Computer Simulation of Multiphase Binary Diffusion in Gas–Solid Type Couples

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Model 1 for describing multiphase diffusion and Model 2 for determining the interdiffusion coefficient of each phase in binary gas–solid couples were developed by modifying models previously presented. No restrictions on the number of phases, the values of interdiffusion coefficients, or the homogeneity ranges of phases were placed on the present models.

Composition profiles, mass changes per unit area of surface and dimensional changes normal to the surface for N–Cr, N–Fe, and N–Ti couples were numerically calculated from diffusivity and phase equilibrium data with Model 1. A good agreement between experimental and calculated results was found. It was confirmed that Model 1 is compatible with Model 2, which can be easily applied and is useful when no references are available for diffusivity data.

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1. Introduction

In binary gas–solid couples, new phases often form as layers parallel to the surface. For example, if pure iron is oxidized, Fe₂O₃, Fe₃O₄ and FeO form on the surface under given conditions. Similar behavior is observed during case hardening processes such as carburizing and diffusion coating processes such as chromizing. Estimation of the layer width and simulation of the composition profile in the diffusion zone at any diffusion time are interesting, not only from a theoretical but also from a practical point of view.

An analytical solution for two-phase diffusion in a binary semi-infinite medium was presented by Jost, but no solution has been derived for more than one product phase. Jäger and Matauschek presented approximate solutions for the layer growth of one and two product phases in a semi-infinite medium on the assumption of the linear concentration in a phase. The solutions can be easily generalized to a general n-phase system. However, their method is not totally satisfactory because it gives no description of the composition profiles. Two different models, for describing multiphase diffusion (Model 1) and determining the interdiffusion coefficient of each phase (Model 2) were developed for Boltzmann–Matano type diffusion where a variable \( \eta \equiv x/t^{1/2} \) is introduced and the solution \( c_i = c_i(\eta) \) is assumed.

It has already been pointed out that the layer growth rate of a product phase increases proportionally to the product of the square root of the interdiffusion coefficient and the homogeneity range of the phase, if the miscibility gap between adjacent phases is excluded. Therefore, a rise in the number of phases present in a couple and a drop in the amount of the preceding product make the simulation still more difficult. One purpose of the present study was to develop a general model for the numerical description of binary multiphase diffusion without being restricted by the number of phases, the interdiffusion coefficient, or the homogeneity range of a phase. This was done by modifying the preceding Model 1.

Equilibrium phase boundary data and diffusion data are needed to execute Model 1. The former data are available for almost all binary systems (for example, reference 6). The latter data are available for some limited systems only. It is therefore useful to apply Model 2 to systems for which there are no available diffusivity data. Another purpose of the present study is to verify the compatibility between Models 1 and 2.

2. Models

For general gas–solid binary couples, one diffusing component, A, is transferred from the gas phase to the solid phase, and the other component, B, is transferred in the opposite direction. The following assumptions are made:

(a) the composition at each phase boundary, including that at the surface, is time independent;

(b) the interdiffusion coefficient in each phase, \( D(j) \), is composition independent;

(c) the ratio of the number of moles for component A entering the solid phase to that for component B leaving the solid phase, \( \gamma \), is time independent.

In gas–solid couples, for such diffusion processes as nitriding and carburizing, the partial molar volume of the diffusing gas component, A, is much smaller than that of the metallic diffusing component, B. However, most analyses of diffusion in gas–solid couples have ignored possible effects due to variations of molar volume with composition, and have assumed constant molar volume over the composition range considered. Nevertheless, these effects should be of significance in the calculated composition profile, mass change, and dimensional change of the solid phase. The additional assumption is made here that:

(d) molar volume changes linearly with composition.

The present numerical simulation of multiphase diffusion in gas–solid couples consists of the following two models:

1. numerical calculation for describing the Boltzmann–Matano type of diffusion where the concentration of a diffusing component, \( c \), can be expressed in terms of a single variable \( \eta \equiv x/t^{1/2} \);
2) numerical calculation of the interdiffusion coefficient for each phase in the Boltzmann–Matano type of diffusion couple.

2.1 Numerical calculation for describing multiphase diffusion (Model 1)

The equations describing the concentration profiles in the product phase \( j \) and the terminal phase \( n \) are given by

\[
c_A = C_A(j, j - 1) + \frac{C_A(j, j + 1) - C_A(j, j - 1)}{\text{erf}(\omega(j, j + 1)) - \text{erf}(\omega(j, j - 1))} \times [\text{erf}(\xi) - \text{erf}(\omega(j, j - 1))]
\]

and

\[
c_A = C_A(n, n + 1) - \frac{C_A(n, n + 1) - C_A(n, n - 1)}{1 - \text{erf}(\omega(n, n - 1))} \times [1 - \text{erf}(\xi)]
\]

where \( \xi = x/[2^{1/2} \cdot D(j)^{1/2}] \), \( C_A(j, j \pm 1) = N_A(j, j \pm 1)/[N_A(j, j \pm 1) \cdot V_A + \{1 - N_A(j, j \pm 1)\} \cdot V_B] \). The term \( V_i \) stands for the partial molar volume of component \( i \), \( N_A(j, j \pm 1) \) stands for the mole fraction of component \( A \) at the phase boundary in phase \( j \) coexisting with phase \( j - 1 \) or \( j + 1 \), \( N_A(1, 1) \) stands for that at the surface; and \( N_A(n, n + 1) \) stands for that in the solid phase at \( t = 0 \). An example of a schematic \( \eta - c_A \) profile is shown in Fig. 1.

The unknowns \( \omega(j, j \pm 1) \), where \( j = 1, 2, \ldots, n \), can substantially be obtained by a binary bisection method.\(^{3}\) By adding a modification, a general numerical method that is not restricted by the number of phases present in the couple, the interdiffusion coefficient and the solubility range of a phase has been developed. Provided that the parameters \( \omega(j, j \pm 1) \) are all known, the following characteristic values can be obtained:

\( \lambda(j, j \pm 1) \) the rate constant for the moving of interfaces \( (j - 1/j) \) or \((j/j + 1)\) \( [\text{m}^{-1/2}] = 2\omega(j, j \pm 1) \cdot D(j)^{1/2} \);

\( X(j, j \pm 1) \) the displacement of interface \( (j - 1/j) \) or \((j/j + 1)\) relative to the \( x = 0 \) plane \([\text{m}] = t^{1/2} \cdot \lambda(j, j \pm 1) \);

\( X_S \) the displacement of the surface relative to the \( x = 0 \) plane \([\text{m}] = X(1, 0) \);

\( kW(j) \) the rate constant for layer growth of phase \( j \) \( [\text{m}^{-1/2}] = \lambda(j, j + 1) - \lambda(j, j - 1) \);

\( W(j) \) the layer width of phase \( j \) \( [\text{m}] = X(j, j + 1) - X(j, j - 1) \);

\( P(j)[x, N_A] \) the point expressed by the distance and mole fraction of component \( A \);

\( kM \) the rate constant for mass change per unit area of surface \([\text{g} \cdot \text{m}^{-2} \cdot \text{s}^{-1/2}] \);

\( \Delta M \) the change in mass of the solid phase per unit area of surface \([\text{g} \cdot \text{m}^{-2}] = t^{1/2} \cdot kM \).

\( kM \) is given by the following equation which eq. (27) in Ref. 3) has been modified into:

\[
kM = -A(1, 0) \cdot A(1, 0) \cdot (R_A + \gamma R_B)
\]

and \( R_i \) in eq. (3) is the relative atomic mass of component \( i \).

The data necessary for the calculation and some characteristic calculated data are shown in Fig. 2.

2.2 Numerical calculation of interdiffusion coefficients (Model 2)

We developed a model for determining interdiffusion coefficients for all the phases present in a gas–solid couple.\(^{4}\) With this model there is no need to evaluate the concentration gradient in each phase. The method principally consists of the calculation of integrals and determination of \( X_S \) by the following equations, respectively:

\[
S_i(j) = \int_{X(j, j - 1)}^{X(j, j + 1)} [c_i - C_i(n, n + 1)] dx
\]

and

Fig. 1 Schematic \( \eta - c \) profile of three-phase diffusion in a gas–solid couple.

Fig. 2 Input and output data used in Model 1. Here, \( P(j)[x, N_A] \) denotes a group of points as a function of distance and the content of component \( A \) in phase \( j \).
\[ X_s = \frac{R_A \cdot \sum_{k=1}^{n} S_A(k) + R_B \cdot \sum_{k=1}^{n} S_B(k) - \Delta M}{R_A \cdot C_A(n, n+1) + R_B \cdot C_B(n, n+1)} \]

Here, \( \Delta M \) can be obtained, provided that \( X_S \) is known. From eqs. (17a, b) in Ref. 3) and eq. (44) in Ref. 4), the mole ratio \( \gamma \) is given by

\[ \gamma = \frac{\sum_{k=1}^{n} S_B(k) - C_B(n, n+1) \cdot X_S}{\sum_{k=1}^{n} S_A(k) - C_A(n, n+1) \cdot X_S} \]

The number in moles of component \( i \) having passed through interface \( (j/j+1) \) is given by

\[ Q(j/j+1) = \sum_{k=j}^{n} S(k) - C_i(n, n+1) \cdot X(j, j+1) \]

Now, we can numerically calculate interdiffusion coefficients for all the phases present by the initial substitution of \( Q_A(j/j+1) \) and \( Q_B(j/j+1) \) and the sequential substitution of the results obtained into the following equations, i.e.

\[ \phi(j/j+1) = \frac{Q_A(j/j+1)}{Q_A(j/j+1)} \]

\[ A(j, j+1) = A(j+1, j) \]

\[ Nt(j, j+1) = \frac{Nt(j+1, j)}{Nt(j+1, j)} \]

\[ \exp \left[ \frac{X(j, j+1)^2 - X(j, j-1)^2}{4D(j) \cdot t} \right] = \frac{X(j, j+1) \cdot [A(j, j+1) - C_A(j, j+1)]}{X(j, j+1) \cdot [A(j, j+1) - C_A(j, j+1)]} \]

and

\[ f \left( \frac{X(n, n-1)}{2[D(n) \cdot t]^{1/2}} \right) = \frac{C_A(n, n+1) - C_A(n, n-1)}{A(n, n+1) - C_A(n, n+1)} \]

where \( f(\omega) = \pi^{1/2} \cdot \omega \cdot \text{erfc}(\omega) \cdot \exp(\omega^2) \).

The necessary data for the calculation and some characteristic calculated data are shown in Fig. 3.

3. Example of Simulations

Nitriding of chromium, iron, and titanium will be used as examples here since equilibrium and diffusivity data are available as input data for their systems, and the reliable mass changes, dimensional changes and diffusion layer widths needed for comparison with the calculated results have been measured. It is possible by either Model 1 or Model 2 to make simulations of composition profiles and the associated changes, provided that the equilibrium and diffusivity or experimental data are known.

By approximating the linear dependence of molar volumes on composition, the partial molar volumes of both the diffusing components for a given system were calculated from the molar volumes of nitrides and the parent pure metal in reference to the lattice parameter data. Phase boundary compositions excluding the surface composition were taken from the equilibrium phase diagrams.

3.1 Nitriding of Chromium

Nitrogen content profiles of nitried chromium calculated from Table 1 are shown in Fig. 4. The profile for case A stands for expansion normal to the surface, that for case B no change, and those for C and D, shrinkage. On the other hand, the following equations were already deduced in Ref. 3, i.e.

<table>
<thead>
<tr>
<th>( j )</th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Phase}(j) )</td>
<td>( \text{Cr}_2\text{N} )</td>
<td>( \text{Cr} )</td>
</tr>
<tr>
<td>( N(j, j+1) )</td>
<td>( 31.4^a )</td>
<td>0.35</td>
</tr>
<tr>
<td>( N(j, j+1) )</td>
<td>26.3</td>
<td>0</td>
</tr>
<tr>
<td>( D(j) )</td>
<td>( 4.2 \times 10^{-12} )</td>
<td>( 1.33 \times 10^{-10} )</td>
</tr>
<tr>
<td>( V_i ) ( \left[ 10^{-6} \text{m}^3 \text{mol}^{-1} \right] )</td>
<td>( V_N = 3.79 ), ( V_C = 7.23 )</td>
<td></td>
</tr>
<tr>
<td>( \gamma )</td>
<td>0.0, -0.5243, -1.0, -1.5</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 3 Input and output data used in Model 2. Here, \( P(j|x, N_A) \) must be input when a linear approximation is not made of the composition profile in phase \( j \). The bottom item on the left side means that \( X_S \) is output in the case where \( \Delta M \) is input, and \( \Delta M \) is output in the case where \( X_S \) is input.

Fig. 4 Nitrogen content profiles in chromium nitried at 1473 K for 34.2 ks calculated with four different values of \( \gamma \).
π1/2 · α(1, 0)[erf[α(1, 0) − α(1, 2)] · exp[α(1, 0)²]]

\[ \frac{CA(1, 0) - CA(1, 2)}{A(1, 0) - CA(1, 0)} \]  

(12)

When \( γ \) takes the value of case B, it makes the term \( V_A + γV_B \) nearly equal to zero, and then the parameter \( A(1, 0) \) approaches infinity, as is clear from eq. (4). Next, when \( A(1, 0) \) having the value of infinity is substituted into eq. (3), i.e.

\[ X_S = -\frac{ΔM}{A(1, 0) \cdot (R_A + γR_B)} \]  

(13)

it can be seen that \( α(1, 0) \) which is written as \( X_S/[2D(1)t]^{1/2} \) becomes nearly zero. Equation (1), where \( j = 1 \), therefore, yields

\[ c_A = CA(1, 0) + \frac{CA(1, 2) - CA(1, 0)}{erf[α(1, 2)] \cdot erf[α/2/[2D(1)/t]]} \]  

(14)

Equation (14) is identical to the solution\(^1\) to diffusion into a homogeneous phase, a second phase developing from the surface given by Jost. That is, it is apparent that the solution by Jost can be applied only to no net transfer of volume through the surface for both diffusing components. Figure 4 shows that \( X_S \) increases from a negative value to a larger positive value with a decrease in mole ratio \( γ \), that is, the dimensional change of the nitrided chromium normal to the surface continuously varies from expansion to shrinkage with a decrease in \( γ \).

The dependence of the rate constant for layer growth of \( Cr_2N \) and the rate constant for mass change upon the mole ratio are shown in Fig. 5, in which both of them decrease with a decrease in \( γ \) and especially the latter reaches negative values. An ammonia gas used in gas nitriding processes is decomposed into nascent nitrogen and hydrogen at the nitriding temperature, i.e.

\[ NH_3 \to N + 3H \]

For example, the nascent nitrogen reacts with chromium and forms chromium nitride. It is clear from the above reaction equation that the mole ratio \( γ \) is zero when the evaporation rate of chromium from the surface is negligibly small. Therefore, the nitriding processes will not result in the mass losses seen in Cases B, C, and D. On the other hand, in siliconizing processes performed on iron with silicon tetrachloride under neutral atmosphere, the following substitution reaction mainly occurs:

\[ SiCl_4(g) + 2Fe(s) = Si(\text{in Fe}) + 2FeCl_2 \]

where the mole ratio has the value -2. It has been reported by Mitani and Onishi\(^10\) that the mass loss of siliconized steel decreases parabolically with treatment time. Their observations correspond to the negative value of the mole ratio.

The experimental values of \( kW(Cr_2N) \) and \( kM \) obtained by Schwertfeger\(^8\) are less than the calculations in the case where \( γ = 0 \). This is perhaps due to evaporation of chromium at the high nitriding temperature 1473 K employed in his study. Even if this is not so, the calculations show close agreement with the experimental results.

### 3.2 Nitriding of Iron

The parameters \( α(j, j \pm 1) \), calculated from the data in Table 2 are shown in Table 3. Substituting \( α(1, 0) \) and \( α(1, 2) \) for the most outer product phase \( ε-Fe_23N \), \( α(2, 1) \) and \( α(2, 3) \) for the inner product phase \( γ'-Fe_2N \) into eq. (1), and \( α(3, 2) \) for the terminal phase \( α-Fe \) into eq. (2) gives a \( c_A-η \) curve or a \( N_A-ε \) curve. The nitrogen content profile thus calculated is shown in Fig. 6. As is clear from the figure, the \( α-Fe \) layer in which nitrogen atoms diffuse away is much wider than the compound layer, which consists of \( ε-Fe_23N \)

<table>
<thead>
<tr>
<th>( j )</th>
<th>Phase(j)</th>
<th>( ε-Fe_23N )</th>
<th>( γ'-Fe_2N )</th>
<th>( α-Fe )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( N(j, j \pm 1) ) [mol%N]</td>
<td>( N(j, j - 1) )</td>
<td>33</td>
<td>20</td>
<td>0.26(^{11})</td>
</tr>
<tr>
<td></td>
<td>( N(j, j + 1) )</td>
<td>24.6</td>
<td>19.3</td>
<td>0</td>
</tr>
<tr>
<td>( D(j) ) [m²·s⁻¹]</td>
<td>( 9.8 \times 10^{-15})(^{12})</td>
<td>( 2.35 \times 10^{-14})(^{13})</td>
<td>( 3.65 \times 10^{-12})(^{14})</td>
<td></td>
</tr>
<tr>
<td>( V_{i} ) [10⁻⁶·m³·mol⁻¹]</td>
<td>( V_{N} = 4.24 )</td>
<td>( V_{Fe} = 7.04 )</td>
<td>( 0 )</td>
<td></td>
</tr>
</tbody>
</table>
Steel parts increase slightly in size during nitriding. This dimensional change is affected by such factors as the temperature and time of nitriding, the relative thicknesses of the nitriding layer and core, and the shape of the parts. An expansion of the order of a 40 μm increase in diameter occurs in solid round bars made of Nitralloy 135 nitrided at 798 K for 259.2 ks. On the other hand, calculations with the diffusivity and equilibrium data for the N–Fe system under the preceding heating conditions result in expansion of 28.5 μm in diameter. Nitralloy 135 containing such alloying components as aluminum, chromium, and molybdenum with higher affinity for nitrogen than iron will take in a greater mass of nitrogen; furthermore, the partial molar volume of nitrogen for ε–Fe2–3N is 12.4 × 10−6 m³/mol(17) which is much larger than that in Table 2. This leads to greater expansion in diameter for the Nitralloy 135, as is clear from the following equation, which is obtained from the combination of eq. (4) with eq. (13) for the condition γ = 0:

$$X_s = -\frac{\Delta M \cdot V_A}{R_A}$$

(15)

Therefore, provided that these effects are taken into consideration, the expansion calculated will be larger, and the difference between the calculated and experimental results will become a reasonable value.

### 3.3 Nitriding of Titanium

The kW(j), kM, and λ(1, 0) calculated from the data shown in Table 4 and those experimentally obtained, are shown in Table 5. As can be seen in the table, the agreement between the calculated and experimental results in terms of both quantities is quite satisfactory. The layer growth rates calculated for ε–Ti2N and α–Ti are larger than those experimentally obtained, for which ion nitriding was employed. It is generally known that layer growth rates are larger for ion nitriding than for gas nitriding. Figure 7 shows

<table>
<thead>
<tr>
<th>j</th>
<th>Phase</th>
<th>1 ε–Fe2–3N</th>
<th>2 γ–Fe2N</th>
<th>3 α–Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>(j, j ± 1)</td>
<td>(1, 0)</td>
<td>(1, 2)</td>
<td>(2, 1)</td>
<td>(2, 3)</td>
</tr>
<tr>
<td>α(j, j ± 1)</td>
<td>−0.1064</td>
<td>0.2909</td>
<td>0.1879</td>
<td>0.2463</td>
</tr>
</tbody>
</table>

Fig. 6 Calculated nitrogen content profile in iron nitrided at 773 K for 28.8 ks.

<table>
<thead>
<tr>
<th>j</th>
<th>Phase(j)</th>
<th>1 δ–TiN</th>
<th>2 ε–Ti2N</th>
<th>3 α–Ti</th>
<th>4 β–Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(j, j ± 1) [mol%N]</td>
<td>N(j, j − 1)</td>
<td>51.2</td>
<td>33.8</td>
<td>15.5</td>
<td>0.14</td>
</tr>
<tr>
<td></td>
<td>N(j, j + 1)</td>
<td>38.1</td>
<td>32.8</td>
<td>1.2</td>
<td>0.0</td>
</tr>
<tr>
<td>D(j) [m²·s⁻¹]</td>
<td>1.11 × 10⁻¹⁶</td>
<td>8.04 × 10⁻¹⁶</td>
<td>4.09 × 10⁻¹⁵</td>
<td>1.77 × 10⁻¹²</td>
<td></td>
</tr>
<tr>
<td>V_j [10⁻⁹ m³·mol⁻¹]</td>
<td>V_δ = 0.80, V_ε = 10.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>j</th>
<th>Phase(j)</th>
<th>1 δ–TiN</th>
<th>2 ε–Ti2N</th>
<th>3 α–Ti</th>
<th>4 β–Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(j, j ± 1) [mol%N]</td>
<td>N(j, j − 1)</td>
<td>51.2</td>
<td>33.8</td>
<td>15.5</td>
<td>0.14</td>
</tr>
<tr>
<td></td>
<td>N(j, j + 1)</td>
<td>38.1</td>
<td>32.8</td>
<td>1.2</td>
<td>0.0</td>
</tr>
<tr>
<td>D(j) [m²·s⁻¹]</td>
<td>1.11 × 10⁻¹⁶</td>
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<td>4.09 × 10⁻¹⁵</td>
<td>1.77 × 10⁻¹²</td>
<td></td>
</tr>
<tr>
<td>V_j [10⁻⁹ m³·mol⁻¹]</td>
<td>V_δ = 0.80, V_ε = 10.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Rate constant</th>
<th>Product phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>kW(j) [m·s⁻¹/²]</td>
<td>1: δ–TiN</td>
</tr>
<tr>
<td>Experimental values</td>
<td>5.06 × 10⁻⁹</td>
</tr>
<tr>
<td>Calculated values</td>
<td>5.06 × 10⁻³</td>
</tr>
<tr>
<td>kM [g·m⁻²·s⁻¹/²]</td>
<td>Experimental values</td>
</tr>
<tr>
<td>Calculated values</td>
<td>2.37 × 10⁻²</td>
</tr>
<tr>
<td>λ(1, 0) [m·s⁻¹/²]</td>
<td>Experimental values</td>
</tr>
<tr>
<td>Calculated values</td>
<td>1.35 × 10⁻⁷</td>
</tr>
</tbody>
</table>
In the case where a nitrogen content profile is approximated by a linear function, a nitrogen content profile calculated from the values in Table 4. Although the profile in β-Ti seems parallel to the x-axis, a decrease in nitrogen content from 0.14 to 0.01 mol% N extends over 413 μm.

The quantities \( W(j), P(j)[x, N_A], S_i(j) \) and \( \Delta M \) shown in Table 6, which had been calculated from the data in Table 4, were utilized for determination of the interdiffusion coefficients of the phases using Model 2. Here, the following two cases are dealt with:

Case 1, nitrogen content profiles in δ-TiN and ε-Ti₂N were assumed to be linear;

Case 2, those in δ-TiN, ε-Ti₂N and α-Ti were to be linear. In the case where a nitrogen content profile is approximated by a linear function, \( S_i(j) \) is given by

\[
S_i(j) = W(j) \cdot \frac{[C_i(j, j-1) + C_i(j, j+1)]}{2} \quad (16)
\]

In the case where a nitrogen content profile is described by \( P(j)[x, N_A] \), \( S_i(j) \) was evaluated using the Simpson integration formula. Using \( S_i(j) \) thus obtained, \( X_s \) calculated from eq. (6), \( \gamma \) from eq. (7), and \( D(j) \) from eqs. (8), (9), (10), and (11a, 11b) are shown in Table 7 together. Here, \( \Delta D(j) = 100 \times \frac{[D_s^*(j) - D(j)]}{D_s^*(j)} \), where \( D_s^*(j) \) stands for \( D(j) \) in Table 4 and \( D_s^*(j) \) stands for that calculated from eqs. (11a) and (11b) in Model 2. To obtain a more accurate interdiffusion coefficient it is necessary to input data closer to the original concentration profile, as clear from a comparison of Cases 1 and 2 in Table 7. Using the closer input data also gives more accurate \( \gamma \) and \( X_s \), as is understood from a comparison of \( \gamma \) in Table 4 and \( \lambda_s \) (= \( X_s/\sqrt{2} \)) in Table 5 with those in Table 7. The above shows that Model 1 and Model 2 are compatible with no inconsistencies between them.
4. Conclusions

Model 1 for describing multiphase diffusion and Model 2 for determining interdiffusion coefficients for each phase present in binary gas–solid couples have been developed by modifying the models previously presented. It has been confirmed that Model 1 is compatible with Model 2. No restriction is imposed on the number of phases, the interdiffusion coefficients, or the homogeneity ranges of phases.

The good agreements between the numerical and experimental results shows that Model 1 is capable of predicting composition profiles, mass changes per unit area of surface, and dimensional changes normal to the surface. It is apparent that Model 2 can be easily applied, and is useful when no references are available for diffusivity data.

REFERENCES

17) L. S. Richardson and N. J. Grant: Trans. AIME 220 (1954) 69–70.

Appendix

Almost all the symbols in this paper correspond to those used in the previous papers. The parameter \( \lambda(j, j) = \rho(j, j) \cdot D(j)^{1/2} \) and the rate constants \( X(j, j) = \rho(j, j) \cdot 2D(j)^{1/2} \) in Refs. 3 and 4 were written as

\[ \lambda(j, j) = \rho(j, j) \cdot D(j)^{1/2} \]  
\[ X(j, j) = \rho(j, j) \cdot 2D(j)^{1/2} \]

Those in this paper, however, are defined as

\[ \lambda(j, j) = \rho(j, j) \cdot D(j)^{1/2} \]
\[ X(j, j) = \rho(j, j) \cdot 2D(j)^{1/2} \]

In eq. (23) in Ref. 3), which is written as

\[ \frac{dQ_A(0/1)}{dt} = -D(1) \frac{\partial c_A}{\partial x} \]

This leads to the elimination of the term \( C_A(1, 0) \) in eqs. (24), (25), (26), and (27) in Ref. 3).