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Particle Growth of $Co_xFe_{3-x}O_4$ with $x \leq 0.2$ by Air Oxidation of Aqueous Suspensions

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The conditions were studied for promoting the particle growth of $Co_xFe_{3-x}O_4$ with $x \leq 0.2$ by oxidation with air at 70°C of $Fe(OH)_2$ suspensions containing slight amounts of Co(II). The particle growth by oxidation is accelerated notably with increasing concentrations of both excess NaOH and Fe(II) in the starting suspension. The presence of extremely fine Fe_3O_4 particles in the starting suspension retards the particle growth by oxidation. The samples consist of multi-, single-, and sub-domain (or superparamagnetic) particles, each being inhomogeneous in Co(II) concentration, with their intermingled particle ratio as well as the inhomogeneity as governed by the conditions for the particle growth.

KEY WORDS: Air oxidation/ Particle growth/ Cubic particle/ Single-domain particle/ Coercivity/ $Co_xFe_{3-x}O_4$/

The precipitates consisting of cubic Fe_3O_4 particles can be prepared by oxidation of $Fe(OH)_2$ suspensions, provided that the conditions for oxidation are suitably chosen. The appropriate conditions of oxidation have been investigated for the formation of Fe_3O_4.[1] The temperature at which Fe_3O_4 is formed is lowered with decreasing concentration of either excess NaOH or iron (II) salt in the starting suspension, whereas each concentration range suitable for the formation of Fe_3O_4 becomes wider with increasing oxidation temperature beyond 50°C. The Fe_3O_4 samples with greater than 0.01 μm in mean particle sizes could successfully be prepared by selecting the oxidation conditions, and their magnetic properties were dependent on the particle sizes. It has been well known that the substitution of slight amounts of Co(II) for Fe(II) in Fe_3O_4 causes a magnetically harder material. The precipitates of $Co_xFe_{3-x}O_4$ with $0.05 \leq x \leq 0.2$ were also prepared in the presence of slight amounts of Co(II) under oxidation conditions similar to those for Fe_3O_4 formation.

This paper deals with oxidation conditions for the growth of particles of the compositions of $Co_xFe_{3-x}O_4$ with $x \leq 0.2$ and their magnetic properties.

EXPERIMENTAL

The starting suspension, varying in the concentrations of iron(II) and excess NaOH, were prepared as follows: Acidic solutions containing different concentrations of Fe(II) were prepared by dissolving $FeCl_2 \cdot 6H_2O$ or $FeSO_4 \cdot 7H_2O$ (both of analytical grade) in water. To every 1 L (1 L$=$1 dm^3) solution, a NaOH solution whose

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concentration had been suitably controlled was added in various $2OH^-/Fe(II)$ ratios (R). Each suspension was diluted with water to 3 L in a 4 L flask. The oxidation of each 3 L suspension was carried out at 70°C by bubbling CO_2-eliminated air into at a constant rate of 300 L/h. The construction of the flask for the air-oxidation experiments has previously been described.[1)]

To investigate the transformation into Fe_3O_4 in the course of oxidation, a 40–50 cm^3 sample was taken several times from each suspension during oxidation. After sampling each filtered precipitate in muddy form was subjected to X-ray, electron microscopic, and chemical examinations. Oxidation for the suspensions with $R \leq 1$ was stopped when the pH dropped sharply with the disappearance of dark blue (or green) or whitish precipitate in the suspension, whereas the alkaline suspensions with $R > 1$ were oxidized until $Fe(OH)_2$ was completely oxidized. A number of alkaline suspensions were also prepared by using acidic solutions containing Fe(II) and either of Fe(III) or Co(II).

The oxidation products were filtered, washed with water, and treated with acetone. The black slurries prepared by oxidation in the absence or presence of Fe(III) in the starting suspensions were, respectively, dried at 70°C under reduced pressure, or at room temperature in air.

All powdery samples thus obtained were examined by X-ray diffraction using Mn filtered FeKα radiation. The samples consisting only of Fe_3O_4, as revealed by X-ray analysis were further examined by electron microscopic observation, magnetic measurement at room temperature using a vibrating sample magnetometer in magnetic field up to 10 kOe ($1\ Oe = 1000/4\pi\ A\ m^{-1}$), BET surface area determination using nitrogen, and chemical analysis. The mean particle size, D, of Fe_3O_4 samples was estimated from the BET surface area (m^2/g) by assuming that the sample consisted of cubic particles with 5.2 specific gravity. The average particle size, d, for the samples with $D < 0.1\ \mu m$ was further estimated from the line broadening of the X-ray diffraction peak for the (311) plane of Fe_3O_4 crystal structure.

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

RESULTS AND DISCUSSION

Aqueous suspensions each containing 0.24 M ($1\ M = 1\ mol\ dm^{-3}$) Fe(II) were prepared by varying R values in the range 0.3–2.5. On adding a NaOH solution to a $FeCl_2$ solution a whitish (or with a tint of blue) precipitate was formed. When the amount of NaOH added fell short of reaching the equivalence point (i.e., $R < 1$), a bluish white neutral suspension was obtained. When it was equal to or more than that for the equivalence point, a weak or a strongly alkaline suspension was obtained.

When air was bubbled into, a color change took place of a neutral suspension to dark blue. The dark blue precipitates as examined by an X-ray analysis and electronmicroscopy proved to consist of hexagonal plate-like particles with the same crystal structure as that of green rust I.[2] When $R \leq 0.7$, with the progress of oxidation the formation of a black, ferromagnetic precipitate, Fe_3O_4, could be observed in the dark blue suspension with pH 6.0 ± 0.3. For $R=0.9$ or 1.0, the formation of Fe_3O_4 took place at pH 7.5–9.0 in the presence of $Fe(OH)_2$ with or without green rust I. As the precipitates of $Fe(OH)_2$ and green rust I completely transformed themselves into Fe_3O_4, the pH sharply dropped to 4 or less. The white precipitate ($Fe(OH)_2$) in the alkaline suspensions was observed to gradually change without the formation of green rust I to the black, and ferromagnetic precipitate.

It has been found that (a) all the filtered Fe_3O_4 samples in a muddy form has the lattice constant, a_0, nearly constant at 8.38 Å, irrespective of R values, (b) the dried samples prepared for $R \geq 1.1$ consist of cubic particles with 0.2–0.8 μm in size, with 8.37–8.38 Å in a_0 and contain Fe(II) 30–31% of the entire Fe ions, whereas (c) those for $R \leq 1$ consist of spherical and cubic particles with 0.05–0.15 μm in size, with 8.36 Å in a_0 containing Fe(II) 26–27%.

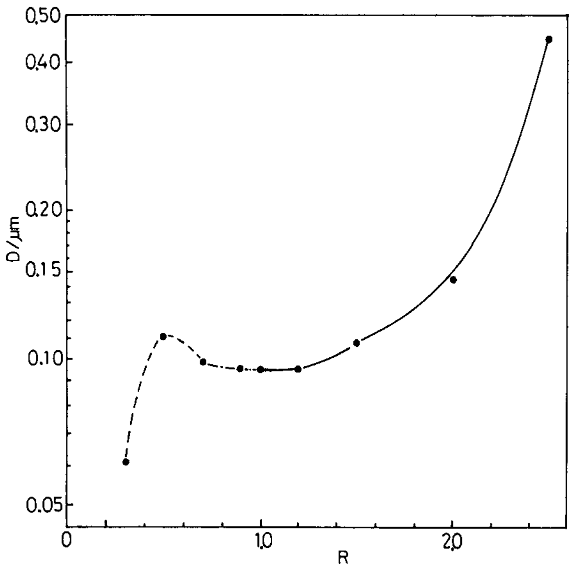


Fig. 1. Mean particle size, D, of Fe_3O_4 samples prepared by oxidation of suspensions with various R values containing 0.24 M $FeCl_2$. Transformation into Fe_3O_4 by oxidation took place in the presence of green rust I (– – –), a mixture of green rust I and $Fe(OH)_2$ (— • —), or $Fe(OH)_2$ (——).

A plot of D values of Fe_3O_4 samples thus obtained *vs.* R values (Fig. 1) demonstrates that the D values are affected by the $Fe(OH)_2$ concentration in the starting suspension when $R \leq 0.7$, and that increasing the concentration of an excess NaOH accelerates the growth of Fe_3O_4 particles (Fig. 2) as a result of retardation in the speed of Fe_3O_4 formation caused by oxidation.

Three kind suspensions with $R=0.5$, 0.9, and 1.5, varying in the Fe(II) concentration in the range of 0.046–0.48 M were prepared from solutions of $FeCl_2$ and

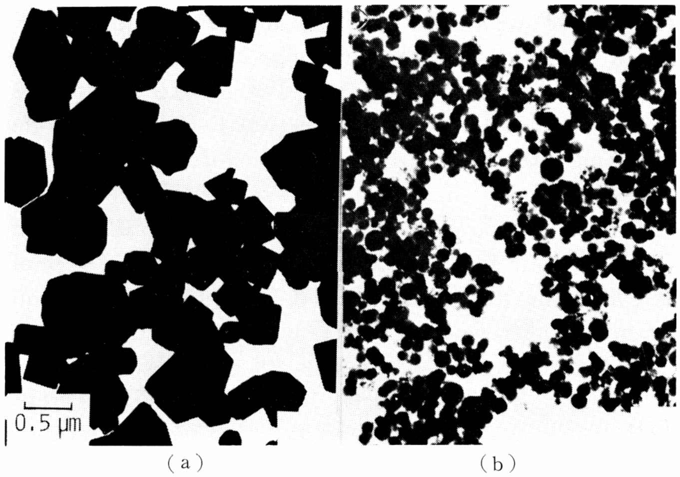


Fig. 2. Electronmicrographs of Fe_3O_4 prepared by oxidation of suspensions containing 0.24 M Fe(II) with R=2.5 (a), and 1.1 (b).

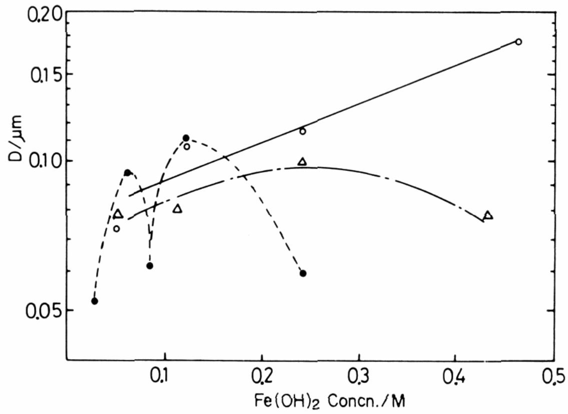


Fig. 3. Mean particle size, D, of Fe_3O_4 prepared by oxidation of suspensions containing different $Fe(OH)_2$ concentrations with R=0.5 (●), 0.9 (△), and 1.5 (○).

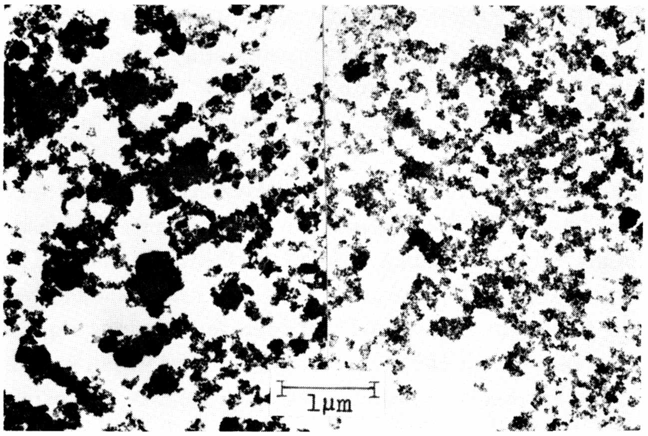
NaOH, and subjected to oxidation. For the $R<1$, the amount of iron (II) precipitates such as $Fe(OH)_2$ increases with increasing R at a given Fe(II) concentration, and is calculated from R values. The D values are plotted against the concentration of $Fe(OH)_2$ at three R values in Fig. 3. The growth of Fe_3O_4 particles by oxidation is promoted with increasing the concentrations of both excess NaOH and Fe(II) in the starting suspension.

Similar experiments were conducted at 0.24 M Fe(II) using $FeSO_4$ in place of $FeCl_2$. No particular differences could be found in the conditions for promoting the growth of Fe_3O_4 particles in alkaline media ($R\geq 1.0$) caused by oxidation. When $R\leq 0.7$, fine needle-like α-FeO(OH) particles were formed besides cubic Fe_3O_4 particles as had been described.[1)]

As has been known, Fe(III) easily reacts with Fe(II) in an alkaline medium to form extremely fine Fe_3O_4 particles.[3] It was found that the presence of such extremely fine Fe_3O_4 particles in the starting suspension tends to retard the growth of Fe_3O_4 particles caused by oxidation. In order to study the effect of Fe(III) concentration in the starting suspension on the particle growth, alkaline suspensions containing 1.0 M excess NaOH, 0.28 M Fe(II), and different amounts of Fe(III) in the range $0.046 \leq M \leq 0.260$ were prepared from solutions of $FeSO_4$ and $FeCl_3$, and subjected to oxidation.

Table I. Properties of typical Fe_3O_4 samples prepared by oxidation at 70°C of suspensions containing 1 M excess NaOH, 0.288 M Fe(II), and different Fe(III) concentrations

Sample	Fe(III)/mol dm^{-3}	D/Å	d/Å	Hc/Oe	M/emu g^{-1}
A	0.060	322	740	120	65
B	0.102	230	357	95	62
C	0.152	145	236	62	49
D	0.200	129	109	20	44



(a) (b)

Fig. 4. Electronmicrographs of Fe_3O_4 prepared by oxidation of suspensions containing 1 M excess NaOH, 0.29 M Fe(II), and either 0.06 M (a) or 0.15 M Fe(III) (b).

Properties of typical samples are given in Table I, and electron micrographs of typical two Fe_3O_4 samples are shown in Fig. 4. The increase in the Fe(III) concentration in the starting suspension up to 0.06 M was found to cause a remarkable decrease in D, but a slight decrease in d. These samples consist of extremely fine particles with 0.01–0.02 μm in size in addition to cubic particles with 0.05–0.1 μm in size (Fig. 4(a)). Further increase in the Fe(III) concentration resulted in the decreases both in D and d.

Their coercivities, Hc, which were independent of the packing densities of cubic Fe_3O_4 particles, are plotted against D in Fig. 5. For the samples with $D > 0.1$ μm their magnetic saturation values, M_s, ranging 85–80 emu/g (1 emu/g$=4\pi\ 10^{-7}$Wb-m

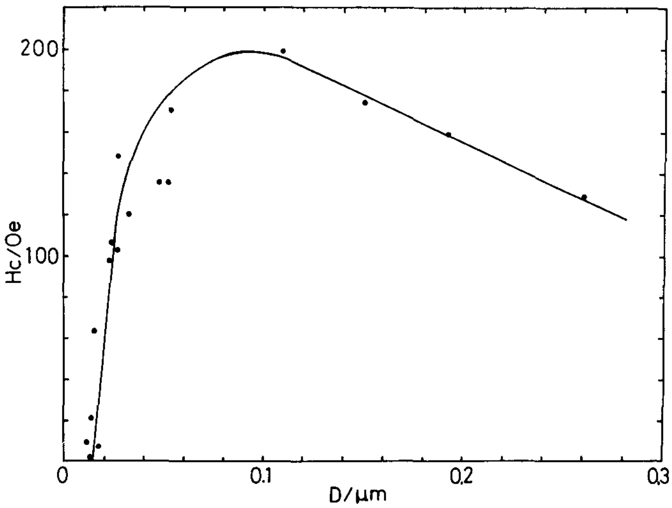


Fig. 5. Coercivity, Hc, of Fe_3O_4 as a function of mean particle size D of Fe_3O_4 samples.

kg^{-1}), were independent of D, whereas their Hc values increased near to 200 Oe with decreasing D to 0.1 μm as a result of increasing single-domain particles. Further decrease in D from 504 to 119 Å causes decreases in Hc to 13 Oe and in magnetisation, *M*, at 10 kOe to 44 emu/g due to an increase in sub-domain (or superparamagnetic) particles.

Alkaline suspensions of hydroxides of Fe(II) and Co(II) in the form of a solid solution of $Co_{x/3}Fe_{1-x/3}(OH)_2$ were prepared by adding an excess NaOH to an acidic solution containing $FeSO_4$ and $CoSO_4$ in the Co(II)/Fe(II) ratios of 0.016 and 0.071, and subjected to oxidation. D values of $Co_xFe_{3-x}O_4$ samples with x=0.05 and 0.20 could be controlled in the range $0.1 \leq D \leq 0.5$ μm by selecting conditions similar to those for promoting the growth of Fe_3O_4 particles. As has been known, the difference in the lattice constant between Fe_3O_4 and cobalt ferrite is appreciably small. The fine particles with the $Co_xFe_{3-x}O_4$ composition ($x \leq 0.2$) could be also prepared by epitaxial coating of cobalt ferrite on the extremely fine Fe_3O_4 particles in an alkaline medium.

The Hc values of typical $Co_xFe_{3-x}O_4$ samples with three D values prepared by

Table II. Magnetic properties of $Co_xFe_{3-x}O_4$ precipitates prepared under various conditions

Sample	Co(II)+Fe(II)/mol dm^{-3}	R	D/μm	x	Hc/Oe	*M*/emu g^{-1}
E	0.360	2.5	0.45	0.20	266	85
F	0.360	1.1	0.12	0.20	633	83
G	0.098	2.5	0.025	0.20	205	75
H	0.360	1.1	0.10	0.05	250	83
I	0.098	2.5	0.025	0.05	175	76

Samples **G** and **I** prepared at 0.29 M excess NaOH in the presence of Fe_3O_4 particles with D=0.025 μm.

varying the conditions are given in Table II. Samples **G** and **I** given in the table were prepared by subjecting alkaline suspensions containing $Co_{y/3}Fe_{1-y/3}(OH)_2$ and fine Fe_3O_4 particles with $D=0.025$ μm and with $Hc=103$ Oe. The Fe_3O_4 particles which had been prepared in the presence of Fe(III) in the alkaline suspension by oxidation as mentioned above were used in a slurry form. Samples **G** and **I** consist of 27 vol% of $Co_yFe_{3-y}O_4$ with $y=0.73$ and 0.18, respectively, as a result of calculation. The Hc values become greater by coating of $Co_yFe_{3-y}O_4$ on the Fe_3O_4 particles and the increment in Hc is affected by the Co content. The Hc increment is presumably due to the participation of a surface magnetic anisotropy as previously described for needle-like particles of γ-Fe_2O_3.[4]

It has been inferred that a Co(II) concentration gradient exists within each particle in the $Co_xFe_{3-x}O_4$ samples prepared even in the absence of Fe_3O_4 seeds, depending on the oxidation conditions and that Hc values of the $Co_xFe_{3-x}O_4$ samples with $D=0.1$ μm vary with heat treatment at 350°C in vacuo as a result of the diffusion of the metal ions in each particle.[5]

Table III. Coercivity, Hc/Oe, of $Co_xFe_{3-x}O_4$ samples subjected to heat treatment in vacuo

Sample	E	F	G	H	I
250°C	—	930	450	290	240
350°C	280	1500	670	350	260

Five samples **E**–**I**, each enclosed in glass tubes under reduced pressure of 10^{-3} Pa were heat treated at temperatures between 250 and 350°C for 5 h and then allowed to cool to room temperature. The Hc values of the samples except for sample **E** begin to increase at 250°C depending on x (Table III), whereas no difference in *M* values of five samples (**A**–**E**) was detected before and after heat treatment.

The Hc value of sample **E** was found to increase at 560 Oe with heat treatment at 200°C in air for 20 h. The Hc increment with heat treatment must be attributed to the fact that the contribution of the crystal anisotropy of Co(II) due to the diffusion of the metal ions in each particle becomes predominant, and the diffusion rate is governed by the concentration of cation vacancies in each particle.

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