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MULTIPHASE DIFFUSION IN BINARY AND TERNARY SOLID-STATE SYSTEMS

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1. INTRODUCTION

If two solid materials are in contact at a sufficiently high temperature, interdiffusion will occur. Depending on the nature of the starting materials, temperature and annealing time, a new concentration distribution of the elements is set up. If the materials are completely miscible at that temperature, the concentration profiles are more or less smooth without any discontinuity. If, however, they are only partially miscible or if they react to form new phases, discontinuities in the concentration profiles occur which are closely related to the phase diagram of the system.

Fig. 1.1. (a) Phase diagram of the binary system A-B.
(b) A diffusion couple A/B annealed at a temperature $T_0$, together with the concentration-penetration curve of component B in mole fraction.

Fig. 1.2. Hypothetical ternary isotherm A-B-C with two possible diffusion paths, 1 and 2.
Figure 1.1 shows an example for a binary system A-B, in which the compounds γ and δ are formed in addition to the solid solutions α and β. After a sufficiently long annealing treatment for such an A-B diffusion couple at a temperature $T_o$, a concentration profile is set up as shown for component B. The exact profile in the various phases cannot be predicted unless the interdiffusion coefficients are known as a function of composition. However, the values of the concentrations at the $α/γ$, $γ/δ$ and $δ/β$ interfaces can be taken from the phase diagram if equilibrium conditions prevail at these interfaces (as is discussed later).

The reason for the creation of straight interfaces with fixed concentration gaps in binary multiphase diffusion couples follows from basic thermodynamic considerations. From the phase rule it follows that only single-phase regions can be formed in such a couple, because three degrees of freedom would be necessary to fix temperature and pressure and to vary the concentration. Two-phase regions (i.e. precipitates or wavy interfaces) are, therefore, forbidden since then only two degrees of freedom are allowed. Temperature and pressure already having been chosen, there would be no possibility left across a two-phase zone for a variation in concentration, i.e. for diffusion.

For interdiffusion in a ternary system at a fixed temperature and pressure, the number of degrees of freedom is three minus the number of phases. This implies that in single-phase regions one might vary the concentration (fraction) of two components, whereas in two-phase regions the concentration of one component can be varied but then the other concentrations are fixed. Therefore, in a ternary diffusion couple two-phase regions are allowed.

In a system where a component is involved which is present both in the solid and in the surrounding gaseous phase it is not easy to fix unambiguously parameters like total pressure or the fraction of this component in the solid phase, since these may be different in the bulk of the couple and at the edges as will be explained later on.

Although nature only chooses one reproducible penetration profile for the elements in such a ternary couple, a prediction of these profiles from the phase diagram is difficult because of the infinite variety of hypothetical possibilities. In Figure 1.2 an isothermal cross-section of a system A-B-C is shown, exhibiting two single-phase fields γ and δ and a two-phase region in which tie lines are drawn connecting coexisting equilibrium phases.

If the element C and the alloy X interdiffuse at the temperature for this cross-section, the resulting concentration profile mapped on this section might resemble the hypothetical diffusion paths 1 or 2 or any other, as long as mass balance is preserved. The concentrations at the $γ-δ$ interface and the morphology of the reaction zone would be completely different for paths 1 and 2 as is discussed later.

In Figs. 1.1 and 1.2, we have related the diffusion phenomena with the relevant phase diagrams. This is only allowed if local equilibrium conditions exist at the interfaces, but cannot be considered generally. For very short annealing times or in thin-film experiments, departure from equilibrium diagram concentrations certainly occur because of surface energy contributions, but also for longer diffusion annealing times, deviations from equilibrium conditions at the phase interfaces are reported [1-3]. The relation between the diffusion phenomena and the phase diagram is then less obvious, although in some cases metastable extensions of equilibrium lines might be helpful in understanding these deviations. In some cases, however, these deviations are only apparent, as is discussed later.

Local equilibrium can always be assumed if volume diffusion is the rate-limiting step. Whether this is the case can be verified by plotting the diffusion profiles for (at least) two sufficiently different annealing times $t$ as a function of $x/t^{1/2}$, where $x$ is the distance parameter. In case of a diffusion-controlled process, the plots then have to coincide.
In this survey the author would like to discuss in a mainly qualitative way the relation between multiphase diffusion phenomena on the one hand, and kinetic and thermodynamic (phase diagram) data on the other hand. This paper then focuses on:

- providing experimental or theoretical evidence to settle some often disputed issues;
- showing how relatively simple experiments can provide information about diffusion and thermodynamics;
- predicting and experimentally verifying multiphase diffusion phenomena from kinetic and thermodynamic data.

This paper is based mainly on the author's own experiences in this research field and is not meant as a comprehensive literature survey or total overview. For instance, not or only partly included in this paper are:

- Non-equilibrium diffusion couples, a situation often encountered at low temperatures and short annealing times, or when nucleation problems exist or interface energies play an important role. However, these problems are mentioned at the appropriate places in the text where the reader is referred to specialised literature on this subject.
- Finite couples in which the sequence of the phase formation as well as the kinetics are time-dependent. This is especially important in thin-film and coating techniques where phases formed in the beginning might be consumed during further annealing. However, generally spoken these phenomena can be understood by applying the theory for infinite diffusion couples using continuously changing end members for such a couple.
- Diffusion in ionic systems in which an extra condition of electric neutrality arises, as well as diffusion in covalent ceramics like certain carbides and nitrides or in completely ordered alloys. In these cases especially the difficult and often coupled formation and migration of point defects is different from metallic materials. However, this restriction is mainly important for the quantitative description of binary multiphase diffusion. The qualitative ideas presented in this paper on ternary multiphase diffusion completely include these types of material.

2. MULTIPHASE DIFFUSION IN BINARY SYSTEMS

Although numerous studies on multiphase binary diffusion have been published, still some little known or even controversial issues exist. Generally, these are mostly mentioned only as side remarks in papers in which another main subject is involved.

After a general introduction, a few typical examples of these issues are discussed in this section in the following sequence:

- the time invariance of the concentration versus \( x/t^{1/2} \) plot. The reasons for deviations are discussed, as well as the use of deviating plots to get reliable diffusion data;
- the absence of bulk-equilibrium phases or the presence of non-equilibrium phases in a diffusion couple;
- deviations of interface concentrations measured in multiphase diffusion couples as compared to bulk-equilibrium values in homogenized alloys;
- the positions of the Kirkendall and Matano planes in a diffusion couple;
- the role of the phase interface(s) in the creation or annihilation of vacancies resulting from the Kirkendall effect;
- the morphology of the phase interface(s) if grain boundary diffusion is taking place;
- comparison of the reaction layer thickness in planar, cylindrical and spherical diffusion couples;
- differences in morphology of reaction zones in the centre and at the edges of a diffusion couple, including differences depending upon the relative diameters of the half couples;
- crystallographic texture in the reaction layer;
- the evaluation of diffusion coefficients in systems where large total volume changes occur (e.g. during interstitial diffusion);
- the evaluation of diffusion coefficients for vapour-solid couples compared with solid-solid couples.

General introduction into multiphase binary diffusion

For a binary interdiffusion process in which volume diffusion is the rate-limiting step the evaluation of diffusion data from concentration plots is the same for single-phase and multiphase systems. The interdiffusion coefficient $D$ can be found from a concentration plot by using the Matano-Boltzmann analysis as given in many excellent reference books, such as e.g. Adda and Philibert [4].

We will start this introduction by giving the necessary and useful equations in their general form. At the end we present these equations in a simplified form for cases where these can be used (e.g. if assumptions of a constant total volume or of equal partial molar volumes are allowed).

The first difficulty is the definition of the dimensions for concentration and distance in these plots. In fact, the frame of reference which is chosen for the description of the interdiffusion process determines the definition of the evaluated diffusion coefficients and indeed quite a variety of definitions exist. As long as one is working in a consistent system every evaluation is equally good and the various diffusion coefficients can be transformed one into another [5]. It is convenient to define the interdiffusion flux $\bar{J}$ for component $i$ by Fick's first law in the form

$$\bar{J}_i = - \bar{D} \frac{dC_i}{dx} \text{ [moles/m}^2\text{s]}$$  \hspace{1cm} (1)

where $\bar{D}$ is the interdiffusion coefficient in $m^2/s$; $C_i$ is the concentration of component $i$ in moles/m$^3$ and $x$ is the distance coordinate in $m$.

In the case of a constant total volume the interdiffusion coefficient $\bar{D}(C_i^*)$ at a certain concentration $C_i^*$ can be found from the penetration plot of $C_i$ versus $x$ by the Matano-Boltzmann equation:

$$\bar{D}(C_i^*) = \frac{1}{2t} \int \frac{dC_i}{C_i} \int_x^{C_i^*} x \, dC_i$$

(2)

The meaning of the symbols follows from Fig. 2.1, for the interdiffusion of the elements A and B between two starting alloys having initial B-concentrations of $C_B^-$ and $C_B^+$, respectively.
Fig. 2.1. Concentration-penetration curve for component B in a diffusion couple between two alloys with starting compositions $C_B^-$ and $C_B^+$, respectively.

The Matano-reference plane $x_o = 0$ is defined in such a way that the horizontally hatched areas are equal. The flux defined in this way is measured with respect to this Matano plane or, alternatively, to one of the ends of the couple (since the total volume is constant). The value of the integral in Eq. (2) is given by the double-hatched area in Fig. 2.1; the reciprocal of the concentration gradient has to be taken at the position $x^*$ where $C_i = C_i^*$. If the total volume changes during the reaction (which means that the partial molar volumes $V_i$ are dependent on concentration), Eq. (2) has to be replaced by [6,7]:

$$
\tilde{D}(Y^*) = \frac{V_m}{2t} \left( \frac{dx}{dY} \right)^* \left[ (1-Y^*) \int_{0}^{X^*} \frac{Y}{V_m} \, dx + Y^* \int_{0}^{X^*} \frac{(1-Y)}{V_m} \, dx \right]
$$

(3)

where the concentration unit $Y$ is defined as $(N_i - N_i^-)/(N_i^+ - N_i^-)$; $N_i$ is the mole fraction of component $i$, being $N_i^-$ and $N_i^+$ at the undisturbed left-hand and right-hand ends of the couple and $V_m$ is the molar volume. In this case the flux is measured with respect to, say, the left-hand end of the couple. A Matano plane $x_o = 0$ cannot be uniquely defined in this frame of reference for a system with varying total volume, since it is split up into two planes depending on whether the left-hand or the right-hand side of the couple is taken as a reference point. It is indeed not necessary to know a plane $x = 0$ since in Eq. (3) the distance parameter appears only in a differential form. Unless stated otherwise, throughout this paper a constant total volume (constant but not necessarily equal partial molar volumes) is supposed in order to avoid needless complications.
The equations (1-3) are related to interdiffusion phenomena, characterized in a binary system by the fact that the same interdiffusion coefficient \( D \) can be used for the description of the diffusion behaviour of both species. If the real - or intrinsic - diffusivities of both components have to be investigated, the diffusion fluxes relative to some lattice plane in a phase have to be known. The origin of this so-called Kirkendall frame of reference can be found in single-phase diffusion couples more or less easily by using inert markers situated at the meeting interfaces at \( t = 0 \). In a later paragraph the situation for multiphase couples is shown to be more complicated.

The unequal diffusion fluxes of the components with respect to the lattice planes in a phase is compensated by a flux of vacancies in the same direction as the flux of the slower component. The relation between the interdiffusion flux \( \tilde{J}_i \) in the Matano and the intrinsic diffusion flux \( J_i \) in the Kirkendall frames of reference is given by [8]:

\[
\tilde{J}_i = J_i + C_i \nu^{X/M}
\]

(4)

where \( \nu^{X/M} \) equals the velocity of Kirkendall frame relative to the Matano frame at that position and time where the concentration of component \( i \) equals \( C_i \).

This velocity \( \nu^{X/M} \) can be defined for each lattice plane in the diffusion zone, but can only be measured easily at the lattice plane corresponding to the original interface at \( t = 0 \) by the relation

\[
\nu^{X/M} = \Delta x / 2t
\]

(5)

where \( \Delta x \) is the marker displacement, i.e. the distance between the Kirkendall plane \( x_K \) and the Matano plane \( x_o = 0 \).

The velocity \( \nu^{X/M} \) is related to the flux of vacancies, which can be seen from Eq. (4) and the relations

\[
\tilde{V}_A J_A + \tilde{V}_B J_B = 0
\]

(6)

\[
\tilde{V}_A J_A + \tilde{V}_B J_B + V_m J_v = 0
\]

(6)

where the subscripts \( A, B \) and \( V \) refer to the components \( A \) and \( B \) and to the vacancies \( V \). This leads to

\[
\nu^{X/M} = V_m J_v
\]

(7)

Substitution into Eq. (4), using the definition of the molar volume

\[
V_m = \frac{1}{C_A + C_B} = \frac{N_A}{C_A} = \frac{N_B}{C_B}
\]

leads to:

\[
\tilde{J}_i = J_i + N_i J_v
\]

(8)
The intrinsic diffusion coefficients \( D_i \) are related to \( v^{X/M} \) and the interdiffusion coefficient \( \tilde{D} \) by the relations

\[
v^{X/M} = \tilde{v}_A (D_A - D_B) \delta C_A / \delta x \tag{9}\]

\[
\tilde{D} = C_A \tilde{v}_A D_B + C_B \tilde{v}_B D_A \tag{10}\]

The values for \( D_i \) can be found at the concentration in the Kirkendall origin (marker position) by combining Eqs. (2,5,9) and (10) with equation [6]:

\[
D_i(x_K) = \frac{1}{2t} \frac{(5X_i)}{6c_i} x_i^T \cdot \frac{1}{c_i^T - c_i^T} \left[ c_i^T \int_0^{x_K} (c_i^T - c_i^T) dx - c_i^T \int_0^{x_K} (c_i^T - c_i^T) dx \right] \tag{11}\]

If the total volume does not remain constant, Eq. (11) has to be replaced by [6]:

\[
D_i(x_K) = \frac{1}{2t} \frac{(5X_i)}{6c_i} \left[ N_i^+ \int_0^{x_K} X/Y dX - N_i^- \int_0^{x_K} (1-Y)/V dX \right] \tag{12}\]

The ratio between the intrinsic diffusion coefficients follows from Eq. (12) and is equal to

\[
\frac{D_A}{D_B} = \frac{\tilde{v}_A}{\tilde{v}_B} \left[ \frac{N_i^+ \int_0^{x_K} (N_i^- - N_i^-) dx - N_i^- \int_0^{x_K} (N_i^+ - N_i^+) dx}{N_i^+ \int_0^{x_K} (N_i^- - N_i^-) dx + N_i^- \int_0^{x_K} (N_i^+ - N_i^+) dx} \right] \tag{12a}\]

In the ratio of the intrinsic fluxes, which equals \( J_A/J_B = -D_A \tilde{v}_B / D_B \tilde{v}_A \), only the expression between brackets remains. This equation considerably simplifies if \( N_i^+ = 1 \) and \( N_i^- = 0 \).

The intrinsic diffusion coefficients are related to the tracer diffusion coefficients \( D_i^T \) in homogeneous alloys of the same composition by [9,10]:

\[
D_A = D_A^T \cdot \frac{\tilde{v}_A}{\tilde{v}_B} \left[ \frac{\text{dln} a_A}{\text{dln} N_A} \right] \cdot r_A \tag{13}\]

where \( \text{dln} a_i / \text{dln} N_A = \text{dln} a_B / \text{dln} a_B \) is called the thermodynamic factor and \( a_i \) is the activity of component \( i \). The term \( r_A \) is a correction factor originating from the vacancy flux effect and is dependent on the crystal structure and the difference in \( D_i^T \) [11]. From Eq. (13) it follows that

\[
\frac{D_A}{D_B} = \frac{D_A^T \cdot \tilde{v}_A \cdot r_A}{D_B^T \cdot \tilde{v}_B \cdot r_B} \tag{14}\]

and
Since the number-fixed frame of reference, which is defined by a constant total amount of moles at each side of the origin \( x = 0 \), is often used in literature [12] it is convenient to give the following relations (superscript N refers to the number-fixed reference frame):

\[
\begin{align*}
\tilde{D} &= \tilde{D}_N \\
\tilde{D}_N &= \frac{V}{V_B} \cdot \tilde{D}_N^N \\
\tilde{D}_N^N &= \frac{d \ln s_{A}}{d \ln N_A} \\
\tilde{D}_N^N &= \tilde{D}_A^N \cdot \frac{d \ln s_{A}}{d \ln N_A} 
\end{align*}
\]

For layers with a very small homogeneity region \( \Delta N = 0 \) it is very difficult to calculate a diffusion coefficient from a penetration curve, since the concentration gradient approaches zero and the apparent diffusion coefficient, therefore, becomes infinite (see Eqs. (3) and (11)). A very useful concept for this case is the integrated diffusion coefficient defined by Wagner [13]:

\[
\tilde{D}_{\text{int}} = \int_{N_1}^{N_2} \tilde{D} \, dN = \tilde{D}_{av} \cdot \Delta N
\]

where \( N_1 \) and \( N_2 \) are the - unknown - homogeneity limits of the phase, \( \Delta N = N_2 - N_1 \) and \( \tilde{D}_{av} \) is the average interdiffusion coefficient in the phase.

This quantity is a material constant like the normal diffusion coefficient and is simply related to the parabolic growth constant as defined in next section.

The equations given in this chapter can often be simplified.

a) In case of a constant total volume, which means that \( V_A \) and \( V_B \) are concentration-independent, Eqs. (2) and (11) can be used for finding \( \tilde{D} \) or \( D_i \). If in such a couple at least one of the starting materials is a pure component, e.g. \( C_1^- = 0 \), then Eq. (11) reduces to:

\[
D_i(x_K) = -\frac{1}{2t} \left( \frac{\partial C_i}{\partial x} \right)_{X_K} \int_{X_K}^{X} C_i \, dx
\]

(11a)

(Note the simple integral which contains, contrary to Eq. (2), the distance parameter as a differential which means that the position of the Matano plane is not involved [6].)
b) In case of constant and equal partial molar volumes, which means $\bar{V}_A = \bar{V}_B = \bar{V}_M$, several equations can be simplified. In Eqs. (2), (11) and (11a), $C_i$ can then be replaced by the mol fraction $N_i$. Further:

$$\sqrt{K/M} = (D_A - D_B) \frac{\delta N_A}{\delta x}$$  \hfill (9a)

$$\bar{D} = N_A D_B + N_B D_A$$  \hfill (10a)

$$\bar{D} = \bar{D}^N \text{ and } D_i = D_i^N$$  \hfill (16a)

If, on top of that, $N_A^- = 0$ and $N_A^+ = 1$ (i.e. diffusion between two pure metals), Eq. (12a) can be simplified to

$$\frac{D_A}{D_B} = \int_0^x N_A \, dx / \int_0^{x_K} (1-N_A) \, dx$$  \hfill (12b)

The time dependence of the penetration plot

The analysis given in the foregoing paragraph assumes that the same diffusion process is rate-limiting throughout the whole annealing procedure. In that case, a plot of the penetration curve versus $x/t^{1/2}$ will be invariant. The treatment is simplified by taking as a diffusion zone the layer of one compound growing between the starting materials, which restricts the problem to the study of the layer growth as a function of time. If the same diffusion process is rate-limiting throughout the whole annealing time, then the layer thickness $d$ and the annealing time $t$ are related through the parabolic growth constant $k_p$ as $d^2 = 2k_pt$. Apart from possible disturbing effects during the heating or cooling procedure, several reasons may exist which invalidate this assumption. A few of these are discussed here.

a) The mating surfaces may initially be covered by a thin layer of different composition, e.g. an oxide film or a segregation layer originating from impurities present in the starting materials. If an oxide film at the interface acts as a barrier for diffusion, then some incubation time will pass before an undisturbed diffusion process can begin. The plots of the width of the diffusion layer $d$ and $d^2$, respectively, versus time then resemble those shown in Fig. 2.2.
An example of this phenomenon was found in the Ti-Al system [14]. An oxide layer between Ti and Al broke down after a period of many hours, during which a slow linear reaction-limited growth of TiAl₂ was found. After this incubation time the layer grew very fast and parabolically with time in a diffusion-limited process. A row of pores in the layer marked the transition point in the process, indicating the residue of the disturbing oxide film.

A segregation layer at the interface is often present as a result of heating the couple or preannealing the starting materials. Especially atoms such as carbon or phosphorus, present in only a few parts per million in the bulk material, may give rise to enriched surface layers of only a few nanometers which in fact change the binary system into a ternary one. The diffusion process can then be totally different, but also time-dependent because of the limited amount of the segregating element [15,16].

b) The reaction between elements to form a new compound may be the rate-limiting step. The layer then starts growing linearly with time, but after reaching a certain thickness the diffusion process eventually becomes rate-limiting. This case is extensively discussed by Dybkov [1]. The plots of \(d\) and \(d^2\), respectively, versus time will then be like shown in Fig. 2.3.

In fact, in bulk diffusion couples no clearly proven case of reaction-limited growth is known to the author for non-porous reaction layers. However, it must immediately be added that the \(d^2/t\) plots in most studies on multiphase diffusion show in-enough measured points and too large a spread to be sure of the exact relation between the layer thickness and time. Small incubation times or periods of non-parabolic growth are then easily overlooked.
In porous layers, the reaction-limited linear growth is well known. In experiments in which the substrate reacts with a surrounding gas or liquid, reaction-limited and diffusion-limited growth can be distinguished by the morphology change of an originally cubic substrate as shown in Fig. 2.4, taken from [17]. In the first case, the typical "Maltese cross" type figure forms from the sharp corners of the substrate, since the gas or liquid can react with the substrate independent of the thickness of the porous reaction layer already formed. In the latter case, volume diffusion of the substrate atoms through the reaction layer towards the gas phase is rate-limiting, leading to complete coverage and rounded edges. Examples of the cross-type attack are the oxidation of metals such as Nb or Ta and of Co–WC alloys [17], the hot-dip aluminizing of titanium [18] and the hot-dip galvanizing of iron [19].
c) In many diffusion couple experiments the layer growth is faster in the beginning of the process because of the small grains present at the start which lead to a fast grain-boundary diffusion process. During the annealing procedure, grain growth occurs, and eventually the slower volume diffusion process will be the rate-limiting step. Plots of $d$ and $d^2$ versus time then appear as shown in Fig. 2.5.

\begin{align*}
\text{Fig. 2.5. Plots of layer thickness } d \text{ (a) and } d^2 \text{ (b) versus time in arbitrary units in a multiphase diffusion couple, if in the beginning of the diffusion process fast grain-boundary diffusion occurs.}
\end{align*}

It is interesting to inquire whether a $d^2/t$ or a $d/t^{1/2}$ plot can better be used in order to describe the proper values for the steady-state parabolic rate constant $k_p$ in the second growth stage. Pieraggi [20] concluded in an interesting discussion that a $d/t^{1/2}$ plot has to be preferred if the layer, formed during an initial transient period of faster kinetics, does not contribute to the steady-state rate control in the later parabolic stage. This situation often arises in oxidation reactions. In that case, the relation

\begin{equation}
\frac{d_p^2}{d^2} = \frac{(d - d_t)^2}{d - d_t} = 2k_p(t - t_i)
\end{equation}

applies, in which $d$ and $t$ are the total thickness and time, respectively, and $d_t$ is the thickness after the transient period ending at time $t_i$ after which the steady-state parabolic growth starts. The value $d_p$ is the thickness of the part of the layer, grown in the parabolic stage after time $t_i$. This relation leads to:

\begin{equation}
d = d_t + (2k_p(t - t_i))^{1/2}
\end{equation}

A plot of $d$ and $d_p$ versus $t^{1/2}$ for a specific case is given in Fig. 2.6a. It shows nearly parallel plots for $d$ and $d_p$ after longer annealing times, leading to a nearly correct value for $k_p$ from the slope of an experimental $d/t^{1/2}$ plot. This is true for cases where $t_i$ is not too large compared to $t$; the apparent value $k_p'$ from the $d/t^{1/2}$ plot and the real value $k_p$ are related through [20]
Fig. 2.6. Plots of $d$ vs. $t^\frac{1}{2}$ (a) and $d^2$ vs. $t$ (b) in arbitrary units in case of the presence of an initial layer of thickness $d = 2$ after a transient period $t = 10$, which does not contribute to the rate-control in the following parabolic stage with $k_p = 0.05$. A value $k_p'$ would have been found from the "experimental" curves. In (c) and (d) the same plots are shown, now for the case in which the initial layer does contribute to the following parabolic growth stage.

$$k_p' = k_p \frac{t}{(t - t_i)} \quad (19)$$

which is independent of the value of $d_i$.

If for this case a $d^2/t$ plot had been used, a wrong value for steady-state $k_p$ would have been found as can be seen by the different slopes of $d^2/t$ and $d_p^2/t$ in Fig. 2.6b. The apparent value $k_p'$ from the $d^2/t$ plot is then related to the real value of $k_p$ through:

$$k_p' = k_p \left[1 + \frac{d_i}{2k_p(t - t_i)}\right]^\frac{1}{2} \quad (20)$$

as shown by Pieraggi [20]. In Fig. 2.6 the sharp transition point between the two growth regimes is smoothed out to a continuous curve.

On the other hand, if the value of the thickness $d_i$ after the transient period does contribute to the steady-state parabolic growth in the second stage, then the following relation applies:

$$d^2 - d_i^2 = 2k_p(t - t_i) \quad (21)$$
In this case, a $d^2/t$ plot leads to the correct value of $k_p$, whereas a $d/t^K$ plot leads to erroneous results as shown in Fig. 2.6 c and d with an apparent $k_p'$ according to

$$k_p' = k_p t / (t - t_i + d_i^2/2k_p)$$

(22)

The same is true in cases where an incubation time is involved without a substantial transient layer thickness like in Fig. 2.2. In that case, $d_i$ is zero and a $d^2/t$ plot will give the proper $k_p$-value, whereas a $d/t^K$ plot leads to an apparent value $k_p'$ given by Eq. (19). It is, therefore, dependent on the kinetic role of the transient layer and the relative thicknesses $d$ and $d_i$ whether a $d^2/t$ or a $d/t^K$ plot is preferred when kinetic data for the parabolic diffusion process are evaluated. Actually, this consideration is often difficult to use because of the possible large spread in layer thickness measurements. It is then necessary to investigate thoroughly morphologic items like porosity and grain size in order to reduce the influence of prejudice in the evaluation of the experimental results!

Phases formed in diffusion couples compared with the phase diagram

This consideration is rather closely related to the former one, since especially in literature on thin-film reaction diffusion a sequential nucleation of various phases has been reported [21]. This, of course, rules out parabolic growth of all layers starting at $t = 0$. Several cases will be discussed:

a) An obvious reason for the absence of an equilibrium phase is the presence of barrier layers at the interface, such as e.g. oxide films, or the presence of impurities in the starting materials. In the latter case, segregation of impurities, present maybe only in the ppm-range in one of the end members, can cause an enrichment in the diffusion zone. This gives rise to a ternary system, and then the diffusion path might easily miss a binary equilibrium phase, as is shown later.

On the other hand, the same effect can cause the formation of a non-equilibrium phase, stabilized by impurities. Notorious examples are carbides like $\text{Mo}_2\text{Si}_3\text{C}$ [22] or $\text{Mo}_6\text{Ni}_6\text{C}$ [15], which might be confused with the purely binary phases $\text{Mo}_2\text{Si}_3$ and $\text{MoNi}$. The same is true for oxides like $\text{Ti}_4\text{Ni}_2\text{O}$ and $\text{Ti}_4\text{Fe}_2\text{O}$, which might be confused with the binary compound $\text{Ti}_2\text{Ni}$ or with an, in fact non-existing, binary "compound" $\text{Ti}_2\text{Fe}$ [23]. This is especially confusing when these ternary phases grow in thin layers in series with genuine binary thicker layers. An easy way to verify the purely binary character of an equilibrium layer is the use of incremental couples. The compositions of the end members are then chosen quite close to the apparent phase in question, in such a way that only this phase might be formed. The end members may be single-phase for two-phase alloys. A true equilibrium phase then grows parabolically with time as a relatively thick layer, whereas an impurity-stabilized phase stops growing after some time since the impurity is totally withdrawn from the end members. Fig. 2.7 schematically illustrates this procedure.
Fig. 2.7. In (a–d) are shown the phase diagram of an A–B system, the penetration plots for component B in a couple A/B and γ/B, and the plot of d^2 β versus time in the γ/B couple. In (a'–d') the δ-phase is a non-equilibrium, impurity-stabilised compound. The growth of the δ-layer in a couple γ/B then reaches soon a maximum value.

b) Especially if thin films are formed, either at the beginning of the experiment or because of a very low diffusivity in the phase, the formation of layers in the diffusion zone might be governed by the nucleation of phases [1,21,24,25]. D'Heurle [21] gives a survey on this subject, treating a number of silicide systems where nucleation may be so difficult that it dominates the process of phase formation. This situation may arise if the driving force (change in free energy ΔG) to build a new phase is very low and might become zero by the counteracting influence of the increase in surface energy. The phase then does not form at all; a threshold value of ΔG = -400 J/cm^3 is indicated [21]. At a specific higher temperature, the formation of the new compound is favoured and growth then starts parabolically with time.

c) If local equilibrium is established in the diffusion zone, each layer has to show up from the beginning of the experiment. Wagner [13] and Gurov et al. [26] derived equations for the growth of each phase in a binary couple, starting from the pure components A and B, of the type

$$\int_{N_A}^{N_A''} N_A \cdot dN_A = K_1 \cdot \frac{d\gamma}{dt} + K_2 \cdot \frac{d\gamma}{dt}$$  \hspace{1cm} (23)
in which \( D(\gamma) \) is the interdiffusion coefficient in the phase \( \gamma \) between the boundary concentrations \( N_A' \) and \( N_A'' \) and \( \delta_\gamma \) is the layer thickness of phase \( \gamma \). \( K_1 \) and \( K_2 \) are functions of the concentrations and diffusion coefficients in the other phases. Since the left-hand part of Eq. (23) is always positive, each phase has to grow to some (possibly very small) thickness \( \delta_\gamma \). Kidson [2] published an often quoted paper which reaches the same conclusion; purely from an equilibrium diffusion-limited growth concept all phases have to be present, albeit in very small widths (see next item). The purely algebraic negative growth constants for a phase mentioned by Kidson may not be interpreted as a reason for the non-existence of a layer of that phase.

If, however, a reaction-limited growth of some phase is involved, its formation can be suppressed according to Dybkov [1], leading to an incubation period for the growth of this phase. The reader has to be aware that this has nothing to do with nucleation problems previously mentioned, but it results from purely kinetic reasons as proposed by Dybkov. In the author's opinion, this prediction has yet to be proven experimentally and will be one of the challenges for accurate experimentalists, especially with regard to the next item.

d) Sometimes phases seem to be missing in diffusion couples when investigated by microscopic or microprobe analysis. In that case they might actually be present in very thin layers, observable only by electron microscopy. Examples which need a thorough analysis in this respect are the diffusion couples Ti-Al [14] and Cu-Si [16]. In both systems various phases should be present according to the phase diagram, but only one phase seems to be present in the diffusion couples, viz. TiAl_3 and Cu_3Si. However, calculations show that the missing phases under the experimental conditions should be present in thicknesses far below 1 micrometer and are, therefore, microscopically not observable. The reason is, that the diffusivity in the "missing" phases is several orders of magnitude lower than those in TiAl_3 and Cu_3Si.

In the titanium-aluminum case, the missing phases (TiAl_2, TiAl and Ti_3Al) were grown in an incremental couple Ti/TiAl_3. After their growth to relatively thick layers the remaining couple was placed versus Al and annealed again. As expected, the layers TiAl_2, TiAl and Ti_3Al microscopically disappeared and only TiAl_3 could be observed [14]. Whether these layers remained present in very thin layers is now being investigated in our laboratory by means of electron microscopy.

Interface concentrations in diffusion couples compared with bulk-equilibrium values

Since the quantitative evaluation of diffusion couples is often used for phase diagram determination, it is important to be sure that bulk-equilibrium values are really attained at the interfaces.

If the diffusion couple technique is not used in a proper way, a number of error sources might appear. Some of them were already mentioned before, such as:
- the large role played by impurities
- the necessity to use incremental couples because of the problem of missing phases.

Apart from these, some practical difficulties may arise, such as:
a] Steep concentration gradients may occur in growing phases or in the end members of the couple. By microprobe analysis it is difficult to measure reliable concentration values at a distance shorter than about 2 \( \mu \)m from the interface. This means, that an extrapolation is always necessary which might cause errors when steep gradients are involved. Again, incremental couples have to be used or an analysis of equilibrated two-phase alloys has to be made in order to get reliable results.
b) Accurate microprobe analyses near interfaces are very difficult if fluorescence effects affect the concentration measurements at distances as large as 40 μm from the interface. Corrections for this effect are possible but difficult [27]. In a binary couple, usually one of the elements does not suffer from the fluorescence effect and one could measure the concentration of that element by microprobe analysis to describe the penetration plot. If, for instance, pure Cu and Co are clamped together without any diffusion taking place, Co-Kα radiation can apparently be measured up to 40 μm in the pure Cu. About 4.8 mole % Co appears to be in Cu at the interface [27]. Measuring Co-Kα radiation diminishes the error, but still an apparent concentration of 2 mole % Cu is found in Co at the interface, whereas the Cu-radiation can still be detected at 15 μm from the interface in Co.

c) As shown for diffusion couples in the Cu-Al system [28], slow cooling rates may easily affect the high-temperature interface concentration values (see further in this section).

d) Adda and Philibert [4] give a number of examples in which the use of an external pressure changes the kinetics of the layer growth as well as the interface concentrations. Large pressures lead to concentration values which are identical with equilibrium bulk phases given by the phase diagram. According to the author's experience, an external pressure of typically 30 kg/cm² (depending on the annealing temperature) is often needed to get reliable and reproducible results. The external pressure is thought to establish good contact between the end members [16, 29, 30].

From a theoretical point of view a more interesting question is whether a supersaturation of one of the elements must occur because of the need for a driving force for the lattice transformation [3]. Also a slight supersaturation of vacancies should be necessary to maintain a vacancy flux [31]. Although very slight differences from binary equilibrium values are predicted, in our laboratory we have never observed differences which exceeded the experimental inaccuracy. Romig [32] came to the same conclusion in a survey paper on this subject. An often quoted experimental proof for large discrepancies between concentrations measured in diffusion couples and in equilibrated alloys was published by Eifert et al. [3] for the Cu-Al system. Newly reported results [28] showed that the discrepancies found by Eifert et al. probably originated from the slow cooling rates in their experiments.

The position of the Kirkendall and Matano planes in a diffusion couple

Let us consider the formation of Ni₃Sn₂ between the adjacent phases Ni₃Sn₄ and Ni₃Sn, which has been studied by van Beek et al. [33]. After annealing at 792°C the result is schematically shown in Fig. 2.8.

The Matano plane x₀ can be found graphically from the penetration curve as treated before, or experimentally e.g. by preventing the reaction between Ni₃Sn₄ and Ni₃Sn at the edges of the couple [34] as shown in Fig. 2.8 or by other ingenuous methods [35].

For simplicity, let us consider the phases in the couple as purely stoichiometric line-compounds. Then, the position of the Matano plane in the Ni₃Sn₂-layer can immediately be found by the reaction equation.
Fig. 2.8. Schematic drawing of a Ni$_3$Sn$_4$/Ni$_3$Sn diffusion couple in which the phase Ni$_3$Sn$_2$ is formed [33].

\[
2 \text{Ni}_3\text{Sn} + \text{Ni}_3\text{Sn}_4 \rightarrow 3 \text{Ni}_3\text{Sn}_2
\]

volume ratio \[103 : 125 : 225\]

Therefore, \(d_2/d_1 = 125/103 = 1.21\). Because hardly any change in total volume occurs, the partial molar volumes \(\bar{v}_{\text{Ni}}\) and \(\bar{v}_{\text{Sn}}\) are nearly constant, viz. about 9 and 24.

The Kirkendall markers, put in the original interface at \(t = 0\), were displaced towards the Ni$_3$Sn-side at the position \(x_K\), leading to a ratio \(x_2/x_1 = 1.85\).

From Table 2.1 it is clear that this ratio equals 0.5 only if Sn diffuses and Ni is immobile (line a in Fig. 2.8) since then at the Ni$_3$Sn-side, two times as many Ni$_3$Sn$_2$ molecules are formed. If only Ni diffuses and Sn is immobile this ratio \(x_2/x_1 = 2\) (line b). From these data it follows that Ni diffuses faster than Sn.

Table 2.1

<table>
<thead>
<tr>
<th></th>
<th>Only Sn diffuses</th>
<th>Only Ni diffuses</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Ni}_3\text{Sn}_4)-side</td>
<td>(\text{Ni}_3\text{Sn}_4 + \text{Ni}_3\text{Sn}_2 + 2 \text{Sn})</td>
<td>(\text{Ni}_3\text{Sn}_4 + 3 \text{Ni} + 2 \text{Ni}_3\text{Sn}_2)</td>
</tr>
<tr>
<td>(\text{Ni}_3\text{Sn})-side</td>
<td>(2 \text{Ni}_3\text{Sn} + 2 \text{Sn} + 2 \text{Ni}_3\text{Sn}_2)</td>
<td>(2 \text{Ni}_3\text{Sn} + \text{Ni}_3\text{Sn}_2 + 3 \text{Ni})</td>
</tr>
<tr>
<td>(x_2/x_1)</td>
<td>0.5</td>
<td>2</td>
</tr>
</tbody>
</table>
If both Ni and Sn diffuse, then the simple chemical equations of Table 2.1 are dangerous to use if the partial molar volumes are not equal. In fact, the mathematically correct Eq. (12a) accounts for this difference in atomic volume as it does for the presence of a homogeneity range of about 5 mole % in Ni3Sn2 and the non-stoichiometry of the end members. The experimentally determined value of \( x_2/x_1 = 1.85 \) then leads to a ratio \( D_{Ni}/D_{Sn} \) of about 1.5. If only the difference in atomic volume had been taken into account, the ratio \( D_{Ni}/D_{Sn} \) would have been calculated as 9.5.

This analysis has been given in some detail to show:

a) The ratio \( d_2/d_1 \), i.e. the relative penetration of the reaction layer into the end members, has nothing to do with the question which atom species is actually diffusing: it is governed purely by the overall reaction equation. Although the penetration is deeper towards the tin-rich side, Ni is the faster diffusing component.

b) A simple mass balance can provide global information about the position of the Kirkendall plane depending on the ratio of the intrinsic diffusion coefficients. A more accurate analysis through Eq. (12a) is needed especially if different partial molar volumes and concentration gradients are involved.

c) The accuracy of the measured position of the Kirkendall plane has to be tremendous in order to get reliable values for the ratio of the intrinsic diffusion coefficients if this is larger than about 5. This has been demonstrated by Bastin et al.[34] and is shown as an example for the above mentioned Ni3Sn4/Ni3Sn couple in Fig. 2.9, where stoichiometric compounds are assumed and Eq. (12a) is used for the calculation of \( D_{Ni}/D_{Sn} \), taking \( \bar{V}_{Ni}/\bar{V}_{Sn} = 0.38 \). In fact, one must admit that the diffusion couple technique is not suited for the accurate determination of the ratio between the intrinsic diffusion coefficients if this is larger than about 5, even if the partial molar volumes of the components are exactly known. For a layer width of 100 \( \mu \)m, the position of the markers for the cases \( D_{Ni}/D_{Sn} = 5 \) and \( D_{Ni}/D_{Sn} = 2 \) differs by 3.4 \( \mu \)m, which is mostly within the accuracy limits of the experiment.

![Fig. 2.9. The ratio of the distances \( x_2/x_1 \) in relation to the ratio of the intrinsic diffusion coefficients \( D_{Ni}/D_{Sn} \).](image-url)
In the foregoing it was assumed that the Kirkendall plane can be found, e.g. by using inert markers. The analysis showed, that the position of this plane has to be determined very accurately in order to find reliable results for the calculation of the intrinsic diffusion coefficients. The markers have, therefore, to be very thin. The best method, although it does not work in all cases, is to use "natural" markers which may be made visible by a proper etching procedure. Small debris or pores, present at the original interface especially at places where the contact between the end members was not established immediately, can then often be seen along a straight row. Often the grain structure of the phase at both sides of this row is different, which can easily be understood from e.g. Fig. 2.8. The part of the Ni$_3$Sn$_2$ layer above the Kirkendall plane is formed by the diffusion of atoms into and out of Ni$_3$Sn$_4$, whereas the part below the Kirkendall plane is formed by the diffusion into and out of Ni$_3$Sn. In some way the different grain morphology of Ni$_3$Sn$_4$ and Ni$_3$Sn is reflected in the different morphology in the Ni$_3$Sn$_2$-phase on both sides of the Kirkendall plane. Nice examples may be found in Ni-Sn [33], Nb-Sn [36], and NiO-Al$_2$O$_3$ [37].

The use of thick markers, like e.g. tungsten wires of 10 μm diameter, is very dangerous as was convincingly demonstrated by Bastin [38]. Fig. 2.10 shows the fate of an originally cylindrical tungsten wire in a Ti-Ni diffusion couple. Since after a short diffusion time the thick wire is in contact with all phases of the couple, in each of which the diffusivities and vacancy fluxes were different, an actual rupture of the wire took place. Various parts of the wire migrated with different velocities. Only very small thoria particles revealed the true position of the Kirkendall plane. The same effect could be seen

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Fig. 2.10. The distortion of an initially circular tungsten wire in a diffusion couple Ni/Ti after 72 hr annealing at 800°C [38].
Fig. 2.11. The distortion and displacement of initially square micro-indentations in a Cu-Zn couple after 4 hr annealing at 400°C [39].

If microhardness indentations were used as markers as shown in Fig. 2.11 [39]. Elongation of the indentations occurs, and in fact from theoretical considerations, depending on the ratio of the intrinsic diffusion coefficients in the various phases, disruption of the indentations might happen. In Ref. [39] it is also shown that if the markers in the Kirkendall plane are fixed to the "laboratory" frame, the ends of the couple will be displaced with respect to that frame. If, on the other hand, one end of the couple is fixed to the laboratory frame, the Kirkendall markers move with respect to this frame. The final morphology and thickness of the diffusion zone is the same for both experimental setups.

Finally, sometimes an easy method can be used to determine the relative diffusion velocities of the elements. By growing a phase γ between the pure end members A and B, and reheating the same couple during the same temperature again as shown in Fig. 2.12, the newly formed part of the layer can often be revealed by specific etching procedures. It is now clear that only A atoms diffuse since the layer grows at the γ/B interface. The method was used e.g. in the Ni-Al [40] and the Ti-Al [14] system.
The role of interphase interface in the creation or annihilation of vacancies resulting from the Kirkendall effect

In recent publications [8,41] the role of interphase interfaces in a diffusion couple on the creation or annihilation of Kirkendall vacancies was investigated. As an example, the most simple multiphase couple, viz. an $\alpha/\beta$ couple with only one interface, was chosen. Dependent on the initial concentrations of the end members, the same interface must be able to act as a source (Fig. 2.13 a,b,e) or a sink (Fig. 2.13 d) for vacancies in the case where the same element diffuses faster in both phases. If the initial concentrations are chosen in such a way that the Kirkendall plane coincides with the position of the interphase interface (Fig. 2.13 c) no discontinuity in the vacancy flux is found.

If the ratio of the intrinsic diffusivities is $> 1$ in one phase but $< 1$ in the other phase, interesting phenomena occur. In Fig. 2.14 the initial concentrations are chosen in such a way that the Matano plane coincides with the phase interface. In Fig. 2.14 a) $B$ diffuses faster than $A$ in the same ratio in both the $\alpha$ and $\beta$-phase, although the interdiffusion coefficient in $B$ is larger than in $\alpha$; in Fig. 2.14 b) $B$ diffuses faster than $A$ in the $\beta$-phase but slower in the $\alpha$-phase, and in Fig. 2.14 c) $B$ diffuses faster than $A$ in the $\alpha$-phase but slower in the $\beta$-phase.

In case a) the interface absorbs vacancies from the $\alpha$-phase and pumps more vacancies into the $\beta$-phase, thus acting as a source for vacancies. In case b) the interface acts as a source, sending vacancies into both the $\alpha$ and the $\beta$-phase. In refs. 8 and 41 it has been shown that in such a case two real Kirkendall planes have to be defined. Markers, placed at the original interface at $t = 0$, have to split up and drift in both the $\alpha$ and the $\beta$-phase. If the ratio $D_A/D_B$ is constant in each phase, this position coincides with the two inflection points in the penetration plot [4,42]. In case c) the interface acts as a sink for vacancies coming from both the $\alpha$ and $\beta$-phase. It is easy to imagine that the arrival of vacancies at the interface from both sides might give rise to the formation of pores, and therefore, bad adherence between the end members. In this case two "virtual" Kirkendall planes may be defined, positioned at the inflection points of the virtual extensions of the penetration plots in both phases. In case a) one real and one virtual Kirkendall plane occurs.
Fig. 2.13. Penetration plots of component B (mole fraction) in a system in which $D_B = 10 D_A$ in both the $\alpha$ and $\beta$ phase for various initial end member concentrations and $D_B = 10 D_A$. Also shown is the vacancy flux $J_v$ and in a) and c) the gradient of the vacancy flux as a function of the position in the couple [8].
Fig. 2.14. Plots of the mole fraction of B and the vacancy flux $J_V$ in couples where the Matano interface does not move. In (a) $D_B/D_A = 10$ in both the $\alpha$- and $\beta$-phases, in (b) $D_B/D_A = 10$ in the $\beta$-phase and 0.1 in the $\alpha$-phase, and in (c) $D_B/D_A = 0.1$ in the $\beta$-phase and 10 in the $\alpha$-phase [6].
These phenomena may be visualized by the behaviour of an initially square indentation at the interface at $t = 0$ as shown in Fig. 2.15. The same authors presented a model for the dynamic action of the interface during the phase transformation, which includes climb of misfit dislocations out of the interface and climb of misorientation dislocations in the interface [43].

Fig. 2.15. The change in morphology of a square indentation marker, originally placed at the $\alpha/\beta$ interface at $t = 0$ after diffusion annealing in the situations given by figs. 2.14a-c. The real or virtual displaced origin of the alpha and beta Kirkendall frames of reference are described by $K^\alpha$ and $K^\beta$ (defined by the constant lateral indentation width) [8].

The morphology of interphase interfaces if grain boundary diffusion is taking place

If a single-crystalline layer of $\gamma$ is growing between single-crystalline substrates $\alpha$ and $\beta$, one might expect completely straight $\alpha/\gamma$ and $\gamma/\beta$ interfaces, provided that no orientation relation effects occur which might cause a faceted interface. In polycrystalline layers grown between polycrystalline end members, the interfaces are often not completely straight. Some typical structures are given in Fig. 2.16.

In many diffusion experiments, case a) is found: an equiaxed layer of $\gamma$ bounded by completely straight interfaces. Often thin needle-like crystals are formed, e.g. Cu$_3$Si formation in Cu-Si couples [16,44,45] as shown in case b) where straight interfaces are found. The explanation is that in case a) only volume diffusion occurs, e.g. because of the use of relatively high temperatures so that grain-boundary diffusion becomes unimportant. In case b), on the other hand, only grain-boundary diffusion takes place. The necessary lateral diffusion at the interfaces might occur by surface or volume diffusion, but in fact this is immaterial because of the thinness of the crystals. In case c) interdiffusion through grain-boundaries is faster than interdiffusion through the bulk as e.g. in the Ni$_3$Al phase grown in Ni/NiAl couples [40]. The morphology gives no information about the relative mobility of the two components.

In case d), found e.g. at the FeSn$_2$/FeSn interface in a FeSn$_2$/Fe couple [33] and in a much more exaggerated form e.g. the formation of Fe$_2$Al$_5$ [46] bulk diffusion is predominant, but is different for various crystallographic directions which leads to a different length of the grains. A non-uniform nucleation accompanied by lateral growth may also lead to morphologies like this [44].
Grain boundaries in the end members may also affect the morphology of the reaction layer at relatively low temperature, especially under the influence of impurities (Fig. 2.16 e,f). For instance, Bastin [34] found extensive formation of $\beta$-Ti by grain-boundary diffusion of Ni into $\alpha$-Ti in the presence of traces of iron. Iron stabilises $\beta$-Ti in the grain-boundaries of $\alpha$-Ti and, therefore, enhances Ni-diffusion. The removal of iron stopped this type of grain-boundary interdiffusion. Whether morphology e) or f) is found depends on the position of the relevant interface with respect to the Matano plane: the total layer width increases by grain-boundary diffusion and the interface, therefore, is further displaced from the Matano plane. Morphology f) can also be found if e.g. the formation of a solid solution in the end member is facilitated by (impurities in) the grain boundary [14].

Influence of a difference in cross-section of the end members on the layer morphology in planar couples

During research on interdiffusion of Cu and Si [45] a typical phenomenon was found, as schematically shown in Fig. 2.17.

If a small piece of Si is used, the Cu$_3$Si-layer grows in exactly the same cross-section into the Cu end member. If the Si has a larger cross-section than Cu, a lens-shaped layer is formed, broader than the original Cu end member. In both cases the columnar grains of Cu$_3$Si always grow perpendicular to the original interface.

The explanation has to be found in the fact, that Cu is the only diffusing component in Cu$_3$Si. In the left-hand figure, Cu atoms diffuse straight through Cu$_3$Si to the available Si, converting the original Si into a Cu$_3$Si mass of the same shape (although with a volume of about 7/3 times the volume of the reacted Si). In the right-hand figure, however, Cu can diffuse by surface diffusion along the Cu$_3$Si to react with Si available outside the original cross-section of Cu, leading to the lens-shaped morphology of the reaction layer. Conversely, the faster diffusing component can be identified from this morphology.
Fig. 2.17. Different morphologies of the Cu$_3$Si reaction layer in a Cu/Si diffusion couple dependent on the relative diameters of the end members. The columnar grains in Cu$_3$Si are indicated.

Generally, the edges and free surfaces of the diffusion couple give extra information on the layer growth mechanism and concentration limits of the various phases. Often surface diffusion or evaporation/condensation processes give rise to the formation of a larger amount of phases rich in substrate material compared to the regular diffusion zone because of an impeded supply of diffusing material (see α-phase in Fig. 2.18). In fact, a kind of incremental couple is present at these edges. In ternary diffusion couples, this phenomenon can be used to even more advantage (see chapter 3).

Fig. 2.18. Development of diffusion layers at the edges of a diffusion couple.
Comparison of the reaction layer thickness in planar, cylindrical and spherical diffusion couples

It makes a difference when layer growth is studied in planar diffusion couples as discussed up to now or in e.g. cylindrical or spherical couples, which are important in e.g. coated wires, fibrous composites or in sintering problems. Let us look to the growth of a layer $A_{By}$ between an infinite matrix $B$ and pure $A$ which has the dimensions of either a plate with thickness $2r_0$, or a cylinder with diameter $2r_o$, or else a sphere of the same diameter. The volume of one mole $A_{By}$ is $z$ times the volume of one mole of pure $A$. After some time $t$, the situation shown in Fig. 2.19 arises, where $a$ equals the unreacted radius, or (for the plate) $a$ equals half the unreacted thickness of $A$.

![Diagram of reaction layer growth](image)

**Fig. 2.19.** The reaction between a plate of pure $A$ with thickness $2r_0$ (a) and of a sphere or cylinder of pure $A$ with diameter $2r_0$ (b) with a matrix $B$, forming the compound $A_{By}$ of layer thickness $d$.

The conversion factor $\alpha$, i.e. the fraction of $A$ which has reacted, is:

$$\alpha = \frac{r_a - a}{r_0} ; \frac{a}{r_0} = 1 - \alpha \quad \text{(Plate)}$$

$$\alpha = \frac{r_a^2 - a^2}{r_0^2} ; \frac{a^2}{r_0^2} = 1 - \alpha \quad \text{(Cylinder)} \quad (24)$$

$$\alpha = \frac{r_a^3 - a^3}{r_0^3} ; \frac{a^3}{r_0^3} = 1 - \alpha \quad \text{(Sphere)}$$
From geometrical considerations the following relations exist between $\alpha$ and the layer thickness $d$:

$$\frac{d_p}{r_o} = \alpha$$  
(Plate)

$$\frac{d_c}{r_o} = (1 + (z - 1)\alpha)^{1/2} - (1 - \alpha)^{1/2}$$  
(Cylinder)  
(25)

$$\frac{d_s}{r_o} = (1 + (z - 1)\alpha)^{1/3} - (1 - \alpha)^{1/3}$$  
(Sphere)

We are interested in $\alpha$ and $d$ as a function of time if volume diffusion is the rate-limiting step. As an example, consider the formation of an $AB_y$-layer, which grows in a planar couple according to the parabolic law $d^2 = 2k_pt$ ($k_p$ = parabolic growth constant). For short annealing times, the layer widths are equal for the three morphologies, but for longer annealing, differences arise from the fact that the surface area of the inner and outer shell of the layer will change, contrary to the constant surface in planar couples.

A number of equations are given in the literature in various degrees of approximation and values of $z$ [47-52]. The author has nowhere found a clear comparison, expressed in the same quantities and, therefore, a number of useful relations is given here between the values of $\alpha$, $r_o$, $t$ and the planar parabolic growth constant $k_p$. The derivation of these equations proceeds along the same lines as used by Carter [47], but special care is taken in defining the various quantities which leads to expressions slightly different from those given in the literature:

$$\left(\frac{\alpha}{z}\right)^2 = 2\frac{k_p}{r_o}t$$  
(Plate)

$$\frac{z}{2} \left[ \frac{1 + (z - 1)\alpha}{z - 1} \right] \ln \left( 1 + (z - 1)\alpha \right) + \frac{\alpha}{2} (1 - \alpha) \ln(1 - \alpha) = 2\frac{k_p}{r_o}t$$  
(Cylinder)  
(26)

For $z = 1$:

$$\frac{z}{2} \left[ \frac{1 + (z - 1)\alpha}{z - 1} \right] \ln \left( 1 + (z - 1)\alpha \right) = 2\frac{k_p}{r_o}t$$  
(Cylinder)

$$\frac{\alpha}{z - 1} (1 - \alpha) \left( 1 - \frac{z}{1 - \alpha} \right) = 2\frac{k_p}{r_o}t$$  
(Sphere)

$$\frac{\alpha}{z - 1} (1 - \alpha) \left( 1 - \frac{z}{1 - \alpha} \right) = 2\frac{k_p}{r_o}t$$  
(Sphere)

For low values of $\alpha$ the Eqs. (25) and (26) reduce to:

$$\left(\frac{\alpha}{z}\right)^2 = \frac{2}{z}t$$  
(Plate)

$$\left(\frac{\alpha}{z}\right)^2 = \frac{2}{z}t$$  
(Cylinder)

$$\left(\frac{\alpha}{z}\right)^2 = \frac{8}{z}t$$  
(Cylinder)

$$\left(\frac{\alpha}{z}\right)^2 = \frac{18}{z}t$$  
(Sphere)

By plotting the conversion factor $\alpha$ versus $t^{1/z}$ according to Eqs. (26) for $z = 2$ as shown in Fig. 2.20, straight lines are found with slopes of 1, 2 and 3 times $(2k_p)^{1/2}$ for values of $\alpha$ lower than about 0.35. Therefore, from each slope the true value for the parabolic rate constant of a planar couple can be found.
Fig. 2.20. A plot of the conversion factor $\alpha$ versus $t^{-\frac{1}{2}}$ for a plate of thickness 200 ($p$), a cylinder ($c$) and a sphere ($s$) both of diameter 200 of material $A$ reacting with a matrix $B$ according to $A + B \rightarrow AB$. Volume diffusion is the rate limiting step. The volume ratio $AB/A = 2$, the parabolic growth constant for the plate $k_p = 50$, all in arbitrary units.

Through Eq. (25) the $\alpha/t^{-\frac{1}{2}}$ plot can be converted into a $d/t^{-\frac{1}{2}}$ plot as shown in Fig. 2.21 for $z = 2$. Consistent with the foregoing result, up to a thickness of about $0.35 \, r_0$, the thicknesses are nearly equal for the three couple types. It takes thickness values up to about $1.1 \, r_0$ ($\alpha = 0.95$) for a cylinder and $0.7 \, r_0$ ($\alpha = 0.90$) for a sphere to find an increase of 10% in layer width compared with a planar couple. For lower values of $z$, the deviations are larger.

However, in practice, the deviations are probably much larger than predicted from these geometrical relations. One reason has been pointed out by Beke [53]: diffusion into a cylinder or sphere may build up stresses which cannot be released as easily as in a planar couple. These stresses may influence the thickness of the growing layer(s), especially when volume changes are involved. Also the Kirkendall effect can cause large deviations, especially when the cylinder or sphere material is diffusing much faster than the surrounding material. In this case, a large increase of the total volume may occur due to the formation of hollow spheres [54].
Fig. 2.21. A plot of the thickness $d$ of the AB reaction layer versus $t^{1/2}$ for the situation described in Fig. 2.20.

**Texture in reaction layers**

Very often the crystals of the phases in diffusion-grown reaction layers have a preferred orientation in the growth (diffusion) direction. This texture has been studied extensively in our laboratory and the following result is found: the direction of the longest crystallographic axis is invariably oriented perpendicular to the diffusion direction, i.e. parallel to the interface [55, 56]. Very often another rule of thumb is found: the shortest repeat-distance in the crystal lattice is aligned parallel to the direction of diffusion (fiber texture). These textures are most pronounced at the growth front of the reaction layer; in the "oldest" part of the layer sometimes changes in texture are found due to recrystallization.
The presence of a texture is important since often chemical and mechanical properties are quite dependent on the crystallographic direction. In the well-known galvanizing process, for instance, the $\delta$-FeZn$_{10}$ layer is formed with its hexagonal axis perpendicular to the diffusion direction [57,58]. In that direction the diffusion of Zn through $\delta$ is very fast which causes relatively thick reaction layers. For economic reasons it would be very helpful if the hexagonal axis could be forced to orient itself parallel to the diffusion direction. Unfortunately, despite the various tricks we used, nature did not allow us to interfere with its above-mentioned rules.

The evaluation of diffusion coefficients in couples in which large volume changes occur

Equations (3) and (12) can be used without any problem for finding the (inter)diffusion coefficients from a penetration curve in multiphase couples, even if very large volume changes occur. A special example is the growth of a titanium carbide layer between pure titanium and carbon [10]. The partial molar volume of carbon in titanium carbide is virtually zero, which leads to equal values for the interdiffusion coefficient $D$ and the intrinsic diffusion coefficient of carbon $D_C$ in titanium carbide:

$$D = C_{Ti} \bar{V}_{Ti} D_C + C_C \bar{V}_C D_{Ti} = D_C$$

The evaluation of diffusion coefficients in vapour-solid couples compared with solid-solid couples

Let us compare, for instance, the growth of a FeO layer between Fe and Fe$_3$O$_4$ on the one hand, and between Fe and oxygen gas with an oxygen activity equal to the FeO/Fe$_3$O$_4$ equilibrium on the other hand [13]. The thickness of the FeO-layer will be larger in the first case than in the latter because of the fact, that FeO grows from two sides: the reaction of oxygen with iron and the loss of oxygen from Fe$_3$O$_4$. The penetration curves, expressed in mole fractions of iron, are schematically shown in Fig. 2.22. For simplicity, the homogeneity range in FeO is taken as zero, which is only a rough approximation but not important for this discussion.

According to Wagner's analysis [13] the integrated diffusion coefficient for the FeO-phase can be written for the Fe/Fe$_3$O$_4$ couple as:

$$\bar{s}_{\text{int}} = \frac{(1-0.5)(0.5-0.7)}{4/7} \cdot \frac{d_1^2/2t}{d_1} = \frac{1}{16} \cdot \frac{d_1^2/2t}{d_1}$$

For the Fe/oxygen couple one finds:

$$\bar{s}_{\text{int}} = \frac{(1-0.5)(0.5-0)}{1-0} \cdot \frac{d_2^2/2t}{d_2} = \frac{1}{4} \cdot \frac{d_2^2/2t}{d_2}$$

Since the integrated diffusion coefficient is a material constant, it follows that $d_1 = 2d_2$. In these simple cases (only line-compounds are involved) the variations in partial molar volumes are irrelevant and a plot with molar fraction can be used.
If the mole fraction of oxygen had been used for the plots, the same results must be obtained. This means that for the oxygen gas the mole fraction must be taken as $N_O = 1$, irrespective of its pressure or activity. Differences in oxygen activity only reflect themselves through differences in the defect structure in changes in the interdiffusion coefficient for the FeO-phase.

The same principle can be used if diffusion is studied between the alloys $A_{q}B_{1-q}$ and $A_{p}B_{1-p}$, heated in a closed vessel with no direct contact. Diffusion then has to proceed through the gas phase. In the ideal case, the same constant surface concentration $N_A = p$ ($q < p < y$) has to occur in the equilibrium condition on the outer surface of both alloys. In practice, sometimes a different but constant value is found for both surfaces [59-61], showing an activity gap in the gas phase.

In Fig. 2.23 it is assumed that only element A evaporates, and that the surface concentration on both alloys equals $N_A = p$. The alloy $A_pB_{1-q}$ has lost material (thickness decrease $x_0 - x_1$) and $A_qB_{1-q}$ has gained material (thickness increase $x_2 - x_0$). If the molar volumes of A and B are equal, and if the total surface of both alloys is equal, then $x_0 - x_1 = x_2 - x_0$.

The total amount of A, lost from the alloy $A_pB_{1-q}$, equals the sum of the area C and D. On the other hand, it also equals the sum of the area D and E. Therefore, one may find the original surface $x_0$ by equating

$$\text{Area C} = \text{Area E}.$$
In the same way the amount of component A gained by the \( A_{qB_{1-q}} \) alloy equals the sum of the area \( G + K + H \), but also equals \( K + G + F \), from which it follows that the original surface \( x_0' \) is found by equating

\[
\text{Area } F = \text{Area } H
\]

Under the above mentioned conditions in which \( x_0 - x_1 = x_2 - x_0' \), one might shift the couple halves in such a way that \( x_0 = x_0' \) and \( x_1 = x_2 \). One then gets Fig. 2.24, showing that

\[
\text{Area } C + F - E = \text{Area } H
\]

and, therefore, the plane \( x_0 = x_0' \) is identical to the Matano plane.

---

Fig. 2.23. The annealing of the alloys \( A_{yB_{1-y}} \) and \( A_{qB_{1-q}} \) together in a closed vessel. After equilibrium is reached, the same surface concentration \( N_A = p \) is present on both alloys. The positions of the Matano planes \( x_{0} \) and \( x_{0}' \) are indicated for both alloys; they coincide with the original surfaces. The new surfaces after diffusion annealing are given by \( x_1 \) and \( x_2 \), respectively.

Fig. 2.24. The situation in a pure solid-state diffusion couple \( A_{yB_{1-y}}/A_{qB_{1-q}} \) obtained by overlapping of Figs. 2.23 a) and b) until the common concentration \( p \).
From this analysis the following conclusions can be drawn:

1) Since the diffusion coefficient, calculated from the profiles in Figs. 2.23 and 2.24, has to be the same for each concentration independent of the total amounts of the alloys it follows that in Fig. 2.23 b the Matano plane has to be the plane \( x_0' \). This position can be found geometrically without any dependence on the actual composition of the master alloy \( A_yB_{1-y} \) by equating the areas \( F \) and \( H \). If the molar volumes of \( A \) and \( B \) are not equal, corrections have to be made as discussed previously.

2) From the diffusion profile shown in Fig. 2.23 a, i.e. the material-losing alloy, the Matano plane (now situated outside the alloy) can be found in such a way that Area \( C = \) Area \( E \). It would lead to completely wrong results if one would define the Matano plane as the plane \( x_3 \), dividing the concentration profile in the alloy in two parts equal in area \( (x_3 - x_1 - p - r = r - s - t) \).

3) If both \( A \) and \( B \) are evaporating, or if the total surface of one alloy is much larger than the other (e.g. a plate of \( A_yB_{1-y} \) embedded in a large excess of \( A_yB_{1-y} \) particles) a same kind of analysis applies provided that infinite diffusion couples still can be assumed. In the first case, the net difference \( (A-B) \) has to be equal to Area \( D+E = \) Area \( K+G+F \). This means that an equal transport of \( A \) and \( B \) leads to a Matano plane coinciding with the outer surfaces of both alloys.

In the second case, the concentration \( p \) at the outer surface would be much closer to the value \( y \), making \( x_0 - x_1 < x_2 - x_0' \). The two penetration curves can then not be joined to one continuous curve like in Fig. 2.24: two different Matano planes can be defined, one for each alloy.

A discontinuity in the slope will arise at the outer surfaces in such a way, that the same diffusion coefficient is found whether the one or the other alloy is evaluated at their outer surface concentration.

In fact, the message is simple: if diffusion coefficients have to be calculated from a penetration curve, the mathematical position of the Matano plane has to coincide with the position of the original surface, which may be situated inside or outside the alloy. From an extension of these considerations interesting conclusions can be drawn concerning the position of, and the composition at the Kirkendall plane [42]. In the specific example chosen here, this plane coincides with \( x_1 \) at \( N_A = p \) in Fig. 2.24.

3. MULTIPHASE DIFFUSION IN TERNARY SYSTEMS

In the introduction the important difference between binary and ternary systems was already mentioned. The extra degree of freedom in a ternary system gives rise to the occurrence of two-phased layers in diffusion couples, and especially the relation between the composition of the diffusion zone and the phase diagram becomes much more complicated.

In a classical paper, Kirkaldy and Brown [62] formulated a number of rules which relate the composition of the diffusion zone with the phase diagram. They used the concept of the so-called diffusion path: this is a line on the ternary isotherm, representing the locus of the average compositions in planes parallel to the original interface throughout the diffusion zone.
Fig. 3.1. Examples of possible morphologies for the reaction layer in a diffusion couple X/C. The corresponding diffusion paths are plotted on the isotherms [65].
In Fig. 3.1 a hypothetical phase diagram shows the existence of six single-phase regions, viz. the three elements A, B and C, two binary compounds X and Z, and the ternary compound T. In Figure 3.1 four diffusion paths are given, together with the corresponding morphologies of the diffusion zone, for the diffusion couple C versus X. They all fulfill the most important constraint, viz. the conservation of mass: no material can be lost or created. This forces the path to cross the straight connection line between C and X at least once, and gives constraints about the relative thicknesses of the various diffusion layers like T and Z in Fig. 3.1b. Obviously, the Z-phase has to be much thinner than the T-phase in order to comply with the mass balance.

Not only the relative thicknesses, but also the total thickness of the diffusion layer is related to the diffusion path. If e.g. in the Z-phase the diffusion is very slow and in the T-phase fast, then obviously the total layer width for Figs. 3.1.b or c will be smaller than in the case of Fig. 3.1.d. In the first examples, the continuous Z-layer acts as a kind of barrier, whereas in the case of Fig. 3.1.d, the total layer thickness is governed by the faster diffusion in the T-phase, which is probably only little hampered by the discontinuous Z-particles. Examples of this phenomenon are given in Refs. 63 and 64.

**Model for the prediction of the layer sequence**

For a number of relatively simple systems it is possible to predict the diffusion path from the phase diagram and kinetic data according to a model extensively described in Refs. 65-67 for so-called displacement reactions of the type

\[
A + BX \rightarrow AX + B
\]

although more intricate reactions can also be understood by using this model.

Referring for details especially to Ref. [65] we will just summarise here the main ideas, using three real systems as examples. The most important starting point is, that no element intrinsically diffuses, i.e. jumps from one lattice site to another, up its own activity gradient. The word "intrinsically" is very important here. An element does often interdiffuse up its own activity gradient, but that transport is then imposed upon this element by the intrinsic diffusion behaviour of the other two: by their atomic jumps from one lattice site to another the third element drifts in a direction which indeed may be up its own activity gradient. This has mathematically been shown in [42].

The reader must be very well aware of the difference between the activity gradient and the concentration gradient for an element in a diffusion couple. In a binary system, these always have the same direction. In a ternary system, this is not the case. In the well-known Darken experiment [68,69], for instance, up-hill diffusion of carbon is found from a concentration point of view, but from an activity point of view carbon diffuses down its own activity gradient throughout the whole couple.

Let us take as a first example the reaction

\[
Co + Cu_2O \rightarrow CoO + 2Cu
\]

at 1000°C. The relevant part of the phase diagram is shown in Fig. 3.2a, whereas the oxygen activity from the Cu/Cu_2O side towards the Co/CoO side is shown in Fig. 3.2.b. From the phase stability diagram, the reaction proceeds because CoO is much more stable than Cu_2O.
Diagram 3.2.b is constructed from a knowledge of the thermodynamic $\Delta G^\circ$-values for CoO and Cu$_2$O, but may in a qualitative way also be constructed from the phase diagram by the slope of the tie-lines [65].

Fig. 3.2. a) Phase relations and diffusion path in Co-Cu-O system at 1000°C.
  b) The oxygen pressure as a function of the metal mole ratio. The dots represent the oxygen pressure in equilibrium with the solid solutions Cu(Co) and Co(Cu).
  c) A schematic representation of the layer morphology and equilibrium oxygen pressure in the couple Cu/Cu$_2$O after a heat treatment of 100 h at 1000°C [65].

Fig. 3.3. Phase relations and diffusion path (a) as well as the equilibrium oxygen pressure (b) in the Fe-Ni-O system at 1000°C; c) represents the layer morphology and oxygen pressure in an Fe/NiO diffusion couple after 100 h annealing at 1000°C [65].
In Fig. 3.2.c the actual layer morphology in a diffusion couple is shown. The activity of oxygen is continuously rising from one side to the other without any extremum. The same holds for the activities of Co and Cu, which are not shown. This means, that from a thermodynamic point of view this morphology is allowed, leading to a diffusion path as given in Fig. 3.2.a. From a kinetic point of view no problem exists, since the diffusion of oxygen through the resulting Cu-layer to form CoO is very fast [70,71]. The rate limiting step is the diffusion of Co-ions through CoO, and indeed quantitative predictions about the total layer thickness turn out to agree with the experiments [65,70].

The reverse path, i.e. Co-Cu-CoO-Cu$_2$O$_2$, is not forbidden for thermodynamic reasons, but very unlikely on kinetic grounds. It would mean that oxygen is immobile and Co has to diffuse through the Cu-layer to form CoO and the solid solution of Co in Cu$_2$O$_2$, whereas Cu ions have to move through CoO. These kinetic steps are much slower than those in the layer sequence shown in Fig. 3.2.c.

In the system Fe-Ni-O, the phase diagram is a type related to Co-Cu-O in the sense that the slopes of all tie lines have the same sign, which leads to a same type of plot for the oxygen activity as a function of the metal ratio, as shown in Fig. 3.3.a and b. A layer sequence Fe/Fe-oxide/Ni/NiO is then predicted. The actual morphology of the reaction layer, however, is different in the sense, that the iron oxides are not formed in a straight layer but penetrate the formed Fe-Ni solid solution in a more or less finger-shaped way. This two-phased layer was predicted and experimentally shown by Rapp and coworkers [70,72] and confirmed by [65]. The reason for this morphology is that the diffusion of oxygen through the Fe-Ni solid solution is now slower and rate-limiting, compared to the fast diffusion of Fe-ions through the oxides. Then each accidental perturbation at the Fe-oxide/Ni boundary grows preferentially: the straight interface is not stable. The original sequence Fe/Fe-oxides/Ni/NiO can, however, still be recognised at the boundaries Fe/Fe-oxide and Ni/NiO.

Fig. 3.4. Phase relations and diffusion path (a) as well as the equilibrium sulfur pressure (b) in the Cu-Ni-S system at 500°C; (c) represents the layer morphology and sulfur pressure in a Cu/Ni$_3$S$_2$ diffusion couple after 100 h annealing at 500°C [65].
An essentially different phase diagram is shown for the Cu-Ni-S system in Fig. 3. Because of the changing sign of the slopes of the tie lines leaving from the metallic solid solution, a maximum in the sulfur activity is found in the three-phase region Cu$_2$S-Ni$_3$S$_2$-CuNi. Then sulfur is thermodynamically not allowed to diffuse intrinsically from Ni$_3$S$_2$ to the Cu-side, because then it would diffuse up its own activity gradient. So at least at the start of the process sulfur is immobile, which leads to an initial layer sequence Cu/CuNi/Cu$_2$S/Ni$_3$S$_2$ as indeed found [65].

The predictions from this kind of considerations for reasonably uncomplicated systems show a perfect agreement with the experimental results, 16 of which are presented in [65,66]. In more complicated systems, adaptions have to be made such as shown for the Fe-Ni-B and Fe-Co-B systems [73]. In summarising, the morphology of the diffusion zone in a ternary couple can be predicted by a scheme such as shown in Fig. 3. Because complicated systems have not yet been studied in this respect (with an exception for the Ti-Al$_2$O$_3$ and Ti-SiO$_2$ systems investigated by Hillal [74]), it might be safer to conclude that the model can definitely predict which layer morphology is impossible, leaving open in some cases more than one possibility which the model cannot decide [73]. Further research is this field to find additional criteria is progressing. The experiments recently published by the group of Chang [e.g. 75] on the interfacial reactions between metals and Gallium Arsenide are interesting in this respect, although in these reactions non-equilibrium situations arise after short annealing times or low temperatures. The phenomena reported for a Pt-GaAs diffusion couple at 600°C [75] are completely in line with the predictions by our model.

Fig. 3.5. Basic morphologies of the reaction zone for the displacement reaction A + BX + B + AX in relation to two possible types of phase diagrams. In (a) the tie lines have the same sign of slopes, leading to morphologies shown in (c) depending on the kinetics in the system. In (b) the different sign of the slopes of the tie lines permits only morphology (d).
Experimental determination of the rate-limiting step

The rate-limiting step in the diffusion process can sometimes be found in a rather elegant way by applying one of the reaction products already to one of the starting materials before making the diffusion couple [71]. For instance, it was experimentally shown that the application of an extra layer of pure Cu on the Cu₂O end member in a diffusion couple with Ni did not influence the thickness of the newly formed Cu and NiO-reaction layers, proving that diffusion of oxygen through Cu is not the rate-limiting step. Applying, however, a NiO-layer on the Ni-surface before making a diffusion couple with Cu₂O drastically decreases the reaction rate, proving that the diffusion of Ni-ions through NiO is the rate-limiting step.

Another way of finding the rate-limiting step is by investigating the sides of the starting materials which are not in direct contact with the other end member. Diffusion layers are often formed on these sides by evaporation of one or more of the elements [65]. This was found in a Ni-Cu₂O couple annealed in an evacuated silica capsule in which extra pieces of Ni were present, as schematically shown in Fig. 3.6. From the free sides of the Cu₂O end member oxygen evaporated and reacted with the excess of nickel, forming a NiO-layer which was equally thick as the one formed in the genuine solid-state diffusion couple. The Cu-layer, however, formed at the outer sides of Cu₂O, was much thicker than in the solid-state diffusion couple, the ratio b/a actually being about 90. The reason is clear: in the diffusion couple the Cu-layer cannot grow faster than allowed by the formation of NiO, which is governed by the slow diffusion of Ni-ions. (From the reaction equation and the molar volumes it follows that the thickness of the Cu-layer is 1.5 times the thickness of the NiO-layer). The thickness of the Cu-layer on the free surfaces of Cu₂O is dependent on the much faster diffusion of oxygen atoms through Cu. The theoretically calculated ratio b/a is about 90 [70], in agreement with the observed value. In a Cu₂O-Fe diffusion couple this effect does not appear, since for both the free surfaces of Cu₂O as well as that in the diffusion couple, the diffusion of oxygen through Cu is rate-limiting.

A third possibility is the use of a diffusion couple in which an alloy of the metals is used instead of a pure metal. This was demonstrated for the Ni-Cu-O system [63] by making couples of the type NiₓCu₁₋ₓ/Cu₂O. For a value of x lower than about 0.4, Ni cannot be supplied fast enough by diffusion in the end member alloy to form a continuous layer of NiO. Then, if fact, internal oxidation occurs, and the diffusion of oxygen through the Cu-Ni alloy is rate-limiting. The total layer width (alloy + NiO-precipitates) is now much larger than in the case where a continuous NiO-layer is formed, proving that the diffusion through NiO was the rate-limiting step in a Ni-Cu₂O couple.

Fig. 3.6. Schematic illustration of the layer morphology in a diffusion couple Ni/Cu₂O at 1000°C, annealed in a closed silica capsule in the presence of excess Ni.
In the same system, a comparable effect was found if small amounts of chloride ions were present in the Cu$_2$O-half of a Ni/Cu$_2$O couple. These prevented the sintering of the NiO-particles to a continuous layer, leading to randomly dispersed NiO particles and much faster total layer growth, again identifying the rate-limiting step in the diffusion process [64].

**Influence of kinetic parameters on the diffusion path**

Up to now we were discussing the morphology of the reaction products in relation to the phase stability diagrams mainly from a thermodynamic point of view. In single-phase regions, and especially in solid solutions formed from the starting materials kinetic factors are also very important as shown in [42,76].

As a general trend, in the single-phase regions of the end members, the diffusion path starts in the direction of the faster diffusing component in the end member poor in this component, and away from the faster diffusing component in the end member which is rich in this component. If the ratio of the mobilities remains the same throughout the whole system, this rule, together with the constraints of the mass balance, permits a rough idea about the course of the diffusion path, which is enough for many practical purposes. Note, however, that the diffusion path in the classical Darken experiment (Fe-Si-C/Fe-C) cannot be found from this kinetic model, since this path follows the direction of decreasing carbon activity and is exclusively determined by the thermodynamics.

For instance, in a phase diagram such as Fig. 3.7, where the element C is the fastest diffusing component in the single-phase region. If we now consider a diffusion couple of pure A versus BC, then the diffusion path can be estimated by these considerations. The prediction of the exact position of point p, as well as the exact curvature of the diffusion path, needs detailed information about the diffusivities of all elements and their mutual dependence. For the author, this calculation seems, generally speaking, a too formidable task to undertake, and an experimental determination is the only way to obtain an exact diffusion path. Backhaus-Ricoult [77,78], who performed both experimental and theoretical work on this problem came to the same conclusion.

![Fig. 3.7. Estimated diffusion path (---) for a diffusion couple A/BC with only the knowledge that the element C is the most mobile component. The tie lines are indicated as thin dotted lines.](image-url)
Influence of the gas partial pressure on the diffusion path

As soon as gases such as oxygen and nitrogen, but under some circumstances also sulfur or phosphorus, take part in the reaction, the gas atmosphere decides which reactions might occur. Take as an example the reaction between Ni and Al₂O₃ (see also [78,66]). The phase diagram in the Ni-rich corner is schematically shown in Fig. 3.8.

If the annealing of a Ni/Al₂O₃ diffusion couple is performed in an atmosphere which is extremely low in oxygen partial pressure the diffusion path will start from virtually the pure Ni-corner along path 1. No new reaction product is formed and only a solid solution of Al and O in Ni is found. Oxygen penetrates much deeper into nickel than aluminum because of their difference in diffusivity, but the absolute values of the dissolved amounts have to obey the mass balance, i.e. have to occur in the ratio 3:2.

If, however, annealing takes place at an oxygen level which already creates a solid solution of oxygen in pure Ni, the diffusion path starts at a point different from the corner position, i.e. path 2. Then, according to the mass balance, the path might develop in such a way that spinel is formed. This is what was predicted and experimentally found by Backhaus-Ricoult [78].

This effect can probably influence the morphology of the reaction layer dependent on the diameter of the couple halves. In Fig. 3.9 the couple pure Ni/Al₂O₃ is annealed in an oxygen atmosphere equal to the equilibrium pressure Ni/NiO. However, it takes time for oxygen to diffuse far enough to reach point a in the couple. At points b, on the other hand, a saturated solid solution of oxygen in Ni is readily formed. Therefore, one expects to find experimentally spinel formation at positions b and only a solid solution of oxygen and aluminum in Ni at point a. Whether or not this is found probably depends largely on the quality of the initial contact between Ni and Al₂O₃. If there is not good contact, oxygen could easily diffuse along the interface and form spinel everywhere. The same holds for reactions between e.g. Ni and Si₃N₄ [79]. In our laboratory we are trying to get more experimental information on this triple-point behaviour.

![Fig. 3.8. Diffusion paths for Ni/Al₂O₃ couples at different oxygen partial pressures [66,78].](image-url)
A related experiment for the Cu-Si-P system has already been performed [80]. The reaction between Cu₃P and Si appears to be largely influenced by the phosphorus partial pressure, as was shown by performing the reaction at 800 K in two ways, viz. in a closed silica vessel or in a dynamic vacuum of 10⁻⁹ atm.

In the first case, the phases Cu₃Si and SiP were formed in the layer sequence predicted by our model according to the phase diagram and the diffusivities as shown in Fig. 3.10 a and b. Inside the capsule the partial P₄-pressure of SiP (about 0.03 atm.) was present.

In the dynamic vacuum circumstances, the SiP phase is not stable because of its high partial phosphorus pressure and the phase diagram then looks like Fig. 3.10 c. According to the same model, the layer sequence as shown in Fig. 3.10 d has to be formed, whereby phosphorus evaporates at the interface Cu₃P/Cu₃Si. This indeed was found experimentally [80].
The phosphorus gas could escape despite applying an external pressure of 20 kg/cm² (2 MPa). The couple did not fall apart. Pores were visible at the interface Cu₃P/Cu₃Si at high temperatures where Cu₃Si was rather ductile and, therefore, plastically deformed. At low temperatures, no plastic deformation of Cu₃Si occurred, so that pores were present in such large dimensions that Cu₃Si seemed to form in isolated columns between Cu₃P and Si [80].

Influence of the stoichiometry of the end members on the diffusion path

Related to the last subject is the question whether small deviations in stoichiometry change a diffusion path. The answer depends on the system actually at hand, as seen by taking two examples.

In the case of Ni/Cu₂O treated before, the stoichiometry of Cu₂O is not very important. If Cu₂O would be slightly supersaturated in oxygen, CuO would be present from the beginning, but it would be reduced to Cu₂O by the formation of NiO. If this is only a small amount, the further reduction of Cu₂O will occur and eventually the layer sequence Cu₂O/Cu/NiO/Ni will form. A large excess of oxygen would lead to a thick NiO-layer, delaying the further reduction of Cu₂O since the necessary transport of Ni ions through NiO is too slow.

If Cu₂O is undersaturated in oxygen, i.e. if some free Cu is present, no difference in reaction is seen because the presence of a Cu layer does not influence the reaction rate or layer sequence.

In other types of systems, the influence of the stoichiometry might be larger. In the system Ti-Si-C the reaction between Ti and SiC might be completely changed by taking SiC with excess Si or C [81]. In the first case, it is not possible to form titaniumcarbide next to SiC, whereas in the last case this is quite well possible. This effect probably accounts for the large differences given by various research groups studying this system [82-84]. In our laboratory, we are currently investigating the system especially in this respect [81].

The occurrence of a periodic layer formation

In their recent book, Kirkaldy and Young [85] give a number of examples in which a periodic precipitation was found in ternary and higher order systems. They are related to the well-known Liesegang bands observed e.g. in some oxidation experiments.

In our laboratory Osinski et al. [86, 87] found examples in the couples Zn-Fe₃Si and Zn-Co₂Si. Mehan and Jackson [88] and Schiepers et al. [89] reported the same type of structure in the case of the diffusion couple Ni-SiC. Recently, periodic structures closely resembling those in Ni-SiC were reported for Pt-SiC couples [90]. It is interesting to consider these systems in a way completely different from Kirkaldy's approach. In Fig. 3.11 a-c the relevant phase diagrams are shown together with the diffusion path and layer sequence for specific diffusion couples, as predicted from our thermodynamic model. The components Zn and Ni are the only diffusing species (as shown by marker experiments), reacting with, respectively, Fe, Co and Si to form the various intermetallics FeₓZnᵧ, CoₓZnᵧ and NiₓSiₓ. The products left are then FeSi, CoSi and C, respectively.

This situation was indeed found experimentally after short annealing times, whereby the phases FeSi, CoSi and C were formed as porous layers. After longer annealing times, however, the diffusion zones showed the FeSi, CoSi and C phases as porous layers, precipitated in the matrices of FeₓZrₓ, CoₓZnₓ and NiₓSiₓ at regular distances and forming an interesting periodic structure.
Fig. 3.11. Schematic isothermal phase diagrams and the predicted layer sequences in specific diffusion couples in the systems Fe-Si-Zn (a), Co-Si-Zn (b) and Si-C-Ni (c).
Our qualitative explanation is the following, taking as an example the most intensively studied cases Fe₃Si-Zn and SiC-Ni. Because of the mechanical stresses built up at the interfaces between Fe₃Si and FeSi or SiC and C, respectively, these phases can only grow to a certain thickness before they lose contact with the end member. Immediately thereafter, the phases are formed again at this end member to the same layer thickness, etc. Then the periodically occurring phases always stay in contact with one end member and are never in contact with the other one, which is not the case if a Liesegang mechanism is operative. The structure reported for Pt-SiC [90] can be explained in the same way.

This idea was corroborated by experiments in the Fe-Si-Zn system in which the Fe₃Si starting material was very thin and, therefore, capable of deformation by mechanical stresses. The initial layer sequence was sustained for much longer times, and the FeSi-layer grew to an appreciable thickness before the layer lost contact.

If less Si is present in the starting material, the interdiffusion of Fe and Si is not fast enough to form a layer of FeSi adjacent to the Fe-Zn compounds. The reaction layer loses its periodic structure, and at low silicon contents, random precipitates of FeSi are found in the Fe-Zn intermetallics.

For the SiC-Ni systems, the experiments with thin SiC end members have not yet been made but are in progress. The closely related SiC-Fe diffusion couples show random precipitates of graphite in Fe₃Si [89], whereas in SiC-FeₓNi₁₋ₓ couples, the bands and random precipitates nicely coincide with a larger or smaller atom ratio of Ni/Fe in the reaction layer [67,91]. This effect might be related to the different influence of Fe and Ni on the sintering behaviour of graphite.

In the couple Co₂Si/Zn [87], a strange effect was found; the phase CoSi formed in periodic bands not parallel to the interface, but parallel to a certain crystallographic direction in the Co₂Si crystal from which the reaction products originated.

It would be worthwhile to understand these phenomena in a more fundamental and quantitative way, rather than in the somewhat vague and qualitative terms used here.

**Determination of a ternary isothermal cross-section using diffusion couples**

Since for each diffusion couple a unique diffusion path is followed, in principle, a large number of diffusion couples must be studied experimentally for a ternary isotherm.

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![Diagram](image-url)  
*Fig. 3.12. Determination of an isothermal section of a phase diagram like (a) from selected multiphase diffusion couples like (b).*
However, this number can be decreased appreciably by using polyphase alloys as starting materials. The chance to hit interfaces at which three phases are in equilibrium is much larger than, but these three-phase triangles have to be exactly known in order to understand the phase diagram. In Fig. 3.12 this procedure is shown schematically.

If a diffusion couple between the alloys P and Q should show a morphology indicated in this figure, then from one couple two three-phase triangles can be found. In area 1, microprobe measurements reveal the three-phase triangle T-Z-C, whereas from area 2 the triangle T-X-B can be found. By making sandwich couples like P/Q/R even more information can be gained. In this way, a few couples can give all the necessary information.

**Extension to quaternary systems**

The graphical difficulties in plotting a diffusion path in a quaternary phase diagram in a clear way are sometimes frustrating. In some simple systems such as the Fe-Ni-Si-C system mentioned before [67, 91] a clear representation is possible. By taking the Fe-Ni-Si triangle as a base and using NC/NFe+NNi+NSi as a vertical axis, the system can be presented as shown in Fig. 3.13 a. All phases at the Si-side of the broken line in the base triangle are in equilibrium with SiC, the other compositions are in equilibrium with graphite. As a consequence of the thermodynamic model, only these latter compositions can be formed in diffusion couples of the type SiC/Fe$_x$Ni$_{1-x}$. For a number of these compositions, the projections of the experimental diffusion paths on the base triangle are shown in Fig. 3.13 b [91].

If quaternary phases are formed, the visualization is more difficult. Yet, this way of presenting diffusion paths is better than using the usual pyramid-type of a quaternary phase diagram.

**4. CONCLUSIONS**

The reader will have noticed that this paper, especially the part on ternary systems, was quite qualitative in character. It is indeed intended to present a feeling for the process of multiphase diffusion, for the possibilities of predicting which reactions might occur, and for the experimental means to get useful information.

The author is fully aware of the fact that several good books have been written on this subject, like e.g. [4, 85]. It is, however, his experience with students and scientists after a number of years that mathematically correct descriptions of, especially ternary, diffusion processes are too intricate to be really used. If one wants to know exactly what happens in a ternary diffusion couple, four diffusion coefficients for each phase, and their concentration and temperature-dependence, have to be known. It is the author's feeling that this giant task to gather these data, will not if ever be completed soon. Therefore, a qualitative feeling about multiphase diffusion remains very important for the coming years, and the author hopes to have contributed to that aim by this work.
Fig. 3.13. a) The isothermal quaternary phase diagram Fe-Ni-Si-C, experimentally determined at 850°C [91].
b) diffusion paths projected on the Fe-Ni-Si section of the couples SiC/Fe$_{80}$Ni$_{20}$, SiC/Fe$_{60}$Ni$_{40}$, SiC/Fe$_{40}$Ni$_{60}$ and SiC/Fe$_{20}$Ni$_{80}$ [67,91].
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LIST OF SYMBOLS

\[ a = \text{unreacted radius or half the unreacted plate thickness in m, Eq. 24} \]
\[ a_i = \text{activity of component } i = N_i \]
\[ C_i = \text{concentration of component } i \text{ in moles/m}^3 \]
\[ C_i^- = \text{initial concentration of component } i \text{ on the left-hand side of the diffusion couple} \]
\[ C_i^+ = \text{initial concentration of component } i \text{ on the right-hand side of the diffusion couple} \]
\[ \bar{D} = \text{interdiffusion coefficient (also called chemical diffusion coefficient) in m}^2/\text{s, Eq. 2} \]
\[ D_i = \text{intrinsic diffusion coefficient of component } i \text{ in m}^2/\text{s, Eq. 11} \]
\[ D_i^T = \text{tracer diffusion coefficient of component } i \text{ in m}^2/\text{s, Eq. 13} \]
\[ D_{av} = \text{average interdiffusion coefficient in m}^2/\text{s, Eq. 17} \]
\[ D_{int} = \text{integrated interdiffusion coefficient in m}^2/\text{s, Eq. 17} \]
\[ d = \text{total layer thickness in m} \]
\[ d_i = \text{layer thickness after a transient period } t_i \text{, Eq. 18} \]
\[ d_p = \text{layer thickness on a plate during the parabolic growth period, Eqs. 18 and 25} \]
\[ d_c, d_p, d_s = \text{layer thicknesses in cylindric, planar and spherical diffusion couples during diffusion-limited growth, Eq. 25} \]
\[ \bar{J}_i = \text{interdiffusion flux of component } i \text{ in the Matano frame of reference in moles/m}^2/\text{s, Eq. 1} \]
\[ J_i = \text{intrinsic diffusion flux of component } i \text{ in the Kirkendall frame of reference in moles/m}^2/\text{s, Eq. 4} \]
\[ k_p = \text{parabolic growth constant in } m^2/s, \text{ Eq. 18} \]
\[ k'_p = \text{apparent value of } k_p \text{ from a } d/t^n \text{ plot, Eq. 19} \]
\[ N_i = \text{mole fraction of component } i. \text{ For superscript - or +, see } C_i \]
\[ \Delta N = \text{homogeneity width of a phase} \]
\[ R = \text{gas constant } = 8.314 \text{ J/mole } K \]
\[ r_i = \text{dimensionless factor originating from the vacancy flux effect, Eq. 13} \]
\[ r_o = \text{radius of cylinder or sphere, or half the plate thickness in } m, \text{ Eq. 24} \]
\[ T = \text{temperature in Kelvin unless stated otherwise} \]
\[ t = \text{diffusion time in seconds} \]
\[ t_i = \text{duration of the transient period before the parabolic growth sets in, in } s, \text{ Eq. 18} \]
\[ V_m = \text{molar volume in } m^3/\text{mole of atoms} \]
\[ \bar{V}_i = \text{partial molar volume of component } i \text{ in } m^3/\text{mole of atoms} \]
\[ \bar{V}_K/M = \text{velocity of local inert markers relative to the Matano frame of reference in } m/s, \text{ Eq. 5} \]
\[ x = \text{coordinate in the diffusion direction in } m \]
\[ x_o = \text{coordinate of the origin of the Matano frame of reference} \]
\[ x_K = \text{coordinate of the Kirkendall plane} \]
\[ \Delta x = x_K - x_0 \text{ in } m, \text{ Eq. 5} \]
\[ Y = \text{concentration unit for component } i = (N_i^- - N_i^+)/N_i^{+ - N_i^-}, \text{ Eq. 3} \]
\[ z = \text{ratio between the volume of one mole } AB_y \text{ and one mole } A, \text{ Eq. 25} \]
\[ \alpha = \text{conversion factor, Eq. 24} \]
\[ \gamma_i = \text{activity coefficient of component } i \]

An asterisk (as in \( C_i^* \) or \( Y^* \)) refers to a definite value of the quantity in question. The superscript N as in Eq. 16 denotes quantities in the number-fixed frame of reference.