield:

$$\begin{aligned} \int d\tilde{J}_i &= \frac{1}{2\sqrt{t}} \int \lambda \left(\frac{\partial C_i}{\partial x} \right)_t dx \\ &= \frac{1}{2\sqrt{t}} \int \lambda \frac{dC_i}{d\lambda} \frac{1}{\sqrt{t}} \sqrt{t} d\lambda \\ &= \frac{1}{2\sqrt{t}} \int \lambda dC_i \end{aligned} \quad (8)$$

If the integration is between C_i^+ at L^+ and C_i at a section x^* , Eq. (8) can be written as:

$$\tilde{J}_i(x^*) = \frac{1}{2t} \int_{C_i^+}^{C_i(x^*)} (x-x_0) dC_i \quad (i=1,2,\dots,n) \quad (9)$$

since $\tilde{J}_i$ is zero at L^+ . Similarly, for the integration between C_i^- at L^- and C_i at x^* :

$$\tilde{J}_i(x^*) = \frac{1}{2t} \int_{C_i^-}^{C_i(x^*)} (x-x_0) dC_i \quad (i=1,2,\dots,n) \quad (10)$$

since $\tilde{J}_i$ is zero at L^- .

If the concentrations are expressed in terms of Y_i , Eq. (9) can be written as:

$$\begin{aligned} \tilde{J}_i(x^*) &= \frac{\Delta C_i}{2t} \int_0^{Y_i^*} (x-x_0) dY_i \\ &= \frac{\Delta C_i}{2t} \left[(x^*-x_0) Y_i^* + \int_{x^*}^{L^+} Y_i dx \right] \quad (i=1,2,\dots,n) \end{aligned} \quad (11)$$

where $\Delta C_i = (C_i^- - C_i^+)$. Similarly, Eq. (10) can be alternatively expressed by:

$$\begin{aligned} \tilde{J}_i(x^*) &= \frac{\Delta C_i}{2t} \left[\int_0^{(1-Y_i^*)} (x_0-x) d(1-Y_i) \right] \\ &= \frac{\Delta C_i}{2t} \left[(x_0-x^*)(1-Y_i^*) + \int_{L^-}^{x^*} (1-Y_i) dx \right] \quad (i=1,2,\dots,n) \end{aligned} \quad (12)$$

Equations (9) to (12) can be employed for the calculation of the interdiffusion flux $\tilde{J}_i$ relative to the Matano coordinate at any section x^* in the diffusion zone of a couple. The Matano plane x_0 in Fig. 1 is located on the basis of mass balance expressed by:

$$\int_0^1 (x-x_0) dY_i = 0 \quad (13)$$

In terms of areas Eq. (13) implies:

$$E = A + B + C \quad (14)$$

$$(E + D) - A = B + C + D = (x^* - x_0) \quad (15)$$

Since $E + D = \int_{L^-}^{x^*} (1 - Y_i) dx$ and $A = \int_{x^*}^{L^+} Y_i dx$, Eq. (15) can be written as

$$\int_{L^-}^{x^*} (1 - Y_i) dx - \int_{x^*}^{L^+} Y_i dx = (x^* - x_0) \quad (16)$$

If Eq. (16) is substituted in Eq. (11), $\tilde{J}_i(x^*)$ can be expressed in another equivalent form given by:

$$\tilde{J}_i(x^*) = \frac{\Delta C_i}{2t} \left[Y_i^* \int_{L^-}^{x^*} (1 - Y_i) dx + (1 - Y_i^*) \int_{x^*}^{L^+} Y_i dx \right] \quad (i=1,2,\dots,n) \quad (17)$$

Equation (17) does not require for its use the location of the Matano plane and is particularly useful in the flux analysis of couples with maxima or minima in their concentration profiles. Hence, from Eqs. (9)-(12) and (17), the interdiffusion fluxes of the individual components in a multicomponent diffusion couple can be evaluated as a function of x from the concentration profiles without a knowledge of interdiffusion coefficients. Although these equations were developed for single phase couples, they are also applicable to flux calculations in multiphase couples, provided the interfaces are planar and the molar volumes of the phases differ little and can be considered identical and constant.

If the variation of molar volume V_m with composition cannot be ignored, Eq. (17) can be modified [19] to:

$$\tilde{J}_i^M(x^*) = \frac{\Delta C_i}{2t} \left[Y_i^* \int_{L^-}^{x^*} \frac{(1 - Y_i)}{V_m} dx + (1 - Y_i^*) \int_{x^*}^{L^+} \frac{Y_i}{V_m} dx \right] \quad (i=1,2,\dots,n) \quad (18)$$

where a mole-fixed reference frame is employed to define the interdiffusion flux $\tilde{J}_i^M$. The assumption of constant molar volume will be employed in this paper.

On the basis of the extended form of Fick's law of Onsager [1,2], $\tilde{J}_i$ for component i in an n -component system is expressed in terms of $(n-1)$ independent concentration gradients $\partial C_j / \partial x$ by:

$$\tilde{J}_i = - \sum_{j=1}^{n-1} \tilde{D}_{ij}^n \frac{\partial C_j}{\partial x} \quad (i=1,2,\dots,n-1) \quad (19)$$

where $\tilde{D}_{ij}^n$ are $(n-1)^2$ independent interdiffusion coefficients. Eqs. (9) and (19) yield:

$$\int_{C_i^+}^{C_i(x^*)} (x-x_0) dC_i = -2t \left[\sum_{j=1}^{n-1} \tilde{D}_{ij}^n \frac{\partial C_j}{\partial x} \right]_{C_i(x^*)} \quad (20)$$

For ternary systems, Eq. (20) becomes:

$$\int_{C_i^+}^{C_i(x^*)} (x-x_0) dC_i = -2t \left[\tilde{D}_{i1}^3 \frac{\partial C_1}{\partial x} + \tilde{D}_{i2}^3 \frac{\partial C_2}{\partial x} \right]_{C_i(x^*)} \quad (i=1,2) \quad (21)$$

Equation (21) can be employed for the evaluation of the four $\tilde{D}_{ij}^3$ coefficients at the common composition of a pair of independent diffusion couples with intersecting diffusion paths. Ternary interdiffusion data based on such calculations are available in literature for several ternary substitutional systems [3-19].

3. Profiles of Concentrations and Fluxes, Zero-Flux Planes and Diffusion Paths

Concentration profiles of the individual components for a multicomponent diffusion couple isothermally annealed at a selected temperature for time t are normally determined by analytical techniques such as microprobe analysis or SEM with energy dispersive analysis. The profiles are presented as C_i vs. x plots where C_i can be expressed in atom fraction or g-moles/cc. Alternatively, the relative concentration variable Y_i as defined in Eq. (1) can be employed for presenting the experimental concentration profiles. Profiles of $\tilde{J}_i$ vs. x can then be generated by employing the flux equations presented in section 2.

The use of the variable Y_i for concentrations is illustrated with the experimental profiles [27] of a ternary Cu-Ni-Zn solid-solid diffusion couple annealed at 775°C for 48 hours. The two terminal alloys of the couple are designated as Alloy I (30.1 Cu - 44.7 Ni - 25.2 Zn, at. pct.) and Alloy II (80.6 Cu - 19.4 Ni) and the plots of C_i (atom fraction) vs. x and of Y_i vs. x are presented in Figs. 2(a) and 2(b), respectively. The fluxes $\tilde{J}_i$ calculated from the concentration profiles on the basis of Eq. (9) or Eq. (17) are presented in Fig. 2(c). Several interesting features in Fig. 2 are discussed below.

3.1. Common Relative Concentration Y_c

Figure 2(b) clearly shows that the concentration profiles of all components can be displayed together over the diffusion zone L^- to L^+ such that $Y_i = 1$ at L^- and $Y_i = 0$ at L^+ for all components, regardless of their individual flow directions. Such a presentation is easy to use for the location of the Matano plane x_0 on the

Fig. 2. Concentration profiles with concentrations expressed in (a) atom fraction and in (b) relative concentrations Y_i for a ternary Cu-Ni-Zn diffusion couple assembled with Alloy I (30.1 Cu - 44.7 Ni - 25.2 Zn) and Alloy II (80.6 Cu - 19.4 Ni) and diffusion annealed at 775°C for 48 hours; (c) calculated profiles of interdiffusion fluxes for the components for the couple with the direction from Alloy I to Alloy II taken as positive [27].

basis of Eq. (13). The locations of the Matano plane determined from the individual profiles are expected to coincide for a constant molar volume diffusion zone.

A more significant feature in Fig. 2(b) refers to the fact that the various profiles cross one another at a common value of Y_i identified as Y_c at the cross-over plane x_c . Y_c is considered to be a characteristic parameter for the diffusion couple.

The individual Y_i values at any section within the diffusion zone of an n-component diffusion couple with constant molar volume satisfy the relation:

$$\sum_{i=1}^n Y_i \Delta C_i = 0 \quad (22)$$

where $\Delta C_i = C_i^- - C_i^+$ for each component. Equation (22) implies that there exist only (n-1) independent Y_i variables for an n-component system. Since

$$\sum_{i=1}^n \Delta C_i = 0 \quad (23)$$

Eq. (22) becomes:

$$\sum_{i=1}^{n-1} (Y_i - Y_n) \Delta C_i = 0 \quad (24)$$

For a ternary system $n = 3$ and Eq. (24) is written as

$$(Y_1 - Y_3) \Delta C_1 + (Y_2 - Y_3) \Delta C_2 = 0 \quad (25)$$

Equation (25) implies that, if $Y_1 = Y_3$ at a section in the diffusion zone of a ternary couple, Y_2 should also be equal to Y_3 . In other words, if the relative concentration profiles for two of the components cross each other, the profile for the third component is also expected to pass through the same cross-over composition, which is identified by $Y_i = Y_c$ for all i .

3.2. Consistency Relations for Profiles.

The check for the internal consistency among the experimental concentration profiles for the various components in a multicomponent diffusion couple can be made on the basis of Eq. (16), which is valid at any section x in the diffusion zone. Writing Eq. (16) for any two components i and j , one gets

$$\int_{L^-}^x (1-Y_i)dx - \int_x^{L^+} Y_i dx = \int_{L^-}^x (1-Y_j)dx - \int_x^{L^+} Y_j dx \quad (26)$$

On rearrangement, Eq. (26) yields:

$$\int_{L^-}^x (Y_j - Y_i)dx = \int_x^{L^+} (Y_i - Y_j)dx \quad (27)$$

or

$$\int_{L^-}^{L^+} (Y_i - Y_j) dx = 0 \quad (i \neq j) \quad (28)$$

For the concentration profiles shown in Fig. 2(b), it follows from Eq. (28) that the area between the profiles of relative concentrations of any two components on either side of x_c must be identical in magnitude. For example, the areas M and N in Fig. 2(b) should be equal. It is also apparent from the figure that the magnitude of the area indicated by the integral $\int_{L^-}^{L^+} (Y_i - Y_j) dx$ ($i \neq j$) is a maximum for $x = x_c$ for two of the components i and j .

3.3. Significance of Y_c

The cross-over composition Y_c can be expressed in terms of the relative depths of the diffusion zone on either side of the Matano plane. As indicated in Fig. 2(b), the locations L^- and L^+ are selected to cover the effective diffusion zone so that $Y_i = 1$ at L^- and $Y_i = 0$ at L^+ for all i . For a given selection of L^- and L^+ locations in Fig. 2(b), Eq. (16) yields:

$$\int_{L^-}^{L^+} Y_i dx = x_o - L^- = \text{area abhg} \quad (29)$$

Similarly,

$$\int_{L^-}^{L^+} (1 - Y_i) dx = L^+ - x_o = \text{area bcih} \quad (30)$$

If the locations L^- and L^+ are conveniently chosen so that area abhg equals area acfd and area bcih equals area dfig, then,

$$x_o - L^- = Y_c (L^+ - L^-) \quad (31)$$

and

$$(L^+ - x_o) = (1 - Y_c)(L^+ - L^-) \quad (32)$$

Hence,

$$\frac{Y_c}{1 - Y_c} = \frac{x_o - L^-}{L^+ - x_o} \quad (33)$$

Equation (33) implies that the effective depths of diffusion ($x_o - L^-$) and ($L^+ - x_o$) on either side of the Matano plane can be considered proportional to Y_c and $1 - Y_c$, respectively. Although these diffusion depths vary parabolically with diffusion time, their ratio is invariant with time and Y_c can be regarded as a characteristic

parameter for a solid-solid couple.

From Eqs. (29) and (31), Y_c can be expressed by

$$Y_c = \frac{1}{(L^+ - L^-)} \int_{L^-}^{L^+} Y_i dx \quad (i=1,2,\dots,n) \quad (34)$$

and from Eqs. (30) and (32), $(1 - Y_c)$ is given by

$$(1 - Y_c) = \frac{1}{(L^+ - L^-)} \int_{L^-}^{L^+} (1 - Y_i) dx \quad (i=1,2,\dots,n) \quad (35)$$

Equations (34) and (35) indicate that Y_c can be interpreted as the average relative concentration of each of the components over the diffusion zone $(L^+ - L^-)$ for the couple and is the same for all components regardless of their diffusion directions. Hence, Y_c reflects not only the relative diffusion depths on either side of the Matano plane but also the average relative concentration for the components for an appropriate choice of L^- and L^+ . A Y_c value of 0.68 for the couple in Fig. 2 reflects the fact that the depth of diffusion on the alloy I side is 2.125 times larger than that on the alloy II side.

3.4. Identification of Zero-Flux Planes

The calculated flux profiles for the couple, Alloy I vs. Alloy II, shown in Fig. 2(c) clearly indicate that the Zn interdiffusion flux is positive in the direction from Alloy I to Alloy II, while that of Cu is negative in the opposite direction over the entire diffusion zone. The Ni flux profile, on the other hand, exhibits two regions with opposite flux directions with the transition occurring through a plane identified as a zero-flux plane (ZFP), where the Ni flux is zero. Such a plane is referred to as a ZFP for Ni. For the sake of clarity and discussion, the concentration and flux profiles of Ni for the Alloy I vs Alloy II couple are presented together in Fig. 3.

Zero-flux planes, where the interdiffusion flux of a component goes to zero in the diffusion zone, can be directly identified from the concentration profiles. Since $J_i = 0$ at a ZFP for component i , it follows from Eqs. (9) and (10) that:

$$\int_{C_i^+}^{C_i(\text{ZFP})} (x - x_0) dC_i = \int_{C_i(\text{ZFP})}^{C_i^-} (x - x_0) dC_i = 0 \quad (36)$$

The application of Eq. (36) for the identification of a ZFP is illustrated with the Ni concentration profile in Fig. 3. The Ni profile exhibits a maximum and the location of the Ni ZFP is dictated by the requirements:

$$\int_{C_{Ni}^+}^{C_{Ni}(\text{ZFP})} (x - x_0) dC_{Ni} = \text{Area D} - \text{Area C} = 0 \quad (37)$$

Fig. 3. The concentration and interdiffusion flux profiles of Ni for the couple Alloy I vs Alloy II in the Cu-Ni-Zn system at 775°C; Ni develops a ZFP located by the requirement that Area A = Area B and Area C = Area D; the dashed curve refers to the profile of Ni activity a_{Ni} .

and

$$\int_{C_{Ni}^-}^{C_{Ni}^+(ZFP)} (x - x_0) dC_{Ni} = \text{Area A} - \text{Area B} = 0 \quad (38)$$

Hence, the ZFP location is such that areas A and B are equal in magnitude and areas C and D are also equal in magnitude. The mass balance over the diffusion zone requires that the total loss indicated by the area (B + C) is equal to the total gain (A + D). Since Ni interdiffuses in opposite directions on the two sides of the ZFP, the two regions of gain, A and D, appear on two different sides of the region of loss.

On the basis of Eqs. (11) and (12), the conditions for a ZFP for component i can be alternatively expressed by

$$(x_0 - x_{ZFP})(Y_i)_{ZFP} = \int_{x_{ZFP}}^{L^+} Y_i dx \quad (39)$$

and

$$(x_{ZFP} - x_o)(1 - Y_i)_{ZFP} = \int_{L^-}^{x_{ZFP}} (1 - Y_i)dx \quad (40)$$

where x_{ZFP} is the location of the ZFP. From Eqs. (39) and (40), it follows that

$$\left(\frac{Y_i}{1 - Y_i} \right)_{ZFP} = \frac{\int_{L^-}^{L^+} Y_i dx}{\int_{x_{ZFP}}^{L^-} (1 - Y_i) dx} \quad (41)$$

Hence, for the identification of a ZFP, a concentration profile needs to exhibit a maximum or a minimum and satisfy equalization of areas as expressed by Eqs. (37) and (38) or equivalently by Eqs. (39) and (40). A maximum or a minimum in the concentration profile does not by itself indicate the development of a ZFP, if such equalization of areas does not exist, but may reflect the interdiffusion of a component up its own concentration gradient without a change or reversal in its flux direction.

3.5. Relative Maxima or Minima in Flux Profiles

The locations where the profiles of the interdiffusion fluxes of the various components exhibit a relative maximum or minimum in Fig. 2(c) can be appreciated on the basis of Eq. (6), which can be written as

$$\frac{\partial \tilde{J}_i}{\partial x} = \frac{(x - x_o)}{2t} \frac{\partial C_i}{\partial x} \quad (42)$$

From Eq. (42) the sections where $\partial \tilde{J}_i / \partial x$ goes to zero are characterized by the requirement that $x = x_o$ or $\partial C_i / \partial x = 0$. It is apparent that all components develop a relative maximum or minimum for its interdiffusion flux at the Matano plane x_o . In addition, a relative maximum or minimum in the interdiffusion flux of a component is observed at each section corresponding to a maximum or a minimum in its concentration profile. Such correspondence can be seen for the Ni profile in Fig. 3.

3.6. Experimental Diffusion Path

The sequence of compositions developed during isothermal diffusion zone of a couple represents the experimental diffusion path or the composition path. The diffusion path for an infinite, ternary solid-solid couple is an S-shaped path when plotted on a ternary isotherm. The path is invariant with time [3], as the

concentration variables are all functions of the Boltzmann parameter λ . The experimental verification of the dependence of C_i on λ has been recently reported [29] for a couple exhibiting a ZFP.

The ternary diffusion path is normally presented on a ternary isotherm. The diffusion path corresponding to the concentration profiles in Fig. 2(a) is presented on the Cu-Ni-Zn ternary isotherm at 775°C in Fig. 4(a). The path crosses the straight

Fig. 4. Experimental diffusion path for the Alloy I vs Alloy II couple presented (a) on the Cu-Ni-Zn ternary isotherm at 775°C, and (b) as a plot of one relative concentration variable against another. The dashed curve in (b) is a calculated path based on procedure presented in section 6 [36].

line joining the terminal composition points of the couple at the cross-over composition C_c . At the two composition points, one on either side of C_c , where the diffusion path is farthest removed from the straight line joining the terminal compositions, the path slopes are given by $\Delta C_1/\Delta C_2$. ΔC_1 and ΔC_2 are the differences in the concentrations of two of the components, Zn(1) and Cu(2), respectively, in the terminal alloys.

The diffusion path can also be displayed in terms of Y_i variables as shown in Fig. 4(b) where Y_1 is plotted against Y_2 . The path crosses the $Y_1 = Y_2$ straight line at the cross-over composition Y_c . The path slope at Y_c is identified as $1/n$. Y_c and $1/n$ are considered to be useful parameters in the analytical representation of diffusion paths. A path calculated on the basis of path parameters is shown as a dashed line in Fig. 4(b). The procedure for the path calculation is presented in section 6.

4. Experimental Diffusion Studies for Zero-Flux Planes and Flux Reversals

The concept of zero-flux planes (ZFP) and flux reversals was first introduced and identified by Dayananda and Kim [26] in their ternary diffusion studies with α (fcc) Cu-Ni-Zn alloys at 775°C. They later identified [28] the development of ZFPs in several past studies of ternary diffusion by an examination of the concentration profiles reported in literature. The studies selected in their examination covered several Cu-based and Fe-based ternary systems and included both solid-solid and vapor-solid couples. ZFPs and flux reversals were identified in the ternary diffusion studies of Wan and DeHoff [38] in the Cu-Ni-Zn system at 900°C, Ziebold and Ogilvie [7] in the Cu-Ag-Au system at 725°C, Dayananda, et al. [9] in the Cu-Zn-Sn system at 750°C, Sabatier and Vignes [8] in the Fe-Ni-Co system at 1136°C, Guy and Leroy [6] in the Co-Ni-Cr system at 1300°C, and Dayananda and coworkers [16,18] in the Fe-Ni-Al system at 1000°C. They [29] further investigated at 775°C several series of single phase and multiphase solid-solid diffusion couples assembled with α (fcc), β (bcc) and γ (cubic) Cu-Ni-Zn alloys for the development of ZFP's and flux reversals for the individual components. Most of these couples were characterized by terminal alloys of similar thermodynamic activity for one of the components. Studies of interdiffusion and ZFP identification have also been carried out by Duh and Dayananda [39] in the Fe-Ni-Cr system at 1100°C, and by Kansky and Dayananda [30] in the quaternary Cu-Ni-Zn-Mn system at 775°C. The development of ZFPs and flux reversals in both single phase and multiphase couples is reviewed below with the aid of selected couples in the Cu-Ni-Zn and Cu-Ni-Zn-Mn systems.

4.1. Isoactivity Couples with α (fcc) Cu-Ni-Zn Alloys.

An isoactivity couple refers to an assembly of two terminal alloys characterized by similar thermodynamic activities for one of the components. In other words, such a couple is identified by terminal compositions lying on an isoactivity line for a component. The diffusion paths for two series of isoactivity couples [29] assembled

Fig. 5. Diffusion paths for two series of isoactivity couples in the Cu-Ni-Zn system annealed at 775°C for 48 hours; (a) for the Ni isoactivity couples in ZFPs for Ni are identified at composition points, p_1, p_2, p_3 and p_4 (b) and for the Cu isoactivity couples in ZFPs for Cu are identified at points p_5 through p_{10} . The dashed lines in (a) correspond to Ni isoactivity lines, while those in (b) correspond to Cu isoactivity lines [29].

with α (fcc) Cu-Ni-Zn alloys and annealed at 775°C for 48 hours are presented in Fig. 5. The paths in Fig. 5(a) are for four Ni isoactivity couples and the Ni isoactivity lines for the various couples are indicated by dashed lines. One of the couples, α_5/α_{12} , whose path appears in Fig. 5(a) is the same couple as Alloy I vs. Alloy II, whose concentration profiles and flux profiles were presented in Fig. 2. The diffusion paths in Fig. 5(b) correspond to six different Cu isoactivity couples and the

dashed curves represent the Cu isoactivity lines. The isoactivity lines for Ni and Cu at 775°C were calculated [17] from the thermodynamic data [40] available for the α Cu-Ni-Zn alloys whose molar volume calculated on the basis of lattice parameter data [41] varies within 5 percent and is considered a constant at 7.1 cc/g-mole. A ZFP for Ni was observed for the various Ni isoactivity couples at the compositions identified by p_1 through p_4 and the interdiffusion flux of Ni was directed away from the ZFP on either side of ZFP for each couple, as indicated in Fig. 5(a). Similarly, a ZFP for Cu was identified at the compositions identified by p_5 through p_{10} in Fig. 5(b) and the Cu interdiffusion flux was directed in opposite directions away from the ZFP for each of the Cu isoactivity couples.

One of the important observations in Fig. 5 is that the compositions of ZFPs for Ni and Cu nearly correspond to composition points of intersection of diffusion paths and isoactivity lines drawn through the terminal alloys of the couples. This observation implies that the location of the ZFP within the diffusion zone of an isoactivity couple nearly corresponds to a section where the activity of a component is the same as its activity in either of the terminal alloys. This can be seen for the location of the Ni ZFP in Fig. 3 where the profile of Ni activity a_{Ni} is drawn over the diffusion zone of the couple Alloy I (α_5) vs. Alloy II (α_{12}) with the aid of thermodynamic data [17] available for Cu-Ni-Zn alloys.

The ZFP development also reflects the fact that a component can interdiffuse against its own thermodynamic activity gradient in a multicomponent system. This can be appreciated in the light of Figs. 3 and 5. It can be seen in Fig. 3 the interdiffusion flux of Ni is not zero at the locations of the maximum and minimum in the Ni activity profile. $\tilde{J}_{Ni}$ is directed in the direction from alloy α_{12} (Alloy II) to alloy α_5 (Alloy I) up the a_{Ni} hill. On the right side of the Ni ZFP, J_{Ni} is directed towards the α_{12} side against a_{Ni} gradient past the a_{Ni} minimum. Hence, there exist two regions in the diffusion zone where the interdiffusion flux of Ni was directed up its own activity gradient. These two regions can also be identified on the diffusion path for the couple α_5/α_{12} in Fig. 5(a), where $\tilde{J}_{Ni}$ is in the direction of increasing Ni activity along the path on the α_5 side in the vicinity of point p_2 and along the path segment close to the α_{12} composition point. Similar path segments characterized by interdiffusion of Ni up its own activity gradient can be recognized for the other Ni isoactivity couples in Fig. 5(a). Similar observations on uphill diffusion of Cu against its own activity gradient may be made for the couples in Fig. 5(b).

4.2. Nonisoactivity Couples with α Cu-Ni-Zn Alloys

Couples whose terminal alloys are characterized by dissimilar thermodynamic activities for all components may be designated as nonisoactivity couples. Diffusion paths for such couples [26] assembled with α Cu-Ni-Zn alloys and annealed at 775°C for 48 hours are presented on the Cu-Ni-Zn ternary isotherm in Fig. 6. Also shown in this figure are the isoactivity lines for Cu, Ni and Zn passing through the terminal alloys of the individual couples. In Fig. 6 the terminal alloys of the couples α_5/α_7 , α_5/Cu , and α_5/α_3 have dissimilar activities for each of the components,

Fig. 6. Diffusion paths for a set of couples assembled with a common terminal alloy α_5 (30.1 Cu - 44.7 Ni - 25.2 Zn) joined to alloys, α_7 (58.1 Cu - 41.9 Ni), α_9 (78.9 Cu - 21.1 Ni), α_3 (59.3 Cu - 13.3 Ni - 27.4 Zn), and Cu and annealed at 775°C for 48 hours. Composition points a and b correspond to ZFPs for Ni and points c, d and e correspond to ZFPs for Cu. The dashed lines are isoactivity lines drawn through the terminal alloy compositions [26].

while the couple α_5/α_9 can be considered a Ni isoactivity couple. The couple α_5/α_7 developed no ZFPs and the couple α_5/α_9 showed a Ni ZFP at the composition point a. The couple α_5/Cu exhibited a ZFP for Ni at point b and a ZFP for Cu at point c. The couple α_5/α_3 developed two ZFPs for Cu, one at the composition point d and the other at point e. For each couple the compositions of the various ZFPs developed are seen to nearly correspond to points of intersection of the diffusion path with the isoactivity lines for the individual components passing through the terminal alloys. For example, the Ni and Cu isoactivity lines passing through α_5 intersect the path of the couple α_5/Cu in the vicinity of the composition points b and c corresponding to ZFPs for Ni and Cu, respectively. Similarly, the composition points d and e for ZFPs for Cu observed for the couple α_5/α_3 nearly coincide with the points of intersections of the path with the Cu isoactivity lines drawn through the terminal compositions α_5 and α_3 , respectively. The development of no ZFPs for the couple α_5/α_7 is consistent with the fact that none of the isoactivity lines for the components drawn through either of the terminal compositions α_5 or α_7 intersects the diffusion path for the couple.

The correspondence between the ZFP compositions and the intersection points of diffusion paths and isoactivity lines drawn through the terminal alloys of the

couples, as indicated in Figs. 5 and 6, is not exact, but is within 0.5 atom percent uncertainty in the concentrations of the individual components.

4.3. Multiphase Couples in the Cu-Ni-Zn System

The concentration profiles as well as the calculated flux profiles for two two-phase couples assembled with a γ (cubic) and two β (bcc) Cu-Ni-Zn alloys and designated as γ_3/β_1 and γ_3/β_8 are presented in Fig. 7. The couples were annealed at 775°C for 2 hours. The couples developed planar γ/β interfaces. Based on lattice parameter data, [42,43,44] the molar volumes of β and γ alloys are similar at about 8.0 cc/g-mole and hence Eq. (9) could be used for flux calculations for the two-phase couples.

Fig. 7. Concentration and interdiffusion flux profiles for two γ (cubic)/ β (bcc) two-phase couples in the Cu-Ni-Zn system annealed at 775°C for 2 hours; (a) the couple assembled with γ_3 (23.4 Ni - 76.6 Zn) and β_1 (30.5 Cu - 20.8 Ni - 48.7 Zn) alloys developed a flux reversal for Ni at the γ/β interface, and (b) the couple assembled with γ_3 (23.4 Ni - 76.6 Zn) and β_8 (55.0 Cu - 45.0 Zn) alloys developed a ZFP for Ni in the γ phase.

In Fig. 7(a), the flux profile for Ni for the couple γ_3/β_1 shows a discontinuous flux reversal at the γ/β interface, since $\tilde{J}_{\text{Ni}}$ exhibits a change in sign or direction at the interface from γ to β side. This follows from the fact that the integral $\int_{C_{\text{Ni}}(+\infty)}^{C_{\text{Ni}}^\gamma} x \, dC_{\text{Ni}}$ is negative, and the integral $\int_{C_{\text{Ni}}(+\infty)}^{C_{\text{Ni}}^\beta} x \, dC_{\text{Ni}}$ is positive, where C_{Ni}^γ and C_{Ni}^β are Ni concentrations on the γ and β sides, respectively, at the interface. Hence, it is important to note that a component can exhibit opposite directions for its interdiffusion flux on the two sides of an interface in a multiphase couple.

The flux profiles for the couple γ_3/β_8 in Fig. 7(b) show the development of a ZFP for Ni on the γ side of the γ/β interface with no discontinuous flux reversal at the interface. This observation implies that the development of a ZFP in a phase layer or a discontinuous flux reversal at an interface in multiphase couples can be controlled with changes in one of the terminal alloys.

The diffusion paths for the two-phase couples are shown in Fig. 8. The composition of the ZFP for Ni developed in the couple γ_3/β_8 corresponds to point p_{20} and

Fig. 8. Diffusion paths for the two-phase couples, γ_3/β_1 and γ_3/β_8 , in the Cu-Ni-Zn system at 775°C; composition point p_{20} corresponds to a ZFP for Ni developed in the couple γ_3/β_8 [29].

the dashed line is a Ni isoactivity line passing through the terminal alloy γ_3 . The isoactivity line is based [29] on activity data [45] for the components for γ Cu-Zn and γ Ni-Zn alloys. The composition of the Ni ZFP nearly coincides with the intersection point of the Ni isoactivity line drawn through γ_3 and the diffusion path for the couple γ_3/β_8 . An additional feature of interest in Fig. 8 is that the Ni isoactivity line drawn through γ_3 meets the diffusion path for the γ_3/β_1 couple almost on the $\gamma/(\beta+\gamma)$ phase boundary line at an end of the tie-line crossing of the diffusion path. Such an intersection between the Ni isoactivity line and the diffusion path for the γ_3/β_1 couple at the entry of the tie-line crossing corresponds to a flux reversal for Ni at the γ/β interface. Hence, a discontinuous flux reversal of a component at an interface appears to occur when the activity of the component at the interface is similar to its activity in one of the terminal alloys of a multiphase couple. Such flux reversals for Ni and Cu have also been reported at interfaces in multiphase Cu-Ni-Zn diffusion couples [29] assembled with γ (cubic) and α (fcc) Cu-Ni-Zn alloys involving the development of an intermediate β (bcc) layer.

4.4. Quaternary Diffusion Couples with Cu-Ni-Zn-Mn Alloys.

Quaternary diffusion has been recently investigated by Kansky and Dayananda [30] in the α (fcc) region of the Cu-Ni-Zn-Mn system at 775°C with solid-solid diffusion couples characterized by terminal alloys with similar concentrations for one

Fig. 9. (a) Concentration profiles and (b) flux profiles for a Cu-Ni-Zn-Mn quaternary diffusion couple assembled with alloy C (71.1 Cu - 10.6 Ni - 8.7 Zn - 9.6 Mn) and alloy I (66.1 Cu - 22.3 Ni - 11.6 Zn) and diffusion annealed at 775°C for 48 hours.

of the components. The concentration profiles of the couples were examined on the basis of relative concentration variables for the components and the profiles exhibited a common cross-over composition. The interdiffusion fluxes of the components were calculated directly from the concentration profiles. Interdiffusion of each component up its own concentration gradient was observed in several couples, while the zero flux planes for the individual components were identified in selected couples.

The concentration profiles and the flux profiles for a couple assembled with alloy C (71.1 Cu - 10.6 Ni - 8.7 Zn - 9.6 Mn, at. pct.) and Alloy I (66.1 Cu - 22.3 Ni - 11.6 Zn) and annealed at 775°C for 48 hours are presented in Fig. 9. Mn interdiffused in the positive direction from Alloy C to Alloy I, while Ni interdiffused in the opposite direction. Cu exhibited a maximum and a minimum in its concentration profile and the Zn concentration profile showed a maximum. Both Cu and Zn developed a ZFP, as shown in Fig. 9. A set of plots obtained by plotting Y_{Ni} vs. Y_{Mn} , Y_{Ni} vs. Y_{Zn} and Y_{Mn} vs. Y_{Zn} for the couple is presented in Fig. 10 and each of the plots may be referred to as a partial diffusion path. The paths indicate a common cross-over composition Y_c for all components. The empirical representation of the partial diffusion paths on the basis of Y_c and the path slopes $1/n$ and $1/m$ of two of the plots in Fig. 10 is discussed in section 6.

5. Comments on ZFP and Flux Reversals.

5.1. General Observations.

On the basis of the selected diffusion couples presented in section 4, there are several general observations which can be made with regard to the development of ZFPs and flux reversals during multicomponent diffusion. These are summarized below:

1. Zero-flux planes where the interdiffusion flux of a component goes to zero can develop within the diffusion zone of an isothermal multicomponent system with three or more components.
2. A ZFP for a component is usually associated with a flux reversal or a change in direction for the interdiffusion flux of the component from one side of the plane to the other. The fluxes are continuous at the ZFP.
3. The development of ZFPs is common to both single phase and multiphase couples. The formation as well as the number of ZFPs is dictated by the terminal alloys of the diffusion assembly.
4. A diffusion couple can develop more than one ZFP for the same component and more than one component can develop ZFPs in the same couple.
5. In multiphase couples, a discontinuous flux reversal for a component can occur at a moving interface, as one phase grows at the expense of the other. In other words, a component can interdiffuse in opposite directions on the two sides of an interface.

Fig. 10. Experimental and calculated plots of Y_{Ni} vs Y_{Mn} , Y_{Ni} vs Y_{Zn} , and Y_{Mn} vs Y_{Zn} for the Cu-Ni-Zn-Mn quaternary diffusion couple CI annealed at 775°C for 48 hours.

6. In general, a multicomponent system may not be considered to be uniform in the flow directions of the individual components over the entire diffusion zone, since the interdiffusion flux of a component can exhibit opposite directions over different segments with the development of a ZFP. Furthermore, the location of a ZFP for a component varies with time during diffusion and hence, a given layer of the diffusion zone experiences within it a reversal in the direction of the interdiffusion flux for that component, as the ZFP sweeps it.

7. The compositions of ZFPs developed in ternary diffusion couples coincided within half an atom pct. uncertainty in concentrations with points of intersection of diffusion paths and isoactivity lines for the components drawn through the terminal alloy compositions on a ternary isotherm. In other words, a ZFP for a component was observed at a section in the diffusion zone, where the activity of the component was nearly the same as its activity in either of the terminal alloys of the couple. Similarly, in a multiphase couple, a discontinuous flux reversal for a component was observed at an interface, if the activity of the component at the interface nearly corresponded to its activity in either of the terminal alloys.

5.2. Significance of ZFP and Flux Reversals

The main significance of the ZFP development in a multicomponent alloy lies in the fact that the interdiffusion flux $\tilde{J}_i$ of component i goes to zero at the ZFP because of the exact balancing of the effects of the various driving forces on its interdiffusion. Phenomenologically, the extended form of Fick's law given by Eq. (19) requires that if $\tilde{J}_i = 0$ at the ZFP

$$\sum_{j=1}^{n-1} \tilde{D}_{ij}^n \frac{\partial C_j}{\partial x} = 0 \quad (43)$$

The sum of the terms in Eq. (43) will normally have opposite signs on the two sides of the ZFP.

For a ZFP in a ternary alloy, Eq. (43) yields

$$\left. \frac{\partial C_1}{\partial C_2} \right|_{\text{ZFP for } i} = - \frac{\tilde{D}_{i2}^3}{\tilde{D}_{i1}^3} \quad (44)$$

Equation (44) indicates that the slope of the ternary diffusion path at a ZFP composition yields directly the ratio of the cross to the main ternary interdiffusion coefficients for component i . Such ratios calculated at the ZFP compositions from the paths for the various couples presented in Figs. 5(a) and 5(b) are presented in Table I.

For the Ni isoactivity couples in Fig. 5(a) exhibiting ZFPs for Ni, Cu is taken as the dependent variable and values of the ratio $\tilde{D}_{\text{NiZn}}^{\text{Cu}} / \tilde{D}_{\text{NiNi}}^{\text{Cu}}$ given by $-(\partial C_{\text{Ni}} / \partial C_{\text{Zn}})$ at ZFP compositions are reported. These values indicate that the cross coefficient $\tilde{D}_{\text{NiZn}}^{\text{Cu}}$ is several times larger than the main interdiffusion coefficient $\tilde{D}_{\text{NiNi}}^{\text{Cu}}$ in magnitude but is of opposite sign. The implication is that the interdiffusion of Ni down a Zn gradient is reduced and the Ni interdiffusion up a Zn gradient is favored. Changes in the directions of $\tilde{J}_{\text{Ni}}$ can thus develop along the diffusion path, as is the case on the two sides of a ZFP, as shown for couples in Fig. 5(a).

For the Cu isoactivity couples, the diffusion paths in Fig. 5(b) are almost parallel to lines of constant Zn in the vicinity of ZFPs. From the experimental values of

Table I. ZFP compositions and ratios of cross to main interdiffusion coefficients in the Cu-Ni-Zn system at 775°C.

Couple Designation	ZFP For	ZFP Composition (at.%)			$\tilde{D}_{\text{NiZn}}^{\text{Cu}}/\tilde{D}_{\text{NiNi}}^{\text{Cu}}$	$\tilde{D}_{\text{CuNi}}^{\text{Zn}}/\tilde{D}_{\text{CuCu}}^{\text{Zn}}$
α_4/α_1	Ni	61.1	12.9	26.0	-2.4	--
α_5/α_{12}	Ni	47.4	35.6	17.0	-4.2	--
α_{22}/α_{13}	Ni	29.0	56.0	15.0	-4.8	--
α_{26}/α_{25}	Ni	11.4	78.1	10.5	-3.7	--
α_{10}/α_{13}	Cu	77.3	6.6	16.1	--	0.8
α_2/α_7	Cu	70.6	16.5	12.9	--	0.9
α_3/α_{18}	Cu	52.5	23.8	23.7	--	1.2
α_3/α_{15}	Cu	51.9	25.2	22.9	--	1.0
α_{16}/α_{20}	Cu	39.0	30.0	31.0	--	1.0
α_5/α_{20}	Cu	25.8	53.4	20.8	--	1.0

— $(\partial C_{\text{Cu}}/\partial C_{\text{Ni}})$ at ZFPs, values of the ratio of $\tilde{D}_{\text{CuNi}}^{\text{Zn}}/\tilde{D}_{\text{CuCu}}^{\text{Zn}}$ were calculated. These values reported in Table I indicate that the cross coefficient $\tilde{D}_{\text{CuNi}}^{\text{Zn}}$ is comparable to the main coefficient $\tilde{D}_{\text{CuCu}}^{\text{Zn}}$. Hence, the flux of Cu will be enhanced down a Ni concentration gradient but will be retarded and possibly reversed, if the gradients of Cu and Ni were large and were of opposite signs as is the case for the couples in Fig. 5(b). Hence, the development of ZFPs and flux reversals can be appreciated in the light of the magnitude of the cross coefficient relative to that of the main coefficient.

If $\tilde{J}_i$ is expressed in terms of chemical potential gradients [3] by

$$\tilde{J}_i = -\tilde{L}_{i1}^3 \frac{\partial(\mu_1 - \mu_3)}{\partial x} - \tilde{L}_{i2}^3 \frac{\partial(\mu_2 - \mu_3)}{\partial x} \quad (i=1,2) \quad (45)$$

the sum of the terms on the right hand side of Eq.(45) goes to zero at the ZFP for i and exhibits opposite signs on the two sides of the ZFP. At the ZFP, one has

$$\left[\frac{\partial(\mu_1 - \mu_3)}{\partial(\mu_2 - \mu_3)} \right]_{\text{at ZFP for } i} = -\frac{\tilde{L}_{i2}^3}{\tilde{L}_{i1}^3} \quad (46)$$

An important corollary related to the ZFP development corresponds to the fact that a component can interdiffuse up its own thermodynamic activity gradient in a

multicomponent system. Such up-hill diffusion of a component against its own activity gradient invariably develops over a region of the diffusion zone in the vicinity of a ZFP on one of its sides, as discussed in section 4.1. Interdiffusion of a component up an activity gradient can be expected, if the cross term in Eq. (45) is larger in magnitude but of opposite sign than the main term.

5.3. Relationship Between Atomic Mobilities and Thermodynamic Data at ZFPs.

The atomic mobilities and thermodynamic data at ZFP composition developed in a ternary diffusion couple can be related through the slope of the diffusion path at ZFP. The interdiffusion flux $\tilde{J}_i$ is expressed in terms of intrinsic fluxes J_i by [46]:

$$\tilde{J}_i = J_i - N_i \sum_{j=1}^3 J_j \quad (i=1,2,3) \quad (47)$$

If a component, say component 2, develops a ZFP, $\tilde{J}_2 = 0$ and hence from Eq. (47) it follows:

$$\frac{J_2}{J_1 + J_3} = \frac{N_2}{1 - N_2} \quad (48)$$

at ZFP for component 2. Equation (48) indicates that at the ZFP the ratio of the intrinsic flux of component 2 to the sum of the intrinsic fluxes of the other components is related to the corresponding ratio of the concentrations of the components. On the basis of a simple atomic mobility model, the intrinsic flux of component i may be defined [47] in terms of its chemical potential gradient $\partial\mu_i/\partial x$ by:

$$J_i = - C_i \beta_i \frac{\partial\mu_i}{\partial x} \quad (i=1,2,\dots,n) \quad (49)$$

where β_i is the atomic mobility for component i . In Eq. (49) the interaction between the diffusing species on the lattice-fixed frame is considered negligible. Substitution of Eq. (49) in Eq. (48) and rearrangement yield:

$$\left. \frac{\partial\mu_1}{\partial\mu_2} \right|_{\text{path at ZFP}} = \frac{N_2 + (1-N_2)(\beta_2/\beta_3)}{N_1[(\beta_1/\beta_3) - 1]} \quad (50)$$

where use has been made of the Gibbs-Duhem equation, $\sum_{i=1}^3 C_i \partial\mu_i/\partial x = 0$.

Since μ_i is a function of two concentration variables C_1 and C_2 in a ternary system, one can write:

$$\frac{\partial\mu_i}{\partial x} = \left(\frac{\partial\mu_i}{\partial C_1} \right)_{C_2} \frac{\partial C_1}{\partial x} + \left(\frac{\partial\mu_i}{\partial C_2} \right)_{C_1} \frac{\partial C_2}{\partial x}$$

or

$$\frac{\partial \mu_i}{\partial x} = \left(\frac{\partial \mu_i}{\partial C_1} \right)_{C_2} \frac{\partial C_1}{\partial x} - \left(\frac{\partial \mu_i}{\partial C_1} \right)_{C_2} \frac{\partial C_1}{\partial C_2} \bigg|_{\mu_i} \frac{\partial C_2}{\partial x} \quad (i=1,2,3) \quad (51)$$

Writing Eq. (51) for components 1 and 2 and dividing one by the other, one gets on rearrangement an expression for the slope of the diffusion path given by

$$\left(\frac{\partial C_1}{\partial C_2} \right)_{\text{path}} = \frac{\left(\frac{\partial \mu_1}{\partial \mu_2} \right)_{\text{path}} \left(\frac{\partial C_1}{\partial C_2} \right)_{\mu_2} - \left(\frac{\partial \mu_1}{\partial \mu_2} \right)_{C_2} \left(\frac{\partial C_1}{\partial C_2} \right)_{\mu_1}}{\left(\frac{\partial \mu_1}{\partial \mu_2} \right)_{\text{path}} - \left(\frac{\partial \mu_1}{\partial \mu_2} \right)_{C_2}} \quad (52)$$

Eq. (50) can be substituted in Eq. (52) for the calculation of the path slope at a ZFP composition for component 2 on the basis of data on atomic mobilities and thermodynamic activities of the components. It is apparent that if a ZFP develops at a ternary composition, the path slope at that composition is uniquely dictated by the atomic mobility and thermodynamic data. Such estimations of path slopes at ZFPs for ternary couples on the basis of Eqs. (50) and (52) are currently under way.

6. Diffusion Path Representation

Analytical solutions for the representation of diffusion paths for ternary diffusion couples cannot be easily obtained, since the four interdiffusion coefficients needed to describe ternary diffusion are, in general, concentration dependent. Even if such ternary diffusion data are available for a ternary system, procedures for solving ternary diffusion equations are complex and are dependent on simplifying assumptions and numerical techniques [34].

In this section an attempt is made to describe a procedure for an empirical representation of ternary diffusion paths for single phase, solid-solid diffusion couples with the aid of two characteristic path parameters. An extension of this procedure for the representation of diffusion paths in quaternary systems is also presented. The method is applied to represent experimental diffusion paths for couples selected in the Cu-Ni-Zn and Cu-Ni-Zn-Mn systems.

6.1. Representation of Ternary Diffusion Paths.

The diffusion path for a solid-solid ternary diffusion couple is S-shaped as shown for the couple Alloy I vs. Alloy II in Fig. 4. The path in Fig. 4(b) consists of two segments, S_1 and S_2 , one on either side of the cross-over composition point Y_c . The path can be empirically represented by [36]:

$$Y_1^n = AY_2 \quad (0 \leq Y_i \leq Y_c) \quad (53)$$

over segment S_1 and by:

$$(1-Y_1)^{n'} = A'(1-Y_2) \quad (Y_c \leq Y_i \leq 1) \quad (54)$$

for segment S_2 , where n , n' , A and A' are constants. At Y_c , $Y_1 = Y_2 = Y_c$ and it follows that $A = Y_c^{n-1}$ and $A' = (1-Y_c)^{n-1}$. Since the path is continuous in slope at Y_c , a differentiation of Eqs. (53) and (54) shows that $n = n'$ and

$$\left. \frac{dY_1}{dY_2} \right|_{Y_c} = \left. \frac{d(1-Y_1)}{d(1-Y_2)} \right|_{Y_c} = \frac{1}{n} \quad (55)$$

Equations (53) and (54) can be written as:

$$Y_1^n = Y_c^{n-1} Y_2 \quad (0 \leq Y_i \leq Y_c) \quad (56)$$

$$(1-Y_1)^n = (1-Y_c)^{n-1} (1-Y_2) \quad (Y_c \leq Y_i \leq 1) \quad (57)$$

On the basis of Eqs. (56) and (57), the diffusion path can be represented with the aid of just two characteristic parameters, Y_c and the slope $1/n$ at Y_c . From the experimental values of Y_c of 0.68 and n of 2.4 for the couple, a diffusion path was calculated on the basis of Eqs. (56) and (57) and is also presented as a dashed curve in Fig. 4(b).

The basic assumption made in this method of path representation is that the path segments, S_1 and S_2 , may be considered essentially symmetric except for a change in scale from Y_c to $1-Y_c$. This symmetry can be appreciated better by considering the two composition points, one on either side of Y_c , where the path is parallel to the $Y_1 = Y_2$ straight line. At these composition points the path deviates by d_1 and d_2 from the straight line joining the terminal alloy compositions, as indicated in Fig. 4(b). A differentiation of Eqs. (56) and (57) yields:

$$\frac{dY_1}{dY_2} = \frac{Y_1}{Y_2} \frac{1}{n} \quad (58)$$

and

$$\frac{d(1-Y_1)}{d(1-Y_2)} = \frac{(1-Y_1)}{(1-Y_2)} \frac{1}{n} \quad (59)$$

At the composition points corresponding to deviations d_1 and d_2 , $dY_1/dY_2 = 1$ and it follows from Eqs. (58) and (59) that:

$$Y_1 = nY_2 \quad (60)$$

and

$$1-Y_1 = n(1-Y_2) \quad (61)$$

From Eqs. (56) and (60), one can show that d_1 is given by:

$$d_1 = \frac{Y_1-Y_2}{\sqrt{2}} = \frac{1}{\sqrt{2}} \frac{Y_c}{n^{1/(n-1)}} \frac{n-1}{n} \quad (62)$$

Similarly, on the basis of Eqs. (57) and (61), d_2 is expressed by:

$$d_2 = \frac{Y_2-Y_1}{\sqrt{2}} = \frac{1}{\sqrt{2}} \frac{(1-Y_c)}{n^{1/(n-1)}} \frac{(n-1)}{n} \quad (63)$$

Hence,

$$\frac{d_1}{d_2} = \frac{Y_c}{1-Y_c} \quad (64)$$

For a couple the ratio $\Delta C_i/\Delta C_j$ of the differences in the terminal concentrations of two of the components i and j corresponds to the slope of the straight line joining the terminal compositions and may be used as a variable to examine the variation in the values of Y_c and n . Table II reports the experimental values of Y_c and n for the four Ni isoactivity couples presented in Fig. 5(a). $\Delta C_{Cu}/\Delta C_{Ni}$ values vary within a factor of 2 but the Y_c and n values are quite similar. The diffusion paths calculated [36] on the basis of Y_c and n values from Eqs. (56) and (57) are shown in Fig. 11 along with the experimental diffusion paths; the agreement between them is quite good except for the limited mismatch on the low Zn side of the couples. Similar representations of diffusion paths have also been made [39] for several couples in the Fe-Ni-Cr system at 1100°C with $\Delta C_{Fe}/\Delta C_{Cr}$ ratio ranging over - 2.8 to 3.0 and

Table II. Values of Y_c and n for the Ni isoactivity couples in the Cu-Ni-Zn system.

Couple	$\Delta C_i = (C_i^- - C_i^+) \frac{\text{g mole}}{\text{cc}}$			$\frac{\Delta C_{Cu}}{\Delta C_{Zn}}$	$\frac{\Delta C_{Cu}}{\Delta C_{Ni}}$	Y_c	n_{CuNi}^*	n_{CuZn}^*
	Zn	Cu	Ni					
α_4/α_1	.038	-.063	.018	-1.66	-3.5	.66	.40	2.0
α_5/α_{12}	.035	-.074	.035	-2.11	-2.11	.68	.59	2.4
α_{22}/α_{13}	.025	-.061	.033	-2.44	-1.85	.69	.53	2.5
α_{26}/α_{25}	.021	-.046	.022	-2.19	-2.09	.69	.60	2.2

* $n_{CuNi} = dY_{Cu}/dY_{Ni}$; $n_{CuZn} = dY_{Cu}/dY_{Zn}$.

Fig. 11. Experimental and calculated diffusion paths for the Ni isoactivity couples in the Cu-Ni-Zn system at 775°C[36].

the agreement between the calculated and the experimental paths has been found to be quite satisfactory.

The main advantage of this analysis is that ternary diffusion paths can be conveniently represented or predicted with the aid of two characteristic path parameters Y_c and $1/n$. These parameters can be determined easily with selected experimental couples characterized by different $\Delta C_i/\Delta C_j$ values. The path representation on the basis of Eqs. (56) and (57) bypasses the need for interdiffusion coefficients and the complexity in their use for the prediction of diffusion paths. The applicability of this procedure should, however, be assessed with experimental ternary diffusion paths. An attempt to test this method for the representation of diffusion paths for a hypothetical ternary system with constant diffusion coefficients has recently been made [48] and such tests cannot be conclusive.

6.2. Representation of Quaternary Diffusion Paths.

A set of three partial diffusion paths characterized by a common cross-over composition Y_c was presented in Fig. 10 for a Cu-Ni-Zn-Mn diffusion couple. Since there exist only three independent concentration variables for a quaternary system, only two of the partial diffusion paths are independent and hence a quaternary diffusion path may be represented as a set of two independent plots obtained by plotting two relative concentration variables, Y_1 and Y_2 , as a function of the third one, Y_3 .

Each of the plots in such path representation is S-shaped and consists of two segments, one on either side of the common composition point, Y_c . If the plots

exhibit no maxima or minima, they may be represented analytically on the basis of Y_c and the path slope at Y_c . Based on the procedure discussed in Section 6.1, the two segments for one of the plots (say Y_1 vs. Y_2), may be empirically represented by

$$Y_1^n = Y_c^{n-1} Y_2 \quad (0 \leq Y_i \leq Y_c) \quad (56)$$

and

$$(1-Y_1)^n = (1-Y_c)^{n-1} (1-Y_2) \quad (Y_c \leq Y_i \leq 1) \quad (57)$$

where $1/n$ corresponds to the slope of the plot at Y_c . Similarly, for the plot of Y_1 vs. Y_3 , one can employ the relations:

$$Y_1^m = Y_c^{m-1} Y_3 \quad (0 \leq Y_i \leq Y_c) \quad (65)$$

and

$$(1-Y_1)^m = (1-Y_c)^{m-1} (1-Y_3) \quad (Y_c \leq Y_i \leq 1) \quad (66)$$

where $1/m$ corresponds to the slope of the plot at Y_c .

Raising the power on both sides of Eq. (56) by m and the power on both sides of Eq. (65) by n and dividing one by the other, one gets a relation between Y_2 and Y_3 given by:

$$Y_2^m = Y_c^{(m-n)} Y_3^n \quad (0 \leq Y_i \leq Y_c) \quad (67)$$

Similarly, from Eqs. (57) and (66) one can derive

$$(1-Y_2)^m = (1-Y_c)^{m-n} (1-Y_3)^n \quad (Y_c \leq Y_i \leq 1) \quad (68)$$

An expression linking all the independent concentration variables Y_1 , Y_2 and Y_3 , can be obtained by raising the power for Eq. (56) by $(m-1)$ and the power for Eq. (65) by $(n-1)$ and dividing one by the other. Thus,

$$Y_1^{(m-n)} = Y_2^{(m-1)} / Y_3^{(n-1)} \quad (0 \leq Y_i \leq Y_c) \quad (69)$$

Similarly, from Eqs. (57) and (66) one can show:

$$(1-Y_1)^{m-n} = (1-Y_2)^{m-1} / (1-Y_3)^{n-1} \quad (Y_c \leq Y_i \leq 1) \quad (70)$$

A geometric representation [49] of the composite quaternary diffusion path in 3-dimensions can be made by plotting Y_1 , Y_2 and Y_3 along the three axes of a cube with unit length for the edge. The diffusion path is a space curve on such a plot and describes Y_1 as a function of Y_2 and Y_3 . The curve originates from the origin of the cube where $Y_i = 0$ for each i , cuts through the cube diagonal at Y_c , and terminates at the corner where $Y_i = 1$ for all i . The 3-dimensional path may be

analytically represented by Eqs. (69) and (70). The projections of this path on the $Y_1 - Y_2$, $Y_1 - Y_3$ and $Y_2 - Y_3$ faces of the cube yield the partial diffusion paths similar to those presented in Fig. 10.

The dashed curves in Fig. 10 correspond to the calculated paths [49] on the basis of Eqs. (56,57,65-68). The values of the three path parameters Y_c , $1/n$ and $1/m$ employed in the calculations are 0.74, 0.264 and 0.482, respectively. Such representation of quaternary diffusion paths is possible, provided the two path segments, one on either side of Y_c , can be considered essentially symmetric with a change of scale from Y_c to $1-Y_c$. The main advantage of this approach to quaternary path representation lies in the fact that it by-passes the need for the nine quaternary diffusion coefficients which are hard to determine and utilizes just three characteristic path parameters.

The method of analytical representation presented here for diffusion paths can be extended to systems with larger number of components. For an n -component single phase couple $(n-1)$ path parameters consisting of the cross-over composition Y_c and the path slopes of $(n-2)$ partial diffusion paths at Y_c are required to describe or predict the composite diffusion path.

7. Conclusions

Isothermal diffusion in multicomponent systems can be investigated for interdiffusion fluxes, zero-flux planes and flux reversals, and diffusion paths without the need for data on interdiffusion coefficients.

The concentration profiles of solid-solid diffusion couples in single phase ternary and quaternary systems displayed on the basis of relative concentration variables Y_i exhibit a common cross-over composition Y_c . The cross-over composition can be interpreted as the average relative concentration of each component over the diffusion zone. The ratio $Y_c/(1-Y_c)$ reflects the ratio of the diffusion depths in the two terminal alloys of a diffusion couple.

Zero-flux planes and flux reversals for the individual components can develop in both single phase and multiphase multicomponent diffusion couples. Discontinuous flux reversals for the components can also develop at an interface.

Analytical representations of diffusion paths for both ternary and quaternary couples can be conveniently made on the basis of characteristic path parameters. These parameters correspond to the cross-over composition Y_c and the slopes at Y_c of partial diffusion paths obtained by plotting one relative concentration variable against another. For an n -component single phase couple exhibiting a common cross-over composition the composite diffusion path can be described in terms of $(n-1)$ characteristic path parameters. Such a description of diffusion paths is based on the symmetry of path segments on the two sides of the cross-over composition with a change of scale from Y_c to $1-Y_c$.

Acknowledgment

This work was supported by U.S. Department of Energy under contract DE-AC02-81ER10814.

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1. Introduction

The phenomenon of diffusion in multicomponent alloy systems is of great interest to materials scientists and engineers both from theoretical and practical points of view. Since commercially important metallurgical systems normally contain more than two components, it is essential to develop a theoretical understanding of the interactions among the various components from diffusional as well as thermodynamic considerations. From a practical viewpoint, diffusion often plays a major role in most of the metallurgical processes involving phase changes, precipitation, oxidation, corrosion, etc. Also, the development and stability of diffusion structures in multicomponent, multiphase assemblies is of great practical relevance in processes such as carburizing, aluminizing, diffusion bonding and cladding.

The phenomenological description of multicomponent diffusion has been based on the Onsager's formalism [1,2] of Fick's law extended to multicomponent systems. The simplest of multicomponent systems is a ternary system. There exist in literature several experimental studies of diffusion in ternary systems. These include those that deal with the determination of diffusion data, such as interdiffusion coefficients [3-19], intrinsic diffusion coefficients [4,6,9,12,17,20] atomic mobilities [21-25] and vacancy wind effects [23,24]. Most of these studies have employed pairs of independent ternary diffusion couples with intersecting diffusion paths for the determination of either intrinsic or interdiffusion data at the common composition of the couples. For an n -component system such a procedure requires the use of $(n-1)$ independent diffusion couples for the determination of $(n-1)^2$ concentration-dependent interdiffusion coefficients at one composition. Hence, the determination of diffusion data in multicomponent systems is rather involved and difficult.

An alternative approach [26,27] in the study of isothermal diffusion in multicomponent systems is to analyze the concentration profiles of couples directly for interdiffusion fluxes of all components without invoking Fick's law. Such an analysis for the interdiffusion fluxes by-passes the need for $(n-1)^2$ interdiffusion coefficients and provides a direct insight into the directions as well as magnitudes of the fluxes at any section within the diffusion zone. An initial application of this flux analysis to ternary diffusion couples in the Cu-Ni-Zn system helped identify zero-flux planes (ZFP) and flux reversals for the individual components [26]. At a ZFP the interdiffusion flux of a component goes to zero and normally exhibits a change in direction from one side of the plane to the other. The development of ZFPs has also been identified for ternary diffusion couples in several systems [28] including Cu-Ag-Au, Cu-Zn-Sn, Fe-Ni-Al and Co-Ni-Cr. The ZFP development is dictated by the terminal alloys of a diffusion couple and can occur in both single phase and multiphase assemblies. In addition, discontinuous flux reversals of a component can also occur at an interface in a multiphase system.

One of the objectives of this paper is to review the flux analysis of concentration profiles and the method of identification of ZFPs in isothermal multicomponent