Experimental Study on Diffusion Induced Recrystallization in Cu/Fe/Cu Diffusion Couples Using Cu Single Crystals

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Diffusion induced recrystallization (DIR) in a face-centered-cubic (f.c.c.) Fe phase was experimentally studied in the Fe(Cu) system. The notation Fe(Cu) means that Cu atoms diffuse into a pure Fe or binary Fe–Cu phase. The Cu/Fe/Cu and Cu/(Fe–4.8Cu)/Cu diffusion couples consisting of a polycrystalline Fe phase specimen and pure Cu single crystals with the same crystallographic orientation were annealed at 1 193 and 1 323 K for various times between 3.0×10^2 and 8.6×10^4 s. The penetration of Cu in the f.c.c. Fe phase was found to occur at rates 100 times greater than the one evaluated from the volume diffusion. This unusually rapid penetration is due to DIR, which takes place in the Fe phase from the interfaces of the diffusion couples. DIR was observed to occur only in the Cu/(Fe–4.8Cu)/Cu diffusion couples annealed at 1 323 K under the present experimental conditions. The thickness w of the Fe phase decreases with increasing annealing time t according to the equation $w/w_0 = 1 - 7.09 \times 10^{-8}(\sqrt{t}/w_0)$, whereas the thickness l of the DIR region increases with increasing annealing time according to the equation $l = 1.58 \times 10^{-6}(t/t_0)^{0.29}$. Here, w_0 is the initial thickness of the Fe phase, and t_0 is unit time, 1 s. The thicknesses w , w_0 and l are measured in m, and the annealing time t is measured in s.

KEY WORDS: diffusion induced recrystallization; Fe–Cu system; grain boundary migration; grain boundary diffusion.

1. Introduction

Diffusion induced recrystallization (DIR) is the phenomenon that new grains with different solute concentrations are produced behind moving grain boundaries owing to recrystallization combined with diffusion of solute atoms along the moving boundaries. On the contrary, during diffusion induced grain boundary migration (DIGM), a region with different composition is left behind a moving grain boundary due to grain boundary migration combined with the diffusion of solute atoms along the moving boundary. DIGM and DIR are known to occur in many binary systems.^{1–3)} Special attention was focused on DIR and DIGM in binary systems, where Zn is the solute, by many investigators because it is relatively easy to control the Zn activity using a zincification technique with an appropriate Zn-source alloy.

DIR in the Cu(Zn) system was experimentally examined by Li and Hillert⁴⁾ using polycrystalline Cu specimens zincified at temperatures between 623 and 873 K and by Giakupian *et al.*⁵⁾ and Schmelzle *et al.*⁶⁾ using oriented Cu specimens zincified at temperatures between 623 and 773 K. 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 their experiments, the Zn concentrations of the DIR regions formed on the surfaces of the Cu specimens were observed to be lower than that of the Zn source alloy. These observations were theoretically analyzed by Kajihara and Gust⁷⁾ on the basis of a new model to evaluate the chemical driving force for the formation of the alloyed region by DIR and DIGM. The analysis could account for the lower Zn concentration in the DIR region formed by the zincification.

Li and Hillert experimentally studied the kinetics of DIR in the Fe(Zn) system using polycrystalline Fe specimens zincified at 733 to 923 K.⁸⁾ They also theoretically analyzed the observations,⁸⁾ combining the chemical driving force model by Hillert and Purdy⁹⁾ with the diffusion equation of grain boundary diffusion. According to their analysis, the thickness l of the DIR region increases proportionately with the zincification time t at early stages of the reaction, whereas l increases in proportion to the square root of t after a certain zincification time. The latter case was observed at 873 K, and the former case was found at 823 K within the experimental zincification times.

A series of studies on DIR have been being carried out by the present authors using Cu/Fe/Cu and Cu/Ni/Cu diffusion couples consisting of Fe and Ni polycrystalline specimens and pure Cu single crystals.^{10–13)} In the Cu/Fe/Cu diffusion couples, DIR was found to occur in the Fe phase from the interfaces during annealing at 1323 K. However, the growth rate of the DIR region in this case cannot be described by the Li and Hillert model. In order to understand general characteristics of DIR in binary systems, more experimental information seems to be needed. In the present work, DIR in the Fe(Cu) system has been experimentally studied using the Cu/Fe/Cu diffusion couples, where a pure Fe or binary Fe–Cu polycrystalline specimen was sandwiched between pure Cu single crystals with the same crystallographic orientation. The single crystals were used to prevent DIGM from taking place in the Cu phase and thus to stabilize the penetration of Cu in the Fe phase. The experimental results were analyzed using an analytical solution of diffusion equations of volume diffusion in a semi-infinite two-phase diffusion couple of binary systems.

2. Experimental

Pure Fe and Fe–4.8mass%Cu (Fe–4.8Cu) alloy specimens were prepared as 30 g button ingots by argon arc melting from pure Fe and Cu with purities of 99.97 and 99.999%, respectively. The Fe–4.8Cu alloy ingot was homogenized in vacuum at 1323 K for 8.6×10^4 s, followed by water quenching. Sheet specimens of the pure Fe and the Fe–4.8Cu alloy were prepared by cold rolling with thicknesses between 115 and 142 μm and an area of $12 \times 5 \text{ mm}^2$. The sheet specimens were electrolytically polished in an etchant containing 95 vol% of acetic acid and 5 vol% of perchloric acid at a voltage of 40 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 sheet specimen was sandwiched between two pure Cu single crystal plates by a technique utilized by

Kajihara *et al.*¹⁴⁾ The assembly was fastened between two plates made of a 25Cr–20Ni austenitic steel with molybdenum screws, which caused thermal compressive stress in the assembly by heating due to a smaller coefficient of thermal expansion for molybdenum. An alumina plate with a size of $12 \times 5 \times 1 \text{ mm}^3$ was inserted between the pure Cu single crystal plate and the austenitic steel in order to avoid diffusional bonding. The clamped assembly was heated in vacuum at 1193 K for 180 s to make the Cu/Fe/Cu and Cu/(Fe–4.8Cu)/Cu diffusion couples, followed by water quenching. In all the diffusion couples, the Miller indices of the Cu single crystals were (111) at the interfaces. The diffusion couples were annealed in an evacuated silica capsule at 1193 and 1323 K for various times between 3.0×10^2 and 8.6×10^4 s, followed by water quenching without breaking the capsule. Cross sections of the annealed diffusion couples were mechanically polished using alumina with a size of $0.05 \mu\text{m}$ and chemically etched in a nital etchant with 5 vol% of nitric acid. The microstructure of the Fe phase in the annealed diffusion couples was observed with an optical microscope. Concentration profiles were measured along the direction normal to the interface by energy dispersive spectroscopy (EDS).

3. Results

Typical cross sections of the annealed diffusion couples are shown in Fig. 1. Figures 1(a) and 1(b) indicate the microstructures of the Cu/(Fe–4.8Cu)/Cu diffusion couples annealed at 1323 K for 3.0×10^2 and 1.2×10^3 s, respectively. The initial thicknesses of the Fe phase are 115 and 126 μm at Figs. 1(a) and 1(b), respectively. For the Fe phase, the face-centered-cubic (f.c.c.) structure is stable at the annealing temperature whereas the body-centered-cubic (b.c.c.) structure becomes stable at room temperature. During water cooling of the diffusion couples after the annealing, the f.c.c. Fe (γ -Fe) phase completely transforms to the b.c.c. Fe (α -Fe) phase in a martensitic manner. The martensitic transformation was observed to occur in all the diffusion couples as can be seen in Fig. 1. The grain size of the prior γ -Fe phase is

Fig. 1. Optical photomicrographs of the Cu/(Fe–4.8Cu)/Cu diffusion couples annealed at 1323 K. The annealing time t and the initial thickness w_0 of the Fe phase are (a) $t = 3.0 \times 10^2$ s and $w_0 = 115 \mu\text{m}$, and (b) $t = 1.2 \times 10^3$ s and $w_0 = 126 \mu\text{m}$.

around 40 μm . In Fig. 1(b), however, new fine grains with sizes between 10 and 20 μm are formed in the γ -Fe phase from both the interfaces during the annealing at 1323 K. Such fine grains were observed in the Fe phase but not in the Cu phase. The microstructure near an interface in Fig. 1(b) is magnified in Fig. 2(a). A concentration profile of Cu was determined by EDS along the line normal to the interface across a fine grain in the Fe phase shown in Fig. 2(a). The result is indicated as open circles in Fig. 2(b). In this figure, an open square shows the solubility of Cu in the γ -Fe phase at 1323 K, 7 mass% Cu, in the binary Cu-Fe system.¹⁵⁾ As can be seen in Fig. 2(b), the concentration of Cu in the fine grain is the same as the solubility. Such fine grains alloyed with Cu in the Fe phase were clearly observed only for the Cu/(Fe-4.8Cu)/Cu diffusion couples annealed at 1323 K. Thus, in this paper, the following attention will be focused on the observations of these diffusion couples.

A pair of interfaces remain planar and parallel in all the diffusion couples during the annealing. The thickness of the Fe phase is plotted against the annealing time as open symbols in Fig. 3. In this figure, the relative thickness of the Fe phase, w/w_0 , and the square root of the annealing time normalized by the initial thickness of the Fe phase, $\sqrt{t}/w_0$, were used in order to make a direct comparison between two sets of experimental data on the diffusion couples with $w_0 = 126$ and 142 μm . Here, w and w_0 are the thickness and the initial thickness, respectively, of the Fe phase, and t is the annealing time.

Fig. 2. (a) Magnified optical photomicrograph of the microstructure near an interface shown in Fig. 1(b); (b) Concentration profile of Cu along the line indicated in (a).

As can be seen in Fig. 3, the relative thickness w/w_0 decreases linearly with the normalized annealing time $\sqrt{t}/w_0$, and thus the following equation is obtained.

$$w/w_0 = 1 - k_1(\sqrt{t}/w_0) \quad \dots\dots\dots(1)$$

The linearity constant k_1 in Eq. (1) was determined to be $k_1 = 7.09 \times 10^{-8} \text{ m s}^{-1/2}$ by a least square method from the experimental points in Fig. 3.

The average thickness l of the fine grains alloyed with Cu in the Fe phase is plotted against the annealing time t in Fig. 4. The ordinate and the abscissa indicate the logarithms of l and t , respectively. According to Fig. 4, the relationship between l and t is expressed by the equation

$$l = k_2(t/t_0)^n, \quad \dots\dots\dots(2)$$

where t_0 indicates unit time, 1 s, and is adopted to make the ratio t/t_0 dimensionless. The proportionality constant

Fig. 3. The relative thickness of the Fe phase, w/w_0 , vs. the square root of the annealing time normalized by the initial thickness of the Fe phase, $\sqrt{t}/w_0$, for the Cu/(Fe-4.8Cu)/Cu diffusion couples annealed at 1323 K.

Fig. 4. The thickness l of the DIR region vs. the annealing time t for the Cu/(Fe-4.8Cu)/Cu diffusion couples annealed at 1323 K.

k_2 has the same dimension as the thickness l , and they are measured in m. The parameters k_2 and n were determined to be 1.58×10^{-6} m and 0.29, respectively, by a least square method from the experimental points in Fig. 4.

4. Discussion

4.1. Penetration Distance of Cu in the Fe Phase

Since the penetration distance of Cu into the Fe phase is much smaller than the thickness of the Fe phase at $t = 1.2 \times 10^3$ s as can be seen in Fig. 2(b), each half part of the diffusion couple is considered to be a semi-infinite diffusion couple. The concentration profile of Cu in the Fe and Cu phases along the direction normal to the migrating interface at this annealing time has been calculated by using an analytical solution of diffusion equations for a semi-infinite two-phase diffusion couple of binary systems. The following assumptions have been adopted for the calculations: (a) Local equilibria are realized at the migrating interface between the Cu and Fe phases for all the elements; (b) The migration is controlled by volume diffusion in each phase; (c) Interdiffusion coefficients in the Cu and Fe phases are independent of the compositions; and (d) Molar volumes of both phases are the same. According to these assumptions, the position ξ of the migrating interface is proportional to the square root of the annealing time or the reaction time t as follows.¹⁶⁾

$$\xi - \xi^0 = K^\alpha \sqrt{4D^\alpha t} = K^\gamma \sqrt{4D^\gamma t} \quad \dots\dots\dots(3)$$

Here, ξ^0 is the initial position of the interface, and D^α and D^γ are the interdiffusion coefficients in the Cu(α) and Fe(γ) phases, respectively. The dimensionless proportionality constants K^α and K^γ are correlated with the mole fractions of Cu in the α and γ phases, $x^{\alpha\gamma}$ and $x^{\gamma\alpha}$ respectively, at the migrating interface by the equation¹⁶⁾

$$x^{\alpha\gamma} - x^{\gamma\alpha} = \frac{(x^{0\alpha} - x^{\alpha\gamma}) \exp\{-(K^\alpha)^2\}}{K^\alpha \sqrt{\pi} \{1 + \operatorname{erf}(K^\alpha)\}} + \frac{(x^{0\gamma} - x^{\gamma\alpha}) \exp\{-(K^\gamma)^2\}}{K^\gamma \sqrt{\pi} \{1 - \operatorname{erf}(K^\gamma)\}} \quad \dots\dots\dots(4)$$

Here, $x^{0\alpha}$ and $x^{0\gamma}$ are the initial compositions of the α and γ phases, respectively. From Eq. (3), it is obvious that only one of K^α and K^γ in Eq. (4) is independent. Thus, the independent parameter, K^α or K^γ , is uniquely determined for a given reaction temperature. The mole fraction x^α of Cu in the α phase is described as a function of the distance y by the equation

$$x^\alpha = x^{0\alpha} + \frac{(x^{\alpha\gamma} - x^{0\alpha})}{\{1 + \operatorname{erf}(K^\alpha)\}} \left\{ 1 + \operatorname{erf}\left(\frac{y - \xi^0}{\sqrt{4D^\alpha t}}\right) \right\} \quad \dots\dots(5a)$$

for $y < \xi$, whereas the mole fraction of Cu in the γ phase, x^γ , is expressed by the equation

$$x^\gamma = x^{0\gamma} + \frac{(x^{\gamma\alpha} - x^{0\gamma})}{\{1 - \operatorname{erf}(K^\gamma)\}} \left\{ 1 - \operatorname{erf}\left(\frac{y - \xi^0}{\sqrt{4D^\gamma t}}\right) \right\} \quad \dots\dots(5b)$$

for $y > \xi$.¹⁶⁾ The γ phase side of the semi-infinite α/γ

diffusion couple is taken to be the positive direction of the distance axis y in Eqs. (5a) and (5b) according to Fig. 2(b).

The concentration profile at 1323 K for 1.2×10^3 s was calculated by Eqs. (3) to (5b) using the following parameters: $D^\alpha = 3.93 \times 10^{-13}$ and $D^\gamma = 3.79 \times 10^{-16}$ m² s⁻¹¹⁷⁾; $x^{\alpha\gamma} = 0.9610$ and $x^{\gamma\alpha} = 0.0615$ ¹⁵⁾; and $x^{0\alpha} = 1.0$ and $x^{0\gamma} = 0.0424$. The result is shown as a dashed curve in Fig. 2(b). The calculated and observed positions of the interface are set at the same in order to make a comparison of the penetration distances. The penetration distance of Cu in the γ -Fe phase is about 1 μ m according to the calculation, and the thicknesses of the γ -Fe phase sheet are $w_0 = 126 \mu$ m at $t = 0$ s and $w = 124 \mu$ m at $t = 1.2 \times 10^3$ s. On the other hand, the observed penetration distance is about 10 μ m. This means that the formation of the fine grains alloyed with Cu in the γ -Fe phase takes place at a rate 100 times greater than the one evaluated from the volume diffusion. This unusually rapid formation of the fine grains is due to DIR. The calculation gives values of $K^\alpha = 2.31 \times 10^{-2}$ and $K^\gamma = 7.43 \times 10^{-1}$ and thus $K^\alpha \sqrt{4D^\alpha} = K^\gamma \sqrt{4D^\gamma} = 2.89 \times 10^{-8}$ m s^{-1/2}. The linearity constant k_1 in Eq. (1) corresponds to the parameters $K^\alpha \sqrt{4D^\alpha}$ and $K^\gamma \sqrt{4D^\gamma}$ in Eq. (3). However, the calculated value of $K^\alpha \sqrt{4D^\alpha}$ or $K^\gamma \sqrt{4D^\gamma}$ is less than half of the experimentally determined value of k_1 . This may also indicate that the migration of the interface is not controlled by the volume diffusion in each phase.

4.2. Composition of DIR

DIR in the Cu(Zn) system was experimentally examined by Li and Hillert⁴⁾ using polycrystalline pure Cu specimens zincified at 623 to 873 K and by Giakupian *et al.*⁵⁾ and Schmelzle *et al.*⁶⁾ using oriented pure Cu bicrystals zincified at 623 to 773 K. They measured the Zn concentrations of the DIR regions formed on the surfaces of the Cu specimens. According to their measurements, the Zn concentrations of the DIR regions are found to be typically lower than that of the Zn source alloy. In order to explain this lower Zn concentration, Kajihara and Gust proposed a new model to evaluate the chemical driving force for the formation of the alloyed region on the surface of a specimen by DIGM and DIR.⁷⁾ In this model, the driving force is obtained as the difference between the molar Gibbs energy of a coexisting state of a specimen and a vapor of a volatile solute and that of an alloyed region by DIR. Assuming that the reaction will proceed at a velocity which maximizes the rate of the Gibbs energy decrease $d\Delta G/dt$, the composition of the growing DIR region is calculated on the basis that it should yield the maximum value of $d\Delta G/dt$. The maximum value of $d\Delta G/dt$ results in a lower concentration of the solute in the DIR region according to the model. The calculations combined with a subregular solution model could well explain the lower Zn concentration in the DIR region. On the other hand, in the present work, the Cu concentration of the DIR region in the Fe phase was observed to be almost the same as the solubility of Cu in the γ -Fe at the annealing temperature. In the Cu/(Fe-4.8Cu)/Cu diffusion couples,

local equilibria are considered to be established at the migrating interface between the Cu and Fe phases for all the elements during the annealing. Under such conditions, the two-phase equilibria between the Cu and Fe phases determine the interface composition of the DIR region formed in the Fe phase. Thus, fortunately, the driving force for the formation of the DIR region is not needed to be taken into consideration for the evaluation of this composition.

In the theoretical analyses by Kajihara and Gust,⁷⁾ it was pointed out that the chemical driving force for the formation of the alloyed region by DIR and DIGM decreases remarkably with increasing concentration of a solute in an untransformed matrix. Thus, for the diffusion couples in the present work, DIR should prefer to occur in the pure Fe phase than in the Fe-4.8Cu solution phase. However, DIR was clearly observed only in the solution phase as mentioned earlier. This may be the reason why DIR was not reported to occur in the Fe(Cu) system. Further studies are needed to be carried out for understanding this unusual behavior of the formation of DIR.

4.3. Growth Rate of DIR

The kinetics of DIR in the Fe(Zn) system was experimentally studied by Li and Hillert using polycrystalline pure Fe sheet specimens zincified at temperatures between 733 and 923 K.⁸⁾ In their experiment, the DIR region alloyed with Zn is formed from the surface of the pure Fe specimen and grows into the inside of the specimen. On the basis of the observations, they obtained the following equation to describe the relationship between the thickness l of the DIR region and the reaction time t , combining the chemical driving force model by Hillert and Purdy⁹⁾ with the diffusion equation of grain boundary diffusion of Zn along the grain boundaries in the DIR region.

$$\tau = 2\lambda + \lambda\sqrt{1+\lambda^2} + \ln(\lambda + \sqrt{1+\lambda^2}) \quad \dots\dots\dots(6)$$

Here, τ and λ are normalized coordinates defined as

$$\tau \equiv \frac{4t(MRTx_{Zn}^s/V_m)^{1.5}}{\sqrt{\delta D^b}} \quad \dots\dots\dots(7)$$

and

$$\lambda \equiv l \sqrt{\frac{MRTx_{Zn}^s}{\delta D^b V_m}} \quad \dots\dots\dots(8)$$

From Eq. (6), we obtain $\tau = 4\lambda$ for $\lambda \ll 1$ and thus

$$\frac{l}{t} = \frac{MRTx_{Zn}^s}{V_m} \quad \dots\dots\dots(9)$$

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

$$\frac{l^2}{t} = 4 \sqrt{\frac{\delta D^b MRTx_{Zn}^s}{V_m}} \quad \dots\dots\dots(10)$$

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_{Zn}^s is the mole fraction of Zn on the Zn source side of the DIR region, V_m is the molar

Fig. 5. The relative thickness of the Fe phase, w/w_0 , and the relative thickness of the DIR region, $2l/w_0$, vs. the annealing time t for the Cu/(Fe-4.8Cu)/Cu diffusion couples annealed at 1323 K.

volume of the DIR region, T is the absolute temperature, and R is the gas constant. Equations (9) and (10) mean that the thickness l of the DIR region increases in proportion to the reaction time t at early stages of the reaction, whereas l increases proportionately with the square root of t after a certain reaction time. However, Eq. (2) indicates that the thickness of the DIR region increases in proportion to the almost cubic root of the annealing time. Equation (6) was obtained for DIR in the A(B) system, where the DIR region grows into a matrix of pure A metal. On the other hand, in the experiment of the present work, the DIR region with a higher Cu concentration is formed in a matrix of the binary Fe-Cu solution phase with a lower Cu concentration. The kinetic equations for the latter case were obtained by the present authors and will be discussed in detail elsewhere.¹⁸⁾

The experimental results on the Cu/(Fe-4.8Cu)/Cu diffusion couple with $w_0 = 142 \mu\text{m}$ in Figs. 3 and 4 are represented in Fig. 5. In this figure, the relative thickness of the Fe phase, w/w_0 , and the total thickness of the DIR regions normalized by the initial thickness of the Fe phase, $2l/w_0$, are plotted against the annealing time t as open symbols. Since the DIR regions are formed in the Fe phase from both the interfaces, the thickness l is multiplied by 2 to obtain the total thickness. Solid curves in Fig. 5 indicate the calculations by Eqs. (1) and (2). Extrapolating these curves and finding their intersection, we can estimate that the DIR regions completely cover the Fe phase at $t = 1.9 \times 10^5 \text{ s}$. At this annealing time, the thickness of the Fe phase decreases to $w = 110 \mu\text{m}$. Using the equation $t = 1.5(w/2)^2/D^v$,¹⁹⁾ we evaluate the annealing time of $t = 1.2 \times 10^7 \text{ s}$ for the concentration of Cu to reach almost the solubility at the center of the Fe phase with a thickness of $110 \mu\text{m}$ by the volume diffusion. Although this annealing time is underestimated due to the assumption of the constant thickness of the Fe phase, it is 63 times greater than the estimated value for the DIR region to reach the center of the Fe phase. Thus,

it can be concluded that due to DIR the complete alloying of the Fe phase with Cu will proceed at reaction rates about two orders of magnitude greater than that expected from the volume diffusion under the present experimental conditions.

5. Conclusions

The kinetics of DIR in the Fe(Cu) system was experimentally studied using the Cu/Fe/Cu and Cu/(Fe-4.8Cu)/Cu diffusion couples consisting of the pure Cu single crystals with the same crystallographic orientation and the polycrystalline Fe phase specimens. The diffusion couples were annealed at 1 193 and 1 323 K, at which the f.c.c. structure is stable for the Fe phase. DIR was clearly observed to occur only in the Fe phase of the Cu/(Fe-4.8Cu)/Cu diffusion couples annealed at 1 323 K. Due to DIR, the penetration of Cu in the Fe phase takes place at rates two orders of magnitude greater than the one evaluated from the volume diffusion. The thickness of the DIR region increases proportionately with the almost cubic root of the annealing time.

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