Magnetic Properties and Cation Distribution of Phosphorous-Doped Co-γ-Fe$_2$O$_3$ Particles

J. G. Na and D. H. Han

Division of Metals, Korea Institute of Science and Technology, Seoul 136-791, Korea
Institute of Physics, CAS, Beijing 100080, P. R. China

The effects of additional P-doping on the magnetic properties, thermal stability and cation distribution of Co-doped γ-Fe$_2$O$_3$ have been investigated by means of magnetic annealing and measurements with vibration sample magnetometer and torque magnetometer. It is found that the P-doping promotes the coercivity and its magnetic-thermal stability, which may be attributed to increase of the cubic magneto-crystalline anisotropy constant, K$_1$ and the activation energy, E, for cation rearrangement, respectively. The cation distribution of P and Co-substituted iron oxide was calculated from the variation of the saturation magnetization with P-doping on the basis of the Neel model. It was found that the most of P ions in the iron oxides occupied the B-site of spinel lattice.

1. Introduction

Acicular Co-doped γ-Fe$_2$O$_3$ is an important particulate medium for magnetic recording technology. However, the short-wavelength signal amplitude of the material reduces continuously with repeated playback because of thermal and mechanical instability. These instability are strongly dependent upon the distribution and chemical environment of Co^{2+} ions in the particles. There have been many efforts to get stable magnetic properties [1, 2].

Itoh et al. and Spada et al. reported that the coercivity, Hc, of acicular iron oxide particles could be increased by surface coating with sodium polyphosphate [3, 4]. They suggested that Hc was enhanced with surface anisotropy increase, which is result of an electrostatic coupling between the ferrous ions on the oxide surface and the phosphate groups in the chainlike polyphosphate.

Although there are many works on the effects of P-surface coating on iron oxide particles, there are few works on the P-doping into the lattice.

In this experiment, P was introduced into the lattice of particles by heat-treatments. The results show that the thermal stability of coercivity, as well as its absolute value is improved. A mechanism of the stability improvement is proposed from torque magnetometric experiments. The cation distribution was calculated from the variation of the saturation magnetization on the basis of the Neel model [5].

2. Experimental Procedure

Co-doped magnetic powders (denoted A$_i$) were prepared by surface coating with precipitation technique on starting acicular γ-Fe$_2$O$_3$ particles with 3.5 wt.% Co^{2+} and different Fe^{2+} contents followed by diffuse-in heattreatment. The starting oxide particles have an average length of 0.5 m, an aspect ratio of 10, a specific surface area of 18 m^2/g, coercivity of 430 Oe and specific saturation magnetization of 73.4 emu/g. The oxide particles were identified to be pure γ-Fe$_2$O$_3$ particles by X-ray diffraction. The mixture of raw materials in alkaline suspension was heated at 80 ℃ and stirred for 2 h. The modified particles were filtered, washed with deionized water, and dried for 12 hr at 80 ℃.

Co and P-doped magnetic powders (denoted B$_i$) were prepared by coating on γ-Fe$_2$O$_3$ particles with Co^{2+}, Fe^{2+} and P ions coincidently. The major procedures for preparing B$_i$ were the same as those of A$_i$, but (NH$_4$)$_2$HPO$_4$ was added in the solution.

The coprecipitated powders were dried at 80 ℃ for 1 day and heated at 370 ℃ in N$_2$ atmosphere for 2 h for diffusing Co^{2+}, Fe^{2+} and P ions into the core of γ-Fe$_2$O$_3$ particles.

The compositions and Fe^{+2} cations of samples were analyzed with the method of inductively coupled plasma (ICP) and wet chemical analysis, respectively. The compositions and Fe^{+2} cations of samples A$_1$-A$_6$ and B$_1$-B$_6$ are listed in Table I.

Magnetic sheets were prepared by coating the organic resin ink of the particles on polyester films and drying in the presence of an external magnetic field of 2 kOe at room temperature.

The magnetic field was applied in-plane direction of the sheets and maintained during the magnetic drying process.

Transverse magnetic field stabilities of the magnetic sheets were measured by using the method proposed by Eiling [6]. The sheets were annealed in a 3 kOe magnetic field perpendicular to the plane of the sheets at 90℃ for 12 h. The coercivities along the orientation direction are measured at various annealing steps.

The cation distribution of the oxide particles was calculated from the saturation magnetization on the basis of the Neel theory.

Table I. The Compositions of samples A_i and B_i.

Sample	Percent in mass			Sample	Percent in mass		
	Co	Fe^{2+}	P		Co	Fe^{2+}	P
A_1	3.61	0	0	B_1	3.60	0	1
A_2	3.47	2.8	0	B_2	3.51	2.1	1
A_3	3.39	5.0	0	B_3	3.41	4.4	1
A_4	3.34	6.4	0	B_4	3.38	5.1	1
A_5	3.25	8.5	0	B_5	3.35	5.9	1
A_6	3.22	9.2	0	B_6	3.35	6.0	1

3. Results and Discussion

Table II. lists that coercivities of sample A_1-A_3 and B_1-B_3 before and after magnetic annealing in perpendicular field.

As shown in Table II, coercivities of Bi particles are higher than those of A_i ones. Also it can be seen that Hc'/Hc, which represent the coercivity stability for the transverse magnetic annealing, shows that the magnetic thermal stability of sample A_1-A_3 is better than that of sample B_1-B_3. It is noticed that the Co^{2+} content of sample A_1-A_3 are nearly the same as that of sample B_1-B_3, correspondingly, but sample B_1-B_3 contain 0 wt.% P. It is obvious that the increased values are the contributions from P-doping.

Table II. The Coercivities of sample A_1-A_3 and B_1-B_3 before and after transverse magnetic annealing.

Sample	Hc$^{(a)}$ (Oe)	Hc'$^{(b)}$ (Oe)	Hc'/Hc (%)
A_1	696	703	100
A_2	815	719	85
A_3	939	717	74
B_1	752	752	100
B_2	840	790	94
B_3	961	787	82

(a) Coercivities before magnetic annealing.
(b) Coercivities after magnetic annealing.

In order to make sure the influence of uniaxial anisotropy on the magnetic coercivity of the particles, the induced uniaxial

anisotropy and cubic magnetocrystalline anisotropy of the particles was measured using a torque magnetometer. To get rid of the effect of Fe^{2+} ions on the magnetic anisotropy, sample A_1 and B_1 were chosen. The typical torque curves of samples A_1 and B_1 are shown in Fig. 1. It can be seen in Fig. 1 that there is a remarkable change between samples A_1 and B_1.
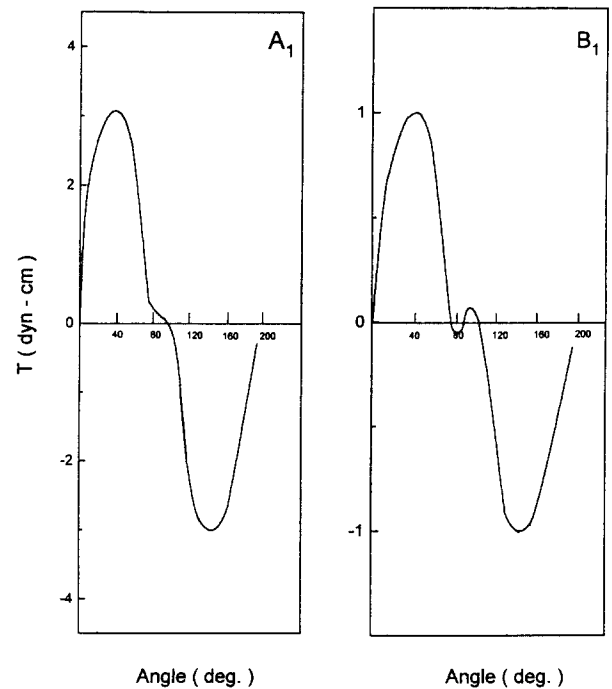

Fig. 1 Torque curves of sample A_1 and B_1.

If the particles contain magnetic uniaxial and cubic magnetocrystalline anisotropies simultaneously, the anisotropic energy E may be written as:

$$E = K_u \sin^2\theta + K_1(\alpha_1^2 \alpha_2^2 + \alpha_2^2 \alpha_3^2 + \alpha_3^2 \alpha_1^2) \qquad (1)$$

where K_u and K_1 are the uniaxial and cubic crystalline anisotropy constants, respectively, α_i the direction cosine of the magnetization, θ the angle between the magnetization and the long axis of the acicular magnetic particles.

Because the easy magnetization directions of γ-Fe₂O₃ and cobalt-substituted magnetite are [110] and [100], respectively, rewriting equation (1) in polar coordinates, gives

$$E = K_1 \cos^2(\pi/4 - \theta) \sin^2(\pi/4 - \theta) + K_u \sin^2 \theta \qquad (2)$$

and the torque is

$$T = -\partial E/\partial\theta = -1/2 K_1 \sin4(\pi/4 - \theta) - K_u \sin^2 \theta \qquad (3)$$

The magnetic torque curves of samples A_1 and B_1 were measured by a torque magnetometer and fitted with the theoretical curve (3).

Table III lists the calculated K_u and K_1 values for the sample

A₁ and B₁. It indicates that K₁ increases with P doping on particles, but K_u remains unchanged. The increasing coercivities of P-doping samples are caused by the increasing cubic crystalline anisotropy of these samples.

The dependencies of the normalized coercivity on the magnetic annealing time were measured to get the activation energy of Co and P and Co-doped iron oxide particles. Fig. 2 shows the results of the magnetic annealing experiments of A₃ and B₃.

Table III. Uniaxial anisotropic constant, K_u, and cubic magneto-crystalline anisotropic constant, K₁, of magnetic sheets A₁ and B₁.

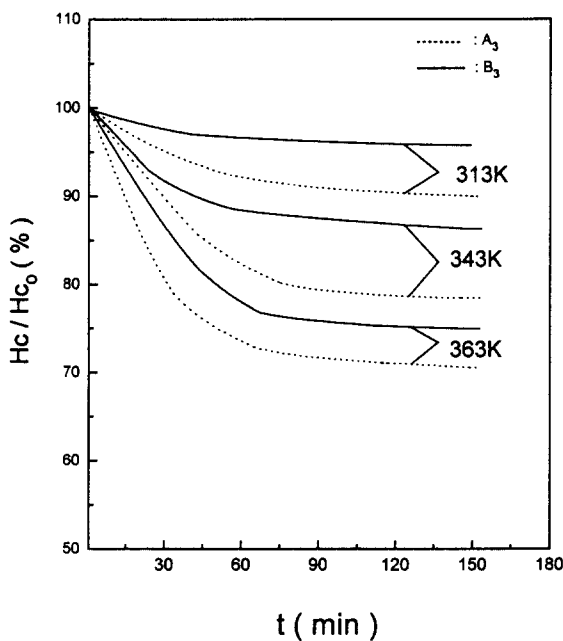| Sample	$K_u (\times 10^5 erg/cm^3)$	$K_1 (\times 10^5 erg/cm^3)$
A₁	1.0	1.8
A₂	1.0	2.2

Fig. 2 Change of coercivities of sample A₃ and B₃ with magnetic annealing time.

For the isothermal annealing in the perpendicular magnetic fields, H, the time dependence of Hc could not be perfectly described by $H_c (T, H, t) = H_c (T, H, 0) \exp (-t/\tau)$: where τ is the relaxation time and T the annealing temperature. Looking at the slope of $H_c (T, H, t)/H_c (T, H, 0)$ for $t \to 0$, the curves of the time dependence of the slope show an exponential behaviour. Thus we take a typical Arrhenius equation

$$h (T, H) = A \exp [- E (H)/ kT] \qquad (4)$$

where h (T, H) is the coercivity of the sample, A a constant, E (H) the field dependent activation energy for cation rearrangement. Taking the logarithm, we get $\ln h (T, H) = \ln A - E (H)/ kT$. A plot of ln h versus 1/T at a fixed magnetic field gave a straight line. The slope of this line determines E (H) with H =

constant while the intercept determines the value of A. Measuring the coercivity of samples Ai and Bi after magnetic annealing for different times, we obtained the values of E (H = 3000 Oe).

Figure 3 shows the typical Arrhenious plots of ln H vs 1/T of sample A₃ and B₃. Table IV lists the activation energy for the thermal coercivity stability of sample A₁ and B₁. It may be seen that the E values of samples B₁ are greater than those of samples A₁. These results are consistent with results presented in Table II that the Hc′/Hc of samples A₁-A₃ are smaller than that of samples B₁-B₃. According to these results, one may conclude that apart from the crucial factor of the presence of Fe^{2+} ions, there may be other factor to affect the thermal stability of P and Co-doped particles. It is well known that the change in coercivity of the magnetic recoding tapes is a crucial source of "print-through problems and this is mainly attributed to the migration and site exchange of the Co ions in the lattice [7]. According to our results, the migration and site exchange of the Co ions are affected by not only Fe ions but also P ions.
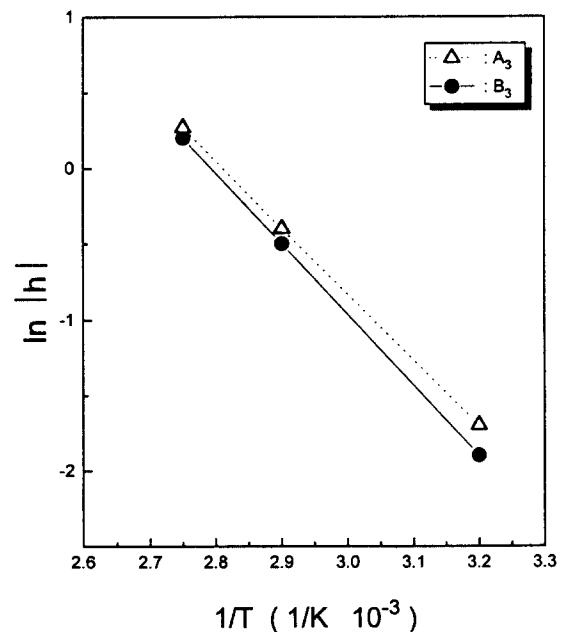

Fig. 3 Arrhenious plots of ln H vs 1/T of sample A₃ and B₃.

Table IV. Activation energy, E (H = 3000 Oe), for the thermal coercivity stability of magnetic sheets A₁ and B₁.

Sample	E (eV)	Sample	E (eV)
A₁	∞	B₁	∞
A₂	0.50	B₂	∞
A₃	0.45	B₃	0.64
A₄	0.39	B₄	0.55
A₅	0.42	B₅	0.52
A₆	0.42	B₆	0.50

The cation distribution of P and Co-substituted iron oxide-

was calculated from the variation of the saturation magnetization with P-doping on the basis of the Neel model. Because the P and Co-substituted iron oxide exhibits ferrimagnetism, the magnetic moment of cations occupying octahedral site (B site) is antiparallel to that of cations in tetrahedral site (A site), and the magnetization is the net magnetic moment between the A site and the B sites ions. Therefore the magnetic moment can be represented as following:

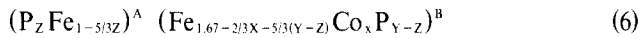$$\sigma_s = M \; \mu_B \; N/160 = (m_B - m_A) \; 3/4 \; \mu_B \; N/160 \qquad (5)$$

where M : molecular weight of γ-Fe$_2$O$_3$,

μ_B : Bohr magneton

N : Avogadro number

m_B, m_A : magnetic moment of A, B site ions

As P ions are introduced in iron oxide particles, the cation distribution can be represented as following:

$$(P_Z Fe_{1-5/3Z})^A \; (Fe_{1.67-2/3X-5/3(Y-Z)} Co_X P_{Y-Z})^B \qquad (6)$$

where X : No. of Co^{2+} ions

Y : No. of P ions

Z : No. of P ions on the A sites

Y−Z : No. of P ions on the B sites

The magnetic moment of the A and B site is represented as following:

$$m_A = 5 \; (1 - 5/3Z)$$

$$m_B = 5 \; [1.67 - 2/3X - 5/3 \; (Y - Z)] + 3X \qquad (7)$$

We calculated sample B$_1$ because sample B$_1$ contained 1 wt.

% P. The results lists in Table V.

From Table V we can see that most of P ions in P and Co-doped iron oxide particles occupied on the B sites, which agrees with Wang's results [8].

Table V. P-ion distribution in PCo-doped iron oxide particles.

σ_s (emu/g)	P (A)/P$_{total}$ (%)	P (B)/P$_{total}$ (%)
57.14	1.9	98.1

4. Conclusion

The phosphorous doping of cobalt-substituted acicular oxides promotes the coercivity and its stability in magnetic and thermal environment, which may be attributed to increase of the cubic magnetocrystalline anisotropy constant, K1 and the activation energy, E, respectively. The most of P ions occupy the B sites of iron oxide particles.

References

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