Shape Anisotropy Evolution of Co Grains in Cu–30at%Co Alloy by Annealing under Magnetic Field

Hideyuki YASUDA, Yasutaka YAMAMOTO, Itsuo OHNAKA and Kohji KISHIO¹⁾

Department of Adaptive Machine Systems, Osaka University, Osaka 565-0871 Japan.

1) Department of Applied Chemistry, University of Tokyo, Tokyo 113-8656 Japan.

(Received on December 10, 2002; accepted in final form on March 6, 2003)

The shape change of the fcc-Co grains during the coarsening process was examined by using the Cu–30at%Co alloys. The fine Co-rich particles were uniformly distributed in the rapidly solidified alloys when the cooling rate was sufficiently large to prevent the dendritic growth of the primary Co phase. The influence of the magnetic field on the shape change of the Co grains was clearly observed when the rapidly solidified particles were annealed at 1173 K under 10 T. The average angle between the long-axis and the magnetic field direction at 10 T is 15 degrees smaller than the average value at 0 T. The coarsening model suggested that the shape magnetic anisotropy energy acts as a driving force of the coarsening in the region that the Co grain size is several μm . The static magnetic energy due to the shape anisotropy has an alternative potential to produce the aligned structure.

KEY WORDS: magnetic anisotropy; shape anisotropy; coarsening; copper-cobalt alloy.

1. Introduction

Application of a magnetic field to solidification processing has been practically developed, *i.e.* improvement of the casting process has been realized for the continuous steel casting.¹⁾ Imposition of the static magnetic field reduces turbulence in the melt flow, while the alternating magnetic field is used for stirring of the melt. Both of them attributed to the Lorentz force. Magnitude of the static magnetic field is typically less than 1 T.

Another effect of the magnetic field is the static magnetic energy and the magnetization force that is derived from the static magnetic energy. There are two different anisotropies in the static magnetic energy. One is the crystalline magnetic anisotropy and the other is shape anisotropy. The magnetization force due to the crystalline magnetic anisotropy has been recognized for the paramagnetic and diamagnetic materials under a high magnetic field. For example, many researches on textured structure of the high T_c superconductors have been examined by using anisotropy of the magnetic susceptibility.^{2–10)} Rango *et al.*¹¹⁾ firstly reported that magnetically aligned structure of Y–Ba–Cu–O systems was obtained by melt processing under a high magnetic field, while magnetic alignment of YBCO particles in suspension of organic substances was studied.^{2,12)} Effect of the shape anisotropy has been realized in the transformation from the paramagnetic fcc-phase to the ferromagnetic bcc-phase for steels.^{4,13)} The studies reported that the transforming nuclei in a magnetic field did not exhibit any anisotropy. The dipolar interaction between the ferromagnetic grains resulted in the alignment of the steel microstructure.

Effect of the magnetic field was also realized in the coarsening process from the rapidly solidified Bi–Mn al-

loys.¹⁵⁾ Ferromagnetic BiMn grains were selected during coarsening under the magnetic field of 10 T in accordance with the crystalline magnetic anisotropy energy of the BiMn crystal. This result indicated that the magnetic field has a potential to produce the aligned structure (crystal orientation and grain shape) through not only the phases transformation but also coarsening in which there is no difference in the constituent phases. However, there is no study on the shape anisotropy induced by the magnetic field during the macroscopic coarsening stage. This paper focuses on the grain shape anisotropy induced by the static magnetic field during coarsening.

The Co particle in the Cu–Co system exhibits cubic structure at temperatures above 695 K, and is a ferromagnet with a rather small crystalline magnetic anisotropy. This system is a suitable system to examine the influence of the magnetic field on the coarsening process of the ferromagnetic grains, since Cu matrix is a paramagnetic. Some studies have been performed to investigate the influence of magnetic field on precipitation of the Co particles in the Cu matrix.^{16–19)} Co particles in dilute Cu–Co alloys, tended to elongate to the [100] direction parallel to the imposed magnetic field during precipitating of the Co particles in Cu matrix. In these studies, size of the precipitating Co particles was the order of 10^{-7} m at most.

It is also interesting to investigate the influence of the magnetic field on the growth of the Co grains after the Co particles precipitated. It is, however, difficult to observe the coarsening process in dilute alloys. Thus, the microstructure in which fine Co grains uniformly distribute in the Cu–Co alloys with higher Co concentration is desirable to examine the coarsening process in the magnetic field. **Figure 1** shows phase diagram of the Co–Cu system.²⁰⁾ The

Fig. 1. Phase diagram of Co–Cu system.²⁰⁾

Cu–Co system shows a shallow liquidus line in the wide composition range. It has been reported that two liquid phase separation occurs in the undercooled melt.^{21–28)} It is expected to obtain the microstructure in which fine Co grains are uniformly distributed when the two liquid phase separation occurs and rapidly solidifies. This paper shows the influence of the magnetic field on the coarsening process of the fcc-Co grains with a small crystalline magnetic anisotropy. The mechanism of the anisotropic microstructure evolution is also discussed.

2. Experimental Procedures

Cu and Co of the grade 99.9% were melted in the vacuum atmosphere in the induction furnace, and the Cu–30at%Co mother alloy was made by metal mold casting. The rapidly solidified particles were made by using a rotating-water-atomization equipment.²⁹⁾ The mother alloy was put into the silica nozzle, it was melted by the induction-heating device and then was injected into a water layer in the rotating drum. The particles were rapidly solidified in the water. The rapidly solidified particles were dried in the vacuum after they were collected from the water and were washed with the ethanol. The particles were classified into diameters. The rapidly solidified particles of which diameters were 250 μm or less were pressed at room temperature under 350 MPa to produce a compact (6 mm in diameter, 2 mm in height). The specimens inserted in the graphite sample holder were enclosed in the argon atmosphere of 10^4 Pa in a silica tube. The annealing under the magnetic field was performed in the furnace set up in the bore of the He-free superconducting magnet. Intensity of the imposed magnetic field is 0 and 10 T. The anneal temperature was 1173 K, and after annealing, the specimen was cooled in the magnetic field until temperature became 573 K. According to the phase diagram of the Cu–Co system, the Cu-rich phase and the Co-rich phase are solid at the anneal temperature (1173 K), and the Co phase is a ferromagnet.

The microstructure of Cu–Co alloy was observed by a conventional SEM using an EDX image. The feature of the Co grain shape was evaluated from the microstructure in the cross section which was parallel to the imposed magnetic field. The shape of the Co crystal grain in the cross section was approximated to the ellipse. Figure 2 shows a

Fig. 2. Schematic illustration of the image analysis to evaluate the anisotropy of the coarsened Co grains in the Cu–Co alloys. The Co grain (solid line) is approximated an ellipse shape (dash line). Lengths of the long-axis and short-axis are defined as a and b , respectively. The angle between the Magnetic field and the long-axis direction is defined as θ .

schematic illustration of the particle shape analysis. The angle θ is defined by the angle between the magnetic field and the long axis of the elliptic particle. The ratio of the short axis to the long axis is defined as m . The magnetization curves of the Cu–30at%Co alloys were measured in two directions, and the anisotropy of the magnetization was examined. One is the direction that is parallel to the magnetic field imposed during annealing, and the other is the direction that is perpendicular to the imposed magnetic field.

3. Experimental Results

3.1. Microstructure of the Rapidly Solidified Cu–30at%Co Alloys

Figure 3 shows the microstructures of the Cu–30at%Co mother alloy and the rapidly solidified particles. The dendrite of the Co-rich primary phase was observed in the cast mother alloys. Rather large Co-rich phase of which size was more than 10 μm was observed in the rapidly solidified particles of which diameter ranged from 470 to 710 μm . In the rapidly solidified particles of 250–420 μm in diameter, the coarse Co-rich phase was still observed in a part of the particles. On the other hand, the microstructure in which fine Co grains with diameter of several μm were uniformly distributed in the Cu matrix was observed in the rapidly solidified particles of which diameter was 250 μm or less.

The grain size dependence on the microstructure originates in the cooling rate. In the case of the larger particles injected into the water layer, the cooling rate was not so high and then the dendritic growth of primary Co occurs in accordance with the equilibrium phase diagram. The cooling rate increases as the particle size becomes small. As a result, the melt temperature became below the metastable immiscibility dome of the two liquid phases (Cu-rich and Co-rich liquid phases), and consequently the liquid phase

Fig. 3. Microstructures of the Cu-30at%Co alloys. (a) Mother alloys cast in metal mold, (b) the rapidly solidified particles (diameter: 470–710 μm), (c) rapidly solidified particles (diameter: 250–470 μm), (d) rapidly solidified particles (diameter: <250 μm).

separation occurs in the melt. In the state of the liquid phase separation, the minor phase tends to be spherical, reducing the total interfacial energy. Thus, the rapid solidification of the two-liquid state causes the uniform distribution of the minor phase in the matrix, since the Co-rich liquid phase is isolated by the Cu-rich liquid phase. The microstructure observed in the rapidly solidified specimens with the diameters less than 250 μm suggested that the liquid phase separation contributed to the formation of the fine and uniform Co particles of which size was typically 1 μm or less. Since the fine and uniform Co grains are suitable to examine the coarsening process, the rapidly solidified particles of which diameter was less than 250 μm was used to examine the influence of the magnetic field on the shape of the coarsened Co grains.

3.2. Influence of the Magnetic Field on Shape of the Co Grains

Figure 4 shows microstructures in the cross section parallel to the imposed magnetic field after the rapidly solidified particles with diameters less than 250 μm were annealed at 1173 K for 4 h, 12 h, 48 h and 200 h under a magnetic field of 0 T or 10 T. Horizontal direction in the photograph corresponds to the magnetic field direction imposed during annealing. The Co grains slightly coarsened, but the influence of the magnetic field was not clear for the specimens annealed for 4 h and 12 h. The Co grains grew up to about 5 μm by annealing the specimens for 48 h. Although no influence of the magnetic field on the size of the Co grains was observed for the specimens annealed under magnetic fields of 0 T and 10 T, influence of the magnetic field on the shape of the Co grains was realized as shown in Fig. 4. There was a tendency that the Co grains elongated in the direction parallel to the imposed magnetic field direction during the annealing under the magnetic field.

Fig. 4. Microstructure of the cross section parallel to the imposed magnetic field for the Cu-30at%Co alloys. Magnetic field was imposed in the horizontal direction of the photographs.

Fig. 5. Shape of the Co grains as a function of the angle between the imposed magnetic field and the long-axis direction, and the spheroidicity " $1/m-1$ ". The m is defined by b/a . Here, a and b are lengths of the long-axis and the short axis, respectively. Size of the marks indicate the cross sectional area of the Co grains.

The influence of the magnetic field on the shape of the Co grain became obvious in the specimens annealed for 200 h at 1173 K. In the specimen annealed without the magnetic field, the shape of the Co grains was almost a circle. When the magnetic field of 10 T was imposed during the annealing for 200 h, the Co grains clearly elongated in the magnetic field direction. Moreover, the microstructure suggested that the Co grains aligned in the magnetic field direction preferably coarsened together and connected with each other.

The shape anisotropy of the ferromagnetic Co grains coarsened under the magnetic field was quantitatively evaluated. Figure 5 shows results of the analysis for the Cu-30at%Co alloys annealed for 48 h and 200 h at 1173 K. The Co grains are plotted as a function of the angle, θ between the magnetic field and the long-axis direction of the approximated ellipse and the ratio of the short-axis length to the long-axis length. Size of the plotted marks is proportional to the grain size. The value of " $1/m-1$ " is a parameter to express the spheroidicity. For example, the value is 0 for the circle and it increases with decreasing spheroidicity. The arrows in the graphs are a mean value of the angle, and the cross sign indicates the average value of " $1/m-1$ ". In the specimen annealed without imposing the magnetic field, the direction of the long-axis of the Co particle was ran-

dom, while the angle θ approached 0 deg for the specimens annealed under the magnetic field. Furthermore, the Co grains with relatively large size tended to exhibit large values of $1/m-1$. It indicated that the Co grains growing under the magnetic field elongated in the direction of the magnetic field imposed during the annealing.

Figure 6 shows the distribution of the angle θ for the Co grains in the specimens annealed under the magnetic field. In the specimens annealed without the magnetic field, number of the Co grains increased with increasing the angle, indicating that random distribution of the long-axis direction. On the other hand, the Co grains obviously gathered in the low angle region for the specimens annealed under the magnetic field. Especially, large Co grains placed in the low angle region. The average angles in the specimens annealed without the magnetic field were 50.4 deg (12 h), 50.0 deg (48 h), and 47.9 deg (200 h). For the specimens annealed under the magnetic field of 10 T, the average angles were 37.2 deg (12 h), 33.1 deg (48 h) and 31.2 deg (200 h). The quantitative analysis of the Co grain shape clearly indicated that the Co grains elongated to the magnetic field direction.

3.3. Magnetization of the Cu-Co Alloys Annealed under the Magnetic Field

Figure 7 shows the result of the magnetization measure-

Fig. 6. Distribution of the angle between the magnetic field and the long-axis direction of the Co grains in the Cu-30at%Co alloys. (a) 48 h, 0 T, (b) 48 h, 10 T, (c) 200 h, 0 T and (d) 200 h, 10 T. The filled patterns indicate the spheroidicity, m .

Fig. 7. Magnetization curves of the Cu-30at%Co alloys. (a) Rapidly solidified particles (diameter $< 1 \mu\text{m}$), (b) annealed at 1173 K for 200 h under 0 T and (c) annealed at 1173 K for 200 h under 10 T.

ment for the Cu-30at%Co alloys. Notation such as “Parallel” and “Perpendicular” indicates the configuration between the imposed magnetic field for the magnetization measurement and the magnetic field direction imposed during the annealing. The anisotropy was not observed in the magnetization curves in the rapidly solidified particles (Fig. 7(a)). Since the Co was supersaturated in the Cu matrix for the rapidly solidified particles, the saturated magnetization that is proportional to content of the Co phase was slightly smaller than that for the annealed specimens (Fig. 7(b)). On the other hand, the saturated magnetization of the annealed specimen was approximately $5.4 \times 10^{-5} \text{ Wb/mkg}$ regardless of the time of annealing or the intensity of the magnetic field, as shown Figs. 7(b) and 7(c). It indicates that the amount of the Co phase was not affected by the imposed magnetic field. Any anisotropy in the magnetization curves

was not realized for the specimen annealed without the magnetic field (Fig. 7(b)), while the anisotropy was clearly detected for the specimens annealed under the magnetic field of 10 T (Fig. 7(c)). For the specimens annealed under the magnetic field, easy direction of the magnetization coincided with the magnetic field direction during the annealing as shown in Fig. 6(c).

Figure 8 shows the saturated magnetization and the induced anisotropy energy estimated from the magnetization curves as a function of the annealing time. The area enclosed by the two magnetization curves (“parallel” and “perpendicular”) in Fig. 7(c) corresponds to the magnetic anisotropy energy induced by the annealing under the magnetic field. The anisotropy energy was estimated by integrating the gap between the two curves from 0 A/m to 1.43 MA/m, since the magnetization in both of the two di-

Fig. 8. Saturated magnetization and the magnetic anisotropy energy estimated from the magnetization curves for the Cu-30at%Co alloys annealed at 1173 K under 10 T.

rections saturated before 1.43 MA/m. The saturated magnetization did not change after the specimens were annealed for 1 h. The precipitation of Co completed before the annealing time of 1 h. The anisotropy energy estimated from the magnetization curves rapidly increased until the annealing time of 4 h. After annealing for 4 h, the magnetic anisotropy energy continued to increase slightly. The slightly increase corresponds to the anisotropic shape formation of Co grains. Therefore, the induced magnetic anisotropy is related to not the precipitation of Co but the coarsening of Co grains.

4. Discussion

It is necessary to compare the crystalline magnetic anisotropy energies with the shape anisotropy energy to examine the formation of anisotropy shape of the fcc-Co grains in the coarsening process under the magnetic field. Crystalline magnetic anisotropy energy E_{crystal} of the fcc-Co grain is expressed by the following equation.³⁰⁾

$$E_{\text{crystal}} = K_1(\alpha_1^2\alpha_2^2 + \alpha_2^2\alpha_3^2 + \alpha_3^2\alpha_1^2) + K_2\alpha_1^2\alpha_2^2\alpha_3^2 \quad \dots(1)$$

Here, K_1 and K_2 are the magnetic anisotropy constants. The α_1 , α_2 , and α_3 are the cosines of the direction of the spontaneous magnetization and [100], [010], and [001] directions, respectively. The equation was developed using the cosines so that the expression of the anisotropy energy satisfies the crystal symmetry of the cubic structure. K_1 and K_2 of the Co crystal are estimated to be 0.9 kJ/m³ and 5.7 kJ/m³, respectively, at the annealing temperature of 1173 K.³¹⁾ On the other hand, the shape anisotropy energy is assumed to be 10²–10³ kJ/m³ when one assumes that the magnetization M_p of the fcc-Co phase is 85% of magnetization 1.57 Wb/m² at room temperature³¹⁾ and the difference of the demagnetizing factor is 0.33. For the fcc-Co grains at the anneal temperature, the shape magnetic anisotropy is about 10³ times as large as the crystalline magnetic anisotropy. Therefore, it is expected that the microstructure changes due to the shape anisotropy occur in the Cu–Co system.

A model on the formation of an anisotropy grain during

the coarsening process is presented when the crystalline magnetic anisotropy energy is ignored. For simplicity, the model deals with a ferromagnetic particle with the spheroid shape which is isolated by the non-magnetic matrix. Lengths in the rotational axis and in the direction perpendicular to the rotational axis are a and b , respectively. The ratio m is defined by b/a . The factors, which contribute to the shape change, are the shape anisotropy energy and the surface energy in the present model.

Magnetic energy U_m that contains the shape magnetic anisotropy is given by

$$U_m = -M_p \left(H_{\text{ex}} - \frac{N_d M_p}{\mu_0} \right) \quad \dots(2)$$

Here, M_p is magnetization, H_{ex} is an external magnetic field, N_d is a demagnetizing factor, and μ_0 is the magnetic permeability in vacuum. Free energy G of the system including the magnetic energy and the surface energy is expressed by

$$\begin{aligned} G = & (N - n) \cdot v_{\text{mole}} \cdot \{H_m - TS_m\} + n \cdot v_{\text{mole}} \cdot \{H_p - TS_p\} \\ & + s_p \cdot \sigma - n \cdot v_{\text{mole}} \cdot M_p \left(H_{\text{ex}} - \frac{N_d M_p}{\mu_0} \right) \\ = & N \cdot v_{\text{mole}} \cdot \{H_m - TS_m\} - v_p \cdot (\Delta H_{m-p} - T \Delta S_{m-p}) \\ & + s_p \cdot \sigma - v_p \cdot M_p \left(H_{\text{ex}} - \frac{N_d M_p}{\mu_0} \right) \quad \dots(3) \end{aligned}$$

Here,

$$\begin{aligned} v_p &= n \cdot v_{\text{mole}} \\ \Delta H_{m-p} &= H_m - H_p \quad \dots(4) \\ \Delta S_{m-p} &= S_m - S_p \end{aligned}$$

N is total moles of the system, n is the moles of the ferromagnetic particles, and v_m is the molar volume of the matrix and the particles (for simplicity, the same molar volume were used for both phases). H and S are enthalpy and entropy, respectively, and the subscripts indicate the matrix (m) and the particle (p). The interfacial energy is σ . The volume and the interfacial area of the ferromagnetic particle are v_p and s_p , respectively. In this case, the local equilibrium condition between the particle and the matrix is given by the following equation.

$$\left(\frac{\partial G}{\partial v_p} \right)_{T, N_d} = 0 \quad \dots(5)$$

Equations (3) and (5) give Eq. (6).

$$\begin{aligned} T = & \left\{ \frac{\Delta H_{m-p}}{\Delta S_{m-p}} \right\} - \left(\frac{ds_p}{dv_p} \right) \cdot \left(\frac{\sigma}{\Delta S_{m-p}} \right) \\ & + \frac{M_p}{\Delta S_{m-p}} \left(H_{\text{ex}} - \frac{N_d M_p}{\mu_0} \right) \quad \dots(6) \end{aligned}$$

In this expression, it is assumed that the imposed magnetic field is sufficiently large to saturate the magnetization. In the present study, the imposed magnetic field was 10 T. Thus, the assumption is valid. A sufficiently large sphere of the ferromagnetic particle is defined as the standard condi-

tion. The value of (ds_p/dv_p) becomes 0 because radius of the curvature is large enough in this standard condition. The local equilibrium temperature of the standard condition is defined as T_{std} . Temperature deviation, ΔT , from the equilibrium temperature of the standard condition is given by

$$\Delta T = T - T_{std} = - \left(\frac{ds_p}{dv_p} \right) \cdot \left(\frac{\sigma}{\Delta S_{m-p}} \right) - (N_d - N_d^0) \frac{M_p^2}{\mu_0 \Delta S_{m-p}} \dots (7)$$

Here, the demagnetizing factor N_d^0 is equal to 1/3. Therefore, ΔT is a parameter to express thermodynamic stability of the particle, and it corresponds to the driving force in the coarsening. In other words, any shape change results in increase of ΔT defined by Eq. (7).

Surface area and curvature (ds_p/dv_p) of the spheroid is derived from the geometric consideration. Volume v_p of the spheroid is given by

$$v_p = \frac{4}{3} \pi a b^2 = \frac{4}{3} \pi m^2 a^3 \dots (8)$$

Surface area s is given by

$$\begin{aligned} s_p &= 2\pi m^2 a^2 + \frac{2\pi m a^2}{\sqrt{1-m^2}} \sin^{-1} \sqrt{1-m^2} \quad (m < 1) \\ &= 4\pi a^2 \quad (m = 1) \\ &= 2\pi m^2 a^2 + \frac{2\pi m a^2}{\sqrt{m^2-1}} \ln \left(\sqrt{m^2-1} + m \right) \quad (m > 1) \dots (9) \end{aligned}$$

In addition, the curvature is defined by the following equation in this study.

$$\left(\frac{ds_p}{dv_p} \right)_m = \left(\frac{ds_p}{da} \right)_m \left(\frac{da}{dv_p} \right)_m = \frac{1}{4\pi m^2 a^2} \left(\frac{ds_p}{da} \right)_m \dots (10)$$

Therefore,

$$\begin{aligned} \left(\frac{ds_p}{dv_p} \right)_m &= \frac{1}{a} \left(1 + \frac{1}{m \sqrt{1-m^2}} \sin^{-1} \sqrt{1-m^2} \right) \quad (m < 1) \\ &= \frac{2}{a} \quad (m = 1) \\ &= \frac{1}{a} \left(1 + \frac{1}{m \sqrt{m^2-1}} \ln \left(\sqrt{m^2-1} + m \right) \right) \quad (m > 1) \dots (11) \end{aligned}$$

On the other hand, the demagnetizing factor N_d of the spheroid is given by

$$\begin{aligned} N_d &= \frac{m^2}{1-m^2} \left[\frac{1}{\sqrt{1-m^2}} \ln \left(\frac{1}{m} + \frac{1}{m} \sqrt{1-m^2} - 1 \right) \right] \quad (m < 1) \\ &= \frac{1}{3} \quad (m = 1) \\ &= 1 - \frac{1}{m^2-1} \left[\frac{m^2}{\sqrt{m^2-1}} \cos^{-1} \left(\frac{1}{m} \right) - 1 \right] \quad (m > 1) \dots (12) \end{aligned}$$

Fig. 9. Temperature deviation, ΔT , from the local equilibrium, defined by Eq. (7), as a function of volume of the grain and the spheroidicity, m . Equivalent radius, R_{eq} , of the grain is estimated by $[a \cdot b^2]^{1/3} = a \cdot m^{1/3}$.

The deviation from the local equilibrium temperature at the standard condition is obtained by substituting Eqs. (11) and (12) to Eq. (7).

Figure 9 shows the deviation from the local equilibrium temperature at the standard condition in terms of volume v_p and the ratio m of the ferromagnetic particles. In this calculation, $\sigma = 0.1 \text{ J/m}^2$ and $\Delta S_{m-p} = 10^6 \text{ J/m}^3 \text{ K}$ are used. The surface energy is the same order as the solid-liquid interfacial energy for the metallic alloys, and the entropy change is the same order as that of the fusion. The magnetization of the fcc-Co phase was assumed to be $M = 1.5657 \text{ Wb/m}^2$.

The isothermal line takes the minimum at $m = 1$ and the spherical shape is most stable when the Co grain size is less than $5 \times 10^{-7} \text{ m}$. In a word, the surface energy is predominant in this region. A minimum point of the isothermal line exists in the vicinity of $m = 0.2$ when the Co grain size is the order of 10^{-6} m . In this region, the shape anisotropy energy greatly influences the particle shape change during the coarsening under the magnetic field. Furthermore, the shape anisotropy energy is dominant when the size of the grain becomes 10^{-5} m or more. Therefore, the particles of which sizes are several μm or more are expected to become the anisotropic shape if there is enough time for diffusion. The tendency indicated by the model is qualitatively consistent with the experimental result.

The numerical calculation suggested that the ellipticity, m , becomes 0.2 or less for the grains with several μm or more in diameter. The ellipticity, m , observed in the experiments is approximately 0.5 even if the specimens were annealed in the magnetic field of 10 T for 200 h at 1173 K. The experimental results were smaller than the values expected from the model calculation. There are some possibilities to cause the discrepancy besides inaccuracy of the physical properties. One is shortage of the annealing time to minimize the free energy of the system. The annealing time of 200 h might be insufficient for solute diffusion in the solid state. Furthermore, the interaction between the particles should be also considered. For example, the Co particle in the Cu matrix was not completely isolated from

other Co grains. The interaction may prevent the Co grains from the shape change due to the shape magnetic isotropy energy. For the quantitative evaluation, it is necessary to consider not only the physical properties but also the interaction between the particles.

It is interesting to consider the magnetic interaction between the particles for evolution of the microstructure under the magnetic field. In the case of steel,^{13,14)} the volume fraction of the ferromagnetic ferrite phase is quite high, and it has been pointed out that the magnetic interaction between ferrite grains significantly contributed to the aligned structure formation. The obtained microstructure suggested that the Co grains, which aligned in the magnetic field preferably, grew and connected with each other in the Cu–Co alloys, as shown in Fig. 4. The interaction between the particles (dipole–dipole interaction^{13,14)} pointed out for the steel system can contribute to the aligned structure in the Cu–Co system. However, since the volume fraction of the Co phase in the Cu–Co alloy used in the present study was roughly 30%, the interaction of the particle–particle was not recognized.

It can be said that the interaction between the particles (the dipolar interaction^{13,14)} is essentially the same as the shape magnetic anisotropy. For instance, if the grain is assumed to be composed of the fine ferromagnetic elements, the shape magnetic anisotropy is derived from the dipolar interaction between the fine elements. Therefore, effect of the magnetic field on the microstructure evolution controlled by diffusion will be consistently understood by considering the static magnetic energy including not only the external magnetic field but also the interaction between the induced magnetic substances. The phase transformation and the coarsening under the magnetic field have a potential to produce the aligned structure due to the shape magnetic anisotropy.

5. Conclusions

This paper examined the shape change of the fcc-Co grains that the crystalline magnetic anisotropy is small at the annealing temperature in the coarsening process from the rapidly solidified structure.

Since the structure change in solid phase is sensitive to the initial microstructure before annealing, uniform and fine microstructure is required as the initial microstructure. In the present experiment, the microstructure in which the fine Co grains were uniformly distributed in the Cu matrix, since the liquid phase separation occurred by using the rapid solidification technique. The influence of the magnetic field on the shape change of the Co grains was clearly observed by using the rapidly solidified microstructure in the particles with diameters less than 250 μm .

It was confirmed that the Co grains grew up to the shape that elongated in the magnetic field direction when the rapidly solidified particles of the Cu–30at%Co alloy were annealed under the magnetic field of 10 T at 1173 K for 48 h and 200 h. The mean value of the angle that the direction of the long-axis and the magnetic field direction at 10 T is 15 degrees smaller than the mean value at 0 T.

The anisotropy structure formation during the coarsening process under the magnetic field was examined from a ther-

modynamic aspect. Not only the surface energy but also the shape anisotropy energy acts as a driving force of the coarsening in the region that the Co grain size is several μm .

Acknowledgments

This work is supported in part by a Research for the Future (RFTF) given by Japan Society for the Promotion of Science and by a Grant-in-Aid for Scientific Research of Priority Areas given by the Ministry of Education, Culture, Sports, Science and Technology, Japan. The author expresses his thanks to Toray Science Foundation for the support. This paper also contains fruition from the continuous discussion in a research group “Advanced Application of Electromagnetic Forces to Materials Processing” supported by the technical division of high-temperature processing, ISIJ.

REFERENCES

- 1) S. Asai: *Sci. Tech. Adv. Mater.*, **1** (2000), 191.
- 2) D. E. Farrell, B. S. Chandrasekhar, M. R. Deguire, M. M. Fang, V. G. Kogan, J. R. Chem and D. K. Finnemore: *Phys. Rev. B*, **36** (1987), 4025.
- 3) A. Lusnikov, L. L. Miller, R. W. McCallum, S. Mitra, W. C. Lee and D. C. Johnston: *J. Appl. Phys.*, **65** (1989), 3136.
- 4) A. Lusnikov, L. L. Miller, R. W. McCallum, S. Mitra, W. C. Lee and D. C. Johnston: *J. Appl. Phys.*, **65** (1989), 3136.
- 5) M. R. Lees, D. Bourgault, P. De Rango, P. Lejay, A. Sulpice and R. Tournier: *Philos. Mag. B*, **65** (1992), 1395.
- 6) A. Holloway, R. W. McCallum and S. R. Arrasmith: *J. Mater. Res.*, **8** (1993), 727.
- 7) P. Courtois, R. P. De La Bahie and R. Tournier: *J. Magn. Magn. Mater.*, **153** (1996), 224.
- 8) K. Sassa, T. Morikawa and S. Asai: *J. Jpn. Inst. Met.*, **61** (1997), 1283.
- 9) P. Gillon: *Mater. Sci. Eng. A*, **287** (2000), 146.
- 10) S. Awaji, K. Watanabe and M. Motokawa: *J. Cryst. Growth*, **226** (2001), 83.
- 11) P. de Rango, M. Lees, P. Lejay, A. Sulpice, R. Tournier, M. Ingold, P. Germi and M. Pernet: *Nature*, **349** (1991), 770.
- 12) J. E. Tkaczyk and K. W. Lay: *J. Mater. Res.*, **7** (1990), 1368.
- 13) S. Shimotomai and K. Maruta: *Scr. Mater.*, **42** (2000), 499.
- 14) K. Maruta and M. Shimotomai: *J. Cryst. Growth*, **237–239** (2002), 1802.
- 15) H. Yasuda, I. Ohnaka, K. Shimamura, T. Fukuda and K. Watanabe: Proc. 3rd Int. Symp. on Electromagnetic Processing of Materials, ISIJ, Tokyo, (2000), 647.
- 16) T. Mitui: *J. Phys. Soc. Jpn.*, **13** (1958), 549.
- 17) C. W. Berghout: *J. Phys. Chem. Solids*, **24** (1963), 507.
- 18) G. Abersfelder, K. Noack, K. Stierstadt, J. Schelten and W. Schatz: *Philos. Mag.*, **41** (1980), 519.
- 19) T. Fujii, T. Ono and M. Kato: *J. Jpn. Inst. Met.*, **61** (1997), 267.
- 20) Desk Handbook Phase Diagrams for Binary Alloys, ed. By H. Okamoto, ASM International, Ohio, USA, (2000), 245.
- 21) M. Shimaoka, I. Ohnaka, I. Yamauchi and M. Maeda: *J. Jpn. Inst. Met.*, **61** (1997), 1115.
- 22) Y. Nakagawa: *Acta Metall.*, **6** (1958), 704.
- 23) A. Munitz and R. Abbaschian: *J. Mater. Sci.*, **26** (1991), 6458.
- 24) A. Munitz, S. P. Elder-Randall and R. Abbaschian: *Metall. Trans. A*, **23A** (1992), 1817.
- 25) A. Munitz and R. Abbaschian: *J. Mater. Sci.*, **33** (1998), 3639.
- 26) X. Song, S. W. Mahon, R. F. Cochrane, B. J. Hickey and M. A. Howson: *Mater. Lett.*, **31** (1997), 261.
- 27) D. Li, M. B. Robinson, T. J. Rathz and G. Williams: *Mater. Lett.*, **36** (1998), 152.
- 28) Z. Sun, X. Song, Z. Hu, S. Yang, G. Liang and J. Sun: *J. Alloys Comp.*, **319** (2001), 266.
- 29) I. Ohnaka: T. Fukusako, T. Ohmichi, T. Masumoto, A. Inoue and M. Hagiwara: Proc. 4th Int. Conf. on Rapidly Quenched Metals, Japan Inst. Metals, Sendai, (1981), 31.
- 30) W. Sucksmith and J. E. Thomson: *Proc. R. Soc. (London) A.*, **225** (1954), 362.
- 31) Magnetic Properties of Metals (Data in Science and Technology), ed. by H. P. J. Wijn, Springer-Verlag, Berlin, (1991), 13.