Growth Rate of Fine Grains Formed by Diffusion Induced Recrystallization in Ni Layer of Cu/Ni/Cu Diffusion Couples[†]

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Diffusion induced recrystallization (DIR) in the Ni(Cu) system was experimentally studied. The notation Ni(Cu) means that Cu atoms diffuse into a pure Ni or binary Ni-Cu phase. The Cu/Ni/Cu diffusion couples consisting of pure Cu single crystals with the same crystallographic orientation and a pure Ni polycrystalline specimen were annealed at 923 and 1023 K for various times between 1.8×10^3 and 1.76×10^5 s. The penetration of Cu in the Ni phase was found to occur at rates three orders of magnitude greater than the ones evaluated from the volume diffusion. This unusually rapid penetration is due to DIR. DIR was observed to take place only in the Ni phase from the interfaces in all the diffusion couples annealed at 923 and 1023 K. The observations indicate that 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 $l = 1.8 \times 10^{-7}(t/t_0)^{0.37}$ at 923 and 1023 K, respectively. Here, l and t are measured in m and s, respectively, and t_0 is unit time, 1 s. The analysis using the kinetic equation proposed by Li and Hillert could account for the observations quantitatively.

(Received June 2, 1997)

Keywords: diffusion induced recrystallization, nickel-copper system, grain boundary migration, grain boundary diffusion

I. Introduction

Diffusion induced recrystallization (DIR) and diffusion induced grain boundary migration (DIGM) are known to take place in many binary systems⁽¹⁾⁻⁽³⁾. DIGM is the phenomenon that a region with different composition is left behind a moving grain boundary owing to the grain boundary migration combined with the diffusion of solute atoms along the moving grain boundary. During DIR, on the contrary, new grains with different solute concentrations are formed behind moving grain boundaries due to recrystallization combined with diffusion of solute atoms along the moving boundaries. A series of studies on DIR in the Fe(Cu) and Ni(Cu) systems have been carried out by the present authors using Cu/Fe/Cu and Cu/Ni/Cu diffusion couples consisting of pure Cu single crystals and Fe and Ni polycrystalline specimens⁽⁴⁾⁻⁽⁸⁾. Here, the notation A(B) means that a solute B diffuses into a pure metal A or a binary A-B alloy according to convention.

In the Fe(Cu) system, the Cu/Fe/Cu and Cu/(Fe-4.8Cu)/Cu diffusion couples were annealed at 1193 and 1323 K for various times⁽⁷⁾. DIR was clearly observed to occur only in the Fe phase of the Cu/(Fe-4.8Cu)/Cu diffusion couples annealed at 1323 K. The DIR regions al-

loyed with Cu are formed in the Fe phase from the interfaces of the diffusion couple and grow toward the center of the Fe phase. The observations of the Cu/(Fe-4.8Cu)/Cu diffusion couples indicate that the thickness l of the DIR region increases with increasing annealing time t according to the relationship $l = 1.58 \times 10^{-6}(t/t_0)^{0.29}$ at 1323 K. Here, l and t are measured in m and s, respectively, and t_0 is unit time, 1 s. This relationship means that the thickness l increases in proportion to the almost cubic root of the annealing time t . Due to DIR, the penetration of Cu in the Fe phase occurs at rates two orders of magnitude greater than the ones evaluated from the volume diffusion. The kinetics of DIR observed for the Cu/(Fe-4.8Cu)/Cu diffusion couples was theoretically analyzed by the present authors⁽⁸⁾. Li and Hillert proposed a kinetic equation for DIR in the A(B) system where a solute B diffuses into a pure metal A⁽⁹⁾. According to their kinetic equation, the thickness l increases proportionately with the annealing time t at early stages of the reaction, whereas l increases in proportion to the square root of t at late stages of the reaction. However, these two relationships between l and t do not hold for DIR in the Fe phase of the Cu/(Fe-4.8Cu)/Cu diffusion couple. Consequently, a new kinetic equation was obtained to describe the growth rate of the DIR region in a binary solution phase⁽⁸⁾. For derivation of the kinetic equation, the columnar-geometry and boundary-diffusion model by Li and Hillert⁽⁹⁾ was combined with the energy balance model by Kajihara and Gust⁽¹⁰⁾. The new kinetic equation quantitatively accounts for the observations of DIR in the Cu/(Fe-4.8Cu)/Cu diffusion couple. The

[†] This paper was partly presented at the 1996 Autumn Meeting of the Japan Institute of Metals.

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analysis indicates that the thickness l increases in proportion to the square root of the annealing time t for DIR in a pure metal whereas l increases proportionately with the cubic root of t for DIR in a solution phase at late stages of the reaction.

As to the Ni(Cu) system, DIGM and DIR were experimentally studied by den Broeder and Nakahara⁽¹¹⁾, Liu *et al.*⁽¹²⁾ and Ma *et al.*⁽¹³⁾ using Cu/Ni/Cu diffusion couples consisting of pure Cu and Ni polycrystalline specimens. The diffusion couples were annealed at various temperatures between 623 and 1223 K. After the annealing, a mixed DIGM+DIR area was observed near the interface whereas DIGM areas were found in both the Ni and Cu phases slightly far from the interface. The kinetics of DIGM was extensively examined from the microstructure observations of the DIGM areas. On the other hand, it seems rather difficult to distinguish the alloyed region by DIR from that by DIGM in the mixed DIGM+DIR area. Thus, the growth rate of the DIR region was not determined in their experimental studies using the polycrystalline Cu/Ni/Cu diffusion couples.

Instead of the polycrystalline diffusion couples, Cu/Ni/Cu diffusion couples consisting of pure Cu single crystals and a pure Ni polycrystalline specimen have been used by the present authors⁽⁴⁾⁻⁽⁶⁾. In this type of Cu/Ni/Cu diffusion couples, fine grains alloyed with Cu were found to be formed only in the Ni phase from the interfaces owing to DIR at 923 and 1023 K. No mixed DIGM+DIR area was observed at these temperatures. Thus, the diffusion couples are suitable for examining the behavior of the fine grain formation due to DIR. Furthermore, unlike the Fe(Cu) system, no solid-solid allotropic transformation occurs during cooling from annealing temperatures to room temperature in the Ni(Cu) system. Therefore, the diffusion couples are appropriate also for determination of the crystallographic orientation relationships between the fine grains and the Cu and Ni phases⁽⁴⁾. In this study, the kinetics of DIR in the Ni(Cu) system was experimentally examined using the Cu/Ni/Cu diffusion couples annealed at 923 and 1023 K. The experimental results were quantitatively analyzed using the kinetic equation proposed by Li and Hillert⁽⁹⁾.

II. Experimental

A pure Ni specimen was prepared as a 30 g button ingot by argon arc melting from pure Ni with purity of 99.97%. Sheet specimens of the pure Ni were prepared by cold rolling with thicknesses around 150 μm and an area of $12 \times 8 \text{ mm}^2$. The sheet specimens were separately annealed in evacuated silica capsules at 873 K for $3.6 \times 10^3 \text{ s}$. The annealed specimens were electrolytically polished in an etchant containing 5 vol% of sulfuric acid and 95 vol% of distilled water at a voltage of 5 V at 273 K. Cu single crystals with parallel (111) surfaces and a thickness of 2 mm were prepared by a Bridgman technique with a graphite crucible from pure Cu with purity of 99.999%. Plate specimens with a size of $12 \times 5 \times 2 \text{ mm}^3$ were cut from the single crystals by spark erosion.

The plate specimens were electrolytically polished in an etchant containing 25 vol% of acetic acid and 75 vol% of ethanol at a voltage of 6 V at 243 K.

The pure Ni sheet specimen was sandwiched between two pure Cu single crystal plates by a technique utilized in a previous study⁽⁷⁾. The sandwich Cu/Ni/Cu diffusion couples were prepared by heat treating in vacuum at 923 K for $3.6 \times 10^3 \text{ s}$. In all the diffusion couples, the Miller indices of the Cu single crystals were (111) at the interfaces. The diffusion couples were separately annealed in evacuated silica capsules at 923 and 1023 K for various times between 1.8×10^3 and $1.76 \times 10^5 \text{ s}$, followed by air cooling without breaking the capsules. Cross sections of the annealed diffusion couples were mechanically polished using alumina with a size of 0.05 μm and chemically etched in an etchant containing 60 ml of acetic acid, 40 ml of nitric acid, and a few drops of hydrochloric acid and phosphoric acid. The microstructure of the Ni phase in the annealed diffusion couple was observed with an optical microscope. Concentration profiles of Cu were measured along the direction normal to the interface by energy dispersive spectroscopy (EDS).

III. Results

Typical cross sections of the annealed diffusion couples are shown in Fig. 1. Figures 1(a) and (b) indicate the microstructures near interfaces of the Cu/Ni/Cu diffusion couples annealed at 923 K for 1.44×10^4 and $1.76 \times 10^5 \text{ s}$, respectively. The grain size of the Ni phase becomes around 200 μm after the annealing for all the diffusion couples. As can be seen in Figs. 1(a) and (b), however, new fine grains with sizes between 4 and 7 μm are formed in the Ni phase from the interfaces during the annealing. Such fine grains were observed in the Ni phase but not in the Cu phase at 923 and 1023 K. The microstructures near the interfaces are magnified in Figs. 2(a) and 3(a). Concentration profiles of Cu were determined by EDS along the lines normal to the interfaces across fine grains in the Ni phase shown in Figs. 2(a) and 3(a). The results are indicated as open circles in Figs. 2(b) and 3(b). As can be seen in these figures, the concentration of Cu is about 30 mass% on the interface side in the fine grain region, whereas it decreases with increasing distance from the interface and reaches about 10 mass% on the Ni phase side in the fine grain region at 7.2×10^4 and $1.26 \times 10^5 \text{ s}$ at 923 K. At this annealing temperature, the Cu concentrations on the interface and Ni phase sides in the fine grain region decrease to about 20 and 5 mass%, respectively, at $1.76 \times 10^5 \text{ s}$.

The average thickness l of the fine grain region alloyed with Cu in the Ni phase is plotted against the annealing time t in Fig. 4. Open circles and squares show the experimental results at 923 and 1023 K, respectively. As can be seen in Fig. 4, the thickness l increases with increasing annealing time t at both temperatures. The rate of increase in the thickness is greater at 1023 K than at 923 K. The results in Fig. 4 are represented in the logarithm scales in Fig. 5. According to Fig. 5, the relationship

Fig. 1 Optical photomicrographs of the Cu/Ni/Cu diffusion couples annealed at 923 K for (a) 1.44×10^4 and (b) 1.76×10^5 s.

Fig. 2 (a) Magnified optical photomicrograph of the microstructure near an interface of the Cu/Ni/Cu diffusion couple annealed at 923 K for 7.2×10^4 s; (b) Concentration profile of Cu along the line indicated in (a).

Fig. 3 (a) Magnified optical photomicrograph of the microstructure near an interface of the Cu/Ni/Cu diffusion couple annealed at 923 K for 1.26×10^5 s; (b) Concentration profile of Cu along the line indicated in (a).

between l and t can be expressed by the equation

$$l = k_1 (t/t_0)^n \quad (1)$$

at each temperature, though the experimental points are slightly scattered. Here, t_0 indicates unit time, 1 s, and is adopted to make the ratio t/t_0 dimensionless. The

proportionality constant k_1 has the same dimension as the thickness l , and they are measured in m. The values of the parameters k_1 and n were determined to be 4.9×10^{-8} m and 0.41, respectively, at 923 K whereas 1.8×10^{-7} m and 0.37, respectively, at 1023 K by a least-squares method from the experimental points in Fig. 5.

Fig. 4 The thickness l of the DIR region versus the annealing time t for the Cu/Ni/Cu diffusion couples annealed at 923 and 1023 K.

Fig. 5 The logarithm of the thickness l of the DIR region versus the logarithm of the annealing time t for the Cu/Ni/Cu diffusion couples annealed at 923 and 1023 K.

IV. Discussion

1. Penetration distance of Cu in the Ni phase

Since the thickness l of the alloyed region or the penetration distance of Cu into the Ni phase is much smaller than the thickness of the Ni phase even at the longest annealing times at both temperatures as can be seen in Figs. 4 and 5, each half part of the diffusion couple is considered to be a semi-infinite diffusion couple. In the binary Ni-Cu system, a complete solid solution phase with the face-centered-cubic (f.c.c.) structure appears at the temperature range between 628 and 1358 K⁽¹⁴⁾. The concentration profile of Cu in the complete solid solution phase along the direction normal to the interface has been calculated by using an analytical solution of a one-dimensional diffusion equation of Fick's second law for a semi-infinite binary single-phase diffusion couple. For the calculations, the interdiffusion coefficient and the

molar volume of the solution phase are assumed to be constant independently of the composition at an annealing temperature. The initial and boundary conditions for the semi-infinite diffusion couple are expressed as

$$\left. \begin{array}{l} x=1, \quad y<0 \\ x=0, \quad y>0 \end{array} \right\} \quad t=0 \quad (2)$$

and

$$\left. \begin{array}{l} x=1, \quad y=-\infty \\ x=0, \quad y=+\infty \end{array} \right\} \quad t>0, \quad (3)$$

respectively. Here, x is the mole fraction of Cu in the solution phase and y is the distance measured from the interface. Under the initial and boundary conditions of eqs. (2) and (3), the following equation⁽¹⁵⁾ is obtained as an analytical solution of the diffusion equation.

$$x = \frac{1}{2} \operatorname{erfc} \left(\frac{y}{2\sqrt{Dt}} \right) \quad (4)$$

Here, D is the interdiffusion coefficient in the solution phase.

The concentration profile of Cu in the solution phase at 923 K was calculated by eq. (4) using the value of $D = 1.43 \times 10^{-19} \text{ m}^2/\text{s}$ ⁽¹⁶⁾. The results for $t = 7.2 \times 10^4$ and $1.26 \times 10^5 \text{ s}$ are shown as dashed curves in Figs. 2(b) and 3(b), respectively. According to the calculations, the penetration distance of Cu in the Ni phase is about 0.1 μm at both annealing times. However, the observed penetration distance was 3 and 6 μm at $t = 7.2 \times 10^4$ and $1.26 \times 10^5 \text{ s}$, respectively, as can be seen in Figs. 2(b) and 3(b). This means that the formation of the fine grain region alloyed with Cu in the Ni phase takes place at rates three orders of magnitude greater than the ones evaluated from the volume diffusion. This unusually rapid formation of the alloyed region is due to DIR. Equation (4) is valid on condition that the interdiffusion coefficient D is independent of the composition as mentioned above. Although D actually increases with increasing x , D is considered to be almost constant within the composition range of $0 < x < 0.6$ at a constant temperature⁽¹⁷⁾. Since the composition of the DIR region in the Ni phase is well within this range, eq. (4) is valid for evaluation of the penetration distance of Cu by the volume diffusion in this region.

2. Growth rate of DIR

DIR in the Ni(Cu) system was experimentally studied by den Broeder and Nakahara⁽¹¹⁾, Liu *et al.*⁽¹²⁾ and Ma *et al.*⁽¹³⁾ using Cu/Ni/Cu diffusion couples consisting of pure Cu and Ni polycrystalline specimens annealed at various temperatures between 623 and 1223 K. In the annealed diffusion couples, a mixed DIGM+DIR area was observed in the Ni and Cu phases along the interface. Thus, it was rather difficult to extract the kinetic behavior of formation of the DIR region from the microstructure observations of the mixed DIGM+DIR area. On the other hand, Cu/Ni/Cu diffusion couples consisting of pure Cu single crystals and a pure Ni polycrystalline speci-

men were used in this study. Since there is no grain boundary in the Cu single crystal, DIGM cannot take place in the Cu phase. In this phase, DIR was not found to occur either. DIR and DIGM were observed only in the Ni phase but no mixed DIGM+DIR area was found at 923 and 1023 K within the experimental annealing times. The polycrystalline Cu/Ni/Cu diffusion couples were prepared by electrodeposition of the Cu phase layer on the Ni phase. Such a Cu layer seems to contain much more point and line defects and thus nucleation sites for DIR compared with the Cu single crystal. This may be the reason why DIR in the Cu phase was observed for the polycrystalline Cu/Ni/Cu diffusion couples but not for the present Cu/Ni/Cu diffusion couples. The microstructure observations of the present diffusion couples give the annealing time dependence of the thickness of the DIR region in the Ni phase as shown in Figs. 4 and 5. The experimental results on the kinetics of DIR in these figures will be analyzed in this section.

Li and Hillert proposed a kinetic equation for DIR in binary systems during alloying of pure metals⁽⁹⁾. Combining the chemical driving force model by Hillert and Purdy⁽¹⁸⁾ with the diffusion equation of grain boundary diffusion of a solute along the grain boundaries in the DIR region, they obtained the following equation.

$$\tau = 2\lambda + \lambda \sqrt{1 + \lambda^2} + \ln(\lambda + \sqrt{1 + \lambda^2}) \quad (5)$$

Here, τ and λ are the normalized annealing time and the normalized thickness of the DIR region, respectively, defined as

$$\tau = \frac{4t(MRTx^s/V_m)^{1.5}}{\sqrt{\delta D^b}} \quad (6)$$

and

$$\lambda = l \sqrt{\frac{MRTx^s}{\delta D^b V_m}}. \quad (7)$$

From eq. (5), we obtain $\tau = 4\lambda$ for $\lambda \ll 1$ and thus

$$\frac{l}{t} = \frac{MRTx^s}{V_m} \quad (8)$$

for small values of l , whereas $\tau = \lambda^2$ for $\lambda \gg 1$ and consequently

$$\frac{l^2}{t} = 4 \sqrt{\frac{\delta D^b MRTx^s}{V_m}} \quad (9)$$

for large values of l . D^b , δ and M are the interdiffusion coefficient, the thickness and the mobility, respectively, of a grain boundary, x^s is the mole fraction of the solute on the solute source side of the DIR region, V_m is the molar volume of the DIR region, T is the absolute temperature, and R is the gas constant. Equation (5) was obtained for the constancy of the parameters M , x^s , δD^b and V_m at a reaction temperature. Equations (8) and (9) mean that the thickness l of the DIR region increases in proportion to the annealing time t at early stages of the reaction, whereas l increases proportionately with the square root of t at late stages of the reaction.

The experimental results shown in Figs. 4 and 5 were analyzed using eqs. (5) to (7). For the analysis, the parameters x^s , δD^b and V_m were assumed to be constant at a reaction temperature, and the mobility M was chosen as the fitting parameter. The value of M was determined to minimize the parameter S defined as

$$S = \sum_{i=1}^n (l_i^{\text{cal}} - l_i^{\text{exp}})^2. \quad (10)$$

Here, l_i^{cal} and l_i^{exp} are the calculated and experimentally determined thicknesses, respectively, of the DIR region at each experimental annealing time t_i . The following parameters were used for the calculations and then the values of $M = 1.86 \times 10^{-18}$ and $2.14 \times 10^{-17} \text{ m}^4/\text{Js}$ were obtained at 923 and 1023 K, respectively: $x^s = 0.25$, $V_m = 6.845 \times 10^{-6} \text{ m}^3/\text{mol}$ ⁽¹⁹⁾, and $\delta D_0^b = 5.25 \times 10^{-16} \text{ m}^3/\text{s}$ and $Q = 133.9 \text{ kJ/mol}$ for $\delta D^b = \delta D_0^b \exp(-Q/RT)$ ⁽²⁰⁾. Using these parameters, the thickness l of the DIR region was calculated as a function of the annealing time t . The results at 1023 and 923 K are shown as solid curves in Figs. 6(a) and (b), respectively. The ordinate and the abscissa indicate the logarithms of l and t , respectively. In these figures, the experimental points in Figs. 4 and 5 are also represented as open symbols. As can be seen in Fig. 6(a), the calculated curve becomes almost straight at annealing times longer than $2 \times 10^3 \text{ s}$ at 1023 K. The straight part of the curve is described by eq. (1) with the parameters of $n = 0.5$ and $k_1 = 5.20 \times 10^{-8} \text{ m}$. A broken line in Fig. 6(a) shows the calculation using these parameters. The experimental points are well located on the broken line as well as the solid curve as can be seen in Fig. 6(a). On the other hand, the calculated curve is considered to be almost straight at annealing times shorter than $3 \times 10^2 \text{ s}$ and longer than $3 \times 10^4 \text{ s}$ at 923 K as indicated in Fig. 6(b). The value of the exponent n in eq. (1) is unity at the short annealing times whereas becomes 0.5 at the long annealing times. As can be seen in Fig. 6(b), half of the experimental points are located at the long annealing times, whereas the other ones are distributed at intermediate annealing times between 3×10^2 and $3 \times 10^4 \text{ s}$. At the intermediate annealing times, the exponent n decreases with increasing annealing time from 1.0 to 0.5. Thus, it is concluded that eq. (9) is applicable to the observations at 1023 K whereas only to the ones for late stages of the reaction at 923 K within the experimental annealing times. At 923 K, eq. (5) should be used to describe the whole annealing time dependence of the thickness l .

Considering the proportionality constant k_1 and the exponent n to be the fitting parameters, the annealing time dependence of the thickness l was described by eq. (1) in Figs. 4 and 5. The values of these two fitting parameters were determined at each annealing temperature from the experimental results by a least-squares method. On the other hand, in Figs. 6(a) and (b), eqs. (5) to (7) were utilized to express the annealing time dependence of the thickness l using the mobility M as the only fitting parameter. At a glance, agreement between the calculations and the experimental results is more satisfactory in

Fig. 6 The logarithm of the thickness l of the DIR region versus the logarithm of the annealing time t calculated by eq. (5) at (a) 1023 and (b) 923 K. The experimental points in Figs. 4 and 5 are also shown.

Figs. 4 and 5 than in Figs. 6(a) and (b). However, the calculation in Fig. 6(b) indicates that the exponent n decreases with increasing annealing time at intermediate stages of the reaction. This means that eq. (1) is no longer applicable at a wide range of annealing times.

In the present analysis, the composition x^s is assumed to be constant, otherwise eq. (5) cannot be utilized. This assumption may be valid for DIR in the Fe(Zn) system experimentally studied by Li and Hillert⁽⁹⁾ using pure Fe specimens zincified at 733 to 923 K by a capsule zincification technique. In this experiment, the DIR regions alloyed with Zn are formed on the surfaces of the pure Fe specimens. If the quantity of the Zn source alloy is much larger than that of the Fe specimen in a capsule, the Zn concentration on the surface of the DIR region is kept to be constant during the zincification. The assumption may also hold good for DIR in the Fe(Cu) system observed by the present authors⁽⁷⁾ using Cu/(Fe-Cu)/Cu diffusion couples annealed at 1323 K. At this temperature, the f.c.c.-Fe solution phase is in equilibrium with the f.c.c.-Cu solution phase in the binary Fe-Cu system⁽²¹⁾. In the Cu/(Fe-Cu)/Cu diffusion couples, the DIR regions with higher Cu concentrations are formed in the f.c.c.-Fe solution phase from the interfaces during the annealing. The Cu concentration on the interface side in the DIR region

was observed to be almost the same as the solubility of Cu in the f.c.c.-Fe phase at 1323 K. Thus, it is appropriate to consider the composition x^s constant during the reaction in the case of DIR in the Fe(Zn) and Fe(Cu) systems. On the other hand, in the binary Ni-Cu system⁽¹⁴⁾, the complete solid solution phase appears at the annealing temperatures in this study. In such a case, the Cu concentration x^s on the interface side in the DIR region cannot be determined only from the phase equilibria and may vary depending on the annealing time during the reaction. Actually, x^s decreases with increasing annealing time from 0.3 to 0.2 according to the experimental results in this study. Unfortunately, so far, there is no kinetic model which gives the interface composition of the alloyed region due to DIR that takes place in complete solid solution alloy systems. Consequently, x^s was assumed to be constant and an intermediate value of $x^s=0.25$ was adopted in the present analysis.

3. Mobility

As mentioned in Section IV.2, the mobility M in eqs. (6) and (7) was chosen as the fitting parameter for the calculations in Figs. 6(a) and (b) and determined to be $M=1.86 \times 10^{-18}$ and 2.14×10^{-17} m⁴/Js at 923 and 1023 K, respectively, from the experimental results. These values are shown as open circles in Fig. 7. In this figure, the ordinate and the abscissa indicate the logarithm of the mobility and the reciprocal of the absolute temperature, respectively. Using the values of M mentioned above, the parameters M_0 and Q in the following equation were determined to be $M_0=1.4 \times 10^{-7}$ m⁴/Js and $Q=192$ kJ/mol:

$$M = M_0 \exp \left(-\frac{Q}{RT} \right) \quad (11)$$

Li and Hillert⁽⁹⁾ evaluated the mobility M for DIR and DIGM in the Fe(Zn) system from the experimentally de-

Fig. 7 The logarithm of the mobility M versus the reciprocal of the absolute temperature T for DIR in the Ni(Cu) system. The results obtained by Kawanami *et al.*⁽⁸⁾ for DIR in the Fe(Cu) system and Li and Hillert⁽⁹⁾ for DIR and DIGM in the Fe(Zn) system are also shown.

terminated composition in the alloyed region and the migration rate of the moving grain boundary at the temperatures between 733 and 923 K. Under these experimental conditions, the DIR and DIGM regions are formed in the body-centered-cubic (b.c.c.) Fe phase. Their values of M are plotted as open triangles in Fig. 7 and give $M_0 = 7.1 \times 10^{-4} \text{ m}^4/\text{Js}$ and $Q = 230 \text{ kJ/mol}$ by a least-squares method. For DIR in the Fe(Cu) system, the value of M was evaluated to be $8.64 \times 10^{-13} \text{ m}^4/\text{Js}$ at 1323 K by the present authors using a new kinetic equation⁽⁸⁾ from the experimental results for the Cu/(Fe-Cu)/Cu diffusion couples⁽⁷⁾. This value is also represented as an open square in Fig. 7. Although there are differences in solute element and lattice structure of the matrix phase, the open square for DIR in the Fe(Cu) system is surprisingly well located on the straight line for DIR and DIGM in the Fe(Zn) system as can be seen in Fig. 7. On the other hand, the values of M for DIR in the Ni(Cu) system are almost two orders of magnitude smaller than those for DIR and DIGM in the Fe(Zn) system between 923 and 1023 K.

The mobility M for DIR and DIGM is relevant to the solute drag effect of the moving grain boundary. The solute drag may mainly be controlled by the grain boundary diffusion of solute atoms across the moving grain boundary and/or the volume diffusion of the solute atoms along the moving direction in the untransformed and alloyed matrices near the moving grain boundary. The value of $Q = 230 \text{ kJ/mol}$ for DIR and DIGM in the Fe(Zn) system is very close to the activation enthalpy of 233 kJ/mol for volume diffusion of Zn in b.c.c. Fe⁽¹⁶⁾. On the other hand, the value of $Q = 192 \text{ kJ/mol}$ for DIR in the Ni(Cu) system is smaller than the activation enthalpy of 258 kJ/mol for volume diffusion of Cu in Ni⁽¹⁶⁾ whereas greater than that of 133.9 kJ/mol for grain boundary diffusion of Cu in Ni⁽²⁰⁾. Although the value of Q for DIR in the Ni(Cu) system was obtained from the two evaluated values of M and thus may not be reliable enough, it can be concluded that for the solute drag effect of DIR the volume diffusion plays the most important role in the Fe(Zn) system whereas the grain boundary diffusion is important as well as the volume diffusion in the Ni(Cu) system.

V. Conclusions

The kinetics of DIR in the Ni(Cu) system was experimentally studied using the Cu/Ni/Cu diffusion couples consisting of the pure Cu single crystals with the same crystallographic orientation and the pure Ni polycrystalline specimen. The diffusion couples were annealed at 923 and 1023 K for various times between 1.8×10^3 and $1.76 \times 10^5 \text{ s}$. DIR was observed to occur only in the Ni phase of the diffusion couples but no mixed DIR+DIGM area was found at both temperatures

within the experimental annealing times. Owing to DIR, the penetration of Cu in the Ni phase takes place at rates three orders of magnitude greater than the ones evaluated from the volume diffusion. The experimental results were theoretically analyzed using the kinetic equation proposed by Li and Hillert for DIR in a pure metal⁽⁹⁾. According to this kinetic equation, the thickness l of the DIR region increases in proportion to the annealing time t at early stages of the reaction whereas l increases proportionately with the square root of t at late stages of the reaction. The analysis indicates that the square root law holds good for $t > 2 \times 10^3 \text{ s}$ at 1023 K whereas for $t > 3 \times 10^4 \text{ s}$ at 923 K. The experimental results for the shorter annealing times at 923 K are located at intermediate stages between the linear and square root laws.

Acknowledgment

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

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