Effects of Liquid Indium Particles on Recrystallization and Grain Growth of α Fe in Fe-In Alloys

Takehito Hagisawa¹, Toshihiro Omori¹, Ikuo Ohnuma², Ryosuke Kainuma¹ and Kiyohito Ishida¹

¹Department of Materials Science, Graduate School of Engineering, Tohoku University, Sendai 980–8579, Japan

²Research Center for Structural Materials, National Institute for Materials Science (NIMS), Tsukuba 305–0047, Japan

Recrystallization, grain growth, and particle ripening behaviors of pre-deformed Fe-In alloy specimens in liquid-particle dispersion microstructures were investigated by microstructural observation. Liquid In particles were trapped by grain boundaries of recrystallized grains, and the trapped particles were dragged by the grain boundaries during grain growth. The recrystallization and the grain growth of the α Fe matrix were extremely retarded by the addition of In. The controlling diffusion mechanism of the growth of matrix grains and the ripening of intergranular liquid In particles changed from interfacial diffusion between matrix and particles to impurity diffusion through liquid In particles with increasing volume fraction of liquid In particles. [doi:10.2320/matertrans.MC201707]

(Received August 23, 2017; Accepted September 19, 2017; Published January 25, 2018)

Keywords: liquid particle, interfacial energy, recrystallization, grain growth, diffusion coalescence, coupled growth

1. Introduction

Koike *et al.* reported that Al-Bi two-phase alloys with a small amount of liquid Bi particles exhibit superplasticity of more than 200% at temperatures above 543 K¹. Although the film-like microstructure of the high-wettable liquid phase on the matrix grain boundary results in liquid metal embrittlement, the particle-dispersion microstructure of the low-wettable liquid phase on the matrix grain boundary in Al-Bi alloys is effective in reducing the stress concentration at the grain boundary during superplastic deformation. It has also been reported in our previous studies on the grain growth of Al-Bi² and Fe-Bi alloys³ that the growth of matrix grains was extremely retarded by the dispersion of liquid Bi particles. Figure 1 shows a typical microstructure of pre-deformed Al-Bi alloy annealed at 573 K². It was confirmed that there were precipitate-free zones (PFZs) along the outside of curvature of matrix grain boundaries and that some large particles formed only on the grain boundaries along the PFZs. These microstructural changes suggest that liquid Bi particles dispersed in matrix grains were trapped and dragged by grain boundaries during their migration and

grew on the grain boundaries by Ostwald ripening as well as by coalescence of trapped particles. Theoretical analysis revealed that the excess interfacial energy between the matrix phase and liquid particles, which is related to the formation of PFZs, can be a driving force of grain boundary migration and that the dragging rate of a liquid particle is controlled by the impurity diffusion of solute atoms through the liquid particle². Furthermore, it has also been found that the ripening rates of the intra- and inter-granular particles can be predicted by the conventional Ostwald ripening theory³.

Figures 2 (a) and 2 (b) show phase diagrams of the Fe-In binary system⁴ of the whole system and of the Fe-rich side, respectively, which indicate that fine liquid In particles form and disperse through a monotectic reaction. In the present study, the grain growth and particle ripening behaviors of the liquid-particle dispersion microstructure in Fe-In alloys were investigated.

2. Experimental Procedures

Fe-1, 3 and 7.5vol% In alloys and a pure Fe were prepared as columnar ingots with a diameter of 12 mm by induction melting under an argon atmosphere. Each ingot was cold-rolled into a plate with a thickness of 6 mm by 50% reduction. Specimens cut from the rolled plates were annealed at 1173 K, which is higher than the melting temperature of In (429 K), for recrystallization and grain growth, and then quenched in ice water. The microstructure was observed by optical microscopy (OM) and scanning electron microscopy (SEM). An etchant consisting of ethanol (50 vol%) and nitric acid (50 vol%) was used for the OM observation. The mean radius of α Fe matrix grains was determined by quantitative microstructural analysis⁵, and the volume fraction and the mean radius of liquid In particles were estimated by image analysis (Win Roof). The progress of recrystallization was evaluated by the Micro-Vickers Hardness (MVH) test and microstructural observation. Chemical compositions of the matrix phase and liquid particles were measured by electron probe micro analysis (EPMA), the calibration being performed by ZAF correction. The experimental data from

Fig. 1 Typical microstructure of pre-deformed Al-Bi alloy annealed at 573 K.

Fig. 2 Fe-In binary phase diagrams⁴⁾ of (a) whole system and (b) Fe-rich side.

more than 5 points for each phase were averaged.

3. Results

3.1 Recrystallization in Fe-In alloys

Figure 3 shows the MVH change of the pre-deformed Fe-7.5vol% In alloy during annealing at 1173 K, in which that of pre-deformed pure-Fe is also plotted for comparison. In the case of pure Fe, the MVH drastically decreased from 185 HV in the as-rolled specimen to 76 HV due to the recrystallization by annealing at 1173 K for 60 s and finally stabilized at about 75 HV after 60 s. On the other hand, the MVH of the pre-deformed Fe-7.5vol%In alloy gradually decreased from 156 HV in the as-rolled specimen to 105 HV until 600 s and became steady at about 100 HV after 900 s.

Figures 4 (a), 4 (b) and 4 (c) show micrographs of an as-rolled specimen, an as-annealed specimen at 1173 K for 60 s and one for 900 s, respectively. Whereas the microstructure of the as-rolled specimen exhibits anisotropy of matrix grains prolonged parallel to the rolling direction, the microstructure after annealing at 1173 K for 900 s is almost completely occupied by isotropic recrystallized grains. An en-

Fig. 3 Vickers hardness of pre-deformed Fe-7.5vol% In alloy annealed at 1173 K.

larged micrograph of the as-annealed sample for 900 s is shown in Fig. 4 (d), where small bright and dark areas correspond to In particles and holes remaining after some In particles fell out during the sample polishing, respectively. Most of the liquid In particles were located at triple junctions of matrix grain boundaries. These experimental results obtained from the MHV test and microstructural observation suggest that the recrystallization of α Fe was significantly influenced by the addition of In.

3.2 Growth of matrix α Fe grains in Fe-In alloys

Figures 5 (a) and 5 (b) show typical micrographs of the pre-deformed Fe-7.5vol% In alloy annealed at 1173 K for 1 day and 2 days, respectively. Most of the liquid In particles were located on grain boundaries, especially at their triple junctions, and few intragranular particles were dispersed. These results suggest that the intergranular liquid particles, which were trapped by interface boundaries during recrystallization, were dragged by grain boundaries of the matrix phase during grain growth.

Figures 6 (a) and 6 (b) respectively show the mean radius of intergranular liquid In particles and matrix grains versus annealing time of Fe-In alloys at 1173 K, in which the experimental data of pure Fe are also shown in Fig. 6 (b) for comparison. The mean radius of liquid In particles and matrix grains increased with increasing annealing time. The ripening rate of liquid In particles of Fe-7.5vol% In alloy was considerably faster than that of other alloys, and the growth rate of matrix grains of Fe-7.5vol% In alloy was the lowest in all specimens. These results also show that the dispersion of liquid In particles plays a significant role in the retardation of the growth of matrix grains.

4. Discussion

4.1 Effects of In addition on recrystallization of α Fe

Some factors are considered to explain the retardation effect of the static recrystallization of α Fe in Fe-In alloys: (i) the pinning effect of liquid In particles, (ii) the solute-drag

Fig. 4 Optical micrograph of (a) as-rolled Fe-7.5vol% In specimen, Fe-7.5vol% In specimens (b) annealed at 1173 K for 60 s, (c) annealed at 1173 K for 900 s, and (d) enlarged micrograph of (c).

Fig. 5 Typical optical micrograph of pre-deformed Fe-7.5vol% In alloy annealed at 1173 K for (a) 1 day and (b) 2 days.

effect due to In atoms in the α Fe matrix, and (iii) the dragging effect of mobile In particles at interface boundaries of recrystallized grains. Here, the retardation mechanism of the recrystallization is discussed in terms of the migration rate of the interface boundary during recrystallization.

On the basis of mass transfer, the migration rate, v , of interface boundary is given by

$$v = \frac{d\bar{R}}{dt} = M \cdot P, \quad (1)$$

where $\bar{R}$, M and P represent the mean radius of matrix grains, the mobility and the driving force of interface boundary migration, respectively. The effect of In addition on M and P is discussed hereafter.

4.1.1 Estimation of pinning effect of liquid In particles during recrystallization

When second-phase particles are randomly dispersed in the matrix, the maximum pinning force on the unit area of grain boundary is described as⁶⁾

$$\Delta G_p = \frac{3 \cdot f \cdot \sigma_m}{2 \cdot \bar{r}}, \quad (2)$$

where f and $\bar{r}$ represent the volume fraction and the mean radius of second-phase particles, respectively. σ_m ($= 0.8 \text{ J} \cdot \text{m}^{-2}$) is the grain boundary energy of the matrix phase⁷⁾. In the case of Fe-7.5vol% In alloy annealed at 1173 K for 900 s, values of $f = 0.075$ and $\bar{r} = 1.3 \text{ } \mu\text{m}$ were obtained from the experimental results. Using these parameters, the maximum pinning force was evaluated to be $\Delta G_p = 0.07 \text{ MPa}$. Because the driving force of recrystallization, ΔG_{rex} , is generally on the order of about $1 \sim 10 \text{ MPa}$ ⁸⁾, the total driving force for grain boundary migration can be esti-

Fig. 6 Mean radius evolutions of (a) intergranular liquid In particles and (b) matrix grains in Fe-In alloys annealed at 1173 K.

mated as

$$P = (\Delta G_{\text{rex}} - \Delta G_{\text{p}}) \cdot V_{\text{m}}, \quad (3)$$

where V_{m} is the molar volume of the α Fe matrix. If the solute-drag effect is ignored, the mobility of grain boundary in pure Fe is written as⁹⁾

$$M_{\text{gb}} = \frac{D_{\text{gb}}}{\delta RT}, \quad (4)$$

where D_{gb} , δ , R and T represent the grain boundary diffusion coefficient, the grain boundary thickness, the gas constant, and the absolute temperature, respectively. By using eqs. (3) and (4), the calculated migration rate of pinned boundary, $v_{\text{pin}}^{\text{cal}}$, can be rewritten using eq. (1) as

$$v_{\text{pin}}^{\text{cal}} = M_{\text{gb}} \cdot (\Delta G_{\text{rex}} - \Delta G_{\text{p}}) \cdot V_{\text{m}}. \quad (5)$$

4.1.2 Estimation of solute drag effect due to In atoms in α Fe during recrystallization

The mobility of the grain boundary is decreased by the solute-drag effect and the mobility in this case can be described as⁹⁾

$$M_{\text{sol.drag}} = \frac{D_{\text{gb}}}{\delta RT} \frac{1}{1 + (K_{\text{seg}}^{\text{gb}})^2 \cdot x}, \quad (6)$$

where x and $K_{\text{seg}}^{\text{gb}}$ represent the solubility of solute in the matrix and the grain boundary segregation coefficient, respectively. By using eq. (6), the calculated migration rate of segregated boundary, $v_{\text{sol.drag}}^{\text{cal}}$, can be rewritten by eq. (1) as

$$v_{\text{sol.drag}}^{\text{cal}} = M_{\text{sol.drag}} \cdot \Delta G_{\text{rex}} \cdot V_{\text{m}}. \quad (7)$$

4.1.3 Estimation of dragging effect of mobile liquid In particles during recrystallization

According to Geguzin and Krivogla¹⁰⁾, the mobility of an intergranular particle with radius r dragged by a grain boundary during its migration can be classified as one of the following three cases.

Case 1. By volume diffusion in the matrix phase surrounding a spherical particle:

$$M_{\text{particle-drag}}^{\text{volume}} = \frac{D_{\text{v}} \cdot V_{\text{m}}}{RT \cdot r^3}, \quad (8)$$

where D_{v} represents the volume diffusion coefficient in the matrix.

Case 2. By interfacial diffusion through the interface between the matrix and a particle:

$$M_{\text{particle-drag}}^{\text{interface}} = \frac{w \cdot D_{\text{s}} \cdot V_{\text{m}}}{10RT \cdot r^4}, \quad (9)$$

where D_{s} and w represent the interfacial diffusion coefficient and the interface thickness, respectively.

Case 3. By impurity diffusion of the solute atoms in a particle:

$$M_{\text{particle-drag}}^{\text{impurity}} = \frac{D_{\text{L}} \cdot n_{\text{p}} \cdot V_{\text{m}}^2}{10RT \cdot V_{\text{p}} \cdot r^3}, \quad (10)$$

where D_{L} , n_{p} and V_{p} represent the impurity diffusion coefficient through the particle, the solubility of solute in the particle, and the molar volume of the particle, respectively.

By using eqs. (8)–(10) and the number of particles in the unit area of grain boundary, N_{s} , the calculated migration rate of particle-dragging boundary, $v_{\text{particle-drag}}^{\text{case-cal}}$, can be rewritten by eq. (1) as

$$v_{\text{particle-drag}}^{\text{case-cal}} = \frac{M_{\text{particle-drag}}^{\text{case}}}{N_{\text{s}}} \cdot \Delta G_{\text{rex}} \cdot V_{\text{m}} \quad (11)$$

where “case” and N_{s} represent one of three cases described by eqs. (8)–(10) and the number of particles on the unit area of grain boundary, respectively.

4.1.4 Comparison between experimental and calculated migration rates of interface boundary during recrystallization

Table 1 shows a comparison between the experimental and calculated migration rates of interface boundary during recrystallization, the parameters of which for the calculation are shown in Appendix A-1. Since the mean radius of matrix grains, $\bar{R}$, is about $5.5 \mu\text{m}$ after heat-treatment at 1173 K for 900 s, the experimental migration rate was estimated to be roughly

$$v_{\text{rex}}^{\text{exp}} = \frac{5.5 \times 10^{-6}}{900} = 6.1 \times 10^{-9} \text{ m} \cdot \text{s}^{-1}. \quad (12)$$

Table 1 Comparison between experimental and calculated migration rates of interface boundary during recrystallization.

Driving force of Recrystallization	Calculated rate of grain boundary migration/ $\text{m} \cdot \text{s}^{-1}$	
	$\Delta G_{\text{rex.}} = 1 \text{ MPa}$	$\Delta G_{\text{rex.}} = 10 \text{ MPa}$
Pinning effect, $v_{\text{pin}}^{\text{cal}}$	1.5×10^{-4}	1.6×10^{-3}
Solute drag effect, $v_{\text{sol.drag}}^{\text{cal}}$	8.3×10^{-9}	8.3×10^{-8}
Particle drag effect, $v_{\text{particle-drag}}^{\text{cal}}$	Controlled by volume diffusion in matrix	
	3.2×10^{-16}	3.2×10^{-15}
	Controlled by interfacial diffusion between matrix and particle	
	2.5×10^{-14}	2.5×10^{-13}
	Controlled by impurity diffusion through liquid particle	
	3.5×10^{-13}	3.5×10^{-12}
Experimental rate of grain boundary migration/ $\text{m} \cdot \text{s}^{-1}$ $v_{\text{rex.}}^{\text{exp}} = 6.1 \times 10^{-9}$		

When the solute-drag effect is assumed to be the rate-controlling process for recrystallization in Fe-In alloys, the experimental result agrees well with the calculated one. On the other hand, when either the pinning effect or the dragging effect of liquid In particles is assumed to be the rate-controlling process, the experimental results are largely different from the calculated ones. Therefore, the solute-drag effect is considered to be dominant in the recrystallization process in Fe-In alloys.

4.2 Relationship between the matrix grain size and the particle size

The relationship between the matrix grain size and the dispersing particle size under the steady state is expressed by^{6,11,12)}

$$\bar{R} = \beta \cdot \frac{\bar{r}}{f^m}. \quad (13)$$

Here, $\bar{R}$, $\bar{r}$, and f represent the mean radius of matrix grains, the mean radius, and the volume fraction of particles, respectively. β and m are constant values given by $\beta = 4/3$ and $m = 1^{(6)}$ in the case of the original Zener equation in which the distribution of second-phase particles is assumed to be random. If all the particles are located on grain boundaries of the matrix, eq. (13) is revised as¹³⁾

$$\bar{R} = 2 \cdot \frac{\bar{r}}{f^{1/2}}. \quad (14)$$

In this case, f equals the volume fraction of intergranular particles, f_{gb} . Microstructural observation in Fe-In alloys revealed most of the liquid In particles to be located on grain boundaries of the αFe matrix. The validity of eq. (14) was then examined by comparing the relationship with experimental data, as shown in Fig. 7. From the slope and the intersection in Fig. 7, the correlation in Fe-In alloys was experimentally estimated to be

$$\bar{R} = 1.95 \cdot \frac{\bar{r}}{f_{\text{gb}}^{1/2}}, \quad (15)$$

which is almost identical to the theoretical equation (14).

Fig. 7 Relationship between $\bar{R}$ and $\bar{r}/f^{1/2}$ in Fe-In alloys.

4.3 Kinetics of matrix grain growth and intergranular particle ripening

It's well known that the ripening rate of second-phase particles is expressed by

$$\bar{r}^3 - \bar{r}_0^3 = k_3 \cdot t, \quad (16)$$

where t is the annealing time, and $\bar{r}$ and $\bar{r}_0$ represent the mean particle radii at t and at $t = 0$, respectively. If the ripening of second-phase particles in a binary alloy system is controlled by volume diffusion, the rate constant $k_3^{\text{vol.}}$ is written as^{14,15)}

$$k_3^{\text{vol.}} = \frac{8D_x \cdot \sigma_{\text{mp}} \cdot x \cdot V_p}{9RT}, \quad (17)$$

where D_x , σ_{mp} , x , and V_p represent the impurity diffusion coefficient of the solute atoms in the matrix phase, the interfacial energy between the matrix and particle phases, the solubility of solute atoms in the matrix phase (atomic fraction), and the molar volume of the particle phase, respectively.

When the ripening of second-phase particles is controlled by grain boundary diffusion, the ripening rate is described by the following equation.

$$\bar{r}^4 - \bar{r}_0^4 = k_4^{\text{gb}} \cdot t. \quad (18)$$

Here, k_4^{gb} is the rate constant and the other variables are equivalent to eq. (16). The rate constant k_4^{gb} in a binary alloy system can be written as¹⁶⁾

$$k_4^{\text{gb}} = \frac{9\delta \cdot D_{\text{gb}}^{\text{impurity}} \cdot \sigma_{\text{mp}} \cdot N_{\text{x}}(\text{gb}) \cdot V_{\text{p}}}{32A \cdot B \cdot RT}, \quad (19)$$

where δ , $D_{\text{gb}}^{\text{impurity}}$, and $N_{\text{x}}(\text{gb})$ represent the grain boundary thickness, the impurity grain boundary diffusion coefficient, and the concentration of solute atoms in the grain boundary, respectively. Moreover, A and B are constant values described by the following equations.

$$A = \frac{2}{3} + \frac{\sigma_{\text{m}}}{2\sigma_{\text{mp}}} + \frac{1}{3} \left(\frac{\sigma_{\text{m}}}{2\sigma_{\text{mp}}} \right)^3 \quad (20)$$

$$B = \frac{1}{2} \ln \left(\frac{1}{f_{\text{b}}} \right) \quad (21)$$

Here, f_{b} is the fraction of grain boundary covered by second-phase particles. The impurity grain boundary diffusion coefficient is usually given by $K_{\text{seg}}^{\text{gb}} \cdot \delta \cdot D_{\text{gb}}^{\text{impurity}}$ in the diffusion database, in which $K_{\text{seg}}^{\text{gb}}$ represents the segregation coefficient, $K_{\text{seg}}^{\text{gb}} = N_{\text{x}}(\text{gb})/x$. Equation (19) can then be revised as

$$k_4^{\text{gb}} = \frac{9K_{\text{seg}}^{\text{gb}} \cdot \delta \cdot D_{\text{gb}}^{\text{impurity}} \cdot \sigma_{\text{mp}} \cdot x \cdot V_{\text{p}}}{32A \cdot B \cdot RT}. \quad (22)$$

To examine the validity of eqs. (16), (17), (18), and (22), the cube and the fourth power of the mean radius $\bar{r}$ of intergranular particles and the mean grain radius $\bar{R}$ were plotted against the annealing time t in Figs. 8 and 9, respectively. The experimental rate constants estimated from the slopes of Figs. 8 and 9, and theoretical rate constants calculated by eqs. (17) and (22), are compared in Table 2. The parameters used for the calculation are shown in Appendix A-2. Although the linear relationship with t seems to be satisfied both for $\bar{r}^3$ and $\bar{r}^4$, as shown in Fig. 8(a) and (b) respectively, these experimental rate constants were 2–3 orders larger than the theoretical ones. This result suggests that another mechanism should be considered to explain the particle ripening in the Fe-In alloys.

Yang *et al.*¹⁷⁾ reported that the ripening of Ag particles in Ni-Ag alloys is controlled by a “coalescence mechanism” due to the coupled growth of the nickel matrix grains and the silver particles, where the rate constant of the particle ripening in the case of “coupled growth mechanism” induced by interfacial tension is given by

$$k_4^{\text{Yang}} = \frac{4}{3} \cdot \frac{D_{\text{s}} \cdot \delta \cdot \sigma_{\alpha\beta} \cdot V_{\text{m}}}{RT}, \quad (23)$$

where $\sigma_{\alpha\beta}$ is the interfacial energy between the Ni matrix (α) and Ag particle (β). Since a constant of $4/3$ in eq. (23) is a fitting value estimated from the experimental data in Ni-Ag alloys, eq. (23) cannot be applied for the present alloy system. Since the volume fraction of second-phase particles is also important to describe the growth of matrix grains, a theoretical equation taking into account the volume fraction of second-phase particles is required to explain the ripening behavior of Fe-In alloys instead of eq. (23). In a manner similar to the discussion by Yang *et al.*¹⁷⁾, eq. (23) was mod-

Fig. 8 (a) cube and (b) fourth power of mean radius of intergranular liquid In particles versus annealing time of Fe-In alloys annealed at 1173 K.

ified on the basis of the migration rate of a particle induced by diffusion phenomena, details of which are summarized in Appendix B.

When the migration of liquid In particles is controlled by the interfacial diffusion at the interface between the matrix and particles, the rate equations of the matrix grain growth and the second-phase particle ripening are described by the following equations.

$$\bar{R}^4 - \bar{R}_0^4 = K_4^{\text{matrix}} \cdot t \quad (24)$$

$$K_4^{\text{matrix}} = \frac{4\pi \cdot D_{\text{s}} \cdot w \cdot \sigma_{\text{m}} \cdot V_{\text{m}} \cdot C}{5RT \cdot f} \quad (25)$$

$$\bar{r}^4 - \bar{r}_0^4 = k_4^{\text{particle-modify}} \cdot t \quad (18')$$

$$k_4^{\text{particle-modify}} = \frac{K_4^{\text{matrix}}}{C^4} = \frac{4\pi \cdot D_{\text{s}} \cdot w \cdot \sigma_{\text{m}} \cdot V_{\text{m}}}{5RT \cdot f \cdot C^3} \quad (26)$$

Here, C equals β/f^m in eq. (13).

On the other hand, when the migration of liquid In particles is controlled by the impurity diffusion in the liquid phase, the rate equations of the matrix grain growth and the second-phase particle ripening are described by the following equations.

$$\bar{R}^3 - \bar{R}_0^3 = K_3^{\text{matrix}} \cdot t \quad (27)$$

$$K_3^{\text{matrix}} = \frac{6\pi \cdot D_L \cdot n_p \cdot \sigma_m \cdot V_m^2}{5RT \cdot V_p \cdot f} \quad (28)$$

$$\bar{r}^3 - \bar{r}_0^3 = k_3^{\text{particle-modify}} \cdot t \quad (16')$$

$$k_3^{\text{particle-modify}} = \frac{K_3^{\text{matrix}}}{C^3} = \frac{6\pi \cdot D_L \cdot n_p \cdot \sigma_m \cdot V_m^2}{5RT \cdot V_p \cdot f \cdot C^3} \quad (29)$$

Theoretical rate constants calculated by eqs. (25), (26), (28)

and (29) are compared with experimental ones in Table 2 and in Figs. 10 and 11, the parameters of which used for calculating theoretical rate constants are also shown in Appendix A-2. In the case of 1 and 3 vol% In alloys, the experimental rate constants agree well with the theoretical ones calculated by eqs. (25) and (26). On the other hand, in the case of the 7.5 vol% In alloy, the experimental rate constant agrees slightly better with the theoretical one calculated by eqs. (28) and (29). These results suggest that the diffusion mechanisms of the particle ripening and grain growth change depending on the volume fraction of liquid In

Fig. 9 (a) cube and (b) fourth power of mean grain radius versus annealing time of Fe-In alloys annealed at 1173 K.

Fig. 10 Comparison between experimental and calculated rate constants of matrix grains in Fe-In alloys.

Table 2 Comparison between experimental and calculated rate constants of intergranular liquid In particles (eqs. (17), (22), (29) and (26)) and those of matrix grains (eqs. (28) and (25)) in Fe-In alloys.

Rate controlling diffusion		Eq.	Calculated rate const.			Experimental rate const.		
			1 vol% In	3	7.5	1 vol% In	3	7.5
Volume diffusion in matrix	k_3^{vol}	(17)		1.0×10^{-25}		1.6×10^{-23}	1.8×10^{-23}	1.8×10^{-22}
Grain boundary diffusion	k_4^{gb}	(22)	1.2×10^{-31}	1.5×10^{-31}	2.1×10^{-31}	4.8×10^{-29}	5.8×10^{-29}	9.0×10^{-28}
Impurity diffusion in liquid	K_3^{matrix}	(28)	9.7×10^{-18}	3.2×10^{-18}	1.3×10^{-18}	1.1×10^{-19}	6.0×10^{-20}	7.2×10^{-20}
Interfacial diffusion	K_4^{matrix}	(25)	4.6×10^{-24}	8.9×10^{-25}	2.3×10^{-25}	5.9×10^{-24}	2.8×10^{-24}	3.8×10^{-24}
Impurity diffusion in liquid	$k_3^{\text{particle-modify}}$	(29)	1.3×10^{-21}	2.3×10^{-21}	3.6×10^{-21}	1.6×10^{-23}	1.8×10^{-23}	1.8×10^{-22}
Interfacial diffusion	$k_4^{\text{particle-modify}}$	(26)	3.2×10^{-29}	5.5×10^{-29}	8.8×10^{-29}	4.8×10^{-29}	5.8×10^{-29}	9.0×10^{-28}

Fig. 11 Comparison between experimental and calculated rate constants of intergranular liquid In particles in Fe-In alloys.

particles. As well as the difference in the volume fraction of liquid In particles, the mean radius of intergranular liquid In particles in the 7.5 vol% In specimen was also largely different from those of 1 and 3 vol% In specimens. As can be seen in eqs. (B2) and (B8), the mobility of a particle depends on the radius of the particle. Figure 12 shows the mobility of a spherical particle calculated by eqs. (B2) and (B8). With increasing radius of the particle, the mobility of a particle decreases and the difference between two diffusional mechanisms becomes larger. According to eq. (B1), the migration rate of a particle dragged by grain boundary is proportional to the product of its mobility (M) and driving force (P). During grain growth under the steady state, the values of P of 1, 3 and 7.5 vol% In alloys heat-treated for 604800 s (1 week) were 0.036, 0.040 and 0.043 MPa, respectively, by which the large difference in the mean particle radius shown in Fig. 6 (a), *i.e.*, the ripening mechanism of the intergranular In particles cannot be explained. These results suggest that both the migration rate of liquid particles and the grain growth rate are very sensitive to the radius of particles.

Although the migration of liquid particles may also depend on the wettability of the liquid phase on the grain boundary, it was not taken into account in the present study. The effect of the wettability in two-phase alloys containing liquid particles will be investigated in a future work.

Fig. 12 Mobility of a spherical particle calculated by eqs. (9) and (10).

5. Summary

The effects of liquid In particles on the recrystallization and the grain growth of α Fe in Fe-In alloys were investigated and the following results were obtained.

- (1) Complete recrystallization of pre-deformed Fe-7.5vol% In alloy at 1173 K was observed for up to 15 minutes. Most of the liquid In particles were located on grain boundaries after the completion of recrystallization.
- (2) The experimental migration rate of the grain boundary during recrystallization agrees well with the theoretical one calculated under an assumption that the solute-drag effect is dominant, which suggests that the recrystallization in Fe-In alloys was retarded mainly by the solute-drag effect.
- (3) During the grain growth at 1173 K, most of the liquid In particles, which had been trapped by grain boundaries during recrystallization, continued to move together with the grain boundaries of the α Fe matrix. The grain growth of the matrix in the Fe-In alloys was extremely retarded by the liquid In particles.
- (4) The relationship between the mean radius of the α Fe matrix grains ($\bar{R}$) and the intergranular particles ($\bar{r}$) in Fe-In alloys was consistent with the theoretical prediction of $\bar{R} = 2\bar{r}/f_{\text{gb}}^{1/2}$.
- (5) The experimental ripening rate of intergranular particles was 2–3 orders faster than the theoretical Ostwald ripening rate, while it agreed well with newly proposed equations deduced on the basis of mass transfer.
- (6) The grain growth of the α Fe matrix was controlled by the ripening mechanism of the intergranular In particles. The mechanisms of grain growth and particle ripening changed from interfacial diffusion to impurity diffusion through liquid particles with increasing volume fraction of liquid In particles.

Appendix

A. Numerical Data Used in Calculations

A-1. Numerical data for the migration rate of the grain boundary during recrystallization

The self-grain boundary diffusion of Fe, $\delta D_{\text{gb,Fe in } \alpha\text{Fe}} = 1.3 \times 10^{-19} \text{ m}^3 \cdot \text{s}^{-1}$ ¹⁸⁾, and the self-diffusion coefficient of αFe , $D_{\text{Fe in } \alpha\text{Fe}} = 4.1 \times 10^{-15} \text{ m}^2 \cdot \text{s}^{-1}$ ¹⁹⁾, were used as δD_{gb} and D_{v} , respectively. When δ is approximated to be 0.75 nm, which corresponds to the thickness of three atomic layers, D_{gb} is calculated to be $1.7 \times 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$. Since there are no reports on the interfacial diffusion coefficient of solute of liquid In particles, D_{s} , and the impurity diffusion coefficient of Fe in liquid In, D_{L} , the impurity diffusion coefficient of Fe in liquid Pb, $D_{\text{Fe in Pb(L)}}^* = 5.4 \times 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$ ²⁰⁾, was used as D_{s} and D_{L} . The molar volumes of the αFe and liquid In phases are $V_{\text{m}} = 7.1 \times 10^{-6} \text{ m}^3 \cdot \text{mol}^{-1}$ and $V_{\text{p}} = 1.3 \times 10^{-5} \text{ m}^3 \cdot \text{mol}^{-1}$ ²¹⁾, respectively. The value of the segregation coefficient of In on the αFe grain boundary, $K_{\text{seg}}^{\text{gb}}$, was roughly approximated to be 2×10^3 according to the relationship between $K_{\text{seg}}^{\text{gb}}$ and the solubility of solute in the matrix ⁹⁾. The solubility of In in αFe , $x = 5.0 \times 10^{-3}$, and that of Fe in liquid In, $n_{\text{p}} = 1.5 \times 10^{-2}$, were measured by EPMA. Instead of the interface thickness w , the lattice constant of αFe , $a_{\alpha\text{Fe}} = 3 \times 10^{-10} \text{ m}$ was used.

A-2. Numerical data for the ripening rate of intergranular liquid particles

$\sigma_{\text{Fe/In}} (= 0.55 \text{ J} \cdot \text{m}^{-2})$ was estimated by the experimental measurement of the wet angle θ for some In particles located on grain boundaries according to the Young's equation $\sigma_{\text{Fe/Fe}} = 2\sigma_{\text{Fe/In}} \cdot \cos \theta$. The value of A in eq. (20) was on the order of 3.1. The values of B in eq. (21) were estimated to be 1.12 (1 vol% In), 0.85 (3 vol% In), and 0.62 (7.5 vol% In) from SEM micrographs. Since there have been no reports on the impurity diffusion coefficient of In in αFe , D_{x} , and the impurity grain boundary diffusion of In in αFe grain boundary, $K_{\text{seg}}^{\text{gb}} \cdot \delta \cdot D_{\text{gb}}^{\text{impurity}}$, the impurity diffusion coefficient of Sn in αFe , $D_{\text{Sn in } \alpha\text{Fe}} = 3.2 \times 10^{-14} \text{ m}^2 \cdot \text{s}^{-1}$ ²²⁾, and $K_{\text{seg}}^{\text{gb}} \cdot \delta \cdot D_{\text{gb}}^{\text{impurity}} = 3.9 \times 10^{-19} \text{ m}^3 \cdot \text{s}^{-1}$ ²³⁾ were used as D_{x} and $D_{\text{gb}}^{\text{impurity}}$, respectively.

B. Modification of the Theoretical Equation for the Ripening Rate of Particles

On the basis of mass transfer, the rate of the migration of a particle is given by

$$\frac{d\bar{R}}{dt} = M \cdot \frac{P}{N_{\text{s}}}, \quad (\text{B1})$$

where M , P and N_{s} represent the mobility of the particle, the driving force of grain boundary migration and the number of particles on the unit area of grain boundary, respectively. If the migration of a spherical particle is controlled by interfacial diffusion, the mobility can be described as

$$M_{\text{particle-drag}}^{\text{interface}} = \frac{w \cdot D_{\text{s}} \cdot V_{\text{m}}}{10RT \cdot \bar{r}^4}, \quad (\text{B2})$$

where D_{s} , w and V_{m} represent the interfacial diffusion coefficient, the thickness of the interface, and the molar volume of the matrix, respectively. The driving force of grain growth,

P , and the number of particles in the unit area of grain boundary, N_{s} , are described as

$$P = \frac{2\sigma_{\text{m}}}{\bar{R}} \quad (\text{B3})$$

and

$$N_{\text{s}} = \frac{\bar{R} \cdot f}{2\pi \cdot \bar{r}^3}, \quad (\text{B4})$$

respectively. Equation (B1) is then rewritten as

$$\frac{d\bar{R}}{dt} = \frac{\pi \cdot D_{\text{s}} \cdot w \cdot V_{\text{m}} \cdot \sigma_{\text{m}}}{5RT \cdot \bar{R}^2 \cdot f \cdot \bar{r}} = \frac{\pi \cdot D_{\text{s}} \cdot w \cdot V_{\text{m}} \cdot \sigma_{\text{m}} \cdot C}{5RT \cdot \bar{R}^3 \cdot f}, \quad (\text{B5})$$

where C equals β/f^m . By solving eq. (B5), the growth rate of the matrix is deduced as

$$\bar{R}^4 - \bar{R}_0^4 = \frac{4\pi \cdot D_{\text{s}} \cdot w \cdot \sigma_{\text{m}} \cdot V_{\text{m}} \cdot C}{5RT \cdot f} \cdot t, \quad (\text{B6})$$

and the ripening rate of the intergranular particles is finally evaluated to be

$$\bar{r}^4 - \bar{r}_0^4 = \frac{4\pi \cdot D_{\text{s}} \cdot w \cdot \sigma_{\text{m}} \cdot V_{\text{m}}}{5RT \cdot f \cdot C^3} \cdot t. \quad (\text{B7})$$

On the other hand, if the migration of a spherical liquid particle is controlled by the impurity diffusion through the liquid particle, the mobility is given by

$$M_{\text{particle-drag}}^{\text{impurity}} = \frac{D_{\text{L}} \cdot n_{\text{p}} \cdot V_{\text{m}}^2}{10RT \cdot V_{\text{p}} \cdot \bar{r}^3}. \quad (\text{B8})$$

Here, D_{L} , n_{p} and V_{p} represent the impurity diffusion coefficient through the liquid phase, the molar fraction of solute in the liquid phase, and the molar volume of the liquid phase, respectively.

Using a similar approach, the growth rate of the matrix grains and the ripening rate of the intergranular particles can be estimated by the following equations:

$$\bar{R}^3 - \bar{R}_0^3 = \frac{6\pi \cdot D_{\text{L}} \cdot n_{\text{p}} \cdot \sigma_{\text{m}} \cdot V_{\text{m}}^2}{5RT \cdot V_{\text{p}} \cdot f} \cdot t \quad (\text{B9})$$

$$\bar{r}^3 - \bar{r}_0^3 = \frac{6\pi \cdot D_{\text{L}} \cdot n_{\text{p}} \cdot \sigma_{\text{m}} \cdot V_{\text{m}}^2}{5RT \cdot V_{\text{p}} \cdot f \cdot C^3} \cdot t \quad (\text{B10})$$

REFERENCES

- 1) J. Koike, K. Miki, H. Takahashi and K. Maruyama: *Mater. Sci. Eng. A* **285** (2000) 158.
- 2) R. Kainuma, I. Ohnuma and K. Ishida: *Mater. Trans.* **44** (2003) 1768.
- 3) T. Hagsawa, H. Mitsui, I. Ohnuma, R. Kainuma and K. Ishida: *ISIJ Int.* **48** (2008) 1001.
- 4) *Binary Alloy Phase Diagrams*: 2nd ed., (eds. T. B. Massalski *et al.*), (ASM International, vol.1 1990), 1712.
- 5) T. Sakuma and T. Nishizawa: *Bulletin of the JIM* **10** (1971) 279 (in Japanese).
- 6) C. Zener, quoted by C. S. Smith: *Trans. Met. Soc. AIME*. **175** (1948) 15.
- 7) E. D. Hondros: *Interfaces Conference*, ed. by R. C. Gifkins, Butterworth, London, (1969), 77.
- 8) F. J. Humphreys and M. Hatherly: *Recrystallization and Related Annealing Phenomena*, Pergamon, Oxford, (1995), 271.
- 9) T. Nishizawa: *Thermodynamics of Microstructures*, ASM International, Materials Park, (2008), pp. 123–166.
- 10) Ya. E. Geguzin and M. A. Krivoglagz: *Migration of Macroscopic*

- Inclusions in Solids, Consultants Bureau, New York, (1973).
- 11) T. Nishizawa, I. Ohnuma and K. Ishida: *Mater. Trans., JIM* **38** (1997) 950.
 - 12) P.A. Manohar, M. Ferry and T. Chandra: *ISIJ Int.* **38** (1998) 913.
 - 13) I. Ohnuma: Doctoral thesis, Tohoku University (2000).
 - 14) I.M. Lifshitz and V.V. Slyozov: *J. Phys. Chem. Solids* **19** (1961) 35.
 - 15) C. Wagner: *Elektrochem* **65** (1961) 581.
 - 16) H.P.K. Kirchner: *Metall. Trans.* **2** (1971) 2861.
 - 17) S.C. Yang, G.T. Higgins and P. Nash: *Mater. Sci. Technol.* **8** (1992) 10.
 - 18) H. Mehrer ed.: *Diffusion in Solid Metals and Alloys*, Landolt-Börnstein, Numerical Data and Functional Relationships in Science and Technology, Vol.26, (Springer-Verlag, Berlin, 1990) p. 642.
 - 19) H. Mehrer ed.: *Diffusion in Solid Metals and Alloys*, Landolt-Börnstein, Numerical Data and Functional Relationships in Science and Technology, Vol.26, (Springer-Verlag, Berlin, 1990) p. 49.
 - 20) "DIFFUSION DATA", DIFFUSION INFORMATION CENTER, OH, Vol.3, No.1 (1969), 45.
 - 21) E.A. Brandes and G.B. Brook eds.: *Smithells Metals Reference Book* 7th ed., (Butterworth-Heinemann, Oxford, 1992) p. 14–7.
 - 22) H. Mehrer ed.: *Diffusion in Solid Metals and Alloys*, Landolt-Börnstein, Numerical Data and Functional Relationships in Science and Technology, Vol.26, (Springer-Verlag, Berlin, 1990) p. 128.
 - 23) H. Mehrer ed.: *Diffusion in Solid Metals and Alloys*, Landolt-Börnstein, Numerical Data and Functional Relationships in Science and Technology, Vol.26, (Springer-Verlag, Berlin, 1990) p. 651.