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Thermodynamic and Kinetic Study of Diffusion Paths in the System Cu-Fe-Ni

K.J. RÖNKÄ, A.A. KODENTSOV, P.J.J. VAN LOON, J.K. KIVILAHTI, and F.J.J. VAN LOO

An understanding and modeling of diffusion paths in ternary systems requires a combined thermodynamic and diffusion kinetic approach. The driving force for the intrinsic diffusion of each component is the gradient of the chemical potential (or activity) which can be calculated from the concentration profile if the thermodynamic properties of the system are known. For studying the diffusion behavior in ternary metallic systems, the Cu-Fe-Ni-system was chosen because of its experimental and thermodynamic simplicity. Concentration profiles and diffusion paths in single-phase areas and across an α/β interface were studied experimentally at 1000 °C using the diffusion couple technique. Coefficients for interdiffusion and tracer diffusion have been calculated at the intersection points of two independent diffusion paths with a common composition. A concentration dependence for the tracer diffusion coefficients for each component was calculated and found to be consistent with the literature data in the binary Cu-Ni and Fe-Ni systems. The calculated vacancy flux in the couples was consistent with the experimentally observed marker shift.

I. INTRODUCTION

ADVANCED materials are of increasing importance in modern technology. For the most part, these are complex multicomponent and multiphase materials such as composites or hybrid structures, which require various types of microjoining and bonding operations. Joinability and compatibility of dissimilar materials largely determine the properties and functionability of these multimaterial assemblies. For mass production soldering, brazing or diffusion bonding are frequently employed methods of joining. New applications of advanced materials require the development of joining materials and processes. This can be carried out effectively by first achieving a better understanding and so controlling the interfacial reactions and diffusion processes. In this respect, thermodynamics and a diffusion-kinetic approach combined with detailed microanalysis techniques can be of great help.

Diffusion and chemical reactions at the interfaces play an essential role in bonding as well as in the mechanical, physical, and chemical performance of the joints. It is noteworthy that these time-dependent structural changes are not only observed in the joining process but are also important during storage and in the use of bonded structures. This is of particular importance in soldering, since the operation temperatures are relatively close to the melting points of conventional solder fillers, and therefore, diffusion is still remarkably fast.

For practical purposes, it is advantageous to develop a model for predicting possible diffusion paths in the joint area. However, in multicomponent systems, the existence of a liquid phase and grain boundary diffusion, as well as

the lack of data on mobility or thermodynamic data, makes a reliable prediction of actual diffusion paths very difficult. Therefore, the relatively simple Cu-Fe-Ni system was chosen in this article to study the diffusion in two-phase systems. Results of this model system will be subsequently applied to more complex systems such as Cu-Ag-Sn, Cu-Ag-Zn, and Cu-Sn-Zn, which are of great interest for brazing and soldering applications. Furthermore, the Cu-Fe-Ni system has the advantage of a wide range of compositions that can be chosen as starting materials in the diffusion couples, and moreover, thermodynamic and kinetic data are fairly well known. It is emphasized, however, that despite their thermodynamic simplicity, the solid solutions of the Cu-Fe-Ni system are not ideal.

The recent development of thermodynamic computer software and data banks provides a much better basis for avoiding the assumption of ideal behavior of solid solutions used commonly in diffusion analysis. Knowing the activities of components as a function of composition and temperature, it is possible to use the gradients of chemical potentials as driving forces for diffusion. This also allows the derivation of intrinsic diffusion properties if the atomic mobilities of each component are available as a function of composition.

II. THEORETICAL BACKGROUND

The limited amount of study in multicomponent systems is, first, due to a lack of reliable analytical and numerical methods for the calculation of interdiffusion, intrinsic diffusion, and tracer diffusion coefficients and their concentration dependence, and second, due to a lack of thermodynamic data.

Analytical methods for calculating diffusion paths and other diffusion properties can be used only when the interdiffusion coefficients are assumed to be constants. Many equations and solutions available in the literature are based on the use of error functions. The assumption of constant interdiffusion coefficients is reasonable in diffusion couples with a relatively small composition difference be-

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tween the terminal alloys. Solutions based on error functions produce symmetric concentration profiles on both sides of the Matano plane unless modified mathematical models are used, for example, as done by van Loo *et al.*^[6] and Thompson and Morral.^[7,8] Therefore, numerical methods are needed, in most cases, to describe the diffusion properties in diffusion couples with concentration-dependent diffusion coefficients and/or large concentration differences. For reliable calculations, the thermodynamic assessment of the system and the concentration dependence of the tracer diffusion coefficients in each phase have to be known.^[9] Other types of approaches such as the atomistic treatment based on the path probability method by Sato^[10] or studies based on "zero-flux planes,"^[11] have also been suggested.

One problem in multicomponent diffusion is the prediction of the diffusion path between the two terminal alloys. By definition, the diffusion path is a line from one terminal alloy to another on the ternary isotherm, corresponding to the locus of the average composition in planes parallel to the original interface throughout the diffusion zone. The diffusion path is dependent on the gradient of chemical potentials and the mobilities of each component, taking into account the mass-balance requirement. If the mobilities of all components are nearly equal and concentration independent, the effect of the thermodynamic driving forces dominates the course of the diffusion path.

The diffusion path reflects the morphology of the diffusion area. If phases are separated by planar interfaces, the diffusion path crosses the two-phase region along a tie-line, and along the entire interface, the same local equilibrium can be assumed. This is not necessarily the case: regions of supersaturation can be formed near the interface. This implies an interface which is thermodynamically unstable, developing wavy interfaces or isolated precipitates. The diffusion path then crosses the tie-lines in the two-phase area. These unstable interfaces can be described by the "virtual paths" suggested by Kirkaldy and Brown.^[12] Rapp *et al.*^[13] used a simple model to predict whether, in displacement-type diffusion couples, single-phase layers separated by planar interfaces or two-phase product layers will be formed.

Van Loo *et al.*^[14] have shown that it is possible to predict qualitatively the layer sequence and morphology in diffusion couples by using kinetic and thermodynamic data on a ternary system. The basic assumption is that no element can diffuse intrinsically against its own activity gradient. If a maximum is found experimentally in the activity profile of a component, this is caused by the intrinsic movement of the other two components.

For reliable diffusion analyses as well as for predictive calculations, data for the interdiffusion, intrinsic diffusion, and/or tracer diffusion coefficients and their concentration dependence have to be known. In ternary systems, the four relevant interdiffusion coefficients and six intrinsic diffusion coefficients have different values dependent on which component is taken as the dependent concentration variable. The tracer diffusion coefficients, in this sense, are preferable. Besides, thermodynamic data for the system have to be known for the calculation of the chemical potentials of each component as a function of composition at constant temperature and pressure. In this section, a method for calculating the three tracer diffusion coefficients in a substitutional ternary system at the intersection points of two diffusion paths is presented.

Kirkaldy^[15] has demonstrated the extension of the Boltzmann-Matano analysis to multicomponent systems. In the ternary case, the four relevant interdiffusion coefficients can be calculated from two independent diffusion couples which have one point with a common composition. This method was first used by Ziebold and Ogilvie in the Cu-Au-Ag system.^[2] In order to get information about the concentration dependence of the interdiffusion coefficients, numerous diffusion couples have to be studied. In multicomponent systems with $n \geq 4$, this method is apparently useless because of the enormous amount of experiments required.^[16] Data on interdiffusion coefficients and diffusion paths can be found on several ternary systems, as reviewed recently by Dayananda.^[17]

The determination of the six intrinsic diffusion coefficients, D_i^* , has been presented by Lane and Kirkaldy.^[18] In the literature, such studies are limited to the cases Fe-Co-Ni,^[19] Cu-Zn-Mn,^[20,21,22] Ag-Zn-Cd,^[23] and Cu-Mn-Ni.^[24] The calculation of intrinsic diffusion coefficients in nonideal and concentrated multicomponent systems has been limited by a lack of reliable thermodynamic data.

In a ternary system, the Onsager's phenomenological diffusion coefficients form an L (3×3) matrix.^[25] Since it is reasonable to assume that in substitutional alloys the metal atoms diffuse only by exchange with the neighboring vacancies, the frequency of direct atom interchanges is small compared with atom-vacancy interchanges.^[26,27] If vacancies are in equilibrium in the system and the contributions of vacancy wind and correlation effects are neglected, it is possible to eliminate the nondiagonal elements in the L_{ij} matrix. Related to the Kirkendall frame of reference, the intrinsic diffusion fluxes J_i ($\text{mol cm}^{-2} \text{ s}^{-1}$) can then be written as^[1]

$$\begin{aligned} J_1 &= -L_{11} \frac{\partial \mu_1}{\partial x} = -D_{11} \frac{\partial c_1}{\partial x} - D_{12} \frac{\partial c_2}{\partial x} \\ J_2 &= -L_{22} \frac{\partial \mu_2}{\partial x} = -D_{21} \frac{\partial c_1}{\partial x} - D_{22} \frac{\partial c_2}{\partial x} \\ J_3 &= -L_{33} \frac{\partial \mu_3}{\partial x} = -D_{31} \frac{\partial c_1}{\partial x} - D_{32} \frac{\partial c_2}{\partial x} \end{aligned} \quad [1]$$

where c_i is the concentration (mol cm^{-3}), x the distance parameter (cm), μ_i the chemical potential (J mol^{-1}), and D_{ij} the intrinsic diffusion coefficient ($\text{cm}^2 \text{ s}^{-1}$). For the relation between phenomenological diffusion coefficients L_{ij} and tracer diffusion coefficients D_i^* , Darken^[28] and LeClaire^[27] have derived the equation

$$L_{ii} = \frac{c_i D_i^*}{RT} \quad [2]$$

This leads to

$$J_i = -\frac{c_i D_i^*}{RT} \frac{\partial \mu_i}{\partial x} = -\frac{N_i D_i^*}{RT V^m} \frac{\partial \mu_i}{\partial x} \quad [3]$$

where N_i is the atomic fraction of component i and V^m is the molar volume ($\text{cm}^3/\text{mole of atoms}$), assumed to be constant in this analysis. The activity a_i is related to the chemical potential, μ_i , through the equation

$$\mu_i = \mu_i^\circ + RT \ln a_i \quad [4]$$

which leads to

$$J_i = \frac{D_i^*}{V^m} \frac{N_i}{a_i} \frac{\partial a_i}{\partial x} = -\frac{D_i^*}{V^m} \frac{1}{\gamma_i} \frac{\partial a_i}{\partial x} \quad [5]$$

where $\gamma_i = a_i/N_i$ is the activity coefficient of component i . The relationship between the interdiffusion fluxes, $\tilde{J}_i$, and the intrinsic diffusion fluxes, J_i , is given by^[6]

$$\tilde{J}_i = J_i - N_i \sum_{j=1}^3 J_j \quad [6]$$

The interdiffusion fluxes related to the Matano plane can be derived as a function of interdiffusion coefficients, $\tilde{D}_{ij}$, and concentration gradients or as a function of tracer diffusion coefficients and chemical potential gradients as follows:

$$\begin{aligned} \tilde{J}_1 &= -\frac{\tilde{D}_{11}^3}{V^m} \frac{\partial N_1}{\partial x} - \frac{\tilde{D}_{12}^3}{V^m} \frac{\partial N_2}{\partial x} \\ \tilde{J}_2 &= -\frac{\tilde{D}_{21}^3}{V^m} \frac{\partial N_1}{\partial x} - \frac{\tilde{D}_{22}^3}{V^m} \frac{\partial N_2}{\partial x} \end{aligned} \quad [7]$$

$$\tilde{J}_3 = -\tilde{J}_1 - \tilde{J}_2$$

or (through Eqs. [3] and [6])

$$\begin{aligned} \tilde{J}_1 &= -\frac{N_1 D_1^*}{RTV^m} \frac{\partial \mu_1}{\partial x} + N_1 \left(\frac{N_1 D_1^*}{RTV^m} \frac{\partial \mu_1}{\partial x} + \frac{N_2 D_2^*}{RTV^m} \frac{\partial \mu_2}{\partial x} + \frac{N_3 D_3^*}{RTV^m} \frac{\partial \mu_3}{\partial x} \right) \\ \tilde{J}_2 &= -\frac{N_2 D_2^*}{RTV^m} \frac{\partial \mu_2}{\partial x} + N_2 \left(\frac{N_1 D_1^*}{RTV^m} \frac{\partial \mu_1}{\partial x} + \frac{N_2 D_2^*}{RTV^m} \frac{\partial \mu_2}{\partial x} + \frac{N_3 D_3^*}{RTV^m} \frac{\partial \mu_3}{\partial x} \right) \end{aligned} \quad [8]$$

$$\tilde{J}_3 = \tilde{J}_1 - \tilde{J}_2$$

Using the Matano-Boltzmann analysis for the multicomponent system,^[15,29] the interdiffusion fluxes can be calculated from the experimental diffusion profile

$$\tilde{J}_i = \frac{1}{2tV^m} \int_{N_i(x)}^{N_i^0} x dN_i \quad [9]$$

where the origin ($x = 0$) coincides with the Matano interface.

When the tracer diffusion coefficients are known, the vacancy flux can be calculated from the equation

$$J_v = -\sum_{j=1}^3 J_j = \frac{N_1 D_1^*}{RTV^m} \frac{\partial \mu_1}{\partial x} + \frac{N_2 D_2^*}{RTV^m} \frac{\partial \mu_2}{\partial x} + \frac{N_3 D_3^*}{RTV^m} \frac{\partial \mu_3}{\partial x} \quad [10]$$

At the original (Kirkendall) plane, the vacancy flux is related to the marker shift, Δx_m , by the relation

$$\frac{\Delta x_m}{2t} = V^m J_v \quad [11]$$

Using thermodynamic data, an experimental composition profile can be converted to a profile of activity or chemical potential. At an intersection point of two independent diffusion profiles, the values for the interdiffusion fluxes in Eq. [9] can be obtained and the four interdiffusion coefficients in Eq. [7] or the three tracer diffusion coefficients in Eq. [8] can be calculated. If one component

has an extremum in its activity profile, one term in Eq. [8] can be neglected and two tracer diffusion coefficients can be calculated at this point from a single diffusion profile.

In all analyses, one has to remember that $\sum_i N_i = 1$, $\sum_i \tilde{J}_i = 0$, and $\sum_i N_i d\mu_i = 0$ (Gibbs-Duhem), which means that according to Eq. [3], $\sum_i \frac{J_i}{D_i^*} = 0$.^[21]

If experimentally determined concentration-penetration ($N_i - x$) curves are converted into $(\mu_i - x)$ or $(a_i - x)$ curves, it is possible that the extrema in these curves will be found. Applying Eq. [1] to these curves will give rise to intrinsic fluxes, J_i , which are positive on one side and negative on the other side of this extremum. On the other hand, van Loo^[6] used another concept in which he introduced "intrinsic" diffusion fluxes, J_i , which are independent of each other and always directed from higher activity of a component in one end member to lower activity in the other end member. Extrema in the activity curves of one component are then caused by the interaction with the intrinsic fluxes, J_j , of the other components, which are also only positive or only negative. This definition was used for predictions of diffusion curves from known tracer diffusion coefficients in thermodynamically ideal systems, but it is less useful in our case in which an experimental curve has to be used to calculate these diffusion coefficients. Therefore, we will further use the dependent intrinsic fluxes, J_i (without prime), as defined in Eq. [1], with the knowledge now that these fluxes, in principle, can change sign because of the occurrence of extrema. The relation between these two flux definitions is presented in the Appendix.

In the ternary Cu-Fe-Ni system, the effects of volume changes due to mixing are negligible^[30] and a constant average value for the molar volume ($V^m = 6.9 \text{ cm}^3/\text{mole}$ of atoms) can be used. The grain size is large enough (average about $100 \mu\text{m}$) to eliminate the effect of grain boundary diffusion in the entire diffusion zone.

III. EXPERIMENTAL PROCEDURE

Copper (99.99 pct purity), iron (99.98 pct), and nickel (99.98 pct) supplied by Goodfellow, (Cambridge, United Kingdom) were used as initial materials. A number of binary (Cu-Ni, Fe-Ni, and Fe-Cu) and ternary (Cu-Fe-Ni) alloys were prepared in an arc furnace under argon using a nonconsumable tungsten electrode. The ingots were remelted five times to improve their homogeneity. The specimens were annealed in an electroresistance furnace in evacuated quartz ampoules at 1000°C for 250 to 530 hours and quenched in water.

The diffusion couples were prepared and heat treated in a vacuum furnace (5×10^{-6} mbar) under an external load of 2 MPa. After annealing and standard metallographic preparation, the diffusion couples and equilibrium alloys were examined with light microscopy, scanning electron microscopy, and electron probe microanalysis. Small particles ($0.5 \mu\text{m}$) of hafnium dioxide or aluminum oxide were used as inert markers between the initial materials prior to heat treatment.

Table I. Compositions (in Atomic Percent) of Ternary Alloys Annealed at 1000 °C for 530 Hours

Alloy	Initial	Phase 1	Phase 2
1	50Cu-40Fe-10Ni	9Cu-76Fe-15Ni	91Cu-5Fe-4Ni
2	55Cu-25Fe-20Ni	20Cu-48Fe-32Ni	79Cu-9Fe-12Ni
3	53Cu-21Fe-26Ni	36Cu-31Fe-33Ni	66Cu-14Fe-20Ni
4	55Cu-15Fe-30Ni	single phase	
5	55Cu-12Fe-33Ni		
6	39Cu-20Fe-41Ni

(a)

(b)

Fig. 1—Backscattered electron images of some ternary Cu-Fe-Ni alloys after annealing at 1000 °C for 530 h and quenching. (a) Alloy 53Cu-21Fe-26Ni consists of two phases: 36Cu-31Fe-33Ni with dark contrast and 66Cu-14Fe-20Ni with light contrast. (b) Alloy 55Cu-15Fe-30Ni shows the single-phase structure.

IV. RESULTS AND DISCUSSION

A. Miscibility Gap in the Cu-Fe-Ni System at 1000 °C

Results of the investigation of equilibrated ternary Cu-Fe-Ni alloys are summarized in Table I. The alloy of composition 53Cu-21Fe-26Ni (at. pct) still lies inside the miscibility gap at 1000 °C. This is revealed by the two-phase microstructure of this alloy after heat treatment and quenching in water (Figure 1(a)). On the contrary, the alloy of composition 55Cu-15Fe-30Ni shows the one-phase mi-

Fig. 2—The miscibility gap in the Cu-Fe-Ni-system at 1000 °C based on the experimental results and the thermodynamic reassessment in the present work (the solid curve) compared with the original assessment^[31] (dashed curve). The nominal compositions of the initial alloys (●) are given in Table I.

crostructure after annealing at the same condition and quenching (Figure 1(b)). Based on electron microprobe analysis of the phases in the alloys, the direction of the tie-lines within the two-phase region and the boundary of the miscibility gap in the Cu-Fe-Ni system at 1000 °C were established (Figure 2).

The thermodynamic calculations on the Cu-Fe-Ni system at 1000 °C are based on the critical assessment of Jansson.^[31] In this evaluation, Jansson has used experimentally determined activities in the binary as well as in the ternary systems at 1000 °C. On the basis of our new experimental solubility results, the ternary system was re-evaluated with a thermodynamic computer program^[32] by optimizing only the ternary parameters in the fcc phase, which leads to a fair agreement between the calculated and experimental boundaries of the miscibility gap, as shown in Figure 2.

The large miscibility gap in the binary Cu-Fe system is a result of a repulsive interaction between copper and iron atoms (the activity coefficient is larger than one). In the Cu-Ni system, the interaction between copper and nickel is also repulsive but not as strong as in case of copper and iron. A miscibility gap exists at low temperatures, but at 1000 °C, copper and nickel are mutually soluble in all compositions. In the Fe-Ni system, the interaction between iron and nickel is slightly attractive. Because of the unequal interactions between copper and nickel vs iron and nickel, the directions of the tie-lines in the two-phase region are not parallel to the Cu-Fe diagram axis but are directed toward the copper-rich corner. The equal activity of nickel at the interface between copper-rich and iron-rich alloys is achieved with a higher concentration of nickel on the iron side. From the direction of the tie-lines, we can predict an "up-hill" diffusion behavior of nickel in diffusion couples between certain copper-nickel alloys and pure iron.

In Figures 3(a) through (c), some calculated isoactivity curves for copper, iron, and nickel at 1000 °C are presented. The activity calculations are based on the pure element reference state at 1000 °C (1 bar). Figure 3 can be applied for

Fig. 3—Calculated isoactivity curves for (a) Cu, (b) Fe, and (c) Ni at 1000 °C. The value of the activity is indicated at the end of each line. The activity calculations are based on the pure element reference state at 1000 °C (1 bar).

Table II. Diffusion Couple Experiments in the Cu-Fe-Ni System at 1000 °C

Diffusion Couple	Time/Hours
Fe vs 85Cu-15Ni	64
Fe vs 85Cu-15Ni	256
Fe vs 70Cu-30Ni	100
Fe vs 50Cu-50Ni	100
50Fe-50Ni vs 85Cu-15Ni	100
65Fe-30Ni-5Cu vs 30Cu-65Ni-5Fe	196
Cu vs 85Fe-15Ni	196
Cu vs 75Fe-25Ni	196
Cu vs 50Fe-50Ni	196
Cu vs 25Fe-75Ni	196

Fig. 4—The experimentally determined diffusion paths in Cu-Fe-Ni system at 1000 °C. The intersection points are indicated by capital letters. For comparison, the calculated miscibility gap is shown by a dashed line.

estimations of the driving forces and intrinsic fluxes. It is difficult to estimate the absolute accuracy of these isoactivity curves in the whole composition range in view of the way they are calculated, but this does not affect the main conclusions of the present work.

The diffusion couples investigated in the present work and the experimentally determined diffusion paths in the Cu-Fe-Ni system at 1000 °C are given in Table II and Figure 4, respectively. The intersection points used for calculations have been indicated.

The time dependence of the penetration plot was studied in the diffusion couple Fe-85Cu-15Ni, which was annealed for two different annealing times. The plot of the concentration profile as a function of $\lambda = x/\sqrt{t}$ (m s^{-1/2}) was found to be invariant within the experimental error. The general trend of the diffusion paths in Figure 4 is clearly determined by the miscibility gap leading to an uphill diffusion behavior of nickel.

In the diffusion couples of the Cu-Fe-Ni system, the interfaces in all cases, were planar; therefore, two-phase areas were crossed along a tie-line and the activities of each component were the same within the experimental errors on both sides along the entire interface (reference state: fcc). Because the thermodynamic assessment is quite reliable, the requirement of equal activities can actually be

Table III. The Calculated Tracer Diffusion Coefficients and Interdiffusion Coefficients of Copper, Iron, and Nickel at the Intersection Points Indicated by Capital Letters in Figure 4

Point	N_{Cu}	N_{Fe}	N_{Ni}	D_{Cu}^* (cm ² /s) $\times 10^{11}$	D_{Fe}^* (cm ² /s) $\times 10^{11}$	D_{Ni}^* (cm ² /s) $\times 10^{11}$	$D_{\text{CuCu}}^{\text{Ni}}$ (cm ² /s) $\times 10^{11}$	$D_{\text{CuFe}}^{\text{Ni}}$ (cm ² /s) $\times 10^{11}$	$D_{\text{FeCu}}^{\text{Ni}}$ (cm ² /s) $\times 10^{11}$	$D_{\text{FeFe}}^{\text{Ni}}$ (cm ² /s) $\times 10^{11}$
Ba	0.84	0.025	0.135	150	34	7	20	6	-8	30
Bb	0.84	0.025	0.135	130	32	10	19	4	3	32
Ca	0.805	0.075	0.125	120	33	18	3	0	7	16
Cb	0.805	0.075	0.125	210	38	22	2	-5	14	31
D	0.81	0.03	0.16	110	17	13	16	19	0	10
E	0.69	0.065	0.245	46	17	7	4	1	4	16
F	0.66	0.095	0.245	23	17	7	1	-1	6	16
G	0.42	0.16	0.42	13	4	3	3	4	2	5
H	0.195	0.245	0.56	5.2	1.8	3.4	2	1.5	1	3
I	0.205	0.34	0.455	3.0	3.1	4.1	2	1.5	0.5	1.5
J	0.085	0.445	0.47	2.5	2.2	3.4	1.6	0.4	-0.3	0.9
Ka	0.185	0.505	0.31	1.1	1.1	0.9	0.7	0.3	0.5	1.1
Kb	0.20	0.50	0.30	2.0	5.2	1.4	0.8	0.3	0.6	1.3
L	0.14	0.52	0.34	1.4	2.8	0.2	0.6	0	0.5	1.2
M	0.10	0.53	0.37	1.0	0.9	0.4	0.6	0.1	0.2	0.7
N	0.06	0.53	0.41	0.8	0.8	0.5	0.5	0.05	0.2	0.7
Oa	0.06	0.77	0.17	0.8	2.8	0.3	0.4	-0.04	0.04	0.2
Ob	0.06	0.77	0.17	0.7	2.5	0.2	0.4	-0.03	-0.1	0.4
P	0.055	0.76	0.185	0.6	1.3	0.2	0.4	0.01	0.02	0.3
Q	0.045	0.755	0.20	0.5	0.4	0.2	0.4	0.02	0.06	0.2

used to obtain the correct interfacial composition when extrapolating the concentration profiles to the interface.

The direction of the tie-lines in the two-phase area strongly affects the course of the diffusion path followed inside the single-phase area before reaching the two-phase area. Which tie-line is chosen is of course also dependent on the kinetics. The shapes of the diffusion paths outside the miscibility gap resemble those touching the two-phase region. When the diffusion path in the single phase runs very close to the critical point of the miscibility gap, the intrinsic fluxes actually converge to zero because the diffusion path runs almost parallel to the isoactivity lines. In the diffusion profile, this part has a very steep concentration gradient. This behavior greatly helps qualitative predictions of diffusion paths and penetration curves.

B. Calculated Tracer Diffusion Coefficients

Using Eq. [8] and the method described in Section II, the three tracer diffusion coefficients have been calculated at the intersection points shown in Figure 4. The results of these calculations are presented in Table III and graphically in Figures 5(a) through (c), where the tracer diffusion coefficients of copper, iron, and nickel are plotted as a function of the atomic fraction of copper (circles). Some data points in the graphs have been calculated in cases where the chemical potential gradient of copper is equal to zero. Estimated average uncertainties for the tracer diffusion coefficients and interdiffusion coefficients are ± 50 and ± 100 pct, respectively (Section D).

The results show clearly the generally ignored concentration dependence of the mobilities. In the Cu-Fe-Ni system, the variation in interdiffusion, intrinsic diffusion, and tracer diffusion coefficient can be as large as 3 decades.

As a general tendency, the mobilities of each component increase strongly as the copper content increases. The difference in the mobilities in high-copper and low-copper al-

loys is roughly 3 decades. The mobility values are actually dependent on two concentration variables. This can be seen in the scattering of data points in Figure 5 with low-copper concentrations. The higher values are from intersection points with higher nickel content, and as the iron content increases, the tracer diffusion coefficients of all three components decrease.

Some tracer diffusion data found in the literature for binary Cu-Ni and Fe-Ni systems^[23] at 1000 °C are shown in Figures 5(a) through (c) as triangles. Good consistency with the calculated values was found. According to the data, copper is the most mobile component in copper-rich alloys followed by iron and nickel. In iron-rich alloys, iron is about as mobile as copper with nickel being again the slowest. In copper-rich alloys, the diffusion is about 2 decades faster than in nickel-rich and 2 to 3 decades faster than in iron-rich alloys. This is observed also in experimental diffusion profiles where, at Fe-rich compositions, the concentration gradients are steep, and therefore, the extent of this part of the diffusion zone is small.

At some points (B, C, K, and O), the calculations were carried out using the profile of the diffusion couple Fe vs 85Cu-15Ni with two different annealing times. The calculated tracer diffusion coefficients seem to be less sensitive to experimental deviations than the interdiffusion coefficients and therefore should be preferred.

C. Predictions of Diffusion Paths in Ternary Solid-State Diffusion Couples

If one knows the mobilities as a function of composition as well as the thermodynamic description, it is possible to calculate the entire diffusion path if there is a sophisticated program available, such as that in Reference 9. For many applications, however, it is enough to have an estimation of in which direction the diffusion path will start.

The dependent intrinsic fluxes in Eq. [5] are dependent

Fig. 5—The tracer diffusion coefficients of (a) copper, (b) iron, and (c) nickel (circles) as a function of the atomic fraction of copper calculated at the intersection points at 1000 °C. The literature data in binary Cu-Ni and Fe-Ni alloys^[33] have been calculated from Arrhenius plots and are presented as triangles. The values in the binary Fe-Ni system are shown on the axis, $N_{\text{Cu}} \rightarrow 0$. The highest values are in pure nickel and the lowest in pure iron.

on the tracer diffusion coefficients and the driving forces. In binary systems, the driving force term is the same for both elements everywhere in the diffusion couple, and the intrinsic or tracer diffusion coefficients can be used directly to determine which component is diffusing fastest. In a ternary system, the driving force of each component can differ greatly. Therefore, if a component has the greatest mobility, it does not necessarily have the largest intrinsic flux. Indeed, the intrinsic flux is the essential quantity in determining, for example, the Kirkendall movement.

In a thermodynamically ideal system, a diffusion path is always S-shaped. If the mobilities of the elements are constant but different, the path can be predicted using the model of van Loo.^[6] The starting direction of the diffusion

Fig. 6—The concentration profiles (above) and the activity profiles (below) in the diffusion couple Fe vs 70Cu-30Ni, annealed 100 h at 1000 °C. Notice the strong up-hill diffusion of nickel against its own concentration gradient. The activity curve instead goes “correctly” downward. In the copper-rich alloy, a “pileup” of both concentration and activity of copper is observed. The vacancy flux goes from right to left. The positions of the Kirkendall and Matano planes are indicated by the letters K and M.

path can qualitatively be estimated without any calculation. If, for instance, in a couple AB vs C the mobilities are in the sequence $D_A > D_B > D_C$, then the diffusion path has to start from AB in the B-rich direction and from end member C in the A-rich direction. This fixes, in principal, the S-shaped diffusion path.

If the interdiffusion coefficients are constant, a prediction method based on the direction of the major and minor eigenvectors can be used.^[7,9] As far as the nonideality in the system increases and/or the differences in mobilities decrease, the driving force term in Eq. [5] becomes more important.

The prediction is then more intricate, as will be shown by an analysis of two diffusion couples taken from the Cu-Fe-Ni system. In Figure 6, the concentration and the corresponding converted activity profiles of the diffusion couple Fe vs 70Cu-30Ni are presented. The concentration and activity profiles of the diffusion couple 75Ni-25Fe vs Cu are shown in Figure 7. In Figure 6, the concentration and activity of copper in the 70Cu-30Ni alloy are increased when compared to the values in the terminal compositions. The same behavior is found for iron in the 75Ni-25Fe alloy in Figure 7. In both cases, the diffusion path from the alloy starts in the direction of lower nickel content (Figure 4). So, in locations on a diffusion couple where two components are diffusing away from an alloy, the component with

Fig. 7—The concentration profiles (above) and the activity profiles (below) in the diffusion couple 75Ni-25Fe vs Cu, annealed 196 h at 1000 °C. A pileup of iron concentration and activity is found. The direction of the vacancy flux is from left to right. The positions of the Kirkendall and Matano planes are indicated by the letters K and M.

the smaller independent intrinsic flux can form a maximum in its activity curve.^[6] Actually, according to the mobility data, nickel is always the slowest diffusing component, and so, using the predictions for a thermodynamically-ideal system, the diffusion-path should start, in both cases, from the initial alloys in a Ni-rich direction. The opposite is true, as seen from Figure 4, showing that thermodynamic interactions play an important role here!

The dependent intrinsic fluxes, vacancy flux, and interdiffusion fluxes given in Table IV are calculated at the points shown in Figures 6 and 7, corresponding to the intersection points described in Table III, using Eqs. [5], [9], and [10].

In the diffusion couple Fe vs 70Cu-30Ni, the dependent intrinsic flux of iron is dominant and the vacancy flux goes from the 70Cu-30Ni alloy (right) toward pure iron (left). Because only a small amount of copper diffuses into the iron, only a small amount of copper can leave the Cu-Ni alloy, which causes an increase in copper concentration. Because of the strong repulsive interaction between iron and copper, the substitution of nickel by iron increases the activity of copper, causing the maximum in the activity profile of copper.

D. Marker Experiments

The marker movement was studied by using small particles (0.5 μm) of hafnium dioxide and aluminum oxide as inert markers between the initial materials. For the diffusion

couples Fe vs 70Cu-30Ni and 75Ni-25Fe vs Cu, their positions are indicated in Figures 6 and 7. The experimentally observed distances between the Kirkendall and Matano planes were 23 and 70 μm, respectively. Based on the calculated vacancy fluxes in Eq. [11], values of 18 and 113 μm are estimated. It should be stressed that the measured values are completely independent of the thermodynamic and kinetic assessment made in this analysis. Therefore, the agreement can be considered as quite satisfactory. Within the limits of accuracy, an extremum of vacancy flux coincides with the Kirkendall plane and an extremum of interdiffusion fluxes coincides with the Matano plane, as can be expected.^[6]

V. CONCLUSIONS

A diffusion kinetic study in nonideal and substitutional systems with three or more components requires a combined thermodynamic and kinetic approach. The gradients of the chemical potentials of each component, as real driving forces, can be found from experimental concentration profiles when the thermodynamic description of the system is known. At the intersection points of the diffusion paths, the mobility (tracer diffusion coefficient) of each component can be calculated, together with the four interdiffusion coefficients. Together with the data of tracer diffusion coefficients and their concentration dependence, the intrinsic fluxes and vacancy flux can be calculated.

The three tracer diffusion coefficients were calculated in the Cu-Fe-Ni system at 1000 °C using this method, and they were consistent with the literature data in the binary Cu-Ni and Fe-Ni systems. A good agreement was found between the calculated and the independently obtained experimental values for the distance between the Kirkendall and Matano planes.

The diffusion paths in a ternary system with a miscibility gap are strongly influenced by the direction of the tie-lines, even if the entire path is running in a single-phase area.

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APPENDIX

In the following, a relationship between the independent (with prime) and dependent intrinsic variables in the thermodynamically ideal case is presented. In a binary system no difference exists between these variables, and therefore, there is no reason to introduce different definitions for the intrinsic flux. In a ternary system, however, the sum of the independent atomic fractions can differ from unity ($\sum N_i \neq 1$) if the independent intrinsic fluxes are used to describe the diffusion behavior.^[6] This corresponds with an extra expansion or shrinkage of the couple. For the atomic fraction, the following relation can be written:

$$N_i = \frac{N_i'}{\sum_{j=1}^3 N_j'} \quad [A1]$$

Table IV. The Calculated Intrinsic Diffusion, Vacancy, and Interdiffusion Fluxes in Diffusion Couples Fe vs 70Cu-30Ni (Figure 6) and 75Ni-25Fe vs Cu (Figure 7)

Couple	Point	$V^m J_{\text{Cu}}$ (cm/s) $\times 10^{10}$	$V^m J_{\text{Fe}}$ (cm/s) $\times 10^{10}$	$V^m J_{\text{Ni}}$ (cm/s) $\times 10^{10}$	$V^m J_V$ (cm/s) $\times 10^{10}$	$V^m \tilde{J}_{\text{Cu}}$ (cm/s) $\times 10^{10}$	$V^m \tilde{J}_{\text{Fe}}$ (cm/s) $\times 10^{10}$	$V^m \tilde{J}_{\text{Ni}}$ (cm/s) $\times 10^{10}$
Fe vs 70Cu-30Ni	P	-1	29	-4	-25	-2.5	10	-7.5
	L	-1.5	28	-1.5	-24	-5	15	-10
	E	13	17	-7	-23	-1	12	-11
75Ni-25Fe vs Cu	H	-14	-1.5	12	3.5	-12	0	12
	G	-35	-3	11	27	-18	2	16
	E	-72	-3	11	64	-22.5	4	18.5
	D	-84	2	9	73	-21.5	3.5	18
	B	-87	1.5	6.5	79	-21	3.5	17.5

which leads to

$$\frac{\partial N_i}{\partial N_j} = \frac{1}{\sum_{j=1}^3 N_j} \left(1 - N_i \frac{\partial \left(\sum_{j=1}^3 N_j \right)}{\partial N_i} \right) \quad [\text{A2}]$$

The relation between the distance variables x and x' can be expressed as

$$x = x' + \int_{-\infty}^{x'} \left(\sum_{j=1}^3 N_j - 1 \right) dx \quad [\text{A3}]$$

and

$$\frac{dx}{dx'} = \sum_{j=1}^3 N_j \quad [\text{A4}]$$

A relation between the gradients of atomic fraction can be derived from the chain rule

$$\frac{\partial N_i}{\partial x} = \left(\frac{\partial N_i}{\partial N_j} \right) \left(\frac{\partial x'}{\partial x} \right) \left(\frac{\partial N_j}{\partial x'} \right) \quad [\text{A5}]$$

which leads to

$$\frac{\partial N_i}{\partial x} = \frac{1}{\left(\sum_{j=1}^3 N_j \right)^2} \left(1 - N_i \frac{\partial \left(\sum_{j=1}^3 N_j \right)}{\partial N_i} \right) \left(\frac{\partial N_j}{\partial x'} \right) \quad [\text{A6}]$$

If we assume that $D_i^*(N_i) = D_i^*(N_j)$, a relation between the dependent and independent intrinsic fluxes J_i and J_j , respectively, can be expressed as

$$J_i = -\frac{D_i^*}{V^m} \frac{\partial N_i}{\partial x} = J_j \frac{1}{\left(\sum_{j=1}^3 N_j \right)^2} \left(1 - N_i \frac{\partial \left(\sum_{j=1}^3 N_j \right)}{\partial N_i} \right) \quad [\text{A7}]$$

These two fluxes have a different direction if

$$\frac{\partial \left(\sum_{j=1}^3 N_j \right)}{\partial x'} > \frac{1}{N_i} \frac{\partial N_j}{\partial x'} \quad [\text{A8}]$$

and both gradients have the same sign. This means that J_i has a different sign at either side of an extremum in the

activity profile, whereas J_j always has the same direction, viz. from the high-activity end member to the low-activity end member.

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