Effect of Vacancy Flow on Interdiffusion in the Binary Alloy System

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Fick’s first law on binary interdiffusion which is given by $-D \frac{\partial C_i}{\partial X}$ becomes approximate and loses its theoretical ground when vacancies flow. If the Kirkendall effect is observed, therefore, the inter- and intrinsic diffusion coefficients are erroneously determined. The effect of the vacancy flow on the interdiffusion coefficient is not so severe and appears to be within the limit of experimental error as long as a diffusion couple consists of one phase. On the contrary, formation and disappearance of the lattice planes at the interface between distinct phase layers in reaction diffusion affect the vacancy flow, so that the value of the interdiffusion coefficient at a given concentration should vary significantly when the magnitude of the vacancy flow in a given phase markedly depends on the experimental method applied.

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I. Introduction

In general, a binary interdiffusion flux in terms of Fick’s first law is given by

$$J_i = -D \frac{\partial C_i}{\partial X},$$

(1)

where $C_i$ is moles of atom species of $i$ in unit volume and $X$ is a usual distance coordinate. If one intends to derive eq. (1) in relation to the jump frequency and the jump distance of atoms, one may follow to the given procedure(1) providing that the jump frequency and the jump distance are always constant independently of atom species of $i$ and the all atoms have the same probability for jump to the (+) and (−) directions on the $X$ coordinate system. In practice, however, the jump frequency depends on the atom species and the chemical potential gradient under concentration gradient acts on the atoms to move in a given direction. From the point of view Guiraldeq(2) stated that it should be regarded as the large approximation to employ eq. (1) for the binary interdiffusion.

Apart from the problem mentioned above Darken(3), Manning(4) and Heumann(5) have presented the equations which express the relation between self diffusion coefficients and interdiffusion coefficient through the so-called intrinsic diffusivities on the assumption that the interdiffusion coefficient in eq. (1) is correctly evaluated by the Matano method(6). If eq. (1) is only the approximate one by losing theoretical background, the relation between the inter- and self diffusion coefficients must be reexamined.

Fick’s first law is originally published as the empirical rule and its object is allowed to be any of the gas, liquid or solid state. The special diffusion mechanism which is not common among the three states and some kinds of forces acting on atoms may yield the deviation from the law. In this paper the authors start from the reconfirmation of Matano method and Darken’s analysis and then consider the invalid case of eq. (1) in binary alloy system.

II. Reconfirmation of Matano Method and Darken Analysis

For simplicity the partial molar volumes, $\bar{V}_1$ and $\bar{V}_2$ of species 1 and 2 are set to be constant

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and equal to each other, so that the total molar volume \( V \) of alloy is kept constant irrespective of the composition. When the necessary conditions for applying the Matano method are satisfied, the interdiffusion flux can be determined. If the plane normal to \( X \) axis has the concentration, \( C^* \), for example, the flux across a unit area of the plane is given by

\[
-\bar{D} \frac{\partial C_1}{\partial X} = \frac{1}{2t} \int_{(C_0)}^{C_1} X dC_1,
\]

where \( t \) is diffusion time. The right term in eq. (2) is obtained by graphical integration of \( C_1 - X \) curve. The magnitude of the flux given by the left term in eq. (2) reaches a maximum at Matano interface, decreasing with increase of the distance between the reference plane and the Matano interface and becomes zero in the semi-infinite region. Here, the remarkable fact under the condition, \( V_1 = V_2 \), is that the following equation holds:

\[
\bar{D} \frac{\partial C_1}{\partial X} + \bar{D} \frac{\partial C_2}{\partial X} = 0. \tag{3}
\]

When \( C_2 - X \) curve is drawn and the flux, \( -\bar{D} \partial C_2/\partial X \), at the concentration, \( C^* = (1/\bar{V}) - C^* \), is evaluated, it is clear that eq. (3) holds between both fluxes as to species 1 and 2. Under the conditions considered the fluxes across the planes normally fixed with respect to the \( X \) axis must always satisfy eq. (3). Because this means that the volume of a diffusion couple does not change before and after diffusion annealing and the number of atoms in a unit volume of the couple is kept constant, outflow or inflow of atom species 1 from a given volume element yields the respective inflow or outflow of species 2 in the same magnitude.

Darken\(^{(3)}\) has presented the intrinsic flux, \( -D_i \partial C_i/\partial X \), as the flux with respect to the marker fixed plane moving with the velocity, \( \omega \), relative to the Matano coordinate system, along the following equation,

\[
-\bar{D} \frac{\partial C_i}{\partial X} = -D_i \frac{\partial C_i}{\partial X} + C_i \omega \tag{4a}
\]

where \( D_i \) is the so called intrinsic diffusion coefficient. The movements of atom species 1 and 2 at lattice point usually proceed at the different rates which directly relate to the fluxes across lattice plane. At the present time, therefore, it is believed that the marker is fixed relative to lattice plane and \( -D_i \partial C_i/\partial X \) corresponds to the atom movement by diffusion.

When the flux relative to the Matano coordinate system, \( -\bar{D} \partial C_i/\partial X \), is given by \( J_i \) and the flux relative to the marker fixed plane, \( -D_i \partial C_i/\partial X \), is given by \( j_i \), two equations as to \( i = 1, 2 \) are expressed by

\[
J_1 = j_1 - C_1 \left( -\frac{j_1 + j_2}{C_1 + C_2} \right) \tag{4b}
\]

\[
J_2 = j_2 - C_2 \left( -\frac{j_1 + j_2}{C_1 + C_2} \right). \tag{4c}
\]

Because of the equality of \( \omega \) in eq. (4a) with the parenthesized terms in eqs. (4b, c), the lattice plane moves with the velocity, \( \omega \), due to the net atomic flow across the lattice plane. This thought arises from that the sum of the left side terms in eqs. (4b, c) becomes zero. Even if Kirkendall effect is practically detected, therefore, the Matano coordinate system cannot have the net atomic flux. Since its reference plane does not coincide with the lattice plane except for the particular case where \( D_1 \) is identical with \( D_2 \), the flux, \( -\bar{D} \partial C_i/\partial X \), does not directly relate to the real atom movement and the interdiffusion coefficient can not be expressed in terms of the real jump frequencies and distance.

A given number of atoms is accomodates in a given size of volume element under the condition \( \bar{V}_1 = \bar{V}_2 \), so that the flowout of atom species 1 from the volume element is just the same as the flowin of atom species 2 in number. The magnitude of the interdiffusion flux depends on \( \bar{D} \) and \( \partial C_i/\partial X \), where \( \bar{D} \) need not be constant. Accordingly, Fick's first law is valid as long as eq. (3) holds, even though the gradient of chemical potential acts on the atoms as the driving force for atom movement.

Substitution of \( -\bar{D} \partial C_i/\partial X \) for \( J_i \) and \( -D_i \partial C_i/\partial X \) for \( j_i \) in eqs. (4b) or (4c) and employment of \( N_i \) (mole fraction of \( i \)) = \( C_i / (C_1 + C_2) \) yield Darken's equation as follows:

\[
\bar{D} = N_1 D_2 + N_2 D_1. \tag{5}
\]
III. Vacancy Flux

There are no lattice planes in the gas and liquid states, and also one can not carry out marker experiment in these states. One may imagine, however, the reference planes on the Matano coordinate system and other reference planes which directly relate to respective movement of constituents. The situation is, for example, such that a semi-permeable film as a marker is moving at the rate depending on the quantity of the constituent across the film, relative to the Matano coordinate system. In order to account for the diffusion phenomenon, Darken(3) has tried to introduce the conception about intrinsic diffusion without considering vacancies. On the contrary, Bardeen and Herring(7) have presented the following equations including vacancy flux in addition to the intrinsic fluxes \( j_1 \) and \( j_2 \),

\[
\begin{align*}
    j_1 &= -M_{11} \frac{\partial \mu_1}{\partial X} - M_{12} \frac{\partial \mu_2}{\partial X} - M_{1v} \frac{\partial \mu_v}{\partial X} \tag{6} \\
    j_2 &= -M_{21} \frac{\partial \mu_1}{\partial X} - M_{22} \frac{\partial \mu_2}{\partial X} - M_{2v} \frac{\partial \mu_v}{\partial X} \tag{7} \\
    j_v &= -M_{v1} \frac{\partial \mu_1}{\partial X} - M_{v2} \frac{\partial \mu_2}{\partial X} - M_{v0} \frac{\partial \mu_v}{\partial X} \tag{8} \\
    j_1 + j_2 + j_v &= 0. \tag{9}
\end{align*}
\]

Here, \( M_{ij} \) is the phenomenological coefficient, \( \mu \) is the chemical potential, subscript \( v \) means the vacancy, and \( j_v \) is the vacancy flux relative to the same plane as the reference plane of \( j_1 \) and \( j_2 \).

Equation (9) is rewritten as

\[
-(j_1 + j_2) = j_v. \tag{10}
\]

After publication of eq. (10) it has been widely appreciated that the marker movement bases upon the existence of the vacancy flux besides the net atomic flux. At the same time, the Kirkendall effect has been regarded as the proof showing that diffusion is controlled by the vacancy mechanism. The sum of the left hand terms in eqs. (4b, c), however, needs to be zero still and so that the vacancy flux must not exist on the Matano coordinate system in the same sense that the system can not have the net atomic flux. In practice, the vacancies flow in the same direction as that of the marker movement and this leads to the invalidity of eq. (3). If Kirkendall effect is detected, therefore, the flux, \(-\partial \mu_0 / \partial X\), and then \( D \) as well as \( D_i \) becomes approximate in theory. Accordingly, it matters to know to what extent the vacancy flow affect the inter- and intrinsic diffusion coefficients and this will be discussed in the next section.

IV. Discussion

As is well known, Darken(3) has demonstrated the relation between the intrinsic diffusion coefficient and the self diffusion coefficients. Manning(4) and in more generalized form Heumann(5) have modified the above relation by adding the term arising from the vacancy wind effect. The self and intrinsic diffusion coefficients, the thermodynamic factor and the vacancy wind factor which appear in their papers should be the respective constants at a given concentration in a binary alloy system. Accordingly, the interdiffusion coefficient is also constant through eq. (5). On the contrary, the inter- and intrinsic diffusion coefficients in terms of the argument in the previous section can not be obtained correctly if the vacancies flow. Because of the equality of the vacancy flow with the vacancy wind, it is more rational to consider that the values of the coefficients at a given concentration erroneously vary with the magnitude of the wind. In binary interdiffusion experiment within the concentration range of a solid solution in which the Kirkendall effect is observed, the vacancy fluxes in the vicinity of the terminal concentrations in the diffusion couple consisting of the concentrations 0 and 15% are nearly zero, for example. Because the vacancy flux becomes significant at 15% in the couple consisting of the terminal concentrations 0 and 30%, the values of the inter- and intrinsic diffusivities at the same concentration of 15% may vary with the type of the couple.

A \( \alpha \) solid solution in the Cu–Zn system has a fcc structure in which a vacancy mechanism appears to control diffusion and much interdiffusion experiments have been carried out in the system. Figure 1 shows the interdiffusion
coefficients together with impurity diffusion coefficient of zinc in copper. In Fig. 1 the interdiffusion coefficients in ref. (13) are smaller than those in ref. (14) by 45%. Except for the coefficients in the vicinity of 0 and 30 at\% Zn where error for the estimation of the coefficients appears easily, the distribution of the coefficients at a given concentration is within about ±50% of those in ref. (14), independently of the type of the diffusion couple and the investigators. The distribution of the coefficients in only ref. (14) is about ±20% around the average regardless of the types of the couples, [pure Cu–(30 at\%Zn–Cu alloy), pure Cu–(15 at\%Zn–Cu alloy) and (15 at\%Zn–Cu alloy)–(30 at\%Zn–Cu alloy)]. Because the distribution of ±20% may arise from the estimation errors of concentration by an electron probe microanalyzer and of the differential quotients in eq. (2) when Matano method is applied to $C_i-X$ curve, the effect of the vacancy flow on the coefficients does not seem to be severe in general.

The interdiffusion coefficients at 0 at\%Zn in Fig. 1 is determined by the extrapolation of the relation between the coefficients and the zinc concentration more than 2 at\%. The value of the coefficient is nearly identical to the impurity diffusion coefficient of zinc in copper obtained by use of the radioactive tracer of zinc. If species 1 and 2 in eq. (5) are zinc and copper, respectively, $\bar{D}$ should equal $D_{Zn}$ at the infinite dilute state of zinc. This is the only theoretical ground that accounts for the equality of the coefficients at zero at\%Zn with the impurity diffusion coefficient. From the viewpoint of the effect of the vacancy flow mentioned above, at zero % the coefficient estimated from the extrapolation should be evaluated more accurately when the concentration of another terminal against pure copper decreases as much as possible.

One of the present authors (15) found the Cu$_3$Si (\theta) phase as an only diffusion layer in the Cu–Si couple annealed at the temperatures between 681 and 734 K. Upon formation of the Cu$_3$Si, the voids which appeared between Cu and Cu$_3$Si layers restricted the diffusion of Cu atoms and arrested the growth of the Cu$_3$Si. Application of a uniaxial compressive stress more than 8 MPa to the couple yielded the parabolic growth of the layer without the void formation. After annealing Kirkendall markers were always observed at the interface between the Cu and Cu$_3$Si. From the results it was concluded that the Cu atoms which reached the interface between the Cu$_3$Si and Si were combined to the Cu$_3$Si lattice together with the Si atoms. Accordingly, there were the one-sided diffusion flux of the Cu atoms and an opposite flux of vacancies in the Cu$_3$Si. Moreover, the interdiffusion coefficient in the Cu$_3$Si were the extremely large value of $1.6 \times 10^{-11} \text{m}^2/\text{s}$ at 681 K. Because the Cu$_3$Si consists of the columnar structure parallel to the diffusion direction, Becht (16) has suggested that diffusion in the boundaries between the columnar crystals yields such large diffusion coefficient. It has also reported that the columnar structure and the extremely large coefficient are detected in the Fe–Zn system under a uniaxial compressive stress. (17) Hence, an application of the Matano method to the case where the one-sided diffusion occurs to accompany with the large magnitude of the vacancy flux should bring about the large
diffusion coefficients and such large coefficient may be obtainable by only boundary diffusion under a uniaxial compressive stress. Iijima et al.\(^{(18)}\) demonstrated that the interdiffusion coefficient in a primary solid solution on Au side in the Au–Fe system depended on whether the diffusion couple consisted of the single phase or the two phases, especially when the difference in the interdiffusion coefficients between the phase was remarkably large. When an interface between two phases is moving during reaction diffusion, the lattice planes are freshly formed or disappear at the interface in usual. The resultant formation or disappearance of the vacancies at the interface may affect the diffusion flux and the interdiffusion coefficient.

Recently, Kirkaldy\(^{(19)}\) has discussed the vacancy wind effect by dividing two cases where the vacancies are conserved or not, having stated that Darken’s equation holds when the vacancies are not conserved and the interdiffusion coefficient is not adequate if the vacancies are conserved. Regardless of whether the vacancies are conserved or not, the interdiffusion coefficients become obscure by the effect of the vacancy flow. The inter- and intrinsic diffusion coefficients obtained by experiments, therefore, are not so accurate as they are related to the self diffusion coefficients by considering the vacancy wind effect according to Manning’s analysis.

V. Summary

The vacancy flow or vacancy wind which always yields reverse flow of atoms contradicts that Matano coordinate system must not have net atomic flux providing the constant total molar volume of alloy. If Kirkendall effect is observed, therefore, \(\frac{\Delta \delta C_i}{\delta X}\) as the interdiffusion flux becomes approximate by losing theoretical ground and the intrinsic diffusion fluxes are in the same situation. The effect of the vacancy flow on the interdiffusion coefficients does not appear to be severe as long as the diffusion couple consists of one phase. The coefficients evaluated by experiment, however, are not so accurate as they are related to the self diffusion coefficients by considering the vacancy wind effect introduced by Manning.

In reaction diffusion, formation and disappearance of lattice planes at the interface between distinct phase layers affect the vacancy flow. When magnitude of the vacancy flow in a given phase markedly depends on the experimental method, the values of the interdiffusion coefficients at a given concentration should vary significantly.

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