Numerical Analysis of Observations on Diffusion Induced Recrystallization in the Ni(Cu) System using A Kinetic Model

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Considering the effect of the friction force due to volume diffusion of a solute on the driving force, a new kinetic model has been proposed for diffusion induced recrystallization (DIR) in the A(B) system in which solute B atoms diffuse into a pure A metal or a binary A-B alloy. The energy balance model [M. Kajihara and W. Gust: Scr. Mater. **38** (1998) 1621] has been combined with the columnar geometry and boundary diffusion model [C. Li and M. Hillert: Acta Metall. **29** (1981) 1949] and the extended model [Y. Kawanami *et al.*: ISIJ Int. **37** (1997) 921] in order to describe mathematically the growth rate of the fine grain region (DIR region) formed by DIR as a function of the reaction time. DIR in the Ni(Cu) system was experimentally observed by Kawanami *et al.* [Y. Kawanami *et al.*: Mater. Trans., JIM **39** (1998) 218] at 923 and 1023 K. The new model has been utilized to analyze their observations theoretically. According to the observations, the migration rate v of the moving boundary gradually decreases with increasing reaction time. However, the decrease in the migration rate v is negligible during a small time interval of $\Delta t = 1$ s at the experimental reaction times. Thus, the value of v was assumed to be constant at each time step with $\Delta t = 1$ s in order to simplify the analysis. Using the mobility M of the moving boundary as the fitting parameter, the thickness of the DIR region was calculated as a function of the reaction time by a numerical technique. The calculation gives values of $M = 3.73 \times 10^{-17}$ and 1.51×10^{-15} m^4/Js at 923 and 1023 K, respectively, and thus $M_0 = 1.03$ m^4/Js and $Q_M = 290$ kJ/mol for $M = M_0 \exp(-Q_M/RT)$. The temperature dependence of the mobility indicates that the grain boundary migration may be governed by the solute drag effect for which the volume diffusion of the solute along the moving direction in the untransformed matrix ahead of the moving boundary has the most important role.

1. Introduction

Diffusion induced recrystallization (DIR) is the phenomenon that new fine grains with discontinuously different solute concentrations are formed behind moving grain boundaries owing to recrystallization combined with diffusion of solute atoms along the moving boundaries. DIR in the Fe(Zn) system was experimentally studied by Li and Hillert using polycrystalline Fe specimens zincified at temperatures between 733 and 923 K for various times.[1] Here, according to convention, the notation A(B) means that a solute B diffuses into a pure A metal or a binary A-B alloy. In their experiment, the fine grain region alloyed with Zn is produced at the surface of the Fe specimen and grows towards the inside of the specimen. It is pointed out by many investigators that the compositional discontinuity between the alloyed region and the untransformed matrix ahead of the moving boundary is the most important driving force.[2-7] The driving force due to such compositional discontinuity is called the chemical driving force. On the basis of this idea, Hillert and Purdy proposed a chemical driving force model.[2] For a theoretical analysis of the observations on DIR in the Fe(Zn) system, Li and Hillert suggested a kinetic model (Li-Hillert model) to describe the growth rate of the fine grain region (DIR region) as a function of the zincification time by combining the chemical driving force model with their own columnar geometry and boundary diffusion model.[1] The Li-Hillert model is valid for DIR in the A(B) system in which solute B atoms diffuse into a pure A metal. According to this model, the thickness l of the DIR region increases in proportion to the zincification

time t at early stages of the reaction, whereas it becomes proportional to the square root of t at late stages of the reaction. This means that the exponent n takes values of 1 and 1/2 at the early and late stages, respectively, if l is expressed as a function of t by the equation $l = k(t/t_0)^n$. Here, k has the same dimension as l, t is measured in s, and t_0 is unit time, 1 s. At the intermediate zincification times between the early and late stages, the exponent n decreases from 1 to 1/2 with increasing zincification time.

The kinetics of DIR in the Ni(Cu) system was experimentally studied by Kawanami *et al.* using Cu/Ni/Cu diffusion couples consisting of pure Cu single crystals and a pure Ni polycrystalline specimen.[8,9] The diffusion couples were annealed at 923 and 1023 K for various times between 1.8×10^3 and 1.76×10^5 s. In this experiment, the DIR region alloyed with Cu was observed to form at the Cu/Ni interface in the diffusion couple and to grow into the Ni phase. The thickness l of the DIR region increases with increasing annealing time t according to the relationships $l = 4.9 \times 10^{-8}(t/t_0)^{0.41}$ and $1.8 \times 10^{-7}(t/t_0)^{0.37}$ m at 923 and 1023 K, respectively.[9] Since Cu atoms diffuse into pure Ni, the Li-Hillert model is expected to be applicable to DIR in this experiment. Unfortunately, however, the observations indicate that the exponent n is smaller than 1/2. Such small values of n cannot be realized even at the late stages in this model.

The Li-Hillert model was extended by Kawanami *et al.*[10] to DIR in the A(B) system where a solute B diffuses into a binary A-B alloy. It is pointed out by Kajihara and Gust[6] that the chemical driving force for formation of the DIR region remarkably decreases with increasing mol fraction x_B of the solute in an untransformed matrix. Such remarkable decrease in the chemical driving force affects the growth behavior of the DIR region. According to the extended model, the exponent

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n at the late stages becomes smaller than 1/2 for the values of x_B greater than zero, and reaches to 1/3 at $x_B = 0.001$. This means that the thickness of the DIR region is proportional to the cubic root of the annealing time at the late stages if x_B is equal to or greater than 0.001. Consequently, the extended model apparently seems to explain the values of $n < 1/2$ observed on DIR in the Ni(Cu) system. In both the Li-Hillert and extended models, however, it is assumed that the whole chemical driving force is effective for the grain boundary migration without any friction forces. This assumption is valid on condition that the migration rate v of the moving boundary is large enough to make the penetration distance d of the solute due to volume diffusion in the untransformed matrix ahead of the moving boundary atomic dimensions or less. However, if v is very small, d becomes much greater than atomic dimensions. In such a case, most part of the chemical driving force will be consumed by the volume diffusion in the penetration zone. The observed values of the migration rate v for DIR in the Ni(Cu) system indicate that the penetration distance d may not be smaller than atomic dimensions at the experimental annealing times.[9] Under such conditions, the energy consumption due to the volume diffusion should be taken into account for evaluation of the driving force.

Recently, an energy balance model was proposed by Kajihara and Gust[7] to evaluate the driving force for DIR during alloying in binary systems. The energy consumption due to the volume diffusion is explicitly considered in this model. The energy balance model gives a mathematical expression of the effective driving force as a function of the migration rate v for a very wide range of the penetration distance d. In the present work, a new model has been proposed to take account of an influence of the energy consumption due to the volume diffusion on the kinetics of DIR by combining the energy balance model with the Li-Hillert and extended models. The new model has been applied to a numerical analysis of the observations on DIR in the Ni(Cu) system[9] by estimating the energy consumption in a simplified manner.

2. Model

In the binary Ni–Cu system, a complete solid solution phase with the face-centered cubic (fcc) structure appears at the temperature range between 628 and 1358 K.[11] The observations by Kawanami et al.[8,9] indicate that DIR occurs in the fcc single-phase region of this binary system at 923 and 1023 K. The chemical composition changes discontinuously across the boundary between the DIR region and the untransformed matrix. In the case of the complete solid solution phase, however, the compositional discontinuity cannot be related with the phase diagram. On the other hand, the two-phase region consisting of the fcc-Cu (α) and fcc-Fe (γ) phases exists at 1123 to 1369 K in the binary Fe–Cu system.[12] According to the observations by Kawanami et al.[13] on DIR in this binary system, the DIR region alloyed with Cu is formed at the α/γ interface and grows into the γ phase at 1193 and 1323 K. In this case, the compositional discontinuity across the interface is known from the phase diagram as long as the local equilibrium is established at the interface. In order to simplify an explanation of a kinetic model, it is more convenient to focus our attention on DIR that takes place

in a two-phase region of an appropriate binary system like the Fe–Cu system. Consequently, we consider a hypothetical substitutional binary A-B system in which A and B are the solvent and solute elements, respectively, and the A-rich (α) and B-rich (β) solid solution phases are in equilibrium with each other. In this binary system, DIR is supposed to occur only in the α phase at a reaction temperature. Figure 1 schematically shows that fine grains alloyed with the solute are produced at the interface due to DIR and grow into the α phase in an α/β two-phase diffusion couple. The growth of the fine grain DIR region is realized by the transport of solute atoms along the grain boundaries from the interface to the moving boundaries. The migration rate v of the moving boundary is related to the driving force ΔG by the equation

$$v = \frac{dl}{dt} = M \Delta G. \qquad (1)$$

Here, l is the thickness of the DIR region, t is the reaction time, M is the mobility of the moving boundary, and ΔG has the dimension of force per unit area or energy per unit volume. If the quantities l, t and ΔG are measured in m, s and J/m^3, respectively, the mobility M takes a unit of m^4/Js. Equation (1) indicates that the migration rate v or the growth rate of the DIR region dl/dt is proportional to the driving force ΔG. On the basis of this equation, Li and Hillert proposed a kinetic model (Li-Hillert model) for DIR in the A(B) system in which solute B atoms diffuse into a pure A metal. In a new model, the Li-Hillert model has been extended to DIR in the A(B) system where the solute B diffuses into a binary A-B solution phase. Furthermore, the energy consumption due to the volume diffusion of the solute in the untransformed matrix ahead of the moving boundary has been taken into consideration in the present new model. These models will be explained in detail for the reaction shown in Fig. 1.

2.1 Li-Hillert model

In order to estimate the rate of supply of solute atoms to the moving boundary, Li and Hillert assumed that the shape of each fine grain in the DIR region is columnar and the diffusion coefficient along the moving boundary parallel to the α/β interface is much greater than that along the stationary
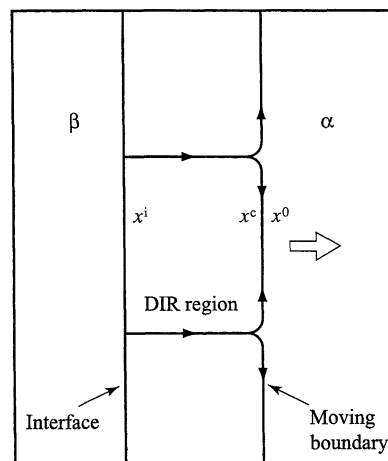

Fig. 1 Schematic diagram of fine grains formed in the α phase from the interface of the α/β diffusion couple in the binary A-B system due to DIR.

circular grain boundaries normal to the interface.[1] Thus, they obtained the following equation to describe the rate of supply of the solute along the circular boundary to the moving boundary.

$$\frac{dm}{dt} = -\frac{1}{2}\pi s\delta \frac{D^b}{V_m}\frac{dx}{dy} = \frac{\pi s\delta}{2}\frac{D^b}{V_m}\frac{x^i - x^c}{l} \tag{2}$$

Here, m is the amount of the solute supplied to the moving boundary, s is the diameter of the columnar fine grain, D^b is the interdiffusion coefficient along the circular boundary, δ is the thickness of the grain boundary, V_m is the molar volume, x is the mol fraction of the solute, and y is the distance along the circular boundary measured from the interface. The quantities x^i and x^c stand for the solute concentrations in the DIR region at the interface and the moving boundary, respectively. In eq. (2), the concentration profile of the solute along the circular boundary is assumed to be straight and thus $dx/dy = (x^c - x^i)/l$. This assumption is valid as long as the boundary diffusion occurs sufficiently fast compared with the grain boundary migration and there is no composition dependency in D^b. The factor 1/2 means that the diffusional flux along the circular boundary is shared with the neighboring fine grains. For the columnar geometry of the fine grain, the supply rate dm/dt is correlated with the growth rate dl/dt by the equation

$$\frac{dm}{dt} = \pi\left(\frac{s}{2}\right)^2\frac{x^c}{V_m}\frac{dl}{dt}. \tag{3}$$

When the α phase is initially a pure A metal and the DIR region with composition x^c grows into the α phase, the chemical driving force $\Delta^c G$ acting on the moving boundary is evaluated as follows using the chemical driving force model proposed by Hillert and Purdy[2]

$$\Delta^c G = -\frac{RT}{V_m}\ln(1 - x^c), \tag{4}$$

if the α phase is thermodynamically ideal. This chemical driving force model is hereafter called the Hillert-Purdy model. For the values of x^c much smaller than unity, eq. (4) reduces to

$$\Delta^c G = \frac{RT}{V_m}x^c. \tag{5}$$

If any friction forces are neglected, $\Delta^c G$ is considered as the driving force ΔG in eq. (1). In such a case, ΔG is proportional to x^c according to eq. (5). From eqs. (1) and (5), the following relationship is obtained.

$$\frac{dl}{dt} = M\Delta^c G = \frac{MRT}{V_m}x^c \tag{6}$$

Equation (6) indicates that the growth rate dl/dt is directly proportional to the composition x^c. Combining eq. (6) with eqs. (2) and (3) and eliminating the term dm/dt, we obtain the equation

$$(x^c)^2 = \frac{2\delta D^b V_m(x^i - x^c)}{MRTls}. \tag{7}$$

For $s = l/2$, eq. (7) yields the relationship

$$x^c = \frac{2x^i}{1 + \sqrt{1 + \dfrac{MRTx^i l^2}{\delta D^b V_m}}}. \tag{8}$$

Inserting eq. (8) into eq. (6), the following equation is obtained.

$$\left(1 + \sqrt{1 + \frac{MRTx^i l^2}{\delta D^b V_m}}\right)\frac{dl}{dt} = \frac{2MRTx^i}{V_m} \tag{9}$$

Equation (9) is an ordinary differential equation of the first order in which t and l are the independent and dependent variables, respectively. This differential equation can be integrated analytically as follows

$$\tau = 2\lambda + \lambda\sqrt{1 + \lambda^2} + \ln\left(\lambda + \sqrt{1 + \lambda^2}\right), \tag{10}$$

if the quantities M, δD^b, V_m and x^i are constant during the reaction. Here, τ and λ are the normalized reaction time and the normalized thickness of the DIR region, respectively, defined as

$$\tau = t\frac{4(MRTx^i/V_m)^{3/2}}{\sqrt{\delta D^b}} \tag{11}$$

and

$$\lambda = l\sqrt{\frac{MRTx^i}{\delta D^b V_m}}. \tag{12}$$

The thickness l is mathematically expressed as a function of the reaction time t in an implicit manner by eq. (10) through eqs. (11) and (12).

2.2 Present model

In the Li-Hillert model, it is assumed that the whole chemical driving force is effectively utilized for the grain boundary migration without any friction forces. This assumption is valid, when the grain boundary migration occurs sufficiently fast and thus the penetration distance of the solute due to volume diffusion in the untransformed matrix ahead of the moving boundary becomes atomic dimensions or less. However, if the migration rate of the moving boundary is very small, the penetration distance becomes much greater than atomic dimensions. In this case, the chemical driving force is considerably consumed by the volume diffusion of the solute in the penetration zone. Under such conditions, the energy consumption due to the volume diffusion should be taken into consideration for evaluation of the driving force.

Recently, an energy balance (EB) model was proposed by Kajihara and Gust[7] in order to evaluate the driving force for DIR during alloying in binary systems as a function of the migration rate. When one mol of the DIR region with composition x^c is formed from $(x^c - x^0)/(1 - x^0)$ mol of solute atoms and $(1 - x^c)/(1 - x^0)$ mol of the α phase with composition x^0, the chemical driving force $\Delta^c G$ is described by the following equation according to the EB model

$$\Delta^c G = \frac{RT}{V_m}(1 - x^c)\left(\ln\frac{1 - x^0}{1 - x^c} + \frac{x^0}{1 - x^0}\ln\frac{x^0}{x^c}\right), \tag{13}$$

if the α phase is again thermodynamically ideal. It should be noted that the term $\Delta^c G$ in eqs. (4) and (5) is evaluated with respect to the initial composition of the untransformed matrix but that in eq. (13) indicates the quantity at the composition in the DIR region. The friction force $\Delta^{vd} G$ owing to the volume diffusion in the penetration zone is given as

$$\Delta^{vd} G = \frac{RT}{V_m}(1 - x^c)\left(\ln\frac{1 - x^0}{1 - x^{nf}} + \frac{x^0}{1 - x^0}\ln\frac{x^0}{x^{nf}}\right)$$
$$+ Y\eta^2\frac{1 - x^c}{1 - x^0}(x^{nf} - x^0)^2 \tag{14}$$

according to the EB model. Here, x^{nf} is the composition in the untransformed matrix at the interatomic distance λ from the moving boundary, Y is the biaxial elastic modulus of the untransformed matrix along a plane parallel to the moving boundary, and η is the misfit parameter. The quantity $\Delta^{ef} G$ defined as the following equation is the effective driving force that remains against the friction force $\Delta^{vd} G$ and then contributes to the grain boundary migration.

$$\Delta^{ef} G \equiv \Delta^c G - \Delta^{vd} G \tag{15}$$

From eqs. (13) to (15), we obtain the relationship

$$\Delta^{ef} G = (1 - x^c)\left\{\frac{RT}{V_m}\left(\ln\frac{1 - x^{nf}}{1 - x^c} + \frac{x^0}{1 - x^0}\ln\frac{x^{nf}}{x^c}\right) - Y\eta^2\frac{(x^{nf} - x^0)^2}{1 - x^0}\right\}, \tag{16}$$

which describes $\Delta^{ef} G$ as a function of x^c and x^{nf}. If ΔG is replaced with $\Delta^{ef} G$, the following equation is obtained from eqs. (1) and (16).

$$\frac{dl}{dt} = M\Delta^{ef} G$$
$$= M(1 - x^c)\left\{\frac{RT}{V_m}\left(\ln\frac{1 - x^{nf}}{1 - x^c} + \frac{x^0}{1 - x^0}\ln\frac{x^{nf}}{x^c}\right) - Y\eta^2\frac{(x^{nf} - x^0)^2}{1 - x^0}\right\} \tag{17}$$

Let x^{pf} be the composition in the penetration zone at the interface between the untransformed matrix and the moving boundary. This interface is designated the front interface. The composition x^{nf} in eq. (17) is a function of the composition x^{pf} and the growth rate dl/dt or the migration rate v as follows.

$$x^{nf} = f(v, x^{pf}) \tag{18}$$

A mathematical expression of the function $f(v, x^{pf})$ will be obtained, if the reaction time dependence of the migration rate v is known for a given value of x^{pf}. Considering the local equilibrium between the moving boundary and the penetration zone at the front interface, x^{pf} is determined by the parallel-tangent construction (PTC) method.[14] The PTC method gives the equation

$$\ln\frac{x^{pf}}{1 - x^{pf}} + \frac{2YV_m\eta^2}{RT}(x^{pf} - x^0) = \ln\frac{x^c}{1 - x^c}, \tag{19}$$

if the concentration gradient of the solute across the moving boundary is negligible. Since the DIR region with composition x^c grows into the untransformed matrix with composition x^0 in the present case, the composition x^c in eq. (3) should be replaced with the compositional difference $(x^c - x^0)$ as follows.

$$\frac{dm}{dt} = \pi\left(\frac{s}{2}\right)^2\frac{x^c - x^0}{V_m}\frac{dl}{dt} \tag{20}$$

Eliminating the term dm/dt from eqs. (2) and (20), the following relationship is obtained to describe the composition x^c as a function of l, s and dl/dt for given values of x^i and δD^b.

$$x^c = \frac{x^i + x^0\dfrac{sl}{2\delta D^b}\dfrac{dl}{dt}}{1 + \dfrac{sl}{2\delta D^b}\dfrac{dl}{dt}} \tag{21}$$

Equations (17), (18), (19) and (21) are the simultaneous dif-

ferential equations of the first order where t and l are again the independent and dependent variables, respectively, if the quantities x^i, V_m, δD^b, Y, η and M are known, the mathematical expression of $f(v, x^{pf})$ is given, and s is described as a function of t or l at a reaction temperature. When the simultaneous differential equations are solved in an appropriate manner under given initial and boundary conditions, the relationship between t and l is determined.

3. Analysis

3.1 Observations by Kawanami et al.

DIR in the Ni(Cu) system was experimentally studied by Kawanami et al.[9] using the Cu/Ni/Cu diffusion couples composed of a pure Ni polycrystalline specimen and pure Cu single crystals. In all the diffusion couples, the Miller indices of the Cu single crystals were (111) at the interfaces. In their experiment, the diffusion couples were annealed at 923 and 1023 K for various times between 1.8×10^3 and 1.76×10^5 s, and then the DIR region alloyed with Cu was observed to form at the interface and to grow into the Ni phase. Their observations on the relationship between the thickness l of the DIR region and the reaction time or annealing time t are represented in Fig. 2. In this figure, open circles and squares show the experimental points at 923 and 1023 K, respectively. Although the experimental points are slightly scattered, the observations indicate that the thickness l increases with increasing annealing time t according to the relationship

$$l = k(t/t_0)^n. \tag{22}$$

Here, t_0 is unit time, 1 s. The proportionality constant k and the exponent n take values of $10^{-7.31\pm0.22}$ m and 0.41 ± 0.05, respectively, at 923 K whereas those of $10^{-6.74\pm0.17}$ m and 0.37 ± 0.04, respectively, at 1023 K. Solid lines in Fig. 2 show the calculations from eq. (22) for the mean values of $k = 4.9 \times 10^{-8}$ and 1.8×10^{-7} m and $n = 0.41$ and 0.37.
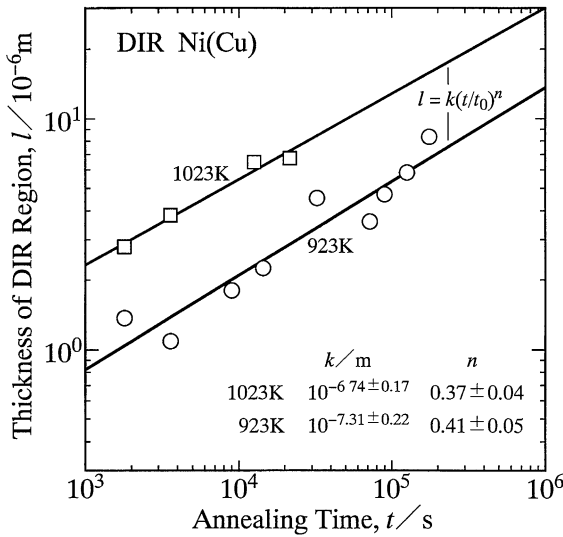
Fig. 2 The thickness l of the DIR region versus the annealing time t for DIR in the Ni(Cu) system observed by Kawanami et al. at 923 and 1023 K.[9]

Fig. 3 The thickness l of the DIR region versus the annealing time t for DIR in the Ni(Cu) system calculated by Kawanami et al.[9] using eqs. (10) to (12) at (a) 1023 and (b) 923 K. The experimental points in Fig. 2 are also shown.

Using the Li-Hillert model, Kawanami et al. analyzed the observations.[9] In their analysis, the mobility M in eqs. (11) and (12) was chosen as the fitting parameter and determined to be 1.86×10^{-18} and 2.14×10^{-17} m^4/Js at 923 and 1023 K, respectively, from the experimental points in Fig. 2. For these values of M, the thickness l was calculated as a function of the annealing time t from eq. (10). The results at 1023 and 923 K are shown as solid curves in Figs. 3(a) and (b), respectively. In these figures, the experimental points in Fig. 2 are also represented. At 1023 K, the solid curve is almost straight at annealing times longer than 2×10^3 s as indicated in Fig. 3(a). The straight part of the solid curve is expressed by eq. (22) using values of $k = 5.20 \times 10^{-8}$ m and $n = 0.5$. A dashed line in Fig. 3(a) indicates the calculation for these values of k and n. As can be seen, the open squares are located on both the solid curve and the dashed line at 1023 K. On the other hand, at 923 K, the solid curve is almost straight at annealing times shorter than 3×10^2 s and at those longer than 3×10^4 s as shown in Fig. 3(b). The exponent n is 1 at the shorter annealing times, but it becomes 0.5 at the longer annealing times. At intermediate annealing times between 3×10^2 and 3×10^4 s, the exponent n decreases with increasing annealing time t. Half of the open circles are distributed at the longer annealing times, whereas the other ones are located at the intermediate annealing times. Considering the slightly scattered experimental points, agreement between the observations and the calculations using the Li-Hillert model may be satisfactory. As mentioned earlier, however, the observations provide the values of $n = 0.41 \pm 0.05$ and 0.37 ± 0.04 at 923 and 1023 K, respectively. Such small values of n cannot be realized in the Li-Hillert model.

3.2 Penetration distance in untransformed matrix

As already mentioned in Section 2.1, it is assumed in the Li-Hillert model that the whole chemical driving force is effectively utilized for the grain boundary migration without any friction forces. In order to determine whether this assumpt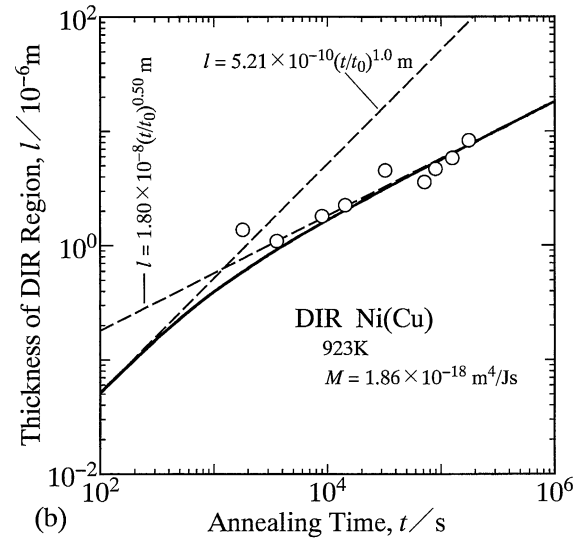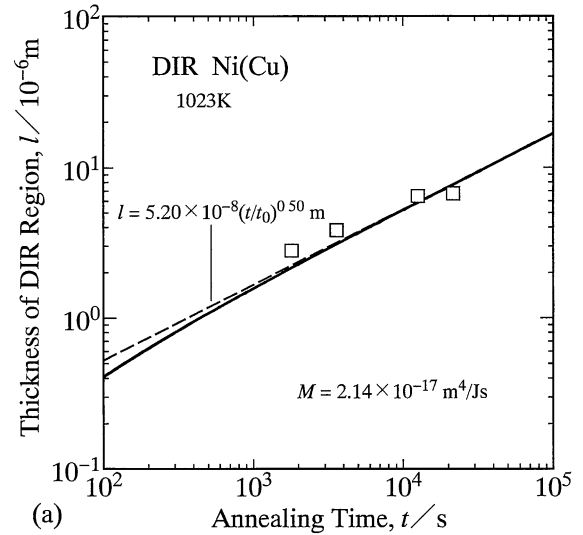ion is valid, the penetration distance of the solute due to volume diffusion in the untransformed matrix ahead of the moving boundary should be known under the experimental conditions. The penetration distance d from the front interface is estimated from the following equation as a function of the migration rate v of the moving boundary, if the grain boundary migrates in a steady state manner.

$$d = D/v \qquad (23)$$

The observations in Fig. 2 indicate that the thickness l of the DIR region is expressed as a function of the annealing time t by eq. (22). Thus, the annealing time dependence of the migration rate is described as follows.

$$v = \frac{dl}{dt} = \frac{nk}{t_0} \left(\frac{t}{t_0} \right)^{-(1-n)} \qquad (24)$$

According to eq. (24), the migration rate v varies depending on the annealing time t, and thus the steady state migration is not realized under the experimental conditions. However, in order to test the validity of the assumption mentioned above, it is still useful to combine eq. (23) with eq. (24). Hence, we

obtain the equation

$$d = \frac{Dt_0}{nk}\left(\frac{t}{t_0}\right)^{(1-n)} \qquad (25)$$

to estimate the penetration distance d as a function of the annealing time t. Using eq. (25), the annealing time dependence of the penetration distance was calculated at 923 and 1023 K with the following parameters: $n = 0.41$ and $k = 4.9 \times 10^{-8}$ m at 923 K; $n = 0.37$ and $k = 1.8 \times 10^{-7}$ m at 1023 K; and $D_0 = 5.7 \times 10^{-5}$ m^2/s and $Q = 258$ kJ/mol for $D = D_0 \exp(-Q/RT)$.[15] The results are shown as solid lines in Fig. 4. In this figure, open squares and circles show the calculations corresponding to the experimental annealing times at 1023 and 923 K, respectively, whereas a horizontal dashed line indicates the interatomic distance λ. As can be seen in Fig. 4, the penetration distance d monotonically increases with increasing annealing time t. At 1023 K, d is always greater than λ at the experimental annealing times. On the other hand, at 923 K, d is smaller than λ at $t < 10^4$ s, but it becomes greater than λ at $t > 10^4$ s. Three open circles are located at $t < 10^4$ s, whereas the other open circles are distributed at $t > 10^4$ s. Consequently, we may conclude that the friction force due to the volume diffusion is negligible at the three shorter experimental annealing times at 923 K.

Recently, the relationship between the penetration distance and the friction force due to the volume diffusion was quantitatively analyzed for an ideal solution phase in a binary system by Kajihara and Gust using the EB model.[7] According to this analysis, the friction force is negligibly small at $d < \lambda/8$, but it gradually increases with increasing penetration distance at $d > \lambda/8$. Hence, the critical penetration distance, which determines whether the friction force is negligible or not, should be $\lambda/8$ instead of λ. The critical value of $d = \lambda/8$ is indicated as a horizontal dotted line in Fig. 4. As can be seen in this figure, d is greater than $\lambda/8$ at all the experimental annealing times. Thus, it is concluded that the chemical driving force is partially or considerably consumed

by the volume diffusion in the penetration zone ahead of the moving boundary during DIR under the present experimental conditions.

3.3 Growth rate of DIR region

If the energy consumption due to the volume diffusion is not negligible, the driving force cannot be evaluated from eq. (4) nor (5) and thus eqs. (10) to (12) are no longer applicable. In such a case, the effect of the energy consumption on the driving force should be taken into account. Hence, in this Section, eqs. (17), (18), (19) and (21) were applied to a theoretical analysis of the observations in Fig. 2.

In order to carry out the analysis, a mathematical expression of $f(v, x^{pf})$ in eq. (18) should be known. When v is constant during the reaction, we obtain a very simple expression of $f(v, x^{pf})$ as follows.

$$x^{nf} = f(v, x^{pf}) = x^0 + (x^{pf} - x^0)\exp(-v\lambda/D) \qquad (26)$$

According to eq. (24), however, the value of v gradually decreases with increasing annealing time t. Nevertheless, for a small time interval of $\Delta t = 1$ s, v merely varies by 0.03% at the shortest annealing time of $t = 1.8 \times 10^3$ s at 1023 and 923 K. The variation of v for the same time interval monotonically decreases with increasing annealing time, and then reaches to 0.003 and 0.0003% at the longest annealing times of $t = 2.16 \times 10^4$ and 1.76×10^5 s at 1023 and 923 K, respectively. This means that v is considered almost constant during $\Delta t = 1$ s. Consequently, in the present analysis, $f(v, x^{pf})$ was approximately described by eq. (26) at each time step with a time interval of $\Delta t = 1$ s. However, it should be noted that this approximation is just for the sake of convenience and the validity of the present model is independent of the approximation. Since the polycrystalline pure Ni specimens were used in the Cu/Ni/Cu diffusion couples, there may not exist special crystallographic orientation relationships between the Ni phase and the DIR region. Therefore, the Ni (α) phase was assumed to be elastically isotropic. This assumption results in $Y = E/(1 - v)$. Here, E and v are the Young's modulus and the Poisson's ratio, respectively. Inserting $x^0 = 0$ into eqs. (17), (19) and (26), considering the relationship $Y = E/(1 - v)$, and then replacing the differential coefficient dl/dt with the difference coefficient $\Delta l/\Delta t$, we obtain the equations

$$\frac{\Delta l}{\Delta t} = M(1 - x^c)\left\{\frac{RT}{V_m}\ln\frac{1 - x^{nf}}{1 - x^c} - \frac{E}{1 - v}\eta^2(x^{nf})^2\right\}, \qquad (27)$$

$$\ln\frac{x^{pf}}{1 - x^{pf}} + \frac{E}{1 - v}\frac{2V_m\eta^2}{RT}x^{pf} = \ln\frac{x^c}{1 - x^c} \qquad (28)$$

and

$$x^{nf} = x^{pf}\exp\left(-\frac{\lambda}{D}\frac{\Delta l}{\Delta t}\right). \qquad (29)$$

Here, Δl is the increment of the thickness of the DIR region for the time interval Δt. According to the observations,[9] the ratio s/l is almost unity independent of the annealing time for DIR in the Ni(Cu) system. Inserting $s = l$ and $x^0 = 0$ into eq. (21) and replacing again dl/dt with $\Delta l/\Delta t$, the following
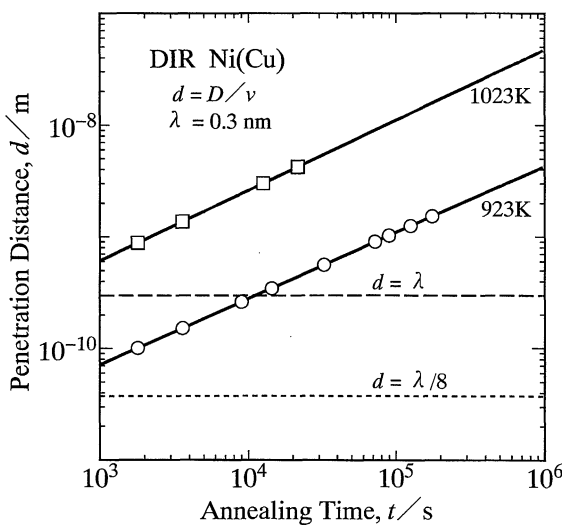

Fig. 4 The penetration distance d of the solute due to volume diffusion in the untransformed matrix ahead of the moving boundary calculated by eq. (25) as a function of the annealing time t. Open squares and circles indicate the calculations for the experimental annealing times at 1023 and 923 K, respectively.

equation is obtained.

$$x^c = \frac{x^i}{1 + \dfrac{l^2}{2\delta D^b}\dfrac{\Delta l}{\Delta t}} \qquad (30)$$

Equations (27) to (30) are simultaneous difference equations of the first order. Using these equations, the increment Δl was calculated for a given value of the interval Δt at time step t_i. For the calculation, it is assumed that the quantities E, ν, V_m, D, δD^b and x^i are constant at a reaction temperature. The mobility M was chosen as the fitting parameter and determined to minimize the parameter S defined as

$$S = \sum_{j=1}^{n}(l_j^{cal} - l_j^{exp})^2. \qquad (31)$$

Here, l_j^{exp} and l_j^{cal} are the observed and calculated values of l, respectively, at each experimental annealing time t_j. From the experimental points in Fig. 2, the mobility was determined to be $M = 3.73 \times 10^{-17}$ and $1.51 \times 10^{-15}\,\mathrm{m^4/Js}$ at 923 and 1023 K, respectively, adopting the following parameters: $D_0 = 5.7 \times 10^{-5}\,\mathrm{m^2/s}$ and $Q = 258\,\mathrm{kJ/mol}$ for $D = D_0\exp(-Q/RT)$;[15] $\delta D_0^b = 5.25 \times 10^{-16}\,\mathrm{m^3/s}$ and $Q_b = 133.9\,\mathrm{kJ/mol}$ for $\delta D^b = \delta D_0^b\exp(-Q_b/RT)$;[16] $V_m = 6.845 \times 10^{-6}\,\mathrm{m^3/mol}$;[17] $x^i = 0.25$;[9] $E = 168\,\mathrm{GPa}$;[18] $\nu = 0.3$;[19] $\eta = 0.0253$;[20] $\lambda = 0.3\,\mathrm{nm}$; and $\Delta t = 1\,\mathrm{s}$. The relationships between l and t calculated at 1023 and 923 K using these values of M are shown as solid curves in Figs. 5(a) and (b), respectively. In these figures, the experimental points at 1023 and 923 K are represented as open squares and circles, respectively, whereas the solid lines in Fig. 2 are indicated as dashed lines. As can be seen, the solid curve coincides well with the dashed line at each temperature. Since the dashed line is described by eq. (22) with a constant value of the exponent n, it has a constant slope. On the other hand, the slope of the solid curve gradually decreases with increasing annealing time at both temperatures. According to the results in Fig. 5, the exponent n varies from 0.350 to 0.347 between $t = 1.8 \times 10^3$ and $2.16 \times 10^4\,\mathrm{s}$ at 1023 K, whereas it changes from 0.437 to 0.349 between $t = 1.8 \times 10^3$ and $1.76 \times 10^5\,\mathrm{s}$ at 923 K. This means that the annealing time dependence of the thickness of the DIR region cannot be simply expressed by a power function with a constant exponent.

The value $n = 0.5$ at the late stages in the Li-Hillert model implies that the growth of the DIR region is controlled by diffusion of solute atoms. Through a theoretical analysis of the observations on DIR in the Cu(Zn) system, it is concluded by Goukon et al.[21] that the boundary diffusion of the solute is actually the rate-controlling process of DIR. This conclusion is considered valid also for DIR in the Ni(Cu) system. In this case, however, the chemical driving force is considerably consumed by the volume diffusion of the solute in the penetration zone ahead of the moving boundary as mentioned earlier. As the annealing time increases, the migration rate of the moving boundary decreases, and hence the consumption of the chemical driving force increases. As a result, the exponent n takes values smaller than 0.5 and gradually decreases with increasing annealing time under the present experimental conditions.
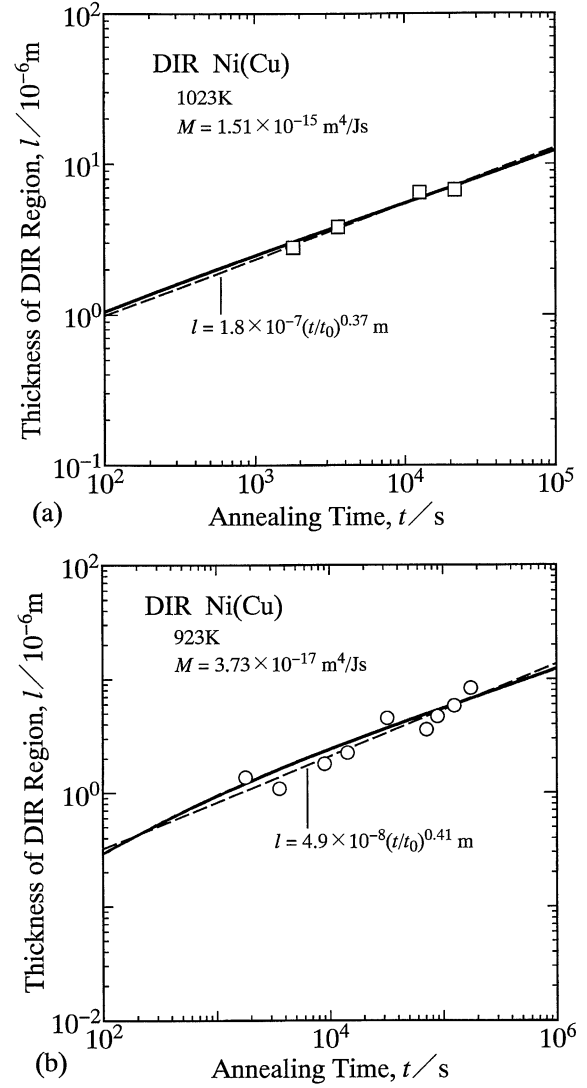

(a)

(b)

Fig. 5 The thickness l of the DIR region versus the annealing time t for DIR in the Ni(Cu) system calculated by eqs. (27) to (30) at (a) 1023 and (b) 923 K. The experimental points and the fitting lines in Fig. 2 are also shown as open symbols and dashed lines, respectively.

3.4 Mobility

For the calculations of the solid curves in Figs. 5(a) and (b), the mobility M was chosen as the fitting parameter. The values of M determined at 1023 and 923 K are plotted as open circles in Fig. 6. In this figure, the ordinate and the abscissa show the logarithm of the mobility M and the reciprocal of the absolute temperature T, respectively. The temperature dependence of the mobility may be described as follows.

$$M = M_0 \exp(-Q_M/RT) \qquad (32)$$

The parameters M_0 and Q_M were determined to be $1.03\,\mathrm{m^4/Js}$ and $290\,\mathrm{kJ/mol}$, respectively, from the open circles in Fig. 6. In this figure, the values of M evaluated by Kawanami et al.[9] using the Li-Hillert model are also represented as open squares. Since the chemical driving force in the Li-Hillert model corresponds to the maximum value of the effective driving force, the result by Kawanami et al. may overestimate the driving force and thus underestimate the mobility. Their result yields $M = 2.14 \times 10^{-17}$ and $1.86 \times 10^{-18}\,\mathrm{m^4/Js}$ at 1023 and 923 K, respectively, and therefore $M_0 = 1.4 \times 10^{-7}\,\mathrm{m^4/Js}$
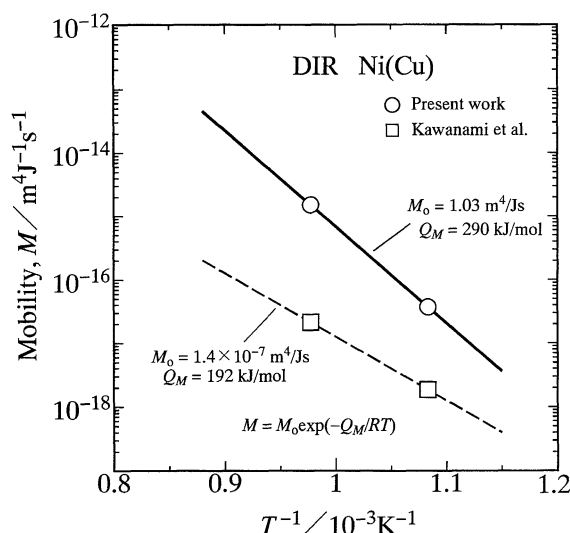
Fig. 6   The logarithm of the mobility M versus the reciprocal of the absolute temperature T for DIR in the Ni(Cu) system. The values of M obtained by Kawanami et al.[9] are also shown as open squares.

and $Q_M = 192$ kJ/mol. These values of M are one to two orders of magnitude smaller than those obtained in the present analysis.

The mobility of the moving boundary for DIR may be relevant to the solute drag effect. The solute drag is usually governed by the boundary diffusion of the solute across the moving boundary and/or the volume diffusion of the solute along the moving direction in the matrices ahead of and behind the moving boundary. The value $Q_M = 192$ kJ/mol obtained by Kawanami et al. is greater than the activation enthalpy of 133.9 kJ/mol for boundary diffusion of Cu in Ni,[16] but smaller than that of 258 kJ/mol for volume diffusion of Cu in Ni.[15] Hence, they concluded that both the volume diffusion and the boundary diffusion might play important roles for the solute drag effect on DIR in the Ni(Cu) system. On the other hand, the value $Q_M = 290$ kJ/mol in the present analysis is greater than the activation enthalpy of the boundary diffusion, whereas it is nearly close to that of the volume diffusion. Therefore, the volume diffusion seems predominant for the solute drag. However, both values of Q_M were determined from the experimental points at only two annealing temperatures. In order to draw conclusions reliably, more detailed experimental information is needed.

4.   Conclusions

A new kinetic model was proposed to describe the growth rate of the fine grain DIR region as a function of the annealing time for DIR in the A(B) system where solute B atoms diffuse into a pure A metal or a binary A-B alloy. The energy balance model by Kajihara and Gust[7] was combined with the columnar geometry and boundary diffusion model by Li and Hillert[1] and the extended model by Kawanami et al.[10] The effect of the friction force due to the penetration of the solute by volume diffusion in the untransformed matrix ahead of the moving boundary was explicitly taken into consideration to evaluate the effective driving force as a function of the migration rate v of the moving boundary. The new model was utilized to analyze theoretically the observations by Kawanami

et al.[9] on DIR in the Ni(Cu) system at 923 and 1023 K. According to their observations, the migration rate v gradually decreases with increasing annealing time. However, the value of v merely varies by 0.03% even at the shortest annealing time during a small time interval of $\Delta t = 1$ s. The variation of v for $\Delta t = 1$ s monotonically decreases with increasing annealing time, and then reaches to 0.003 and 0.0003% at the longest annealing times at 1023 and 923 K, respectively. Consequently, in order to simplify the analysis, the migration rate v was assumed to be constant at each time step with $\Delta t = 1$ s. The growth behavior of the DIR region could be quantitatively accounted for by the analysis. The analysis indicates that the chemical driving force for the grain boundary migration is considerably consumed by the volume diffusion of the solute in the untransformed matrix ahead of the moving boundary during DIR under the present experimental conditions. From the temperature dependence of the mobility for the moving boundary, it may be concluded that the volume diffusion in the untransformed matrix plays the most important role for the solute drag effect on the grain boundary migration.

Acknowledgements

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