Temperature Dependence of Kinetics for Reactive Diffusion in a Hypothetical Binary System

Masanori Kajihara*

Department of Materials Science and Engineering, Tokyo Institute of Technology, Yokohama 226-8502, Japan

A hypothetical binary system consisting of two primary solid solution phases (α and γ) and one compound phase (β) was considered in order to analyze theoretically the temperature dependence of kinetics for reactive diffusion. Assuming that migration of interface is controlled by volume diffusion in neighboring phases, the growth of the β phase due to the reactive diffusion between the α and γ phases in a semi-infinite diffusion couple was mathematically expressed as a function of the interdiffusion coefficients and the solubility ranges of the α , β and γ phases. The assumption yields that the square of the thickness l of the β phase is proportional to the annealing time t according to the parabolic relationship $l^2 = Kt$, where K is the parabolic coefficient. The present attention was focused on the relationship between the temperature dependency of the growth rate and those of the interdiffusion coefficients, and hence the solubility ranges were assumed to be constant independently of the temperature and to take the same value for all the phases. On the contrary, the interdiffusion coefficient D^θ ($\theta = \alpha, \beta, \gamma$) was expressed as a function of the temperature T by an Arrhenius equation of $D^\theta = D_0^\theta \exp(-Q^\theta/RT)$. For simplicity, however, D_0^α , D_0^β and D_0^γ were considered equivalent. The temperature dependence of the parabolic coefficient K was described also by an Arrhenius equation of $K = K_0 \exp(-Q_K/RT)$, and then K_0 and Q_K were evaluated for various combinations of Q^α , Q^β and Q^γ . The evaluation yields that Q_K is equal to Q^β at $Q^\alpha = Q^\beta = Q^\gamma$ and close to Q^β at $Q^\beta \leq Q^\alpha$ and $Q^\beta \leq Q^\gamma$. Under such conditions, the temperature dependence of D^β is estimated directly from that of K . On the other hand, Q_K is greater than Q^β at $Q^\beta > Q^\alpha$ or $Q^\beta > Q^\gamma$. In this case, such estimation becomes invalid.

(Received July 25, 2005; Accepted August 26, 2005; Published October 15, 2005)

Keywords: intermetallic compounds, bulk diffusion, analytical methods, reactive diffusion, kinetics

1. Introduction

There exist many binary alloy systems where intermetallic compounds appear as stable phases.¹⁾ If a diffusion couple is prepared from two different pure metals in such a binary system and then annealed at an appropriate temperature T , some of the compounds may be recognized to form as layers at the interface between the two metals after certain periods due to reactive diffusion. Kinetics of the reactive diffusion was experimentally studied by many investigators for various alloy systems.^{2–20)} When the reactive diffusion is controlled by volume diffusion, the total thickness l of the compound layers is described as a function of the annealing time t by the parabolic relationship $l^2 = Kt$. Here, K is the parabolic coefficient. The temperature dependence of K may be expressed by an Arrhenius equation of $K = K_0 \exp(-Q_K/RT)$, where R is the gas constant. From experimental values of K at different annealing temperatures, the pre-exponential factor K_0 and the activation enthalpy Q_K can be determined by the least-squares method. Most of the experimental studies indicate that the temperature dependence of K is reasonably described by the Arrhenius equation within experimental uncertainty.^{2–20)} Thus, it is expected that the Arrhenius equation of K derives representative properties of the interdiffusion in the diffusion couple. However, K_0 and Q_K contain complex information of the temperature dependencies of the diffusion coefficients and the solubility ranges of the relevant phases. Consequently, such derivation is not so straightforward.

Recently, the reactive diffusion controlled by volume diffusion was theoretically analyzed by the present author using a mathematical model.²¹⁾ In the theoretical analysis, a hypothetical binary alloy system composed of two primary solid solution phases and one intermetallic compound was

considered, and then the growth rate of the compound was evaluated for various semi-infinite diffusion couples initially consisting of the two primary solid solution phases. The mathematical model was also used to analyze numerically the relationship between the temperature dependence of the interdiffusion in each phase and the kinetics of the reactive diffusion.²²⁾ In the numerical analysis, the interdiffusion coefficient D was described as a function of the annealing temperature T by an Arrhenius equation of $D = D_0 \exp(-Q/RT)$, and the following assumptions were adopted: (a) the molar volume, the solubility range and the pre-exponential factor D_0 are constant and equivalent for all the phases; and (b) the activation enthalpy Q is equivalent for the solution phases but different between the solution phase and the compound. The numerical analysis indicates that the equation $K = K_0 \exp(-Q_K/RT)$ is reliable enough to express the temperature dependence of experimental values of K but not necessarily completely exact. If Q is smaller for the compound than for the solution phases, Q_K is nearly equal to Q of the compound. In such a case, the temperature dependence of K corresponds well with that of D of the compound. This relationship cannot hold good any longer, if Q is greater for the compound than for the solution phases. In order to examine whether such conclusions are universally valid, assumption (b) was eliminated for numerical analysis in a previous study.²³⁾ However, only limited combinations of Q were treated between the two solution phases, and thus the validity could not be confirmed conclusively. In the present study, similar numerical analysis has been carried out extensively for various combinations of Q among all the phases. Nevertheless, attention is still focused on the relationship between the temperature dependency of the kinetics and those of the interdiffusion coefficients of the constituent phases. Therefore, assumption (a) still remains for the numerical analysis in the present study.

*E-mail: kajihara@materia.titech.ac.jp

2. Analysis

A hypothetical binary A–B system composed of two primary solid solution phases and one intermetallic compound was adopted in previous studies.^{21–23)} The same binary system was treated also in the present study. The α and γ phases are the primary solid solution phases of elements A and B, respectively, and the β phase is the compound. For the analysis, we consider a semi-infinite diffusion couple consisting of the α and γ phases with initial compositions of $y^{\alpha 0}$ and $y^{\gamma 0}$, respectively. Here, y is the mol fraction of element B. In the semi-infinite diffusion couple, the thickness is semi-infinite for the α and γ phases, and the α/γ interface is flat. Therefore, the interdiffusion of elements A and B takes place unidirectionally along the direction perpendicular to the flat interface. This direction is hereafter called the diffusional direction. When the diffusion couple is annealed at temperature T for an appropriate time, the β phase will be produced as a layer at the interface due to the reactive diffusion between the α and γ phases. The concentration profile of element B across the β phase layer along the diffusional direction is schematically shown in Fig. 1.²¹⁾ In this figure, the ordinate indicates the mol fraction y , and the abscissa shows the distance x measured from the initial position of the α/γ interface. Dashed lines and solid curves indicate the concentration profiles before and after annealing, respectively, and $z^{\alpha\beta}$ and $z^{\beta\gamma}$ show the positions of the α/β and β/γ interfaces, respectively, after annealing. If the local equilibrium is established at each migrating interface during annealing, the compositions of the neighboring phases at the interface coincide with those of the corresponding phase boundaries at temperature T in the phase diagram of the binary A–B system. As a result, the migration of the interface is controlled by the volume diffusion in the neighboring phases. In Fig. 1, $y^{\alpha\beta}$ and $y^{\beta\alpha}$ are the compositions of the α and β phases, respectively, at the α/β interface, and $y^{\beta\gamma}$ and

$y^{\gamma\beta}$ are those of the β and γ phases, respectively, at the β/γ interface. The compositions $y^{\alpha\beta}$, $y^{\beta\alpha}$, $y^{\beta\gamma}$ and $y^{\gamma\beta}$ provide the boundary conditions, and those $y^{\alpha 0}$ and $y^{\gamma 0}$ give the initial conditions.

If the reactive diffusion is controlled by the volume diffusion, the positions $z^{\alpha\beta}$ and $z^{\beta\gamma}$ of the α/β and β/γ interfaces are expressed as functions of the annealing time t by the equations

$$z^{\alpha\beta} = K^{\alpha\beta} \sqrt{4D^{\alpha}t} = K^{\beta\alpha} \sqrt{4D^{\beta}t} \quad (1a)$$

and

$$z^{\beta\gamma} = K^{\beta\gamma} \sqrt{4D^{\beta}t} = K^{\gamma\beta} \sqrt{4D^{\gamma}t}, \quad (1b)$$

respectively.²⁴⁾ Here, D^{α} , D^{β} and D^{γ} are the interdiffusion coefficients for volume diffusion in the α , β and γ phases, respectively, and $K^{\alpha\beta}$, $K^{\beta\alpha}$, $K^{\beta\gamma}$ and $K^{\gamma\beta}$ are dimensionless coefficients. The thickness l of the β phase layer is readily obtained as the difference between $z^{\alpha\beta}$ and $z^{\beta\gamma}$, and hence the following equation is deduced from eq. (1) to express l as a function of t .

$$l^2 = (z^{\alpha\beta} - z^{\beta\gamma})^2 = 4D^{\beta}(K^{\beta\alpha} - K^{\beta\gamma})^2 t = Kt \quad (2)$$

Here, K is the parabolic coefficient defined as

$$K \equiv 4D^{\beta}(K^{\beta\alpha} - K^{\beta\gamma})^2. \quad (3)$$

The dimensionless coefficients are related to the initial and boundary conditions as follows:

$$\begin{aligned} c^{\beta\alpha} - c^{\alpha\beta} &= \frac{c^{\alpha 0} - c^{\alpha\beta}}{K^{\alpha\beta} \sqrt{\pi} \{1 - \operatorname{erf}(K^{\alpha\beta})\}} \exp\{-(K^{\alpha\beta})^2\} \\ &+ \frac{c^{\beta\gamma} - c^{\beta\alpha}}{K^{\beta\alpha} \sqrt{\pi} \{\operatorname{erf}(K^{\beta\alpha}) - \operatorname{erf}(K^{\beta\gamma})\}} \\ &\times \exp\{-(K^{\beta\alpha})^2\} \end{aligned} \quad (4a)$$

and

$$\begin{aligned} c^{\gamma\beta} - c^{\beta\gamma} &= \frac{c^{\beta\alpha} - c^{\beta\gamma}}{K^{\beta\gamma} \sqrt{\pi} \{\operatorname{erf}(K^{\beta\alpha}) - \operatorname{erf}(K^{\beta\gamma})\}} \exp\{-(K^{\beta\gamma})^2\} \\ &+ \frac{c^{\gamma 0} - c^{\gamma\beta}}{K^{\gamma\beta} \sqrt{\pi} \{1 + \operatorname{erf}(K^{\gamma\beta})\}} \exp\{-(K^{\gamma\beta})^2\}. \end{aligned} \quad (4b)$$

Here, c is the concentration of element B measured in mol per unit volume. The initial and boundary conditions are shown with the concentration c in eq. (4), but indicated with the mol fraction y in Fig. 1. However, y is readily converted into c by the equation $c = y/V_m$, where V_m is the molar volume of the relevant phase. The following relationships are obtained from eq. (1):

$$K^{\alpha\beta} = K^{\beta\alpha} \sqrt{D^{\beta}/D^{\alpha}} \quad (5a)$$

and

$$K^{\gamma\beta} = K^{\beta\gamma} \sqrt{D^{\beta}/D^{\gamma}}. \quad (5b)$$

Equation (5) shows that only two of the four dimensionless coefficients are independent. In the present analysis, $K^{\beta\alpha}$ and $K^{\beta\gamma}$ are chosen as the independent variables. Insertion of eq. (5) into eq. (4) yields two independent equations. Consequently, the two independent variables are finally determined from the two independent equations.

Fig. 1 Concentration profile of element B across the β phase along the diffusional direction in the semi-infinite diffusion couple.²¹⁾

3. Results and Discussion

Equations (2) to (5) indicate that the growth rate of the compound layer is controlled by the solubility ranges and the interdiffusion coefficients of the constituent phases in the diffusion couple. Hence, there are many parameters to determine the growth rate. As already mentioned in Section 1, however, the attention is focused on the relationship between the temperature dependency of the growth rate and those of the interdiffusion coefficients. Thus, in the present analysis, the solubility ranges of all the phases are considered constant independently of the temperature. Furthermore, it is assumed that the molar volume V_m is independent of the composition and equivalent for all the phases. According to this assumption, the concentrations $c^{\alpha 0}$, $c^{\alpha \beta}$, $c^{\beta \alpha}$, $c^{\beta \gamma}$, $c^{\gamma \beta}$ and $c^{\gamma 0}$ in eq. (4) are automatically replaced with the mol fractions $y^{\alpha 0}$, $y^{\alpha \beta}$, $y^{\beta \alpha}$, $y^{\beta \gamma}$, $y^{\gamma \beta}$ and $y^{\gamma 0}$, respectively. The following initial and boundary conditions are adopted in the present analysis: $y^{\alpha 0} = 0$, $y^{\alpha \beta} = 0.1$, $y^{\beta \alpha} = 0.45$, $y^{\beta \gamma} = 0.55$, $y^{\gamma \beta} = 0.9$ and $y^{\gamma 0} = 1$. Hence, independently of the temperature, the solubility range Δy is equal to 0.1 for all the phases, and the mean composition y^β of the compound is identical to 0.5: $\Delta y = y^{\alpha \beta} - y^{\alpha 0} = y^{\beta \gamma} - y^{\beta \alpha} = y^{\gamma 0} - y^{\gamma \beta} = 0.1$; and $y^\beta = (y^{\beta \alpha} + y^{\beta \gamma})/2 = 0.5$. The temperature dependence of the interdiffusion coefficient D is described by the equation $D = D_0 \exp(-Q/RT)$. Here, D_0 is the pre-exponential factor, and Q is the activation enthalpy. The values of Q^α , Q^β and Q^γ are varied from 50 to 100 kJ/mol, whereas the same value of $D_0 = 10^{-4} \text{ m}^2/\text{s}$ is used for all the phases in order to simplify the analysis. Using these parameters, the parabolic coefficient K was numerically calculated as a function of T from eqs. (3)–(5) at a range of $T = 700$ – 1000 K. The temperature dependence of K was expressed by the equation $K = K_0 \exp(-Q_K/RT)$, and the pre-exponential factor K_0 and the activation enthalpy Q_K were determined in a manner similar to previous studies.^{22,23)}

On the basis of the determination, dependencies of K_0 on Q^α and Q^γ were evaluated for various values of Q^β . The results are shown as solid curves with constant values of $Q^\gamma = 50$ – 100 kJ/mol in Fig. 2. In this figure, the abscissa indicates Q^α , and the ordinate shows the logarithm of K_0 . Figures 2(a), (b), (c), (d), (e) and (f) indicate the evaluations for $Q^\beta = 50, 60, 70, 80, 90$ and 100 kJ/mol, respectively. At $Q^\beta = 50$ kJ/mol in Fig. 2(a), K_0 monotonically increases with increasing value of Q^α for each solid curve. For all the phases, the solubility range Δy and the pre-exponential factor D_0 are identical to 0.1 and $10^{-4} \text{ m}^2/\text{s}$, respectively, as mentioned earlier. Furthermore, the mean composition y^β of the compound is equal to 0.5. Thus, the effects of Q^α and Q^γ on the temperature dependence of K are equivalent each other. As a result, K_0 monotonically increases also with increasing value of Q^γ at a constant value of Q^α . On the other hand, at $Q^\beta = 60$ kJ/mol in Fig. 2(b), K_0 slightly decreases with increasing value of Q^α , and reaches the minimum value at $Q^\alpha \cong 60$ kJ/mol. After taking the minimum value, K_0 gradually increases with increasing value of Q^α . Due to the equivalence between the effects of Q^α and Q^γ on the temperature dependence of K , the appearance of the minimum point is also the reason why K_0 is smaller for the solid curves with $Q^\gamma = 60$ and 70 kJ/mol than for those with $Q^\gamma =$

50 and 80 kJ/mol but greater for those with $Q^\gamma = 90$ and 100 kJ/mol than for those with $Q^\gamma = 50$ and 80 kJ/mol. At $Q^\beta = 70$ kJ/mol in Fig. 2(c), however, the minimum point shifts to $Q^\alpha \cong 70$ kJ/mol for the solid curves with $Q^\gamma = 60$ – 100 kJ/mol, but almost stays at $Q^\alpha \cong 60$ kJ/mol for that with $Q^\gamma = 50$ kJ/mol. On the contrary, at $Q^\beta = 80$ kJ/mol in Fig. 2(d), the minimum point nearly remains at $Q^\alpha \cong 60$ and 70 kJ/mol for the solid curves with $Q^\gamma = 50$ and 60 kJ/mol, respectively, but relocates to $Q^\alpha \cong 80$ kJ/mol for those with $Q^\gamma = 70$ – 100 kJ/mol. In the case of $Q^\beta = 100$ kJ/mol, K_0 increases with increasing value of Q^γ at $Q^\alpha = 50$ kJ/mol, but decreases with increasing value of Q^γ at $Q^\alpha = 100$ kJ/mol. Consequently, K_0 varies depending on Q^α and Q^γ in a complicated manner as shown in Fig. 2(f).

For various values of Q^β , dependencies of Q_K on Q^α and Q^γ were evaluated together with those of K_0 on Q^α and Q^γ . The results are indicated as solid curves with constant values of $Q^\gamma = 50$ – 100 kJ/mol in Fig. 3. The evaluations for $Q^\beta = 50, 60, 70, 80, 90$ and 100 kJ/mol are shown in Figs. 3(a), (b), (c), (d), (e) and (f), respectively. Figures 3(a) and (f) represent the results obtained in a previous study.²³⁾ At $Q^\beta = 50$ kJ/mol in Fig. 3(a), Q_K lightly decreases with increasing value of Q^α , and attains the minimum value at $Q^\alpha \cong 60$ kJ/mol. After attaining the minimum value, Q_K gradually increases with increasing value of Q^α . However, such variations of Q_K are rather small, and thus Q_K is close to Q^β . On the other hand, at $Q^\beta = 60$ kJ/mol in Fig. 3(b), the minimum point migrates to $Q^\alpha \cong 70$ kJ/mol for all the solid curves. Q_K is close to Q^β at $Q^\alpha = 60$ – 100 kJ/mol and $Q^\gamma = 60$ – 100 kJ/mol, but slightly greater than Q^β at $Q^\alpha = 50$ kJ/mol or $Q^\gamma = 50$ kJ/mol. It is interesting to note that the minimum point of the solid curve appears at different values of Q^α for K_0 and Q_K as indicated in Figs. 2(b) and 3(b). According to the results in Figs. 3(c)–(f), Q_K is close to Q^β at $Q^\alpha = 70$ – 100 kJ/mol and $Q^\gamma = 70$ – 100 kJ/mol for $Q^\beta = 70$ kJ/mol, at $Q^\alpha = 80$ – 100 kJ/mol and $Q^\gamma = 80$ – 100 kJ/mol for $Q^\beta = 80$ kJ/mol, at $Q^\alpha = 90$ – 100 kJ/mol and $Q^\gamma = 90$ – 100 kJ/mol for $Q^\beta = 90$ kJ/mol, and at $Q^\alpha = 100$ kJ/mol and $Q^\gamma = 100$ kJ/mol for $Q^\beta = 100$ kJ/mol. However, Q_K is greater than Q^β at $Q^\alpha = 50$ – 60 kJ/mol or $Q^\gamma = 50$ – 60 kJ/mol for $Q^\beta = 70$ kJ/mol, at $Q^\alpha = 50$ – 70 kJ/mol or $Q^\gamma = 50$ – 70 kJ/mol for $Q^\beta = 80$ kJ/mol, at $Q^\alpha = 50$ – 80 kJ/mol or $Q^\gamma = 50$ – 80 kJ/mol for $Q^\beta = 90$ kJ/mol, and at $Q^\alpha = 50$ – 90 kJ/mol or $Q^\gamma = 50$ – 90 kJ/mol for $Q^\beta = 100$ kJ/mol. Thus, it is concluded that Q_K is close to Q^β at $Q^\alpha \geq Q^\beta$ and $Q^\gamma \geq Q^\beta$ but greater than Q^β at $Q^\alpha < Q^\beta$ or $Q^\gamma < Q^\beta$.

The results in Fig. 3 are shown in a different manner in Fig. 4. In this figure, solid curves indicate the evaluations with constant values of $Q^\beta = 50$ – 100 kJ/mol. Open circles show values of Q_K at $Q^\alpha = Q^\beta$, and a dashed straight line indicates a relationship of $Q_K = Q^\alpha$. Figures 4(a), (b), (c), (d), (e) and (f) show the results for $Q^\gamma = 50, 60, 70, 80, 90$ and 100 kJ/mol, respectively. The results in Figs. 4(a) and (f) were reported in a previous study.²³⁾ At $Q^\gamma = 50$ kJ/mol in Fig. 4(a), Q_K is rather insensitive to the variation of Q^α , and close to Q^β for the solid curve with $Q^\beta = 50$ kJ/mol. The open circle of this solid curve lies on the dashed line. However, Q_K is greater than Q^β for the solid curves with $Q^\beta = 60$ – 100 kJ/mol. Thus, the open circles of these solid curves are distributed on the upper-side of the dashed line. On

Fig. 2 Dependencies of K_0 on Q^α and Q^γ for (a) $Q^\beta = 50$ kJ/mol, (b) $Q^\beta = 60$ kJ/mol, (c) $Q^\beta = 70$ kJ/mol, (d) $Q^\beta = 80$ kJ/mol, (e) $Q^\beta = 90$ kJ/mol and (f) $Q^\beta = 100$ kJ/mol.

the other hand, at $Q^\gamma = 60$ kJ/mol in Fig. 4(b), Q_K is close to Q^β at $Q^\alpha \geq 50$ kJ/mol for the solid curve with $Q^\beta = 50$ kJ/mol and at $Q^\alpha \geq 60$ kJ/mol for that with $Q^\beta = 60$ kJ/mol, but slightly greater than Q^β at $Q^\alpha < 60$ kJ/mol for the latter solid curve. The open circle of the solid curve with $Q^\beta = 60$ kJ/mol is completely located on the dashed line, but that of the solid curve with $Q^\beta = 50$ kJ/mol lies slightly below the dashed line. For the solid curves with $Q^\beta = 70$ – 100 kJ/mol, however, Q_K is greater than Q^β . As can be seen in Figs. 4(c)–(f), Q_K is nearly equal to Q^β at $Q^\alpha \geq Q^\beta$ for $Q^\beta = 50$ – 70 kJ/mol at $Q^\gamma = 70$ kJ/mol, for $Q^\beta = 50$ – 80 kJ/mol

mol at $Q^\gamma = 80$ kJ/mol, for $Q^\beta = 50$ – 90 kJ/mol at $Q^\gamma = 90$ kJ/mol and for $Q^\beta = 50$ – 100 kJ/mol at $Q^\gamma = 100$ kJ/mol. For such combinations of Q^β and Q^γ , however, Q_K is greater than Q^β at $Q^\alpha < Q^\beta$. On the contrary, independently of Q^α , Q_K is greater than Q^β for $Q^\beta = 80$ – 100 kJ/mol at $Q^\gamma = 70$ kJ/mol, for $Q^\beta = 90$ – 100 kJ/mol at $Q^\gamma = 80$ kJ/mol and for $Q^\beta = 100$ kJ/mol at $Q^\gamma = 90$ kJ/mol. These relationships indicate that Q_K is close to Q^β at $Q^\alpha \geq Q^\beta$ for $Q^\beta \leq Q^\gamma$. If such conditions are not realized, Q_K becomes greater than Q^β .

From the evaluations in Fig. 3, the dependence of Q_K

Fig. 3 Dependencies of Q_K on Q^α and Q^γ for (a) $Q^\beta = 50 \text{ kJ/mol}$, (b) $Q^\beta = 60 \text{ kJ/mol}$, (c) $Q^\beta = 70 \text{ kJ/mol}$, (d) $Q^\beta = 80 \text{ kJ/mol}$, (e) $Q^\beta = 90 \text{ kJ/mol}$ and (f) $Q^\beta = 100 \text{ kJ/mol}$.

on Q^β is illustrated for various values of Q^α and Q^γ . The results with constant values of $Q^\gamma = 50$ – 100 kJ/mol are shown as solid curves in Fig. 5. In this figure, the abscissa indicates Q^β , and the ordinate shows the ratio of Q_K to Q^β . Open circles indicate values of the ratio Q_K/Q^β at $Q^\beta = Q^\gamma$, and a horizontal dashed line shows a value of $Q_K/Q^\beta = 1$. The evaluations for $Q^\alpha = 50, 60, 70, 80, 90$ and 100 kJ/mol are indicated in Figs. 5(a), (b), (c), (d), (e) and (f), respectively. At $Q^\alpha = 50 \text{ kJ/mol}$ in Fig. 5(a), the ratio Q_K/Q^β is equal to unity at $Q^\beta = 50 \text{ kJ/mol}$ for the solid curve with $Q^\gamma = 50 \text{ kJ/mol}$, and close to unity at $Q^\beta =$

50 kJ/mol for those with $Q^\gamma = 60$ – 100 kJ/mol . As Q^β increases, the ratio Q_K/Q^β monotonically increases, and becomes greater for $Q^\gamma = 50 \text{ kJ/mol}$ than for $Q^\gamma = 60$ – 100 kJ/mol . On the other hand, at $Q^\alpha = 60 \text{ kJ/mol}$ in Fig. 5(b), the ratio Q_K/Q^β is equal to unity at $Q^\beta = 60 \text{ kJ/mol}$ for $Q^\gamma = 60 \text{ kJ/mol}$, and close to unity at $Q^\beta \leq 60 \text{ kJ/mol}$ for $Q^\gamma = 70$ – 100 kJ/mol . Although the ratio Q_K/Q^β for $Q^\gamma = 60 \text{ kJ/mol}$ is still smaller than that for $Q^\gamma = 50 \text{ kJ/mol}$, it becomes greater than that for $Q^\gamma = 70$ – 100 kJ/mol at $Q^\beta > 60 \text{ kJ/mol}$. At $Q^\alpha = 70 \text{ kJ/mol}$ in Fig. 5(c), the ratio Q_K/Q^β is equal to unity at $Q^\beta = 70$ for $Q^\gamma = 70 \text{ kJ/mol}$, and

Fig. 4 Dependencies of Q_K on Q^α and Q^β for (a) $Q^\gamma = 50$ kJ/mol, (b) $Q^\gamma = 60$ kJ/mol, (c) $Q^\gamma = 70$ kJ/mol, (d) $Q^\gamma = 80$ kJ/mol, (e) $Q^\gamma = 90$ kJ/mol and (f) $Q^\gamma = 100$ kJ/mol.

close to unity at $Q^\beta = 50$ kJ/mol for $Q^\gamma = 50$ kJ/mol, at $Q^\beta \leq 60$ kJ/mol for $Q^\gamma = 60$ kJ/mol and at $Q^\beta \leq 70$ kJ/mol for $Q^\gamma = 70$ –100 kJ/mol. In the case of $Q^\alpha = 80$ kJ/mol in Fig. 5(d), however, the ratio Q_K/Q^β is equal to unity at $Q^\beta = 80$ for $Q^\gamma = 80$ kJ/mol, and close to unity at $Q^\beta \leq 80$ kJ/mol for $Q^\gamma = 90$ –100 kJ/mol as well as at $Q^\beta = 50$ kJ/mol for $Q^\gamma = 50$ kJ/mol, at $Q^\beta \leq 60$ kJ/mol for $Q^\gamma = 60$ kJ/mol and at $Q^\beta \leq 70$ kJ/mol for $Q^\gamma = 70$ kJ/mol. Considering the results at $Q^\alpha = 90$ and 100 kJ/mol in Figs. 5(e) and (f), it is finally concluded that Q_K is exactly equal to Q^β at $Q^\alpha = Q^\beta = Q^\gamma$ and close to Q^β at $Q^\beta \leq Q^\alpha$ and $Q^\beta \leq Q^\gamma$. Under such conditions, the activation enthalpy of the interdiffusion

coefficient in the growing compound layer is estimated directly from that of the parabolic coefficient. On the other hand, Q_K is greater than Q^β at $Q^\beta > Q^\alpha$ or $Q^\beta > Q^\gamma$. In this case, such estimation becomes invalid.

The reactive diffusion was experimentally studied for many binary systems consisting of elements with considerably different melting temperatures.^{10–20} When the melting temperature is much higher for the α phase than for the β and γ phases, the interdiffusion occurs much slower in the former phase than in the latter phases at a constant annealing temperature. Furthermore, the stable crystal structure of a compound is usually an ordered lattice in many binary

Fig. 5 Dependencies of the ratio Q_K/Q^β on Q^β and Q^γ for (a) $Q^\alpha = 50 \text{ kJ/mol}$, (b) $Q^\alpha = 60 \text{ kJ/mol}$, (c) $Q^\alpha = 70 \text{ kJ/mol}$, (d) $Q^\alpha = 80 \text{ kJ/mol}$, (e) $Q^\alpha = 90 \text{ kJ/mol}$ and (f) $Q^\alpha = 100 \text{ kJ/mol}$.

systems.¹⁾ Thus, the interdiffusion in the β phase should be more sluggish than that in the γ phase unless the melting temperature is much lower for the β phase than for the γ phase. Under such conditions, we may expect $Q^\alpha > Q^\beta > Q^\gamma$. According to the conclusions mentioned above, the temperature dependence of the interdiffusion coefficient in the β phase cannot be estimated directly from that of the parabolic coefficient at $Q^\alpha > Q^\beta > Q^\gamma$. In this case, experimental information on the interdiffusion is essentially important for reliable estimation of the activation enthalpy of the interdiffusion coefficient in the compound.

4. Conclusions

The temperature dependence of the kinetics of reactive diffusion was theoretically analyzed for the hypothetical binary system composed of one compound phase (β) and two primary solid solution phases (α and γ). The growth rate of the β phase during the reactive diffusion between the α and γ phases in a semi-infinite diffusion couple was expressed as a function of the interdiffusion coefficients and the solubility ranges of the α , β and γ phases using the mathematical model reported in a previous study.²¹⁾ For simplicity, however, the solubility ranges of all the

phases were assumed to be constant and equivalent. On the contrary, the interdiffusion coefficient D^θ was described as a function of the temperature T by the equation $D^\theta = D_0^\theta \exp(-Q^\theta/RT)$. Here, D_0^θ is the pre-exponential factor, Q^θ is the activation enthalpy, R is the gas constant, and θ stands for α , β and γ . Furthermore, we assumed $D_0^\alpha = D_0^\beta = D_0^\gamma$. For the reactive diffusion controlled by the volume diffusion, the square of the thickness l of the β phase is proportional to the annealing time t as $l^2 = Kt$. The temperature dependence of the parabolic coefficient K was expressed by the equation of $K = K_0 \exp(-Q_K/RT)$, and then the pre-exponential factor K_0 and the activation enthalpy Q_K were evaluated for different combinations of Q^α , Q^β and Q^γ . In the case of $Q^\alpha = Q^\beta = Q^\gamma$, Q_K is exactly equal to Q^β . Q_K is still close to Q^β at $Q^\beta \leq Q^\alpha$ and $Q^\beta \leq Q^\gamma$. Under such conditions, the temperature dependence of D^β is estimated directly from that of K . Unfortunately, however, Q_K becomes greater than Q^β at $Q^\beta > Q^\alpha$ or $Q^\beta > Q^\gamma$. In such a case, Q^β cannot be estimated directly from Q_K .

Acknowledgements

The present study was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

REFERENCES

- 1) T. B. Massalski, H. Okamoto, P. R. Subramanian and L. Kacprzak: *Binary Alloy Phase Diagram* (ASM International, Materials Park, OH, 1990) vol. 1–3.
- 2) B. Lustman and R. F. Mehl: *Trans. Met. Soc. AIME* **147** (1942) 369–394.
- 3) D. Horstmann: *Stahl Eisen* **73** (1953) 659–665.
- 4) S. Storchheim, J. L. Zambrow and H. H. Hausner: *Trans. Met. Soc. AIME* **200** (1954) 269–274.
- 5) G. V. Kidson and G. D. Miller: *J. Nucl. Mater.* **12** (1964) 61–69.
- 6) K. Shibata, S. Morozumi and S. Koda: *J. Jpn. Inst. Met.* **30** (1966) 382–388.
- 7) K. Hirano and Y. Ipposhi: *J. Jpn. Inst. Met.* **32** (1968) 815–821.
- 8) M. M. P. Janssen: *Metall. Trans.* **4** (1973) 1623–1633.
- 9) G. F. Bastin and G. D. Rieck: *Metall. Trans.* **5** (1974) 1817–1826.
- 10) M. Onishi and H. Fujibuchi: *Trans. JIM* **16** (1975) 539–547.
- 11) El-B. Hannech and C. R. Hall: *Mater. Sci. Tech.* **8** (1992) 817–824.
- 12) P. T. Vianco, P. F. Hlava and A. L. Kilgo: *J. Electron. Mater.* **23** (1994) 583–594.
- 13) M. Watanabe, Z. Horita and M. Nemoto: *Interface Science* **4** (1997) 229–241.
- 14) S. Choi, T. R. Bieler, J. P. Lucas and K. N. Subramanian: *J. Electron. Mater.* **28** (1999) 1209–1215.
- 15) T. Yamada, K. Miura, M. Kajihara, N. Kurokawa and K. Sakamoto: *Mater. Sci. Eng. A* **390** (2005) 118–126.
- 16) T. Takenaka, S. Kano, M. Kajihara, N. Kurokawa and K. Sakamoto: *Mater. Sci. Eng. A* **396** (2005) 115–123.
- 17) K. Suzuki, S. Kano, M. Kajihara, N. Kurokawa and K. Sakamoto: *Mater. Trans.* **46** (2005) 969–973.
- 18) T. Takenaka, S. Kano, M. Kajihara, N. Kurokawa and K. Sakamoto: *Mater. Trans.* **46** (2005) 1825–1832.
- 19) M. Mita, M. Kajihara, N. Kurokawa and K. Sakamoto: *Mater. Sci. Eng. A* **403** (2005) 269–275.
- 20) T. Takenaka, M. Kajihara, N. Kurokawa and K. Sakamoto: *Mater. Sci. Eng. A* **406** (2005) 134–141.
- 21) M. Kajihara: *Acta Mater.* **52** (2004) 1193–1200.
- 22) M. Kajihara: *Mater. Sci. Eng. A* **403** (2005) 234–240.
- 23) M. Kajihara: *Defect and Diffusion Forum*, in press.
- 24) W. Jost: *Diffusion of Solids, Liquids, Gases* (Academic Press, New York, 1960) p. 68.