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The relationship between the microstructure and the magnetic properties of nano-scale magnetic particles in a Cu–Fe–Co ternary alloy

The relationship between the microstructures and the properties of nano-scale Fe–Co magnetic particles formed in a copper alloy was investigated. Several structural aspects and physical properties of Fe–Co precipitates were investigated simultaneously using transmission electron microscopy, high resolution transmission electron microscopy, and superconducting quantum interference device magnetometry. The microstructure and magnetic properties of precipitates comprising both Fe and Co atoms evolved with isothermal annealing at 873 K. We found that the evolution of small coherent precipitates obeys the Ostwald ripening law; however, the coarsening rate of the particles increased after coherent particles transformed into incoherent precipitates. The coercive force varied, correlating with the evolution of precipitates.

Keywords: Cu–Fe–Co; Precipitation; Nano-scale magnetic particles; TEM; HRTEM

1. Introduction

In recent years, granular magnetic materials, in which magnetic particles are embedded in metal matrices, have been studied intensely because of their widespread application for ultra-compact magnetic storage devices. Besides their practical applications, granular magnetic materials are of fundamental interest for studying physical phenomena such as spin-/cluster-glass behavior, superparamagnetism, and the kinetics of coarsening and precipitation. The discovery of giant magneto-resistance (GMR) by Berkowitz [1] in an immiscible binary Cu–Co alloy system has further stimulated attention towards these materials especially in the last decade. A number of studies have been made on nano-scale magnetic precipitates in copper alloys, using neutron and X-ray diffraction, transmission electron microscopy (TEM), Mössbauer spectroscopy, superconducting quantum interference device (SQUID) magnetometry, and other techniques. These studies have demonstrated that the magnetic properties of metallic particles are sensitive to their microstructure including their sizes, shapes, and composition.

According to the Cu–Fe phase diagram, large Fe-rich precipitates in Cu–Fe alloys are expected to have the body-centered cubic lattice (bcc) structure below a temperature of 1130 K. However, small Fe particles keep the

face-centered cubic lattice (fcc) structure even below 1130 K in the initial stage of precipitation, retaining their coherency to the Cu matrix. Furthermore, a lattice modulation similar to pre-martensite or some type of diffusionless transformation has also been reported [2]. In this context, Kubo et al. claimed that Fe precipitates which formed at the edges of thin foils transformed without plastic deformation [3], although Abraham concluded that fcc precipitates do not transform into the bcc phase on simple cooling [4]. In a TEM study conducted by the present authors, bcc Fe precipitates with layered domains, which are similar to those reported by Kubo, were observed during isothermal annealing without plastic deformation. It was confirmed by high resolution transmission electron microscope (HRTEM) that layered domains with alternating light and dark contrast in Fe precipitates were due to a twin-like structure. These characteristic features of nano-scale Cu–Fe particles have not been seen explicitly in other alloy systems such as Cu–Co, although a linear alignment of coherent Co precipitates without any external stress field have been observed by TEM [5–7]. Relatively little is known about the microstructure of Cu–Fe–Co alloys as compared with Cu–Fe or Cu–Co alloys [8]. The different trends of precipitation occurring in Cu–Fe and Cu–Co alloys also suggest that it is of interest to investigate precipitation in a ternary Cu–Fe–Co alloy system. The present study aimed to clarify the precipitation process and magnetic properties appearing in Cu–Fe–Co alloys, combining TEM observations with measurements of magnetic properties by SQUID magnetometry.

2. Experimental

The specimens of Cu–Fe–Co alloy investigated in this study were prepared from pure metals by arc melting. We prepared four alloys with differing solute compositions and Fe:Co ratios as listed in Table 1. After arc melting, the ingots were cold rolled to a thickness of approximately 130 μm , with intermediate annealing at 923 K in a salt bath. In order to obtain the microstructure in solid solution, a solution-treatment was carried out at 1273 K in evacuated quartz capsules using an infrared furnace, following by quenching into ice water (273 K). The specimens were then annealed at 873 K and 973 K for various periods up to 10000 min, and subsequently quenched into ice water.

Table 1. The chemical compositions of the alloy specimens.

	composition (at.%)				
	Cu	Fe	Co	Percentage of solute	Fe : Co
Cu-0.8 at.% Fe-0.2 at.% Co	99	0.8	0.2	1 %	4 : 1
Cu-0.6 at.% Fe-0.4 at.% Co	99	0.6	0.4	1 %	3 : 2
Cu-2.4 at.% Fe-0.6 at.% Co	97	2.4	0.6	3 %	4 : 1
Cu-1.8 at.% Fe-1.2 at.% Co	97	1.8	1.2	3 %	3 : 2

Bright field TEM observations were performed to confirm the microstructures of specimens for each stage of the annealing process. The final specimens for TEM observations were prepared by conventional electro-polishing in a solution of methanol and nitric acid, and observed using a HITACHI H-800 transmission electron microscope operated at 200 kV for bright-field image observations and a 300 kV JEOL JEM-3010F field emission transmission electron microscope for high-resolution imaging. All TEM images were taken along the [001] zone axis of the Cu matrix. The magnetization measurements were conducted with a Quantum Design MPMS SQUID magnetometer. Complete hysteresis loop (M-H curves) were obtained with magnetic field, $-4 \text{ T} \sim 4 \text{ T}$.

3. Results and discussion

3.1. The microstructure of Cu-Fe-Co alloys

We first examined the evolution of the microstructures of four specimens after isothermal annealing at 873 K. Figure 1 shows bright field TEM images of the microstructures of Cu-2.4 at.% Fe-0.6 at.% Co aged for (a) 0 min, (b) 1000 min, (c) 2000 min, and (d) 10000 min, respectively. As shown in Fig. 1a, immediately after the solution-treatment, no precipitates were visible. It is possible that precipitates were present but were too small to be seen in the instrument we used, but neither streaks nor extra spots were observed in electron diffraction patterns. Figure 1b shows the precipitates in a specimen annealed for 1000 min. The precipitates were about 15 nm in size and were randomly distributed throughout the Cu matrix, as is often seen in other alloys such as Cu-Cr. The electron microscope contrast seems consistent with coherent, spherical precipitates in this early stage of precipitation. The equilibrium structure of bulk Fe-Co, according to the equilibrium phase diagram, is bcc (A2), B2 or hexagonal close-packed structure (hcp). This was confirmed by electron diffraction, which showed that the crystal structure of the precipitates was fcc, as inherited from Cu matrix. After annealing for 2000 min, the coherent precipitates, now about 20 nm in size, were linearly aligned in pairs along the $\langle 100 \rangle$ directions of the Cu matrix as seen in Fig. 1c. This feature was also found in our previous study of Co precipitates in a Cu matrix [6]. After annealing for 5000 min, large irregular-shaped precipitates, which were tangled with interfacial dislocations, appeared among spherical coherent precipitates. The interfacial dislocations indicate that the large precipitates had lost their coherency to the Cu matrix and had become incoherent, as seen in Fig. 1d.

Fig. 1. Bright-field images of Cu-2.4 at.% Fe-0.6 at.% Co aged at 873 K for (a) 0 min, (b) 1000 min, (c) 2000 min, and (d) 10000 min. The arrows in (c) indicate of a pair linearly arranged Fe particles

Fig. 2. High-resolution TEM images of Cu-1.8 at.% Fe-1.2 at.% Co aged at 973 K for (a) 100 min, and (b) 1000 min.

Since it is difficult to investigate the detailed shapes of particles by conventional TEM due to dynamical diffraction effects, we conducted HRTEM observations. Figure 2 shows HRTEM images of Cu-1.8 at.% Fe-1.2 at.% Co annealed at 973 K for (a) 100 min and (b) 1000 min. At the earlier stage of the annealing process, particles had diameters of 10–15 nm and were spherical in shape, as shown in Fig. 2a. After annealing for 5000 min, cubic precipitates with nearly (100) planes and round corners were observed. Similar-shaped coherent precipitates have been observed in Cu-Co [9]. It seems that coherent precipitates are initially spherical, and gradually change into a cubic shape with round corners as they grow. Onaka et al. interpreted the transition from spherical to cubic shape, by taking the strain field energy and interfacial energy into consideration [10].

In order to examine the coarsening processes of Cu-Fe-Co, we measured the volume fraction, growth rate and size

Fig. 3. Total volume of Fe-Co precipitates formed in a Cu matrix of Cu-0.8 at.% Fe-0.2 at.% Co and Cu-0.6 at.% Fe-0.4 at.% Co.

distribution of the precipitates. Figure 3 shows the change of the volume fraction of Fe-Co precipitates with annealing time for Cu-0.8 at.% Fe-0.2 at.% Co and Cu-0.6 at.% Fe-0.4 at.% Co. For both materials, the volume of the precipitates initially increased with annealing time up to 500 min, and then remained constant between 500 min and 2000 min. Beyond an annealing time of 5000 min, the total volume of precipitates for each composition seems nearly saturated. Figure 4 shows curves of the mean size of the precipitates vs. the one-third power of annealing time for (a) Cu-0.8 at.% Fe-0.2 at.% Co, (b) Cu-0.6 at.% Fe-0.4 at.% Co, (c) Cu-2.4 at.% Fe-0.6 at.% Co, and (d) Cu-1.8 at.% Fe-1.2 at.% Co. For the first 2000 min, the particle size in each case is proportional to the one-third power of the annealing time. However for annealing times greater than 5000 min,

all of the curves deviate upwards from a straight line. It has been reported that the coarsening process of Cu-Fe and Cu-Co alloys is subject to the theory of Ostwald ripening [6, 11, 12]. According to this theory, the following conditions should hold: first, the shape of precipitates remains essentially unchanged; second, the volume fraction of precipitates remains constant; and third, the particle size is proportional to the one-third power of the annealing time. The present TEM observations confirm that all of these conditions are met at annealing times <2000 min. This indicates that the growth of Fe-Co precipitates in a Cu matrix is essentially similar to Ostwald ripening in the initial stage of annealing [16]. At annealing times longer than 5000 min, both the total volume of precipitates and their mean sizes are larger than those predicted by Ostwald ripening theory. Little information is available on the relationship between the lattice coherency and growth rate of particle. However it is reported experimentally that loss of coherency leads to an increase in the growth rate of particles in Cu-Co and Al-Sc alloys [6, 13]. The equilibrium structure of large Fe-Co precipitates is bcc. A structural transformation from fcc to bcc is therefore expected to occur when the precipitates reach a size large enough to overcome the constraint from the Cu matrix. Kuwano et al. reported that Fe-Co precipitates transformed martensitically from fcc into bcc even with no plastic deformation under an annealing condition similar to that employed in this study [14]. As mentioned above, the present TEM observations confirmed that large precipitates accompanied by interfacial dislocations appeared among coherent precipitates after a long ageing time, Fig. 1d. Figure 5 shows the size distribution of precipitates formed in Cu-0.8 at.% Fe-0.2 at.% Co. These distributions fall into two types, with narrow and broad peaks respectively. The size distributions in specimens annealed for periods up to 2000 min show a narrow distribution with a

Fig. 4. The mean size of Fe-Co precipitates vs one-third power annealing time for (a) Cu-0.8 at.% Fe-0.2 at.% Co, (b) Cu-0.6 at.% Fe-0.4 at.% Co, (c) Cu-2.4 at.% Fe-0.6 at.% Co, and (d) Cu-1.8 at.% Fe-1.2 at.% Co.

Fig. 5. The size distributions of the precipitates formed in Cu-0.8 at.% Fe-0.2 at.% Co aged at 873 K.

sharp peak. However, in specimens annealed for more than 5000 min there are broader distributions in size. The same trends have been reported in a Cu-Co alloy [6]. Broader size distributions reflect the transformation of Fe-Co precipitates from fcc into bcc.

3.2. The magnetic properties of Cu-Fe-Co alloys

In the previous section, we described how the microstructures of Cu-Fe-Co alloys evolve with annealing time. Since the magnetic properties of the precipitates depend on their microstructure, we examined the magnetic properties of the specimens using a SQUID magnetometer, measuring

the hysteresis curves of the specimens at each stage of the annealing process. Figure 6 shows the saturation magnetization and coercivity of Cu-0.8 at.% Fe-0.2 at.% Co. The saturation magnetization increased with annealing time at the early stage of the precipitation process. The saturated curve attained a maximum value of approximately $1.8 (\mu_B/\text{atom})$ at 1000 min, and the saturation remained constant up to 10000 min. This fact suggests that precipitation has almost been completed within the early stage of the annealing process. This is also consistent with the TEM measurement of volume fraction of precipitates, shown in Fig. 3.

Few close studies have been performed so far on the relationship of the microstructure and the coercive force of materials containing nano-scale magnetic particles. The present measurements revealed that the coercivity first increased, reached a maximum value of $1.711 \times 10^4 \text{ A} \cdot \text{m}^{-1}$ (215 Oe) at an annealing time of 2000 min, and then decreased. As seen in Fig. 1c, at an annealing time of 2000 min particles were assembled and linearly aligned, whereas at an earlier stage of annealing they were randomly distributed in the matrix. At this stage, the separations of paired particles became smaller. Based on the previous work by Luborsky and Paine [15], the increase in the coercive force suggests that precipitates consist of single magnetic domains at the early stage of annealing process. In this case it is expected that the peak of the coercivity occurs as a result of magnetic interaction between paired particles. The reason that the coercive force decreased after annealing for more than 2000 min is not fully understood, but it may suggest that multi-domain precipitates are formed. It is expected that the coercivity is dominated by the mobility of magnetic domain walls in bulk materials, and spin rotation is much more easily performed by domain-wall motion. One possible interpretation is that the transformation from single- to multiple-domain particles is associated with the structural transformation from fcc to bcc.

Fig. 6. The change of saturation magnetization and coercive force of Cu-0.8 at.% Fe-0.2 at.% Co with annealing time.

In order to test this hypothesis, in future studies of Cu–Fe–Co alloys we intend to apply Lorentz microscopy, which is capable of providing information on the magnetization of individual particles.

4. Conclusion

We have investigated the relationship between the microstructure and magnetic properties of Cu–Fe–Co alloys using TEM and SQUID magnetometry. The present investigation revealed:

1. At an early stage of evolution, particles were spherical and had an fcc structure, inherited from the Cu matrix. Particles were initially located randomly but at a somewhat later annealing stage a linear alignment of particles was found.
2. At a late stage of annealing, particles lost their coherency to the matrix.
3. The growth rate of incoherent particles was greater than that of coherent particles.
4. As the transformation of microstructure occurred, the coercivity of particles reduced.

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