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The microstructure and magnetic properties of nano-scale Fe magnetic particles precipitated in a Cu–Fe alloy

The evolution of nano-scale Fe particles precipitated in a Cu–Fe alloy has been examined from the viewpoint of the relationship between the microstructure and magnetic properties, using conventional, high-resolution and Lorentz electron microscopy, and magnetic measurements. It has been revealed that spherical Fe particles have a tendency to align along the $\langle 001 \rangle$ direction in a Cu matrix at the early stage of precipitation. A twin-like structure developed when spherical Fe particles grew to approximately 40 to 60 nm in size. Lorentz microscopy was successfully applied to determine the direction and magnitude of the magnetic momentum of Fe particles.

Keywords: Cu–Fe alloy; Lorentz microscopy; Precipitation; Nano-scale particle

1. Introduction

Ferromagnetic particles have recently attracted considerable attention, as it may be possible to use them in various magnetic devices and next-generation storage applications. Despite the desirability of reducing the size of magnetic domains to further improve magnetic storage devices, refining the magnetic recording unit does not always lead to improvements, due, for example, to the appearance of superparamagnetism when the particle size is of the order of several nanometers. In addition to the innovative practical applications, the discovery of the giant magnetoresistance-effect in substances containing nano-granular magnetic particles has made it necessary to conduct fundamental research to understand the structures and the magnetic properties of nano-scale magnetic particles. According to the equilibrium phase diagram, the fcc γ -Fe phase is stable at temperatures between 1185 and 1667 K, whereas bcc α -Fe becomes stable below 1185 K. However, Bitter reported that small Fe particles had an fcc structure even below 1185 K [1]. Kinsman claimed that α -Fe particles comprised $\{112\}$ twins of the order of 5 to 50 nm in width [2]. There have been a number of studies on the structure and the magnetic properties of Cu–Fe alloys investigated by Mössbauer measurements and X-ray and neutron diffraction. Abraham has reported that neutron diffraction revealed Fe precipitates in a Cu matrix to be antiferromag-

netic γ -Fe [3]. Using low-temperature X-ray diffraction, Tsunoda pointed out that the lattice modulation of nano-scale Fe particles can be described as a periodic spin wave [4]. Gonser et al. investigated the Néel temperature of γ -Fe precipitates in a Cu matrix by Mössbauer measurements [5]. Mössbauer and X-ray analysis give us locally-averaged information about the structure. The magnetic properties of nano-scale particles are, however, also very sensitive to their local microstructures. Thus it is essential to investigate how the microstructure relates to the magnetic properties. Transmission electron microscopy (TEM) and Lorentz microscopy allow us to observe the details of microstructures and the distribution of the magnetic domains in a localized area. The purpose of this study was to investigate the relationship between the precipitation behavior of nano scale Fe particles and the magnetic properties in a Cu–Fe alloy.

2. Experimental procedure

The present study used Cu-3 at.% Fe alloy specimens. The alloy ingots were produced by arc-melting in an argon atmosphere. After subsequent annealing and rolling, disk-shaped specimens of thickness 200 μm were obtained and sealed in an evacuated silica tube. The specimens were solution-treated at 1323 K (1050 °C) for 180 min, then quenched in iced water at 273 K (0 °C). After the solution treatment, isothermal annealing was conducted at 873 K (600 °C) for various periods. The TEM specimens were finally obtained by electro-polishing. TEM observations were performed using a 200 kV HITACHI H-800 and a JEOL JEM-3010F transmission electron microscopes. The magnetic domain structure was observed in the low-angle diffraction (LAD) mode using a TOPCON EM-002BL Lorentz microscope. SQUID measurements were conducted to obtain the magnetization vs. temperature curves from 5 K to 350 K under a small applied-field of 7958 A m⁻¹ (100 Oe) using a Quantum Design MPMS-XL SQUID Magnetometer.

3. Results and discussion

3.1. Precipitation processes in a Cu–Fe alloy

TEM observations were conducted to examine the precipitation processes occurring in a Cu–Fe alloy. Figure 1

Fig. 1. Bright field TEM images of Cu-3 at.% Fe alloy aged at 873 K for (a) 500 min, (b) 2000 min, and (c) 20000 min.

shows bright-field TEM images of Cu-3 at.% Fe alloy annealed isothermally at 873 K for (a) 500 minutes, (b) 2000 min, and (c) 20000 min. No precipitates were found immediately after iced-water quenching, indicating that Fe atoms are still in supersaturated solid solution. After annealing for 100 min, very small precipitates appeared in the Cu matrix. After further annealing at 873 K, Fe precipitates evolved as spherically-shaped particles 10 to 20 nm in size. The Fe precipitates continued growing to 40 nm in size, and finally incoherent precipitates over 40 nm in size appeared, accompanied by interfacial dislocations. Figure 2a shows the microstructure of the specimen annealed for 1000 min, corresponding to the late coherent stage of the precipitation process. An interesting feature in the formation of the precipitates may be seen in this micrograph, namely that pairs of precipitates of similar size were linearly arranged along the $\langle 001 \rangle$ direction of the Cu matrix. This tendency was also found in a Cu–Co alloy, reported by Takeda et al. [6]. In Cu–Fe the tendency is less marked than in a Cu–Co alloy. After the precipitates grew to 35 to

45 nm in size, narrow stripes approximately 5 to 10 nm wide appeared in the Fe particles, as shown in Fig. 2b. The average width of the layered domains comprising the stripes increased as the particles became larger.

3.2. High resolution TEM observations

Previous studies on Cu–Fe alloys have adopted the interpretation that both fcc γ -Fe and bcc α -Fe are present in the Fe precipitation process. However, the details of the transition between the two phases have not been fully investigated. We conducted HRTEM observations, SQUID magnetic property measurements, and Lorentz microscopy to investigate this point. Figure 3 shows high-resolution TEM images of the coherent (a), and incoherent precipitates (b), respectively. Lattice fringes were observed outside the Fe particles, corresponding to the (200) planes of the Cu matrix. Two lattice fringes perpendicularly crossing with each other are observed in a Fe particle in Fig. 3a. Using the (200) lattice spacing value of the Cu matrix as a reference,

Fig. 2. Bright field TEM images of Cu-3 at.% Fe alloy aged at 873 K (a) The arrow indicates a pair of linearly arranged Fe particles, (b) twin-like structure.

Fig. 3. High resolution TEM images of precipitates in a Cu-3 at.% Fe alloy aged at 873 K (a) linearly arranged Fe particles, (b) twin. Inset top-right is an enlarged image of the microstructure of the particle.

Fig. 4. (a) Magnetization vs. temperature curves for Cu-3 at.% Fe alloy aged at 873 K for 100 min, 2000 min, 10000 min, and 20000 min. (b) ZFC curve obtained from the specimen annealed for 2000 min (c) FC curve obtained from the specimen annealed for 2000 min. Vertical scale is Bohr magneton per α -Fe atom.

the widths of the two orthogonal lattice fringes are estimated at 0.177 nm and 0.180 nm, respectively. We calculated the lattice spacings under the assumption that the crystal structure of Fe particles is fcc or bcc. This calculation showed that the lattice fringes observed in the TEM images could be from either the {200} planes of the fcc structure or from {110} planes of the bcc structure. Thus two possibilities are suggested that coherent Fe particles in a Cu matrix have either the fcc structure or the bcc structure. Figure 3b shows a microstructure different from the feature shown in Fig. 3a. The Fe particles consist of layered domains. The width of the lattice fringes inside the layers is approximately 0.203 nm. This value almost corresponds to the lattice spacing of {110} planes of α -Fe in a bcc structure. The lattice fringes are symmetrically inclined at an angle 55 degrees to the interfaces of the layers. It is probable that the lattice fringes observed in Fig. 3b correspond to the {110} planes of bcc Fe. This result also agrees with the fact that the twin plane of bcc bulk Fe is the {112} plane. This present result is similar to that obtained by Kubo et al. [7].

3.3. Measurements of magnetic properties

Magnetization vs. temperature ($M(T)$) measurements were performed using a SQUID magnetometer to investigate the magnetic properties of the Cu-3 at.% Fe specimens. Figure 4a shows $M-T$ curves obtained for specimens annealed at 873 K for 100 min, 2000 min, 10000 min, and 20000 min, under an applied field of 7958 A m^{-1} (100 Oe) in a temperatures range 5 K to 350 K. The magnetization of $M(T)$ curve was larger, the longer the annealing time. This indicates that Fe particles tend to become ferro-

magnetic with increasing annealing time. Figure 4b and c show the ZFC and FC curves obtained from the specimen annealed for 2000 min. Both curves exhibit a small cusp at around 40 K. Similar features were found in other specimens annealed for ≤ 10000 min, except the specimen annealed for 100 min. These cusps are commonly observed in $M(T)$ curve and associated with antiferromagnetism. Table 1 shows the relationship between aging time and the temperature at which the small cusp appeared. All the values are close to the Néel temperature of 44 K for bulk Fe [8]. We refer that the cusps originate from the formation of antiferromagnetic γ -Fe particles. As shown in Fig. 4a, the maximum magnetization value of 0.04 (μ_B per Fe atom) of the sample annealed for 20000 min was much higher than that of the others. No cusp was observed at around 40 K in this sample. These results indicate that γ -Fe transforms to α -Fe after a long period of annealing without plastic deformation. In the TEM observations, there is the possibility that the transition from fcc to bcc is caused by thinning of the foil during electropolishing, as suggested by Kubo [7].

Table 1. Relationship between the average particle size and the temperature at which small cusps appeared on $M(T)$ curves.

Aging time (min)	Average particle size (nm)	Cusp Temperature (K)
500	14.14	55
1000	19.77	40
2000	39.15	40
5000	44.24	40
10000	52.70	55

Fig. 5. (a) Electron diffraction spot of (220) reflection obtained from a specimen containing Fe particles ~ 15 nm in size using Lorentz microscope. Satellite spots are seen along the [100] and [010] directions. The beam deflection corresponds the direction of magnetization of Fe particles. (b) Electron diffraction spot obtained from a specimen containing Fe particles ~ 50 nm in size. Satellite spots are observed in the [110] direction.

However, the specimens for SQUID magnetic measurements were not polished or thinned. Therefore, γ -Fe precipitates are likely to transform spontaneously to α -Fe without a change of strain field around the precipitates. If we regard the cusp as the Néel temperature, the present results suggest that the particles retained the gamma structure up to a size of 50 nm after which they transformed to α -Fe.

3.4. Lorentz microscopy observations

In order to verify the direction and magnitude of the magnetization of Fe particles, we conducted low-angle diffraction (LAD) using Lorentz microscopy [9]. When electrons travel in magnetic materials, the incident electrons are deflected by the Lorentz force due to magnetization of the specimen. The deviation from the normal Bragg reflections due to the Lorentz force can be detected using Lorentz microscopy. We examined eight specimens with particle sizes of approximately 10 to 60 nm. Two examples of LAD are shown in Fig. 5. Previous studies have reported that the easy axis of magnetization of bcc α -Fe is almost parallel to the $\langle 100 \rangle$ orientation. The deviation of the Bragg reflection occurs in the direction perpendicular to both the electron beam and magnetic field. Thus it is essential to observe the deflection of the electron beam from the [001] zone axis. Satellite spots are seen along the [100] and [010] directions. Because the particles are very small, the spots are rather fuzzy, so the deflection spots assume to shape of a cross with arrows along [100] and [010]. We also observed $\langle 110 \rangle$ additional spots in Fig. 5b when particles have a size exceeding 45 nm. As far as the elongation along $\langle 100 \rangle$ is concerned, the present result confirms that the easy axis of magnetization of α -Fe is the $\langle 100 \rangle$ orientation. The origin of the $\langle 110 \rangle$ additional spots has not yet been identified. Tsunoda et al. reported that a lattice modulation occurred in a small Fe particle [4]. The $\langle 110 \rangle$ extra spots may relate to such a lattice modulation. Using LAD, the intensity of magnetization can also be estimated. We measured the distance between the fundamental and extra spots, and estimated the intensity of magnetization at each stage of the precipitation process. The Lorentz force generated by magnetic field $\mathbf{B}$ is given by:

$$\mathbf{F} = -e(\mathbf{v} \times \mathbf{B}) \quad (1)$$

where e is the electric charge and $\mathbf{v}(v_x, v_y, v_z)$ is the electron velocity. By Newton's law, the rate of change of the momentum of an electron caused by the Lorentz force is

written as:

$$\left\{ \begin{array}{l} m \frac{dv_x}{dt} = ev_y B \\ m \frac{dv_y}{dt} = -ev_x B \\ m \frac{dv_z}{dt} = 0 \end{array} \right\} \quad (2)$$

where m is the electron mass. Since the deflection of the electrons is very small, the direction of $\mathbf{B}$ is set along the z axis. By setting the initial condition and the velocity of the incident electron to v , we obtain the following equation:

$$\left\{ \begin{array}{l} x = \frac{mv}{eB} \sin \frac{eB}{m} t \\ y = \frac{mv}{eB} \left(\cos \frac{eB}{m} t - 1 \right) \end{array} \right\} \quad (3)$$

As is evident from Eq. (3), the incident electrons rotate with a radius of $\frac{mv}{eB}$. Hence, the deflection angle ϕ is written as

Fig. 6. The relationship between deflection angle and particle size. The solid and broken lines refer to the calculated angles for the α -Fe and γ -Fe particles, respectively. The deflection angles experimentally obtained increases at ~ 45 nm in size. The large increment of the angle suggests that the structural transformation from γ -Fe to α -Fe occurs at particles sizes of around 45 nm.

follows:

$$\varphi = \frac{eB d \lambda}{h} \quad (4)$$

where λ is the wavelength of the electron beam and h is Planck's constant. The results of the present investigation are shown in Fig. 6. The solid and broken lines refer to the calculated angles for the α -Fe and γ -Fe particles, respectively. We found that the experimental values of the deflection angles are somewhat greater than calculated with Eq. (4). An approximate correction for the deflection angle has been made by shifting the value obtained for smallest particle size (15 nm) onto the fcc calculated line. After this correction, the experimental values obtained from the particles greater than 45 nm in size tended to deviate from the fcc calculated value and transfer to the bcc theoretical curve. These results seem consistent with structural transformation $\gamma \rightarrow \alpha$, described in Section 3.3. The reason for the difference between the experimental and calculated values is not yet clear. The corrected angles obtained from particles of size less than 45 nm lie close to the theoretical value of γ -Fe, while those from particles larger than 45 nm roughly coincide with the theoretical value of α -Fe. This suggests that the structural transformation from γ -Fe to α -Fe occurs when the particle grows to around 45 nm in size. This value is somewhat greater than the value obtained from the magnetic measurements. This difference may be attributed to the size distribution. Thus the present study has obtained some important information about the microstructure and the magnetic properties of nano-scale Fe particles formed in a Cu matrix. The details of the magnetic domain structures provide a very interesting subject for further study. Lorentz TEM in Foucault mode is suggested as a suitable approach to gain information on the structure. A further study is intended by the present research group.

4. Conclusions

We have examined the relationship between the microstructure and the magnetic properties of Cu-3 at.% Fe using TEM observations, SQUID magnetic measurements, and Lorentz microscopy. It has been found that:

1. Fe particles gradually evolved from spherical coherent particles to incoherent particles.
2. At the late coherent stage, α -Fe particles comprise layered domains with a twin relation.
3. The particles with twin-like structure most probably have a bcc structure.
4. The transformation from γ -Fe to α -Fe occurs when Fe particles grow to around 45 nm in size.

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