The Formation of Needle-like Particles of $x\mathrm{CoFe_2O_4}\cdot(1-x)\mathrm{Fe_3O_4}$ with $x\leq 0.2$

Masao KIYAMA* and Toshio TAKADA

Institute for Chemical Research, Kyoto University, Uji, Kyoto 611

(Received February 12, 1982)

An experimental study was made of the oxidation with air of alkaline suspensions containing needle-like Fe_3O_4 particles and slight amounts of $Co_{1/3}/Fe_{2/3}(OH)_2$ at temperatures between 60 and 90 °C, together with the properties of the resulting oxidation products. It has been found that the H_c (coercivity) values of the products were greatly affected by both the excess NaOH concentration and the oxidation temperature—*i.e.*, the two essential factors in determining the difference in the properties of a cobalt ferrite layer coated on the Fe_3O_4 particles, that these values increased with the heat treatment *in vacuo* of the products within the temperature range of 200 to 450 °C, without decreasing the saturation magnetization values, and that the H_c increment was mainly governed by the Co content.

Needle-like particles of γ-Fe_2O_3, containing a slight amount of Co(II), have been widely used as a ferromagnetic material for high-density recording tapes. The coercivity (coercive force), H_c, of γ-Fe_2O_3 particles has been known to become greater with an increase in the shape anisotropy.[1)] The γ-Fe_2O_3 particles become magnetically harder—*i.e.*, the H_c increase, by either the adsorption of Co(II)[2,3)] or the epitaxial coating of cobalt ferrite[3—5)] on their surfaces, with the participation of the properties of a surface magnetic anisotropy.

The precipitate of $Co_{x/3}Fe_{1-x/3}(OH)_2$, prepared by adding an excess NaOH solution to a mixed solution of Co(II) and Fe(II) salts, can transform itself by oxidation into a ferromagnetic precipitate consisting of cubic $Co_xFe_{3-x}O_4$ particles, whose H_c value is governed by the conditions of oxidation.[6)] As has been known, the difference in the lattice constant between Fe_3O_4 and cobalt ferrite is appreciably small relative to that between γ-Fe_2O_3 and cobalt ferrite.

The present authors considered that the use of Fe_3O_4 particles instead of γ-Fe_2O_3 would contribute to the ease of the epitaxial coating of cobalt ferrite, with a consequent attainment of a magnetically harder material. The authors have found that magnetic properties of the products prepared by subjecting aqueous suspensions containing needle-like Fe_3O_4 particles and slight amounts of $Co_{1/3}Fe_{2/3}(OH)_2$ to oxidation were greatly affected by the conditions of oxidation.

This paper is an account of the properties of such products and of the conditions for the formation of $x\mathrm{CoFe_2O_4}\cdot(1-x)\mathrm{Fe_3O_4}$ with $0.2\geq x$, featuring greater H_c values created by coating cobalt ferrite on the surfaces of needle-like Fe_3O_4 particles.

Experimental

A number of α-FeO(OH) samples, each consisting of needle-like particles, were prepared as follows. Alkaline suspensions (each 3 dm^3) of $Fe(OH)_2$, which had been prepared by mixing aqueous solutions of $FeSO_4$ and NaOH (both of an analytical grade), were heated and then oxidized at 40 °C by bubbling CO_2-eliminated air into them at various constant rates until the precipitate of $Fe(OH)_2$ completely disappeared. The oxidation method for these suspensions was the same as that previously reported.[7)] The yellowish precipitates of α-FeO(OH) were separated by filtration, washed well with water, treated with acetone, and then dried at 70 °C in air. The mean particle size of the α-FeO(OH) samples was estimated from the BET surface area, S, which had been measured using nitrogen; it could successfully be controlled in the S range between 20 and 45 $m^2\,g^{-1}$ by varying the concentrations of Fe(II) and of the excess NaOH in the starting suspension, and the air-flow rate.

The α-FeO(OH) samples were then directly reduced in hydrogen at 330 °C to Fe_3O_4. The Fe_3O_4 sample with the highest H_c value (Fig. 1(b)), which had been prepared from the α-FeO(OH) sample with $S=30\ m^2\,g^{-1}$ (Fig. 1(a)), was selected from the Fe_3O_4 samples and used as the starting ferromagnetic material. The α-FeO(OH) sample (Fig. 1(a)) was prepared by bubbling air at a constant rate of 500 dm^3/h for 20 h into the individual 3-dm^3 suspensions, each containing 0.22 M(1 M$=$1 mol dm^{-3}) $Fe(OH)_2$ and 1.25 M excess NaOH; the resulting suspensions were mixed and subjected to further treatment.

The starting suspensions, consisting of the particles of Fe_3O_4 and the hydroxides of Co(II) and Fe(II), were prepared in each 4-dm^3 spherical flask, as will be described. $FeSO_4\cdot 7H_2O$ and $CoSO_4\cdot 7H_2O$(both of an analytical grade) in the required amounts were dissolved in the atomic ratio of 1:2 into 1 or 2 dm^3 of water, followed by the dispersion of the Fe_3O_4 sample (60—100 g) in the mixed solution. The Fe(II) and Co(II) in the black suspension were precipitated by adding an excess of NaOH to the acidic suspension. Each alkaline suspension in the flask was diluted with water to 3 dm^3, quickly heated to the desired temperature, and then stirred in air with a mechanical stirrer for 3 to 5 h until the precipitate of $Co_{1/3}Fe_{2/3}(OH)_2$ has been completely transformed by oxidation into $CoFe_2O_4$. The construction

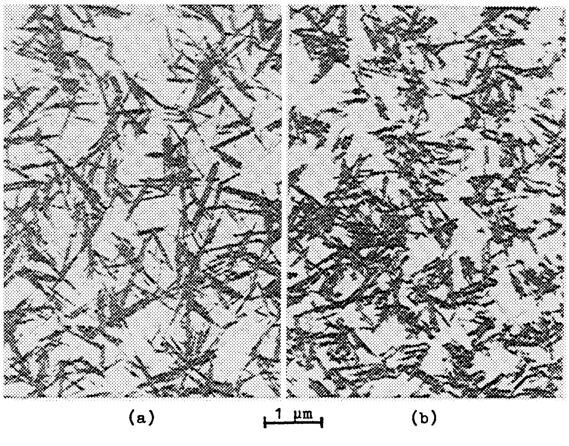

Fig. 1. Fe_3O_4 particles(b) obtained by subjecting α-FeO(OH) particles(a) to direct reduction in H_2 at 330 °C.

TABLE 1. PROPERTIES OF SOME TYPICAL $x\mathrm{CoFe_2O_4}\cdot(1-x)\mathrm{Fe_3O_4}$ SAMPLES PREPARED AT VARIOUS OXIDATION TEMPERATURES, t, AND EXCESS NaOH CONCENTRATIONS

Sample	Excess NaOH (mol dm^{-3})	t/°C	x	S/m^2 g^{-1}	M_s/emu g^{-1}	H_c/Oe
A	1.54	90	0.12	16.3	85	588
B	0.50	90	0.07	17.0	85	521
C	0.02	90	0.12	18.1	83	480
D	1.54	80	0.07	17.5	86	580
E	1.54	60	0.07	18.1	85	536

of the flask for the oxidation was the same as has previously been described, except that the stirrer was inserted in place of an air-introducing tube.[7] The Co-ion contents in the oxidation products were controlled by varying the mixing ratio of the $\mathrm{Fe_3O_4}$ and $\mathrm{Co_{1/3}Fe_{2/3}(OH)_2}$. The oxidation products with the $x\mathrm{CoFe_2O_4}\cdot(1-x)\mathrm{Fe_3O_4}$ composition were filtered, washed well with water, treated with acetone, and then dried at 50 °C under reduced pressure.

Five kinds of $x\mathrm{CoFe_2O_4}\cdot(1-x)\mathrm{Fe_3O_4}$ samples, selected from the numerous samples, were packed into brass cylinders 6 cm in length and 0.6 cm in diameter with packing densities, p (g/cm^3), ranging from 0.1 to 1.2. Some samples with $p<0.5$ had to be immersed in paraffin. After the sample had been magnetized up to 4 kOe (1 Oe$=1000/4\pi$ A m^{-1}) in a solenoid, the demagnetization curve was taken at room temperature with a self-recording permeameter. An inspection of these curves indicated that the H_c values of each sample were independent of the p for $p<0.5$, as could be anticipated from an earlier publication.[8] For $p\geq0.5$, the H_c values manifested a decrease of $-100p$, regardless of the difference in kind of samples, presumably due to the use of the same starting material.

Exactly the same samples were also packed in brass cylinders 0.6 cm in diameter and 0.2 cm in height in the $0.6\leq p\leq0.9$ range. Magnetic measurements with these samples were carried out at room temperature in a magnetic field up to 10 kOe using a vibrating sample magnetometer (VSM). The H_c values for each of these samples were found to be lowered approximately $-50p$ with an increase in the p. In this case, the difference in saturation-magnetization, M_s, values for each sample was within 0.5 emu g^{-1} (1 emu g$^{-1}=4\pi10^{-4}\,\rho$ Wb m^{-2}, where ρ=specific gravity in units of 10^3 kg m^{-3}).

As a result of normalizing for $p=0.5$ the H_c values for each sample with $p\geq0.5$, after these values had been obtained using the previously mentioned two methods, it has been found that the difference between the two sets of normalized H_c values could be held within 15 Oe. Magnetic measurements of the remaining samples were also made using a VSM at room temperature in 10 kOe. The H_c values normalized for $p=0.5$ are presented in the present paper.

The cobalt and iron-ion contents of some samples were determined by atomic absorption after the samples had been dissolved in a HCl solution. The Fe(II) content in the $\mathrm{Fe_3O_4}$ sample was decided by titrating with $\mathrm{KMnO_4}$ after it had been dissolved in a mixed solution of $\mathrm{H_2SO_4}$ and $\mathrm{H_3PO_4}$ under a nitrogen atmosphere.

Results and Discussion

The H_c values of the $\mathrm{Fe_3O_4}$ samples prepared from the α-FeO(OH) samples with $S\leq25$ and $S\geq35$ m^2 g^{-1} were found to be less than the H_c value of the $\mathrm{Fe_3O_4}$ sample (Fig. 1(b)) prepared from the α-FeO(OH) sample with $S=30$ m^2 g^{-1} (Fig. 1(a)). This was due to the formation of microscopic pores in each needle-like particle (for $S\leq25$) or the decrease in the shape anisotropy (for $S\geq35$ m^2 g^{-1}). The starting ferromagnetic material with $S=18.0$ m^2 g^{-1} (Fig. 1(b)) contained 26% Fe(II) of the total iron ions, and its H_c and M_s values were 467 Oe and 87 emu g^{-1} respectively.

The conditions for the formation of five typical samples with the $x\mathrm{CoFe_2O_4}\cdot(1-x)\mathrm{Fe_3O_4}$ composition and their magnetic properties at room temperature are given in Table 1, together with the S values. Table 1 demonstrates that, with the increase in the excess NaOH concentration and the elevation of the oxidation temperature, the H_c value increases and the S value decreases.

According to our electron-microscopic observation, no cubic particles could be detected with Samples A and D. This indicates that the $\mathrm{Co_{1/3}Fe_{2/3}(OH)_2}$ was almost entirely changed by oxidation to $\mathrm{CoFe_2O_4}$ on the surfaces of the needle-like $\mathrm{Fe_3O_4}$ particles. The fact that cubic particles 0.05—0.1 μm in size were intermingled in Samples B, C, and E demonstrates that part or all of the $\mathrm{Co_{1/3}Fe_{2/3}(OH)_2}$ was transformed into $\mathrm{CoFe_2O_4}$ off the surfaces.

Insoluble oxides suspended in an aqueous solution are known, in general, to be electrically charged by adsorbing $\mathrm{H^+}$ or $\mathrm{OH^-}$ ions. At pH values greater than the point of zero charge (PZC), the metal ions that have been combined only with $\mathrm{O^{2-}}$ ions are known to be formed in the subsurface of an oxide such as $\mathrm{Fe_2O_3}$[9] or ZnO[10] by the dissociation of surface protons, thus providing the insoluble particles with negatively charged sites, whose number becomes greater with an increase in the pH.

In the present experiments, it is presumed that the metal ions, probably bivalent, in the alkaline-suspension medium tend to be adsorbed at negatively charged sites where the iron ions combined only with $\mathrm{O^{2-}}$ ions exist in the subsurfaces of needle-like particles of $\mathrm{Fe_3O_4}$, whose PZC is 6.55 at 25 or 5.4 at 90 °C.[11] It is considered from these results that the surface area coated with the Fe(II) and Co(II) on the needle-like particles becomes wider with an increase in the excess NaOH concentration and that a rise in the oxidation temperature facilitates the formation of $\mathrm{CoFe_2O_4}$.

Some samples, each divided into several parts and enclosed in glass tubes under a reduced pressure of 1.33×10^{-3} Pa, were heat-treated at temperatures between 200 and 600 °C for 4 h and then allowed to cool to room temperature. Figure 2 shows a plot of the H_c values of two typical samples A and D, *vs.* the heat-treated temperature to demonstrate that the

Table 2. Properties of some typical samples subjected to heat treatment at 400 °C *in vacuo*

Sample	A	B	C	D	E
$S/\mathrm{m^2\,g^{-1}}$	16.0	16.9	14.9	15.8	17.1
H_c/Oe	920	603	687	701	632

H_c values become greater upon heat treatment, even at such low temperatures as 200 °C. It has been found that there was no marked difference in M_s values between samples A and D for heat-treatment temperatures$\leq$450 °C, except that the M_s for 500 °C became less than that for 450 °C due to the formation of α-Fe_2O_3.

As is indicated in Table 2, the S and H_c values of the five samples prepared at 400 °C *in vacuo* become less than and higher than those of the original samples, respectively. As is evident from a comparison of Tables 1 and 2, the increase in H_c is mainly governed by the Co content.

The H_c values were also measured with the original samples, A and D, and their heat-treated samples under the magnetic fields of 10 and 20 kOe within the temperature range from 77 to 350 K. Figure 3 is a plot of [H_c] (ratio of H_c at various measuring temperatures, T, to that at 295 K) against T/K.

The temperature dependence of [H_c] for the other original samples was substantially the same as for the original samples, A and D, regardless of the conditions of oxidation and the Co(II) content. From the gradual variations in [H_c] with the temperature for the original samples, the H_c increase at room temperature may be attributed to the participation of the effect of the magnetic-surface anisotropy caused by the formation of the cobalt ferrite layer on the surface of Fe_3O_4 particles, as has previously been described for γ-Fe_2O_3 ones.[3] The H_c increase at room temperature would be determined by the properties of a ferrite layer coated on the surfaces, notably the percentage of the surface coverage, and the homogeneity and thickness of the ferrite layer, governed by the conditions of oxidation.

The cobalt ferrite layer coated on the surfaces presumably possesses a Co(II) concentration gradient similar to that of the cubic particles of ferrite formed outside the needle-like particles.[6] The reason for the differences in the temperature dependence and in the H_c increase at room temperature among the five kinds of samples prepared by heat treatment *in vacuo* can be attributed to the facts that some of the fine cubic particles of $CoFe_2O_4$ form a ferrite layer on the needle-like particles of Fe_3O_4 and that the participation of the crystal anisotropy effect of Co(II) attributable to the internal diffusion of part of the Co(II) ions into the needle-like particles becomes predominant with the tendency towards the uniform concentration of Co(II) ions in the coated ferrite layer.

The authors wish to thank Messrs. T. Kusuda (this Institute), Y. Enoki (Matsushita Electric Industrial Co., Ltd.), and N. Horiishi (Toda Kogyo Co., Ltd.) for their extensive assistance in conducting a number of experiments.

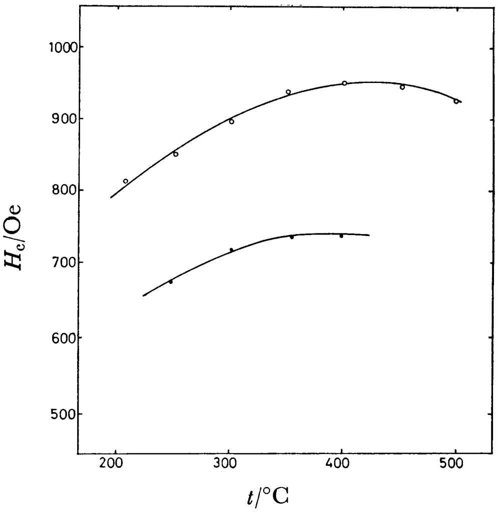

Fig. 2. Plot of coercivity, H_c, as a function of heat treatment temperatures *in vacuo* for samples A(○) and D(●).

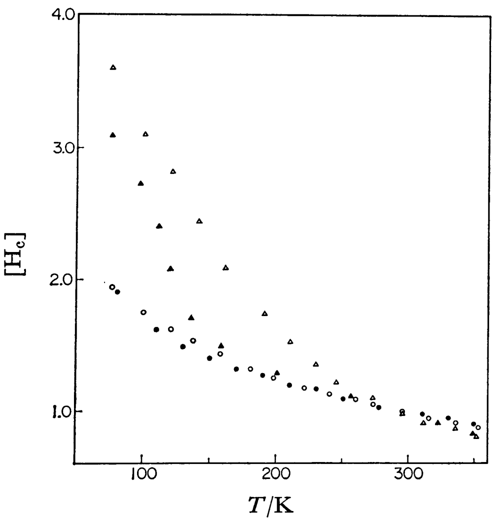

Fig. 3. Plot of relative coercivity, [H_c], as a function of measuring temperatures for original samples A(○) and D(●) and their heat-treated samples A(△) and D(▲) prepared at 300 and 400 °C *in vacuo*, respectively.

References

1) A. H. Morrish and L. A. K. Watt, *J. Appl. Phys.*, **29**, 1029 (1958).
2) Y. Tokuoka, S. Umeki, and Y. Imaoka, *J. Phys. (Paris)*, **38**, Cl-337 (1977).
3) H.-L. Lo and W. Gung, *J. Appl. Phys.*, **50**, 2414 (1979).
4) M. Kishimoto, T. Sueyoshi, J. Hirata, M. Amemiya, and F. Hayama, *J. Appl. Phys.*, **50**, 450 (1979).
5) K. Sumiya, T. Matsumoto, S. Watani, and F. Hayama, *J. Phys. Chem. Solid*, **40**, 1097 (1979).
6) M. Kiyama, *Bull. Chem. Soc. Jpn.*, **51**, 134 (1978).
7) M. Kiyama, *Bull. Chem. Soc. Jpn.*, **47**, 1646 (1974).
8) L. A. K. Watt and A. H. Morrish, *J. Appl. Phys.*, **31**, 72s (1960).
9) G. A. Parks and P. L. de Bruyn, *J. Phys. Chem.*, **66**, 967 (1962).
10) H. F. A. Trimbos and H. N. Stein, *J. Colloid Interface Sci.*, **77**, 397 (1980).
11) P. H. Tewari and A. W. Mclean, *J. Colloid Interface Sci.*, **40**, 267 (1972).