Order-Disorder Transformation in Fe₅₀Co₅₀ Particles Synthesized by Polyol Process

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X-ray diffraction applied anomalous dispersion effect was used for characterizing the order-disorder transformation in Fe₅₀Co₅₀ fine particles synthesized by polyol process. The long range order parameter was estimated from the superlattice peak intensities in the diffraction pattern of particles annealed in the temperature range between 20 and 800°C. The results showed that fine particles of as-synthesized Fe-Co have a disordered structure at room temperature, while the ordered structure is present, to a great extent, in Fe-Co bulk alloys. The fine particles of the disordered alloy were transformed to the ordered state by annealing up to about 450°C. The magnetic properties of the Fe-Co alloy fine particles annealed at different temperatures were also investigated using a vibrating sample magnetometer, in which magnetic fields of up to 15 kOe were applied to samples at room temperature. The saturation magnetization of the as-synthesized particles increased with annealing temperature. This may be attributed to transformation from disordered to ordered structure, along with sintering. [doi:10.2320/matertrans.M2009251]

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1. Introduction

Fe-Co alloys are useful magnetic materials due to their soft magnetic properties with high magnetization and high Curie temperature.^{1,2)} Fe-Co alloys exhibit a face-centered cubic (fcc) structure (γ -phase) above 983°C and a body-centered cubic (bcc) structure (α -phase) below 983°C. They also show order-disorder transformation at about 730°C at Fe-50at% Co in the α -phase. Several studies have investigated the phase equilibrium³⁻⁵⁾ and order-disorder transformation^{6,7)} in Fe-Co binary systems. For studies on phase transformation, bulk Fe-Co alloys were prepared by melting. On the other hand, fine Fe-Co particles have been successfully synthesized by using a polyol process.⁸⁻¹⁰⁾ In the polyol process, Fe-Co alloy particles are prepared in a poly alcohol such as ethylene glycol (EG), which is used as both solvent and reducing agent to fabricate fine particles from dissolved cations. The solution reaction derived fine Fe-Co alloy particles are prospective to have any useful difference in the property of thermal order-disorder transformation from the bulk for which it is well known. The structural change, i.e. the order-disorder transformation in Fe-Co bulk alloys has previously been studied with respect to their physical properties such as the electrical resistivity, the specific heat and the magnetization.¹¹⁻¹³⁾ On the other hand, to determine directly the long range order parameter S from the intensity of diffraction, so-called “superlattice line” is useful to investigate the thermal order-disorder transformation behavior in the alloy system. For bulk Fe-Co alloys, although such structural analysis approached using neutron¹⁴⁾ or electron diffraction¹⁵⁾ have been studied, there is almost no report using X-ray diffractometry due to the marginal difference between Fe and Co in the amplitude value of the atomic X-ray scattering factor. In this study, the anomalous X-ray dispersion effect was applied to enhance the difference between the atomic scattering factors, and the order-disorder transformation behavior was investigated by using the superlattice diffraction intensity in the annealed fine Fe₅₀Co₅₀ alloy particles.

When conventional XRD measurements of Fe-Co alloys are carried out, it should be noted that a superlattice diffraction peak is hardly detected in the diffraction patterns of the alloys. This is due to very similar values of atomic scattering factors, f_{Co} for Co and f_{Fe} for Fe. The diffraction peak intensities of the superlattice peak lines, which is proportional to the square of structure factor $|F|^2 = (f_{\text{Co}} - f_{\text{Fe}})^2$, will be very small even if they were perfectly ordered. However, the superlattice lines can be detected with high enough intensity to analyze quantitatively by application of the anomalous X-ray dispersion phenomenon i.e. the variation of the atomic X-ray scattering factor in the energy region close to the specific absorption edges of corresponding elements.

The X-ray scattering factor of an atom is described by the following equation:

$$f(\sin \theta / \lambda, E) = f_0(\sin \theta / \lambda) + f'(E) + if''(E), \quad (1)$$

where f' and f'' are the real and imaginary parts of the anomalous dispersion terms, respectively. Figure 1(a) shows anomalous dispersion terms for Fe and Co as a function of X-ray energy. In general, because the structure factors F_{hkl} are proportional to the intensity I_{hkl} of the corresponding reflections h , k , and l , we have

$$I_{hkl} = |F_{hkl}|^2 \cdot p \cdot LP, \quad (2)$$

where $|F_{hkl}|^2$ are structure factors of hkl , p is the multiplicity factors and LP is the Lorentz polarization factor. Thus, the intensity of the 100 superlattice peak is expressed as $I_{hkl} \propto |F_{hkl}|^2$. Figure 1(b) shows the calculated structure factor or the relative intensity of 100 superlattice peak versus the X-ray energy. In XRD measurements using Cu K α with 8048 eV, the calculated intensity of a superlattice peak is considerably small. On the other hand, the diffraction intensity of the superlattice measured using Co K α with 6932 eV near the Fe K absorption edge (7111 eV) is relatively high due to the anomalous dispersion effect.

Fig. 1 (a) Anomalous dispersion terms in the atomic scattering factor and (b) $|F_{100}|^2$ versus x-ray energy.

2. Experimental Procedure

2.1 Sample synthesis

The Fe-Co alloy particles were synthesized by the polyol process. Fe chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$), Co acetate tetrahydrates ($\text{Co}(\text{CHOO})_2 \cdot 4\text{H}_2\text{O}$), and sodium hydroxide (NaOH) were dissolved in EG. For the synthesis of the Fe-Co alloy particles, the total concentrations of Fe and Co cations were fixed at 0.05 mol/L, while that of sodium hydroxide concentration was 40 mol/L. The EG-metal salt-OH salt solution was heated to the reaction temperature of 130°C and refluxed at this temperature for 1 h. After cooling to room temperature, the solid product was centrifuged and washed with ethanol several times to remove organic materials remaining in the final product.

2.2 Measurements

The XRD patterns of the $\text{Fe}_{50}\text{Co}_{50}$ alloy particles were measured by the X-ray diffractometer, Rigaku RINT2000 using Co K α radiation. The long range order parameter (S) of the as-synthesized and annealed fine particles was estimated from the intensity ratio between 100 superlattice and 110 fundamental lines. The morphology and chemical composition of the $\text{Fe}_{50}\text{Co}_{50}$ fine particles were analyzed by scanning electron microscopy (SEM) and electron probe micro analyzer (EPMA), respectively. The alloy particles were annealed from room temperature to 800°C for 1 h in an $\text{Ar} + 10\% \text{H}_2$ atmosphere. The magnetic properties were measured by a vibrating sample magnetometer (VSM), in

Fig. 2 XRD patterns of $\text{Fe}_{50}\text{Co}_{50}$ alloy fine particles using Co K α radiation.

which magnetic fields of up to 15 kOe were applied to samples at room temperature.

3. Results and Discussion

3.1 As-synthesized $\text{Fe}_{50}\text{Co}_{50}$ alloy fine particles

Figure 2 shows the XRD pattern of as-synthesized Fe-Co fine particles. The peak positions in the diffraction pattern are almost consistent with those given by the JCPDS data (Fe-Co: PDF#44-1433), and no oxide phase was observed. The lattice constant calculated from the XRD pattern is $a = 0.2858 \text{ nm}$, which is consistent with the value of $a = 0.2857 \text{ nm}$ reported for Fe-Co alloy sample prepared by mechanical alloying.¹⁶⁾ From the 110 reflection, the crystallite size of the fine particles was calculated to be 26 nm by Scherrer's formula, that is, $t = 0.9\lambda/B \cos \theta$ ($B = \text{FWHM}$).

As revealed by the narrow-range profile in Fig. 2, the diffraction peak of 100 and 111 superlattice line expected to be observed at $2\theta = 36.5^\circ$ and 65.7° , respectively, were not detected in this experiment.

This suggests that Fe-Co fine particles synthesized by the polyol process have a disordered structure.

The composition, shape and size of Fe-Co alloy particles can be controlled by varying the synthesis conditions such as metal ion concentration, reaction temperature, and hydroxyl ion concentration, as reported by Kodama *et al.*¹⁷⁾ The atomic composition of the Fe-Co alloy particles synthesized by the polyol process in this work was estimated to be Fe : Co = 50.7 : 49.3.

Figures 3(a) and (b) show a SEM image of as-synthesized Fe-Co alloy particles and a histogram of their size distribution. The results revealed that the $\text{Fe}_{50}\text{Co}_{50}$ particles were nearly cubic shaped and about 170 nm in size with a narrow size distribution. This indicated that they were formed through homogeneous nucleation and growth with little agglomeration.

The resultant different value of average crystallite size and particle size obtained from XRD and SEM analyses revealed that as-synthesized $\text{Fe}_{50}\text{Co}_{50}$ particles are polycrystalline with crystalline size as measured by XRD.

Fig. 3 (a) SEM image and (b) histogram of size distribution of Fe₅₀Co₅₀ fine particles synthesized from EG containing 0.05 mol/L metal ions. Here, particle size is defined as an averaged length of particle cube-edges in the SEM images.

Fig. 4 B-H hysteresis loops of Fe₅₀Co₅₀ fine particles synthesized from EG containing 0.05 mol/L metal ions and Fe₅₀Co₅₀ fine particles annealed at 725°C.

The magnetic hysteresis loops of the as-synthesized and annealed at 725°C FeCo alloy particles are shown in Fig. 4. These results indicated that the as-synthesized particles are ferromagnetic, and the saturation magnetization (M_S) of annealed sample increased to 230 emu/g from a value 187 emu/g for as-synthesized particles. Therefore, the magnetization values of the Fe-Co particles seemed to be lower than those of bulk materials.¹⁸⁾

3.2 Structural changes in Fe₅₀Co₅₀ fine particles by annealing

The crystallite size of annealed Fe₅₀Co₅₀ alloy particles was analyzed by means of XRD measurements. Figure 5(a) shows the XRD patterns of Fe₅₀Co₅₀ alloy particles annealed from room temperature to 800°C for 1 h in an Ar + 10% H₂ atmosphere. As the annealing temperature was increased,

Fig. 5 (a) XRD patterns and (b) crystallite size (110) of Fe₅₀Co₅₀ alloy fine particles annealed at different temperatures in Ar + 10% H₂ atmosphere.

the diffraction peaks became sharper and intense, indicating that the particles became well-crystallized.

Figure 5(b) shows the crystallite size of Fe₅₀Co₅₀ alloy particles annealed at different temperatures; the crystallite size was estimated based on the 110 diffraction peak profile. The crystallite size of as-synthesized Fe₅₀Co₅₀ alloy particles increased gradually with the annealing temperature up to 300°C and then increased more sharply at higher temperatures. In order to investigate the changes in crystallite size of Fe₅₀Co₅₀ alloy particles due to annealing, the morphology of samples annealed at 300, 600, and 700°C was observed by SEM as shown in Fig. 6. These micrographs show that the mean diameter of the particles was about 170 nm and sintering was not observed in the particles annealed at 300°C. On the other hand, sintering was observed in particles annealed at 600°C. These results can be explained with the results by the variation in crystallite size due to annealing, as shown in Fig. 5(b). The particles annealed below 300°C show structural change caused by sintering between crystallites in particle.

3.3 Structural transformation in Fe₅₀Co₅₀ fine particles by annealing

Figure 7 shows the X-ray diffraction peak profiles of 100 superlattice line of Fe₅₀Co₅₀ alloy particles annealed from room temperature to 800°C. The 100 superlattice peak was

Fig. 6 SEM images of annealed Fe₅₀Co₅₀ alloy fine particles at 300°C, 600°C, and 700°C.

detected in the range between 450 and 800°C. This indicates that disordered structures in the Fe₅₀Co₅₀ alloy particles synthesized by the polyol process were transformed to ordered structures by annealing and the critical transformation temperature is around 400°C.

In order to estimate the long range order parameter (S) of alloy particles, integrated intensities of 100 superlattice and 110 fundamental peaks were obtained from the measured diffraction patterns. S is related to the ratio $(I_{100}/I_{110})_s$ (observed from XRD peaks) to $(I_{100}/I_{110})_{s=1}$ (calculated under the assumption of complete ordering in Fe₅₀Co₅₀), as given by

$$S^2 = (I_{100}/I_{110})_s / (I_{100}/I_{110})_{s=1}. \quad (3)$$

The S value of the Fe-Co alloy particles synthesized by polyol process was almost zero at annealing temperatures up to 400°C and further increased above the temperature as shown in Fig. 8. In the case of rapidly quenched bulk Fe-Co alloy, the order-disorder transformation temperature (T_C) was 720°C and the maximum S value at 550°C was 0.92.¹⁹ On the other hand, the present results on fine particles appear to be different from those for the bulk alloy, as maximum S value of 0.94 was rerecorded at 800°C. This is considered to be consequence of slow cooling rate used in

Fig. 7 (100) Superlattice peak in the X-ray diffraction patterns of Fe₅₀Co₅₀ annealed at different temperatures; the patterns are obtained using Co K α radiation.

Fig. 8 Long range order parameter of Fe₅₀Co₅₀ versus annealing temperature.

this study. Disordered Fe₅₀Co₅₀ particles became ordered above 400°C and the crystallinity of the samples improved and become similar to that of bulk at 600°C. In the temperature region above T_C , the alloy particles became disordered with little defect in their crystallites. Therefore, the S value of Fe-Co particles slowly cooled from 800°C recorded the maximum.

When the alloy annealed up to 800°C is slowly cooled, the alloy temperature gradually decreases passing through the temperature range of high degree of order. Under this condition, the atomic ordering easily proceeds due to the high atomic mobility in the defect-free annealed crystallites. In the present experimental condition, the atomic ordering during the cooling process must be suppressed when the annealing temperature is decreased below 500°C.

Figure 9 shows the saturation magnetization (M_S) versus annealing temperature for the Fe₅₀Co₅₀ particles annealed from room temperature to 800°C for 1 h in an Ar + 10% H₂ atmosphere. The M_S of the as-synthesized sample was 187 emu/g and that of the samples annealed up to 400°C was

Fig. 9 Saturation magnetization of Fe₅₀Co₅₀ alloy fine particles versus annealing temperature.

210 emu/g. This M_s increasing at 400°C is considered to indicate starting to become ordered. After then, the M_s showed little changed up to 550°C due to almost no changing of the S value, and increase to 230 emu/g at 625–750°C above the critical temperature of sintering, 600°C.

4. Conclusions

The order-disorder transformation of Fe₅₀Co₅₀ fine particles synthesized by the polyol process was studied by X-ray diffraction structural analysis and magnetic property measurements. The synthesized Fe₅₀Co₅₀ fine particles were 170 nm in diameter and disordered structure. Long range order parameter estimated from a superlattice peak using anomalous dispersion effects showed that the ordering of this alloy occurs temperature above 400°C. Superlattice peaks, detected by X-ray diffraction using Co K α radiation, are effective in characterizing the ordered structures of Fe-Co particles. The saturation magnetization of the particles annealed in the range between 625 and 750°C increased to

about 230 emu/g, which may be attributed to transformation from disordered to ordered structure, along with sintering.

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