

INTERFACE MIGRATION AND THE KIRKENDALL EFFECT IN DIFFUSION-DRIVEN PHASE TRANSFORMATIONS

F. J. J. van LOO¹, B. PIERAGGI² and R. A. RAPP³

¹Laboratory of Physical Chemistry, Eindhoven University of Technology, Eindhoven, The Netherlands,

²Laboratoire Métallurgique Physique, UA 445 CNRS, ENSC Toulouse, F-31077 Toulouse, France,

³Department of Materials Science and Engineering, Ohio State University, Columbus, OH 43210, U.S.A.

(Received 27 July 1989)

Abstract—An analysis is presented for the mass and vacancy fluxes within the reacting phases and at the interface for a diffusion-driven phase transformation between disordered binary solid solutions. As decided by the intrinsic diffusion coefficients and the initial and interface concentrations for each phase, vacancies must either be created or annihilated in the bulk phases but also at their interface. A general analysis is formulated for the growth or recession of a phase in terms of the Kirkendall reference frame and this result is compared to the analysis based on the reference frame centered on the number of moles. Specific example calculations demonstrate the various possibilities for vacancy creation/annihilation and for the growth/recession of phases. The growth rate expressed in the Kirkendall reference frame can be found by taking into account the associated vacancy exchanges for the interface reaction.

Résumé—L'analyse des flux de matière et de lacunes, au sein de phases réagissantes et à l'interface, est présentée dans le cas d'une transformation de phase, contrôlée par la diffusion, entre deux solutions solides binaires désordonnées. Selon les valeurs des coefficients intrinsèques de diffusion et des concentrations initiales et interfaciales de chaque phase, des lacunes doivent être créées ou annihilées au sein des phases accolées et également à leur interface. Une analyse générale des conditions de croissance ou décroissance d'une phase donnée, par rapport au repère de Kirkendall associée à cette phase, est présentée et comparée à l'analyse basée sur le repère de Matano (centre du nombre de moles). Les calculs effectués, pour différent cas, mettent en évidence les diverses possibilités de création/annihilation de lacunes et de croissance/décroissance des phases. La vitesse de croissance, dans le repère Kirkendall, peut aussi être déterminée en considérant l'échange de lacunes associées aux réactions interfaciales.

Zusammenfassung—Für eine diffusionsgesteuerte Phasenumwandlung zwischen entordneten binären Mischkristallen werden die Materie- und Leerstellenflüsse in den reagierenden Phasen und an der Grenzfläche analysiert. Wie von den intrinsischen Diffusionskoeffizienten und den Anfangs- und Grenzflächenkonzentrationen für jede Phase bestimmt, müssen Leerstellen im Phasenvolumen und an den Grenzflächen entweder erzeugt oder annihiliert werden. Die Analyse wird allgemein im Kirkendall-Bezugsrahmen für Wachstum oder Schrumpfung einer Phase formuliert; das Ergebnis wird verglichen mit der Analyse, die auf einem Bezugsrahmen auf Basis der Molzahlen aufbaut. Besondere Beispielrechnung zeigen die verschiedenen Möglichkeiten für Leerstellenerzeugung/-annihilation und für Wachstum/Schrumpfung der Phasen auf. Die Wachstumsrate, ausgedrückt im Kirkendall-Rahmen, kann erhalten werden, wenn der entsprechende Leerstellenaustausch bei der Grenzflächenreaktion berücksichtigt wird.

1. INTRODUCTION

For the interdiffusion of solid solutions in a binary isomorphous system (e.g. Cu/Ni, Au/Ag, etc. . .) both theory and experimental interpretations consider that lattice sites are conserved at least far from the free surface [1–3]. Because one component of the binary diffusion couple diffuses faster than the second component, a vacancy flux passes in the direction of the flux of the slower component. The vacancies are both created and annihilated in the metal couple at sources and sinks such as dislocations or internal interfaces (grain boundaries). Otherwise, vacancy condensation

leads to the formation of the well known Kirkendall voids.

The situation is more complex in the case of a migrating interphase interface leading to the growth of one phase and the consumption of another by a vacancy diffusion mechanism. Existing theories [1–8] generally have been restricted to the consideration of bulk diffusion as the rate-limiting step with fixed local equilibrium concentrations at the interfaces. Under these assumptions, the interface displacement or the growth rate depends only on the differences in the interdiffusion fluxes in the two contacting phases at the interface, which generally leads to parabolic

rate behavior. However, because the frame of reference is usually chosen as the Matano (volume fixed) plane, the consideration of vacancy fluxes, sources, and sinks is commonly neglected for multiphase diffusion.

Nevertheless, for fixed interfacial concentrations and given intrinsic diffusivities for the components in the contacting phases, vacancy diffusion is again needed to balance the different intrinsic diffusion fluxes and thereby conserve the lattice sites. Likewise, to accommodate the difference in vacancy fluxes in each phase, any interphase boundary must be able to serve as either a source or sink for vacancies in a manner that has not been clearly demonstrated. The succeeding paper will develop specific models for interfacial creation/annihilation of vacancies and for interface migration/lattice transformation at a semicoherent interphase interface. The purpose of this paper is twofold: (1) to analyze generally the role of vacancy fluxes in multiphase diffusion and interphase boundary migration and (2) to develop and demonstrate conditions for interface migration in a binary two-phase diffusion couple. A preliminary presentation of this analysis has been made previously [9].

2. ANALYSIS OF DIFFUSION FLUXES AND INTERFACE VELOCITY

For the interdiffusion of solid solutions in a binary isomorphous A-B system, unequal diffusion rates of the two components A and B induce a displacement of lattice planes. This displacement generates the well known Kirkendall effect [1-3]. For such isomorphous systems, two types of reference frames can be used in the analysis: (i) the frame centered on the number of moles (number-fixed frame), denoted as the N-frame in the following, (ii) the Kirkendall-frame which is referred to as the K-frame. Similarly, in the case of a two-phase diffusion couple (Fig. 1), the analysis of the Kirkendall effect would necessitate the use of two different sets of Kirkendall reference frames for the two contacting α and β phases.

The N-frame, common to the α and β phases, is defined by the flux equation

$$\tilde{J}_A^i + \tilde{J}_B^i = 0 \quad (i = \alpha \text{ or } \beta) \quad (1)$$

where $\tilde{J}_j^i$ are the interdiffusion fluxes of the species j (A or B). The fluxes are defined as positive for diffusion from α toward the β phase. The origin of the N-frame is the Matano plane, here defined as the plane separating a constant number of A plus B species.

The K-frames are defined by the flux equation associated with the diffusion in the α and β phases

$$J_A^i + J_B^i + J_V^i = 0 \quad (2)$$

where J_A^i and J_B^i are the intrinsic fluxes of the species A and B, and J_V^i the vacancy flux, associated with lattice plane shift in the i phase (α or β). The lattice plane at the original interface defines the origins of the two K-frames. For diffusion in an isomorphous system, this plane can be experimentally identified by the insertion of inert markers into the interface at $t = 0$, but the situation is more complicated (as discussed later) for a two-phase diffusion couple because of the different rates of lattice plane shift in the two phases.

The interrelation between the N- and K-frames can be described through the relation between the diffusion fluxes of the species j

$$\tilde{J}_j^i = J_j^i + c_j^i v^{K/N} \quad (3)$$

where $v^{K/N}$ is the velocity of the K-frame relative to the N-frame and c_j^i denotes the concentration of species j in phase i in number of atoms per unit volume. The combination of equations (1), (2) and (3) yields

$$\tilde{J}_j^i = J_j^i + X_j^i J_V^i \quad (4)$$

where X_j^i denotes the mole fraction of species j in phase i (see Appendix).

In a system such as that shown in Fig. 1, the interfacial diffusion fluxes of A and B would induce the growth or recession of the α or β phases through the interfacial reactions describing the relative

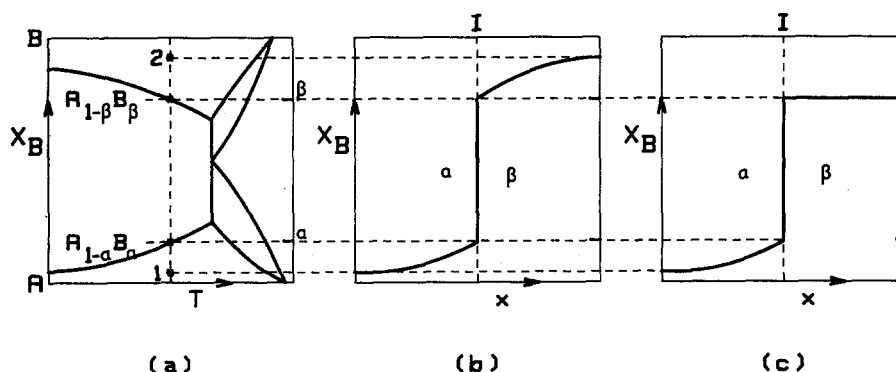


Fig. 1. Schematic representation of (a) phase diagram and concentration profiles for diffusion reactions (b) between two unsaturated compositions (1 and 2), or (c) between one saturated and one unsaturated composition.

transformation of α into β and/or the reverse transformation. In the N-frame, the rate of growth or recession is the rate of change $\dot{N}$ in the total number of A and B atoms per unit diffusion cross-section present in the phases α and β ; this rate would be positive as the α phase grows. The atomic balance, or equivalently the mole number balance, at the α - β interface can be expressed by the usual growth equation

$$(\beta - \alpha) \dot{N} = \bar{J}_{\text{BI}}^{\beta} - \bar{J}_{\text{BI}}^{\alpha} \quad (5)$$

where, as indicated in Fig. 1, α and β are the mole fractions of B in the α and β phases at equilibrium, and $\bar{J}_{\text{BI}}^i$ the interfacial interdiffusion flux of B in phase i . By applying equation (4) to the α and β phases, equation (5) is transformed to

$$(\beta - \alpha) \dot{N} = J_{\text{BI}}^{\beta} - J_{\text{BI}}^{\alpha} + \beta J_{\text{VI}}^{\beta} - \alpha J_{\text{VI}}^{\alpha} \quad (6)$$

where J_{BI}^i denotes the interfacial intrinsic diffusion flux of B in the phase i . Equation (2) can be applied to any planes of the α or β phases and thus to the interface plane. Then equation (6) can be transformed into two equivalent expressions for the rate $\dot{N}$

$$\dot{N} = -\frac{\beta}{\beta - \alpha} \Delta J_{\text{AI}} + \frac{1 - \beta}{\beta - \alpha} \Delta J_{\text{BI}} + J_{\text{VI}}^{\alpha} \quad (7a)$$

or

$$\dot{N} = -\frac{\alpha}{\beta - \alpha} \Delta J_{\text{AI}} + \frac{1 - \alpha}{\beta - \alpha} \Delta J_{\text{BI}} + J_{\text{VI}}^{\beta} \quad (7b)$$

where ΔJ_{AI} and ΔJ_{BI} are the flux differences for A and B species at the α/β interface ($\Delta J \equiv J^{\beta} - J^{\alpha}$). In equations (7a) and (7b), the rate $\dot{N}$ is expressed in terms of intrinsic fluxes defined relative to the K^{*i*}-frame. The rate of growth $\dot{K}^i$ of the phase i relative to its K^{*i*}-frame represents the rate of change of the total number of lattice sites of phase i resulting from the atomic interfacial exchange reactions and/or other interface action (vacancy creation or annihilation). Because vacancies are the predominant defects for the diffusion processes, the difference between $\dot{N}$ and $\dot{K}^i$ would just correspond to the interfacial flux of vacancies into the α and β phases so that (see Appendix)

$$\dot{N} = \dot{K}^{\alpha} + J_{\text{VI}}^{\alpha} = -\dot{K}^{\beta} + J_{\text{VI}}^{\beta} \quad (8)$$

Equations (7) and (8) lead to the expression for $\dot{K}^i$ as a function of ΔJ_{AI} and ΔJ_{BI} independent of the exact interfacial reactions

$$\dot{K}^{\alpha} = -\frac{\beta}{\beta - \alpha} \Delta J_{\text{AI}} + \frac{1 - \beta}{\beta - \alpha} \Delta J_{\text{BI}} \quad (9)$$

$$\dot{K}^{\beta} = \frac{\beta}{\beta - \alpha} \Delta J_{\text{AI}} - \frac{1 - \alpha}{\beta - \alpha} \Delta J_{\text{BI}} \quad (10)$$

Equations (8) show that the growth (or recession) rate of the phase i relative to the N-frame is not necessarily equal to, or of the same sign as, the rate relative to the K-frame. This means, for example, that the α phase can grow relative to the N-frame and recede relative to its K-frame. From equation (8), the relative magnitudes of $\dot{K}^{\alpha}$ and $\dot{K}^{\beta}$ depend on the difference ΔJ_{VI} between interfacial vacancy fluxes in the α and β phases

$$\dot{K}^{\alpha} + \dot{K}^{\beta} = J_{\text{VI}}^{\beta} - J_{\text{VI}}^{\alpha} = \Delta J_{\text{VI}} \quad (11)$$

For the particular case where $\Delta J_{\text{VI}} = 0$, there would be no discontinuity in the interfacial vacancy fluxes so that no vacancies are created or annihilated at the interface. In that case, from equations (8) and (11)

$$\dot{K}^{\alpha} = -\dot{K}^{\beta} = \dot{N} - J_{\text{VI}}^{\alpha} \quad (12)$$

so that the origins of the K ^{α} - and K ^{β} -frames coincide with the α - β interface. This corresponds to the implicit assumptions in the existing analyses [4, 6-8] for the growth kinetics of intermediate product phases by diffusion reactions.

But in the more general case, $\Delta J_{\text{VI}} \neq 0$ so that vacancies (or equivalently lattice sites) must be created or annihilated at the interface, which means that depending on the sign of ΔJ_{VI} , the interface would act as a vacancy source or sink. Several different possible combinations of atomic and vacancy fluxes are illustrated in Fig. 2. As a consequence of equations (9)-(11), the sign and magnitude of $\dot{K}^{\alpha}$ and $\dot{K}^{\beta}$ can be such that both phases can grow or recede with respect to their K-frames, or even one phase can be stationary while the other one grows or

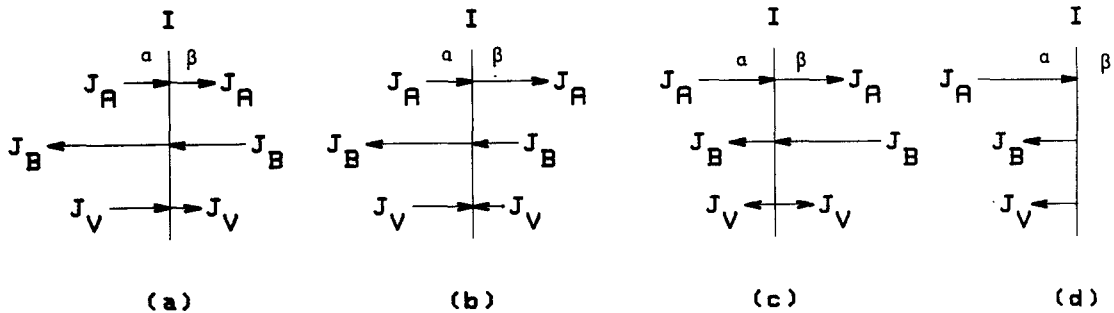


Fig. 2. Some different possible cases for interfacial fluxes of α - β diffusion reactions of Fig. 1: (a) B diffuses faster than A in both α and β phases so that $J_{\text{VI}}^{\alpha} > 0$ and $J_{\text{VI}}^{\beta} > 0$. (b) A diffuses faster than B in β phase and slower in α phase so that $J_{\text{VI}}^{\alpha} > 0$ and $J_{\text{VI}}^{\beta} < 0$. (c) A diffuses faster than B in α phase and slower in β so that $J_{\text{VI}}^{\alpha} < 0$ and $J_{\text{VI}}^{\beta} > 0$. (d) Saturated β phase, $J_{\text{VI}}^{\beta} = 0$ and $J_{\text{VI}}^{\alpha} < 0$ (A diffuses faster than B in α phase).

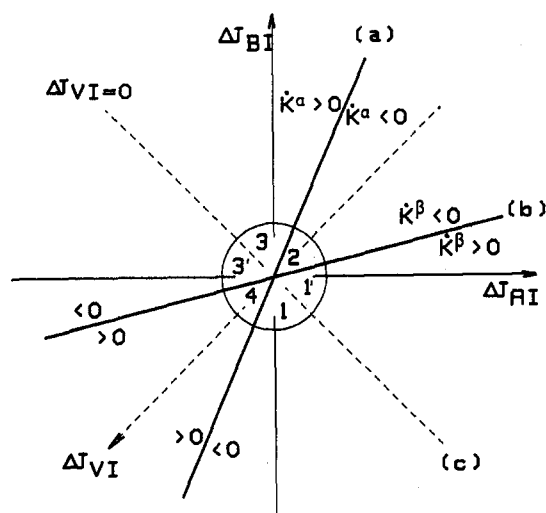


Fig. 3. Graphical interpretation of equations (9), (10) and (11) in terms of the differences in the interfacial intrinsic fluxes ΔJ_{AI} and ΔJ_{BI} . Lines (a) and (b) correspond to $\dot{K}^\alpha = 0$ and $\dot{K}^\beta = 0$, i.e. $\Delta J_{BI} = X_B^0 \Delta J_{AI} / (1 - X_B^0)$ and $\Delta J_{BI} = X_B^0 \Delta J_{AI} / (1 - X_B^0)$.

recedes. This is clearly shown by Fig. 3 where equations (9)–(11) are interpreted graphically. The two intersecting solid lines (a) and (b), drawn for the equilibrium interfacial compositions $X_B^0 = 0.2$ and $X_B^0 = 0.7$, represent the conditions $\dot{K}^\alpha = 0$ [equation (9)] and $\dot{K}^\beta = 0$ [equation (10)], respectively, drawn on the $(\Delta J_{AI}, \Delta J_{BI})$ plane. Furthermore, the line (c) $\Delta J_{VI} = 0$ [equation (11)] subdivides the $(\Delta J_{AI}, \Delta J_{BI})$ plane into two parts where the interface acts as a vacancy sink ($\Delta J_{VI} < 0$) or as a vacancy source ($\Delta J_{VI} > 0$). Thus, in Fig. 3, the lines (a), (b), and (c) define six domains with differing signs for $\dot{K}^\alpha$ and $\dot{K}^\beta$, and differing interface action as a vacancy source or sink. The different situations which can arise in the domains or subdomains defined in Fig. 3 are considered in greater detail in the following section.

3. SPECIFIC EVALUATIONS OF CONCENTRATION PROFILES AND VACANCY FLUXES

To demonstrate the evaluation of the expressions presented in the foregoing, concentration profiles and the associated diffusion fluxes were calculated to show the dependencies of these specific quantities on the intrinsic diffusivities of the A and B components and the initial concentrations of the α and β phases. The calculations were performed by using a computer-assisted finite-difference solution to the diffusion equation (NASA-COSMIC No. LAR-12381) [10]. The program was modified for a linear dependence of the interdiffusion coefficient on concentration and for evaluating the variation of diffusion fluxes and their derivatives along the diffusion direction. In the calculations, the partial molar volumes for A and B are assumed to be equal, so that the

N-frame and the volume-fixed frame are identical, and the origin of the N-frame and the Matano plane coincide. The position of the origin of the K^α - and K^β -frame was determined from equation (8) and an evaluation of the interface displacement and the interfacial vacancy fluxes. Indeed equation (8) can be transformed into

$$x_K^\alpha - x_M = 2t \cdot J_{VI}^\alpha \cdot V_m$$

and

$$x_K^\beta - x_M = 2t \cdot J_{VI}^\beta \cdot V_m \quad (13)$$

where t is the diffusion annealing time, V_m is the molar volume ($V_m = \bar{V}_A = \bar{V}_B$), and x_M , x_I , x_K^α and x_K^β are the abscissa values for the Matano, the interface, and the Kirkendall planes, respectively.

Figures 4, 6 and 7 present the calculated results for interdiffusion between the α and β phases of Fig. 1 with equilibrium interfacial compositions given by $X_B^0 = 0.2$ and $X_B^0 = 0.7$. Figure 5, similar to Fig. 3, shows the location of points corresponding to ΔJ_{VI} values for the different situations described in Figs 4, 6 and 7. On these figures, the positions marked M, K^α and K^β represent the origins for the N-frame and K^α -frames, respectively; the location I corresponds to the position of the α - β interface.

Figure 4 presents plots of the concentration profiles, the vacancy flux, and the vacancy flux divergence, calculated for the following concentration-independent intrinsic diffusion coefficient ratios: $D_B^\alpha = 10 D_A^\alpha$, $D_B^\beta = 10 D_A^\beta$, and $D_B^\beta = 10 D_B^\alpha$ so that B diffusion is faster than A in both phases α and β .

Figure 4(a) corresponds to the interdiffusion between pure A and pure B. The much more rapid diffusion of B in both phases leads to a displacement of the α/β interface I to the left, and the Kirkendall markers, located at the initial α/β interface at $t = 0$, are shifted to the right. Both K^α and K^β move to the right; thus, according to equation (13), the origin of the K^α -frame is located on the β side of the interface and must be considered as a virtual one. Because of the discontinuity in J_V at the interface, a large vacancy flux is created at the α - β interface. Likewise, vacancy annihilation is maximum at a position to the right of the Kirkendall plane where dJ_V/dx is a minimum ($dJ_V^2/dx^2 = 0$).

In Fig. 4(b), the reduction in the initial B concentration in the β phase slows the arrival of B from β to the interface, so that the rate of boundary migration is decreased and the rate of interfacial vacancy creation is reduced. In fact, the initial B concentration in the β phase can be chosen in such a way that the interface stays at the Matano plane position; the volume of neither phase would change, but with respect to their K-frames, the β phase has grown and the α phase has receded.

In Fig. 4(c), a further reduction in the initial B concentration in the β phase results in identical vacancy fluxes in the α and β phases at the interface. Thus, the α/β interface does not create or annihilate

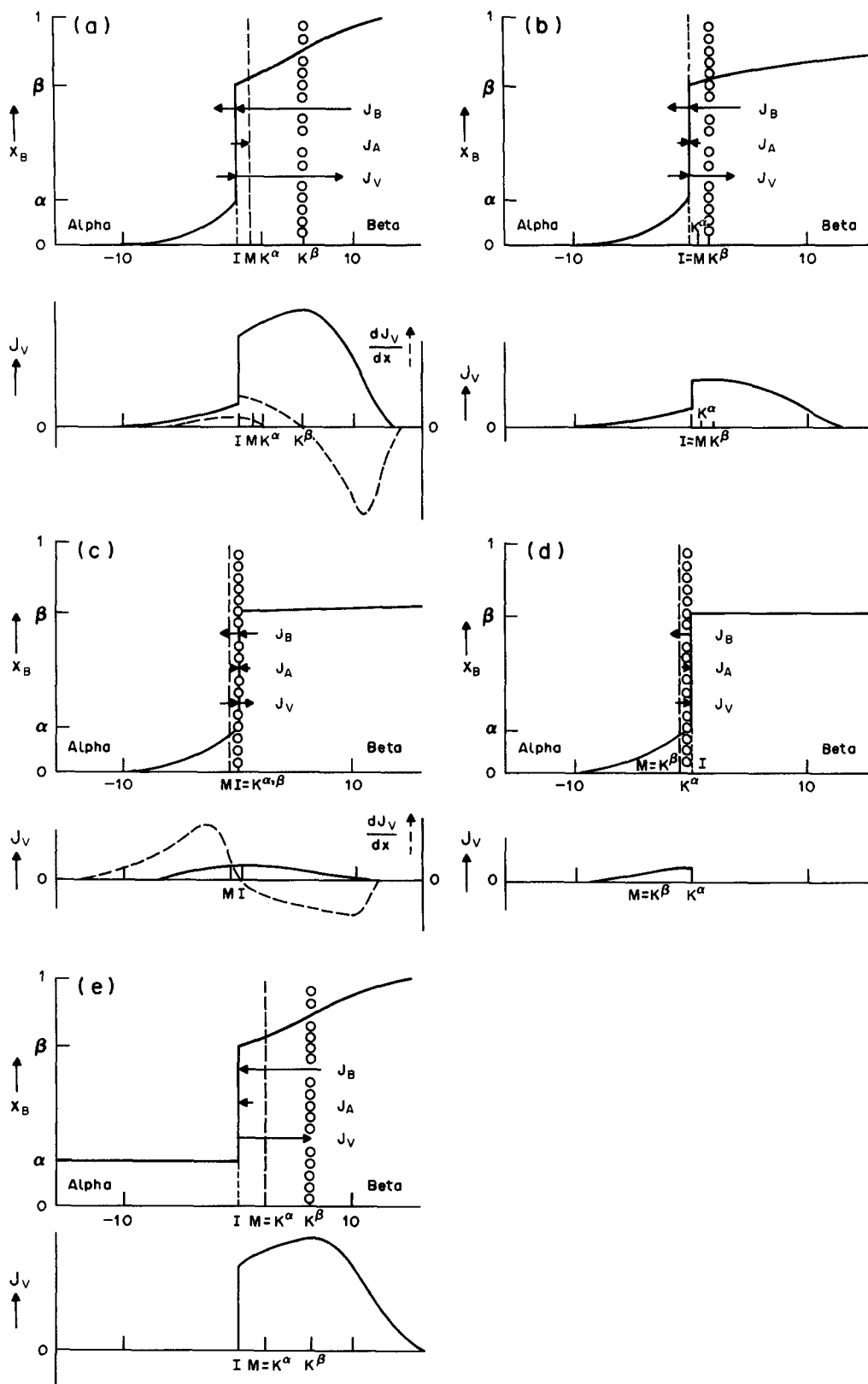


Fig. 4. Concentration profiles (mole fraction X_B vs x in μm), corresponding vacancy flux profiles (J_V vs x , solid lines) and vacancy divergence (dJ_V/dx vs x , broken lines) for a given time (8740 s) for interdiffusion of α and β phases with interfacial concentrations $X_B^\alpha = 0.2$ and $X_B^\beta = 0.7$. The intrinsic diffusion coefficients were chosen as $D_B^\alpha = 10 D_A^\alpha$, $D_B^\beta = 10 D_A^\beta$ and $D_B^\beta = 10 D_A^\beta$, with $D_A^\alpha = D_A^\beta = 10^{-11} \text{ cm}^2/\text{s}$. (a-e) describe cases of different end-member compositions of α and β . The location (I) of the α/β interface coincides with $x = 0$. The origin of the N-frame (Matano plane), K^α -frame and K^β -frame are indicated by M, K^α and K^β , respectively.

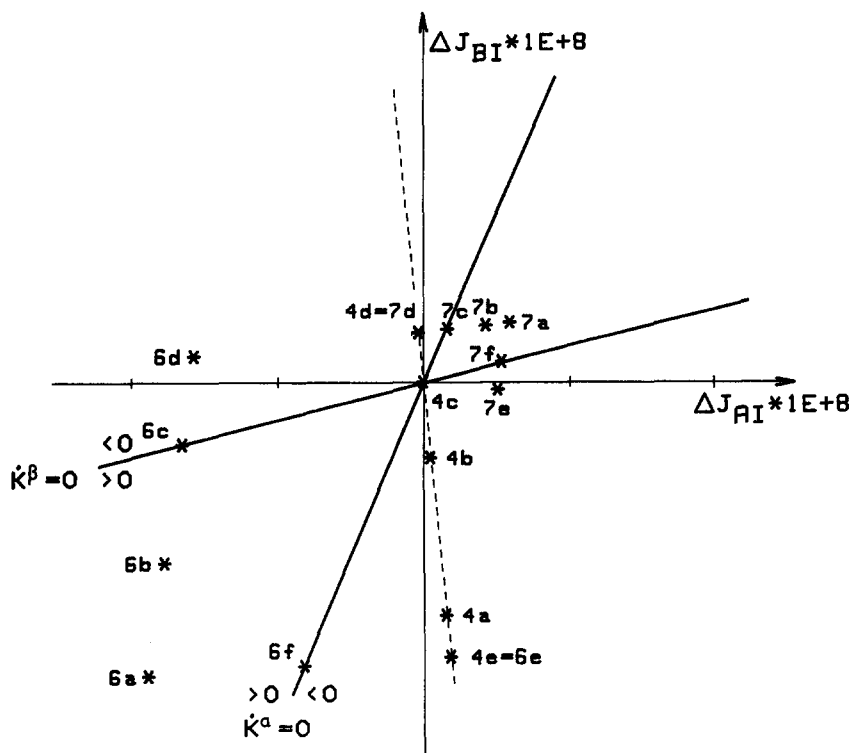


Fig. 5. Map of α - β interdiffusion conditions from Figs 4, 6 and 7 onto a plot similar to Fig. 3 showing the growth conditions relative to the Kirkendall frames of reference. The dimensions of ΔJ are $\text{mol}/\text{cm}^2 \cdot \text{s}$.

vacancies ($dJ_v/dx = 0$), and the K^α and K^β planes remain at the α/β interface. In this case, the α phase grows and the β phase recedes in the N-frame. In the Kirkendall frame of reference, however, no growth of either phase occurs. This emphasizes the necessity of defining carefully the frame of reference when fluxes and the growth of phases are considered.

Figure 4(d) illustrates the concentration profiles and vacancy fluxes for interdiffusion between pure A and the saturated $A_{0.3}B_{0.7}$ phase. In this case, the α/β interface moves to the right, with vacancy annihilation at the interface. The K^α plane is found in the α phase, between the Matano plane and the α/β interface while the virtual K^β plane always coincides with the Matano plane. In both the K^I - and the N-frames, the α phase has grown and the β phase has receded.

Figure 4(e) shows the reverse case of Fig. 4(d), for diffusion between pure B and the saturated α phase. The K^α plane coincides with the Matano plane so that in both the K^I -frame and the N-frame, the β phase has grown and the α phase has receded.

The sequence of examples presented in Fig. 4 illustrates how the action of the interface can depend on the initial α and β concentrations, even for fixed intrinsic diffusion coefficients. Therefore, generally, any α/β interface must be inherently able to create and annihilate vacancies regardless of the diffusion properties or structural characteristics of the phases involved. In the succeeding paper, plausible arguments for the interactions of vacancies with the defect structure of an α/β interface to effect

vacancy creation and annihilation, as well as interface migration, are presented.

In Fig. 5, the locus of points (4a-4e) as a straight line results from the choice of the same constant ratio for the concentration-independent intrinsic coefficients in the α and β phases. In such a case, the ratio $\Delta J_{BI}/\Delta J_{AI}$ is also constant

$$\frac{\Delta J_{BI}}{\Delta J_{AI}} = -\frac{D_B^\alpha}{D_A^\alpha} = -\frac{D_B^\beta}{D_A^\beta}.$$

For the values of D_A^I and D_B^I used in drawing Fig. 4, this line crosses the domains 1 and 3 where $\dot{K}^\alpha$ and $\dot{K}^\beta$ always have opposite signs.

In Fig. 6, interdiffusion of the α and β phases is treated for the same interfacial concentrations as in Fig. 4, but $D_A^\alpha = 10D_B^\alpha$, $D_B^\beta = 10D_A^\beta$ and $D_B^\beta = 10D_B^\alpha$. In contrast to the conditions for Fig. 4, where B diffusion was faster than A in both phases, A diffuses faster than B in the α phase in Fig. 6.

Figure 6(a) provides the concentration profiles, interfacial fluxes, the vacancy flux profiles and vacancy flux divergence for the interdiffusion of pure A with pure B. Large vacancy fluxes of opposite sign are present at the interface. In this case, Kirkendall markers placed initially at the original interface diverge in their migration to positions K^α and K^β in the α and β phases, respectively. Thus both phases grow in their Kirkendall frames, whereas in the Matano frame, the α phase recedes and the β phase grows. In Fig. 6(b), the initial B concentration of the β phase is lowered to a value such that

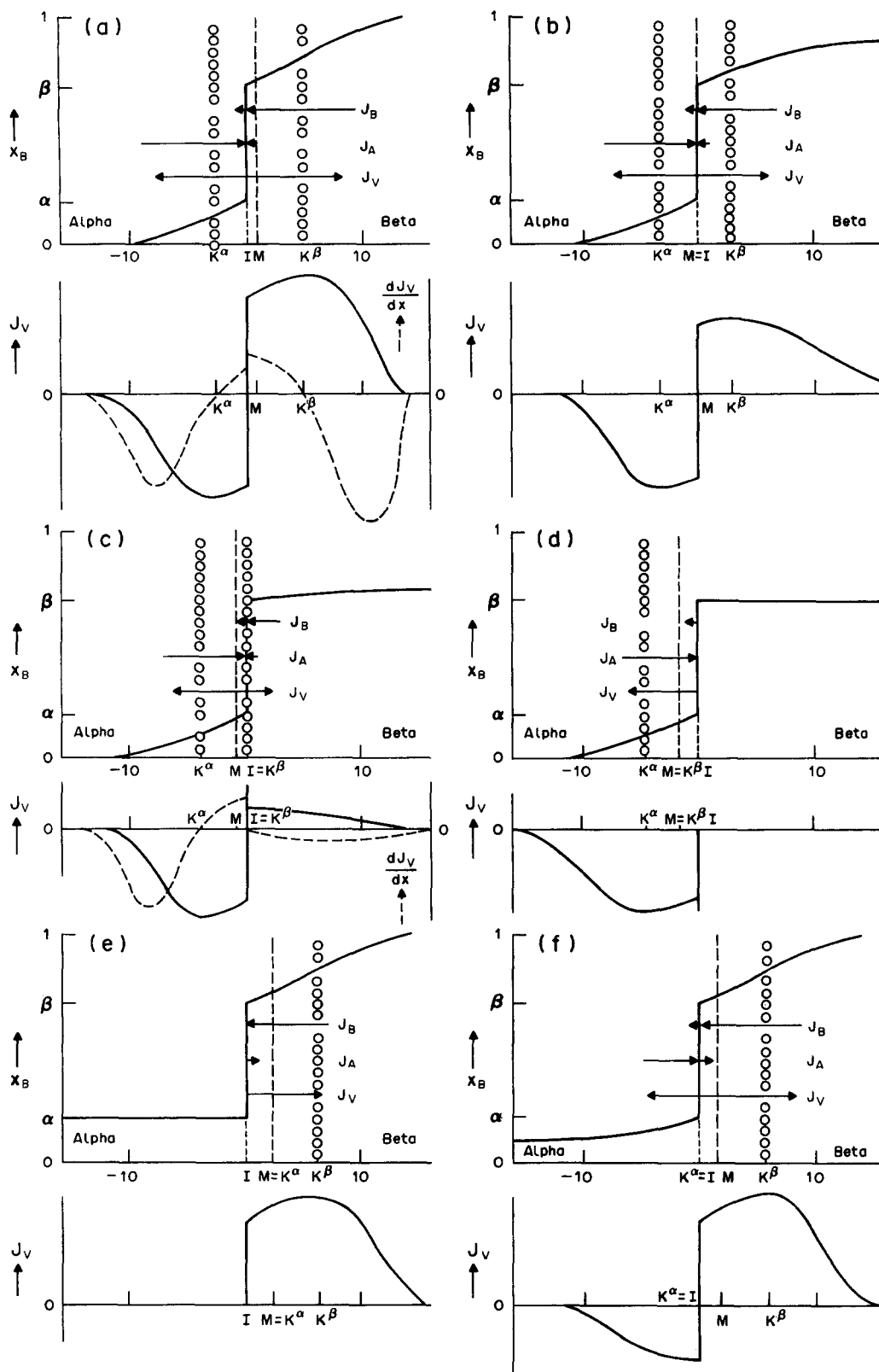


Fig. 6. Concentration, vacancy flux and vacancy flux divergence profiles for alpha/beta interdiffusion with interfacial concentrations $X_B^\alpha = 0.2$ and $X_B^\beta = 0.7$, for $D_A^\alpha = 10 D_B^\alpha$, $D_B^\beta = 10 D_A^\beta$ and $D_B^\beta = 10 D_A^\beta$ with $D_A^\beta = D_B^\beta = 10^{-11} \text{ cm}^2/\text{s}$. (a-f) Describe cases with different end-member compositions.

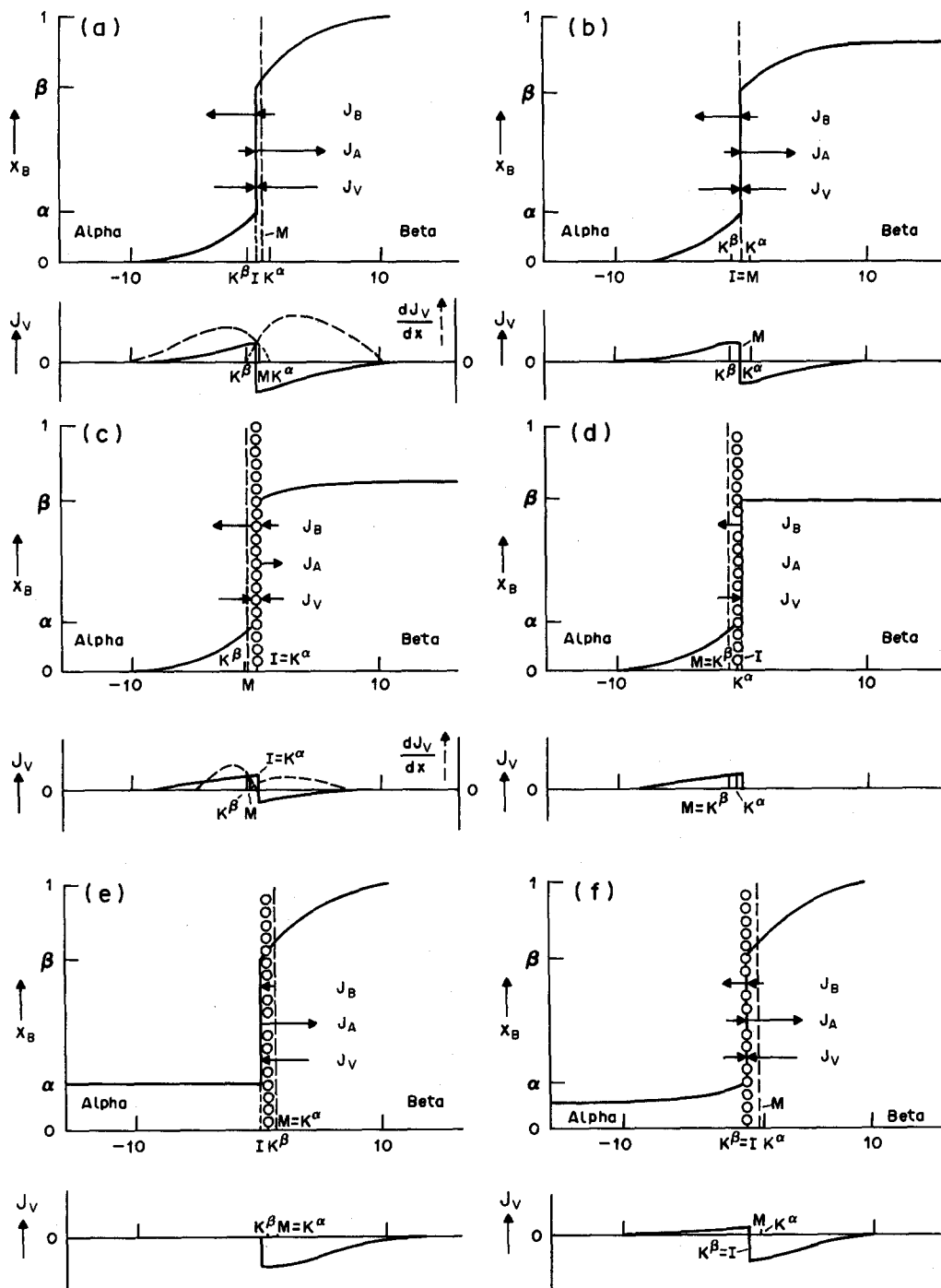


Fig. 7. Concentration, vacancy flux and vacancy flux divergence profiles for alpha/beta interdiffusion with interfacial concentrations $X_B^\alpha = 0.2$ and $X_B^\beta = 0.7$, for $D_B^\beta = 10 D_A^\alpha$, $D_A^\beta = 10 D_B^\alpha$ and $D_B^\beta = 10 D_B^\alpha$ with $D_A^\beta = D_B^\beta = 10^{-11} \text{ cm}^2/\text{s}$.

the Matano plane and the α/β interface coincide. Points 6a and 6b are plotted onto Fig. 5 to indicate these examples.

Further lowering of the B content in the β phase leads to Fig. 6(c), and point 6c in Fig. 5, where the Kirkendall plane K^β coincides with the interface. Relative to the Matano plane, the α phase has grown while the β phase has receded.

For a saturated β solid solution, as seen in Fig. 6(d) and as point 6d in Fig. 5, only the Kirkendall plane in the α phase is visible. The phase has receded relative to both frames of reference.

Correspondingly, Figs 6(e) and (f), with points 6e and f in Fig. 5, present the concentration profiles and vacancy fluxes for the interdiffusion of pure B with saturated and with unsaturated α phases.

In Fig. 7, the following conditions have been assumed: $D_B^{\alpha} = 10D_A^{\alpha}$, $D_A^{\beta} = 10D_B^{\beta}$, and $D_B^{\alpha} = 10D_B^{\beta}$. In comparison to Figs 4 and 6, in Fig. 7 component A diffuses slower than B in the α phase, and B diffuses slower than A in the β phase.

In Fig. 7(a) (described by point 7a in Fig. 5), pure A reacts with pure B. Vacancies arriving from both the α and β phases are annihilated at the interface; thus relative to their K-frames, both phases have receded, although the α phase recedes and β phase grows relative to the Matano frame of reference. Moreover, both the K^{α} - and K^{β} -frames have virtual origins so that the behavior of inert markers placed at the original interface at $t = 0$ is difficult to imagine.

Figure 7(b) (point 7b in Fig. 5) corresponds to the interdiffusion between pure A and a β solid solution of such a composition that after diffusion the Matano plane coincides with the interphase interface. Then neither the α phase nor the β phase grow relative to the N-frame, but both phases recede relative to their K-frames.

If the B concentration in the β phase is again lowered, the situation shown in Fig. 7(c) (point 7c in Fig. 5) would occur. Relative to the N-frame, the α phase grows and the β phase recedes; but relative to their K-frames, the α phase neither grows nor recedes while the β phase recedes, the virtual origin for K^{β} being located in the α phase.

For the saturated β phase in Fig. 7(d) (point 7c in Fig. 5) the phase has grown relative to both the N-frame and its K-frame, and the interface annihilates vacancies arriving from the α phase.

For couples of pure B and either saturated or unsaturated α solid solutions [Fig. 7(e) and (f)], the reverse behavior of Fig. 7(c) and (d) occurs.

4. DISCUSSION

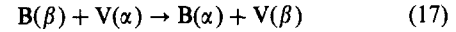
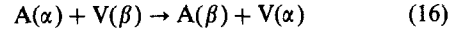
In Section 2, the fundamental expressions describing interdiffusion have shown that a general interphase interface must act as either a vacancy source or sink. Furthermore, the calculation of concentration profiles, vacancy flux and vacancy flux divergence (Section 3), for different ratios of intrinsic diffusion coefficients and differing initial concentrations for the α and β phases showed that the same interphase interface must be able to act as a vacancy source or vacancy sink. This interfacial action must compensate for the difference in diffusion fluxes of the A and B species within the α and β phases. Indeed, the usual assumption of conservation of lattice sites can be expressed as

$$\int_{(-\infty)}^{x_1} (dJ_V/dx) \cdot dx + \int_{x_1}^{(+\infty)} (dJ_V/dx) \cdot dx + \text{Interface action} = 0 \quad (14)$$

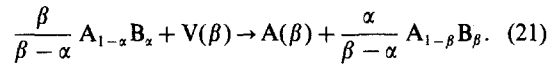
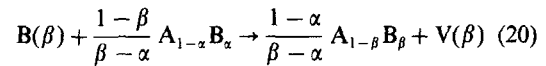
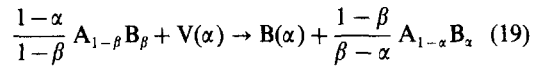
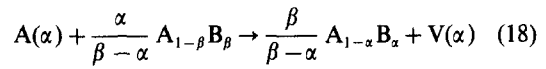
so that

$$\text{Interface action} = J_{V1}^{\beta} - J_{V1}^{\alpha} = \Delta J_{V1}. \quad (15)$$

Alternatively, the interface action can be described in terms of interfacial reactions corresponding to the exchange of A and B species between the α and β phases, such as



where $V(\alpha)$ and $V(\beta)$ indicate vacancies in the α and β phases. These simple exchange reactions (16) and (17) are consistent with the assumed substitutional/vacancy diffusion mechanisms, but they are inadequate to describe accurately the relative magnitudes of the A, B and vacancy fluxes to the α/β interface. However, each of these two equations can be resolved into two other elementary equations describing the reactions of the diffusing species A, B or V within the α and β phases at the interface



From the exchange of the lattice sites occurring by the interfacial reactions (18)–(21), and the consideration of intrinsic diffusion fluxes, the rate of change in the total number of lattice sites per unit area of interface in the α and β phases, i.e. the growth rate, can be expressed in the Kirkendall frames of reference for the α and β phases. In this way, expressions identical to equations (9) and (10) can be deduced from interfacial reactions (18)–(21). Equations (18)–(21) differ from previous analyses [6–8] in that they indicate that the growth (or recession) of the α or β phases involves not only diffusion of both A and B species in both the α and β phases, but also the creation [equations (18) and (20)] or annihilation [equations (19) and (21)] of vacancies at the interface. These four equations also permit the balance of atoms and lattice sites required to describe the growth or recession of the α and β phases resulting from the differences in the fluxes of A, B and V to the α/β interface.

Otherwise, the growth rate relative to the Matano frame of reference can also be deduced from interdiffusion fluxes and the interfacial reactions using expressions different from equations (18)–(21), whereby vacancies are neglected. In that case, the growth rate is expressed by an equation similar to equation (5). Thus, the classical diffusion approach and the partitioning method [6, 7] are strictly equivalent as long as the growth rate for a given phase does not depend on the kinetics of the lattice transformation occurring at the interface (reaction-limited kinetics).

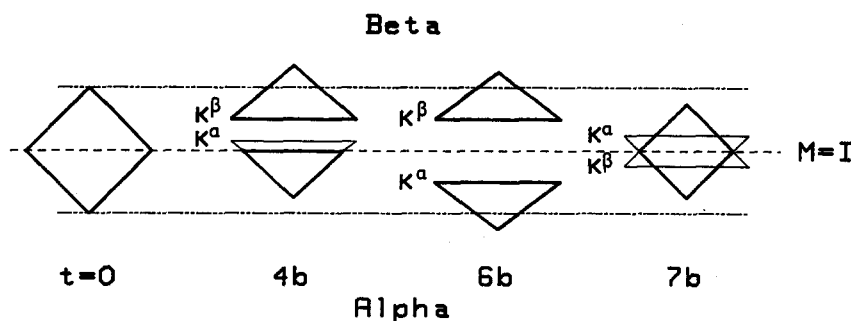


Fig. 8. The change in morphology of a square indentation marker, originally placed at the α/β interface at $t = 0$, after diffusion annealing in the situations given by Figs 4(b), 6(b) and 7(b). The real or virtual displaced origin of the α and β Kirkendall frames of reference are described by K^α and K^β (defined by the constant lateral indentation width).

The preceding analysis shows that two different Kirkendall frames of reference must be considered. Thus, it may be difficult to imagine the behavior of inert markers placed at the original interface at $t = 0$. Indeed, this original interface plane corresponds to the common origin of the K^α - and K^β frames, but, in the more general case, these two planes separate as diffusion proceeds. However, if indentation markers were placed in the original interface, Fig. 8 would describe their shape changes for three cases of interest described in this analysis where the Matano plane coincides with the interface. An originally square indentation marker would split in the diffusion direction for case 6b and shrink for case 7b, whereas for case 4b, it would extend at the β side and contract at the α side. In Fig. 8, the width of the indentation does not change at the real or virtual origins of the K^α - and K^β -Kirkendall frames.

In a multiphase Ti-Ni diffusion couple, Bastin [11] showed experimental evidence for the actual rupture of a tungsten marker wire as a result of differing diffusion fluxes in the various phases.

5. CONCLUDING REMARKS

For the case of a vacancy/diffusion phase transformation in a biphasic system, the present analysis of interface migration and the associated Kirkendall effect has shown:

1. That it is necessary to consider two different Kirkendall frames of reference, one for each adjoining phase.
2. That differing Kirkendall shifts in the reacting phases must be compensated by the action of the interface as a vacancy source or sink.
3. That any given interphase interface, i.e. an interface separating two phases of given equilibrium chemical compositions and crystallographic structures, must be able to act as either a vacancy source or vacancy sink; indeed the specific action of the interface can be reversed by just a

change in the initial compositions of the reacting phases.

4. That it is necessary to define carefully the frame of reference chosen to describe fluxes and phase growth rates. The two adjoining phases can, in some cases, simultaneously grow or recede relative to their own Kirkendall frames of reference.

5. That the definition of growth rate by means of classical diffusion formalisms or from interfacial reactions involving the partitioning of the two diffusing species between the two phases are strictly equivalent. Equations describing interfacial reactions must expressly include vacancies to permit the evaluation of growth rates relative to the Kirkendall frames of reference.

Acknowledgements—The financial assistance of NATO for the Collaborative Research Grant 0777/87 is gratefully acknowledged. The provision of the NASA finite difference computer by J. Nesbitt of NASA Lewis Laboratory in Cleveland (Ohio) is greatly appreciated.

REFERENCES

1. W. Jost, *Diffusion in Solids, Liquids and Gases*. Academic Press, New York (1952).
2. P. G. Shewmon, *Diffusion in Solids*. McGraw-Hill, New York (1963).
3. J. Philibert, *Diffusion et Transport de Matière dans les Solides*. Les Editions de Physique, Les Ulis (1986).
4. C. Wagner, *Acta metall.* **17**, 99 (1969).
5. F. J. J. van Loo and G. D. Rieck, *Acta metall.* **21**, 73 (1973).
6. S. R. Shatynski, J. P. Hirth and R. A. Rapp, *Acta metall.* **24**, 1071 (1976).
7. D. S. Williams, R. A. Rapp and J. P. Hirth, *Metall. Trans.* **12A**, 639 (1981).
8. G. X. Li and G. W. Powell, *Acta metall.* **33**, 23 (1985).
9. B. Pieraggi, F. J. J. van Loo and R. A. Rapp, Fluxes and interface migration in diffusion-driven phase transformations, *Diffusion Analysis and Applications* (edited by A. D. Romig and M. S. Dayananda). T.M.S., Warrendale, Pa (1987).
10. D. R. Tenney and J. Unnam, NASA Tech. Mem. 78636n (1978).
11. G. F. Bastin, Ph.D. thesis, Techn. Univ. Eindhoven (1972).

APPENDIX

Relations Between Fluxes or Rates Expressed in Matano and Kirkendall Frames of Reference

In most of the textbooks [1–3], the lattice shift rate is expressed as a function of the difference in intrinsic diffusion coefficients and the gradient in atomic fractions

$$v^{K/N} = (D_A - D_B) \frac{\delta N_A}{\delta x}.$$

Equivalent expressions can be found by combining equations (1)–(3). For diffusion in a homogeneous system

$$\tilde{J}_A = J_A + c_A v^{K/N}$$

$$\tilde{J}_B = J_B + c_B v^{K/N}$$

so that

$$J_A + J_B + (c_A + c_B) v^{K/N} = 0$$

and

$$v^{K/N} = -(J_A + J_B)/(C_A + C_B) = V_m \cdot J_v$$

with

$$V_m = 1/(C_A + C_B) = X_A/C_A = X_B/C_B$$

Thus

$$c_i v^{K/N} = X_i J_v$$

and

$$\tilde{J}_i = J_i + X_i J_v.$$

The relation between the growth rate expressed in the Matano and Kirkendall frames of reference can be found by expressing $\dot{N}$ and $\dot{K}$ as

$$V_m \cdot \dot{N} = d(x_I - x_M)/dt$$

and

$$V_m \cdot \dot{K} = d(x_I - x_K)/dt = d(x_I - x_M)/dt + d(x_M - x_K)/dt$$

where $d(x_M - x_K)/dt$ is the lattice shift rate, so that

$$\dot{N} = \dot{K} + v^{K/N}/V_m = \dot{K} + J_v.$$

Since the growth of a phase is considered to be positive, $V_m \cdot \dot{K}^z$ is defined as $d(x_I - x_K^z)/dt$ and $V_m \cdot \dot{K}^\beta$ as $d(x_K^\beta - x_I)/dt$, thus $\dot{N} = \dot{K}^z + J_{v1}^z = -\dot{K}^\beta + J_{v1}^\beta$.