The Formation of Manganese and Cobalt Ferrites by the Air Oxidation of Aqueous Suspensions and Their Properties

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Manganese and cobalt ferrites were prepared by the air oxidation of aqueous suspension of $Fe(OH)_2$ and either $Mn(OH)_2$ or $Co(OH)_2$ at 50—80 °C. In alkaline suspensions, all the metal ions are transformed into spinel ferrites, $M_xFe_{3-x}O_4$ (M=Mn or Co), by a suitable combination of the oxidation temperature and the concentration of the excess NaOH. Both manganese and cobalt ferrites consist of ferromagnetic particles (ferrite(A)) when x is smaller than 1.3, nonferromagnetic particles (ferrite(B)) when x is larger than 2, and mixtures of the two in the intervening range. The contents of Mn or Co, both in a solid solution of hydroxides, $M_{x/3}Fe_{1-x/3}(OH)_2$, and in ferrite, increase with the progress of the formation of the ferrite(A) caused by oxidation. The formation of the ferrite(B) begins when x in the solid solution reaches 2. Each particle in the ferrite(A) is less homogeneous in comparison with that in the ferrite prepared by a solid-state reaction, although with the same composition. The difference in the homogeneity causes the essential difference in magnetic properties.

Spinel ferrites with the general formula of $M_xFe_{3-x}O_4$(M being a bivalent metal ion, such as Mn^{2+}, Co^{2+}, Ni^{2+}, or Mg^{2+}), polycrystalline compounds prepared by a solid-state reaction between the constituent oxides, MO and Fe_2O_3, have been thoroughly investigated as regards their properties[1-3] and the conditions needed for their formation.[4] An alternative method of formation, precipitating spinel ferrites from aqueous suspensions containing $M(OH)_2$ and $Fe(OH)_3$ at the boiling point, was worked out by Schuele and Deetscreek.[5] The precipitates thus prepared consist of superparamagnetic particles of MFe_2O_4.

The appropriate conditions of oxidation have been found for the preparation of Fe_3O_4 from a $Fe(OH)_2$ suspension.[6] Since all the spinel ferrites have the same crystal structure as that of Fe_3O_4, it seemed to the present author that it would be possible to prepare the spinel ferrites under conditions similar to those used for the formation of Fe_3O_4, provided that $Fe(OH)_2$ and $M(OH)_2$ coexist in the starting suspension. The formation of a few kinds of spinel ferrites has been achieved from suspensions.[7-9] It was found that the composition of manganese and cobalt ferrites can be optionally varied in the $0 \leq x \leq 3$ range by selecting appropriate oxidation conditions.

This paper will give an account of the conditions and mechanisms for the formation of $Co_xFe_{3-x}O_4$ and $Mn_xFe_{3-x}O_4$ as well as of their properties.

Experimental

The starting suspension containing $Fe(OH)_2$ and either $Mn(OH)_2$ or $Co(OH)_2$ was prepared as follows. The required amounts of $FeSO_4 \cdot 7H_2O$, $MnSO_4 \cdot 5H_2O$ or $CoSO_4 \cdot 7H_2O$ (analytical grade) were dissolved in 1 l water, the resulting solution being acidic. To this NaOH was then added in the required amounts. Each suspension was diluted with water to 3 l. A number of suspensions were thus prepared, varying in the mole ratio of $2OH^-/SO_4^{2-}$ (=R) and in the metal concentration. The oxidation of the suspensions was carried out by bubbling air into them at a constant rate of 300 l/h for a period of 20 h. The details of the procedure of oxidation were previously reported.[6] A series of suspensions were prepared by adding excess aqueous ammonia to the solution. Air containing NH_3, bubbled through 0.5 M aqueous ammonia in a separate vessel, was used for oxidation.

The oxidation products were separated from each solution by filtration, washed with water, treated with acetone, and then dried at 50 °C under reduced pressure. The products, found by X-ray analysis to consist of only ferrites, were subjected to electronmicroscopic observation, and BET surface area and magnetic measurements. The mean particle size, r(μm), of each product was estimated from the BET surface area by assuming that each particle was cubic.

The contents of Fe, Mn, and Co ions in the products were determined by the usual chemical analysis, combined with either X-ray-fluorescence or atomic-absorption spectrometry. The results agreed to within 0.01 in x; that is, $M_{1.00}Fe_{2.00}O_4$ has $x=1.00(\pm 0.01)$.

The excess oxygen content, δ, in a powdery sample of $MnFe_2O_{4+\delta}$ was determined by means of a reaction between the sample and the Fe^{2+} ion in an acidic solution. After the sample had been dissolved in a mixture of 0.05 M $FeSO_4$ and a dilute solution of H_2SO_4 and H_3PO_4 by heating in a nitrogen atmosphere, the amount of the Fe^{2+} ion remaining in the mixture was titrated with $KMnO_4$.

Results and Discussion

Conditions for the Formation of Ferrites. When a solution of NaOH was added to an acidic solution containing 0.72M $FeSO_4$ and either 0.36M $MnSO_4$ or 0.36M $CoSO_4$, a whitish precipitate was formed. When NaOH was added to the acidic solution in the $0.1 < R < 1$ range, a whitish precipitate appeared in a neutral or slightly alkaline suspension. The precipitate was found to be amorphous by X-ray analysis. When $R > 1$, X-ray analysis showed that the precipitate had a CdI_2-type crystal structure. Through oxidation, the ferromagnetic precipitate was formed indirectly via a dark green intermediate oxidation product, or directly from a whitish precipitate, provided that a suitable oxidation temperature was chosen.

When $R < 1$, a dark green precipitate(which is nonferromagnetic at room temperature) appeared upon oxidation. During oxidation, the concentration of the dissolved metal ions in the suspension medium decreased. The dark green precipitate was found by microscopic and X-ray diffraction examinations to consist of hexagonal, plate-like particles with the same crystal structure (a_0 3.17 and c_0 10.7 Å) as that of green rust II.[10] In view of the composition of green rust II, the precipitate is inferred to be a basic sulfate, one-half containing bivalent, and the other half, trivalent metal ions. The dark green precipitate was gradually transformed into a brownish black and ferromagnetic precipitate during oxidation, provided that the temperature of suspension was kept higher than that at which a yellowish brown precipitate, which is nonferromagnetic at room temperature, would occur. The intermediate oxidation product was eventually transformed into the brownish black and ferromagnetic precipitate by oxidation, with an abrupt drop of the pH value to 6 or a little lower, and with the cessation of the occurrence of the ferromagnetic precipitate. At the same time, the concentration of the Mn^{2+} or Co^{2+} ion increased to the concentration in the starting suspension medium. Further oxidation merely caused a very slight dissolution of the Mn^{2+} or Co^{2+} ion contained in the ferromagnetic particles.

When $1<R\leq 3$, the metal ions were precipitated almost entirely as hydroxides of Fe^{2+} and Mn^{2+} or Co^{2+} in the form of a solid solution of $M_{x/3}Fe_{1-x/3}(OH)_2$ (M=Mn or Co). With a decrease in the amount of the solid solution during oxidation, the amount of the black ferromagnetic precipitate increased in the suspension when a suitable oxidation temperature was selected.

Microscopic and X-ray diffraction examinations showed that the ferromagnetic products consist of cubic or spherical particles of the cubic spinel ferrite, whereas the yellowish brown products consist of needle-like particles with the same crystal structure as that of α-FeO(OH).[11] It was found from these experiments that the temperature at which ferrites were formed was lowered with a decrease in the concentration of excess NaOH or a metal sulfate and that the R range suitable for ferrite formation became wider with an increase in the oxidation temperature beyond 50 °C. The composition of the products obtained at 70 °C by varying the R is given in Table 1, together with the change in pH before and after oxidation. The x value of the $Co_xFe_{3-x}O_4$ samples prepared in the presence of aqueous ammonia is 1.00 or less, depending on the concentration of aqueous ammonia present, as a result of the formation of ammine complexes of Co^{2+} in the suspension medium. When $0.6<R<3$, the needlelike particles besides the ferrite particles were formed at 70 °C.

The sample of ferrite prepared at 70 °C from a suspension containing an excess of aqueous ammonia or no excess NaOH ($R<1$) consisted of a mixture of very fine particles(size, 0.01 μm) and spherical particles(size, 0.1—0.2 μm), their mean particle size, r, being less than 0.1 μm. The r value increased as the concentration of excess NaOH in the alkaline suspension was increased.

TABLE 1. COMPOSITION, x, OF FERRITES $M_xFe_{3-x}O_4$ (M=Co or Mn) PREPARED BY THE OXIDATION AT 70°C OF SUSPENSIONS WITH VARIOUS R VALUES

R	$Co_xFe_{3-x}O_4$		$Mn_xFe_{3-x}O_4$	
	pH	x	pH	x
0.70	7.3→3.2	0.44	7.5→3.3	0.14
0.90	7.4→5.2	0.76	8.2→6.0	0.76
1.0	9.5→6.0	0.99	8.9→6.7	0.98
1.06	11.6→10.5	1.00	11.3→10.4	1.00
2.0	12	1.00	12	1.00
>1.0[a)]	9.5	⩽1.00	9.5	1.00

a) Excess aqueous ammonia used as a precipitant.

Properties of Manganese Ferrites. $MnFe_2O_{4+\delta}$ samples were prepared at 50—80 °C from each of the alkaline suspensions with R=1.1—3.0 containing 0.36 mol/l of $Mn_{1/3}Fe_{2/3}(OH)_2$. Table 2 demonstrates that an increasing T and/or R increases r and slightly decreases the lattice constant, a_0, and the excess oxygen content, δ. A Mn NMR spectral pattern of the $MnFe_2O_4$ precipitate prepared from a suspension exhibits two peaks, at 551 and 524 MHz, at room temperature, with the higher peak corresponding to the Mn ions at the A sites in the spinel-crystal structure.[8)] The patterns of the samples obtained showed that the higher peak becomes higher and steeper with an increasing R and T, but the ratio of peak heights remains almost constant, the Curie temperatures estimated from the patterns all being 500 °C.

Samples of $Mn_xFe_{3-x}O_4$ were prepared by subjecting suspensions containing 0.36 mol/l of $Mn_{x/3}Fe_{1-x/3}(OH)_2$ with various x and one of 0.072, 0.72 or 1.44 M excess NaOH(=1.1, 2.0, and 3.0 in R, respectively) to oxidation at 70 °C. The samples with $0\leq x\leq 1.3$ were found to consist only of the cubic spinel ferrite. In the $1.4\leq x\leq 1.8$ range, a small amount of tetragonally deformed spinel ferrite coexisted with the cubic spinel

TABLE 2. PROPERTIES OF $MnFe_2O_{4+\delta}$ FORMED AT VARIOUS OXIDATION TEMPERATURES, T, AND R VALUES

R	T(°C)	r(μm)	a_0(Å)	δ
1.1	70	0.17	8.464	0.025
1.5	70	0.32	8.462	0.006
3.0	70	0.35	8.456	0.000
1.5	50	0.17	8.477	0.024
1.5	80	0.30	8.462	0.004

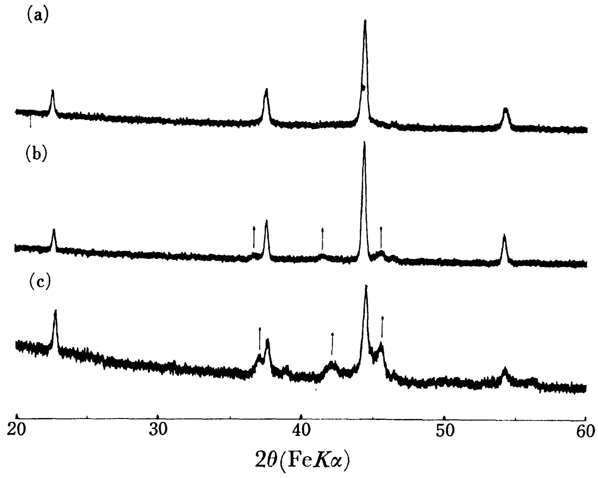

Fig. 1. X-Ray diffraction patterns of $Mn_xFe_{3-x}O_4$ precipitates, (a) x=1.5, R=1.1, (b) x=1.5, R=2.0, and (c) x=2.0, R=1.1. Arrows indicate the peaks caused by the presence of a tetragonal ferrite.

ferrite. As the concentration of excess NaOH increases, the content of the tetragonal ferrite in the mixture slightly increases for a given value of x((a) and (b) in Fig. 1). The content began to increase remarkably at $x=2$ (c) and reached 100% for $x \geq 2.6$. The shape and size of both kinds of ferrite particles with $x \leq 1.3$ and $x \geq 2.6$, prepared at given concentrations of excess NaOH, were found by microscopic examination to be similar. When $x<1$, the a_0 of the cubic spinel ferrites increases with x, regardless of the concentration of excess NaOH(Fig. 2). It approaches 8.5 Å with a further increase in x, depending on the concentrations of excess NaOH. The Mn NMR spectral patterns of these cubic spinel ferrites showed that an increase in x shifts the higher peak to the lower frequency side as a result of lowering the Curie temperature(447 °C for $x=1.3$). Heating the samples of $Mn_xFe_{3-x}O_4$ *in vacuo* at 450 °C decreased the Curie temperature and increased a_0(to the value of the dotted curve shown in Fig. 2), both the values approaching those of a manganese ferrite with the same composition prepared by a solid-state reaction. It was found by electron-microscopic examination that the particle shape and size in each sample with $x \leq 1.3$ remain almost unchanged in spite of heat treatment at 450 °C.

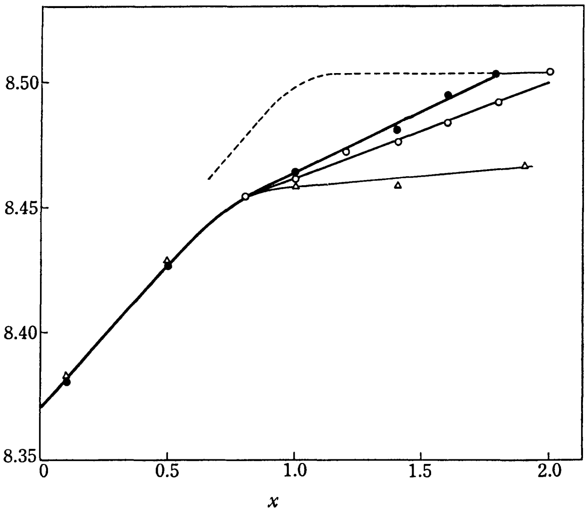

Fig. 2. Lattice constant a_0 of cubic spinel ferrite as a function of x in $Mn_xFe_{3-x}O_4$ preicpitates prepared from the suspensions with $R=1.1$(●), 2.0(○), and 3.0(△) by oxidation at 70 °C.

Properties of Cobalt Ferrites. Samples of $Co_xFe_{3-x}O_4$ were prepared by oxidizing at 70 °C suspensions containing 0.36 mol/l of $Co_{x/3}Fe_{1-x/3}(OH)_2$ with various x and 0.075 M excess NaOH. Figures 3 and 4 show, respectively, electron-micrographs and X-ray diffraction patterns of some typical samples. The black and ferromagnetic samples with $0 \leq x \leq 1.3$ consisted of cubic particles (for $0 \leq x \leq 0.6$), or spherical particles (for $0.9 \leq x \leq 1.3$), and had lattice constants which were nearly constant at 8.38 Å. When $x \geq 1.4$, very fine particles of another kind of ferrite with a_0 8.34—8.31 Å coexist with the spherical particles((a) and (b) in Figs. 3 and 4).

Increasing the x caused a retardation of the rate of transformation of the solid solution of hydroxides, $Co_{x/3}Fe_{1-x/3}(OH)_2$, into ferrites. In the $2 \leq x \leq 3$ range, the solid solution was not completely transformed into ferrites in 20 h(Fig. 4(c)), so that the oxidation was carried out for 50 h. The resulting sample with $x=2.4$ was nonferromagnetic because of its Curie temperature, lower than room temperature,[12] consisting of very fine particles (Fig. 3(c)). Incidentally, the nonferromagnetic samples with $2.7 \leq x \leq 3.0$ had the same crystal structure as that of $CoHO_2(=CoO(OH))$.[13]

Similar experiments were conducted with $Co_xFe_{3-x}O_4$ by varying the excess NaOH concentration in the 0.1—1.5 M range. The results indicated that increasing the concentration of excess NaOH accelerates the particle growth of $Co_xFe_{3-x}O_4$ with $0 \leq x \leq 1.3$ and causes a slight decrease in the content of the nonferromagnetic ferrite for a given value of x(the inset in Fig. 4(b)). In the absence of excess NaOH$(0.9 \leq R \leq 0.95)$, the oxidation products obtained at 70 °C, corresponding to $Co_xFe_{3-x}O_4$ with $2.2 \leq x \leq 3.0$, were nonferromagnetic

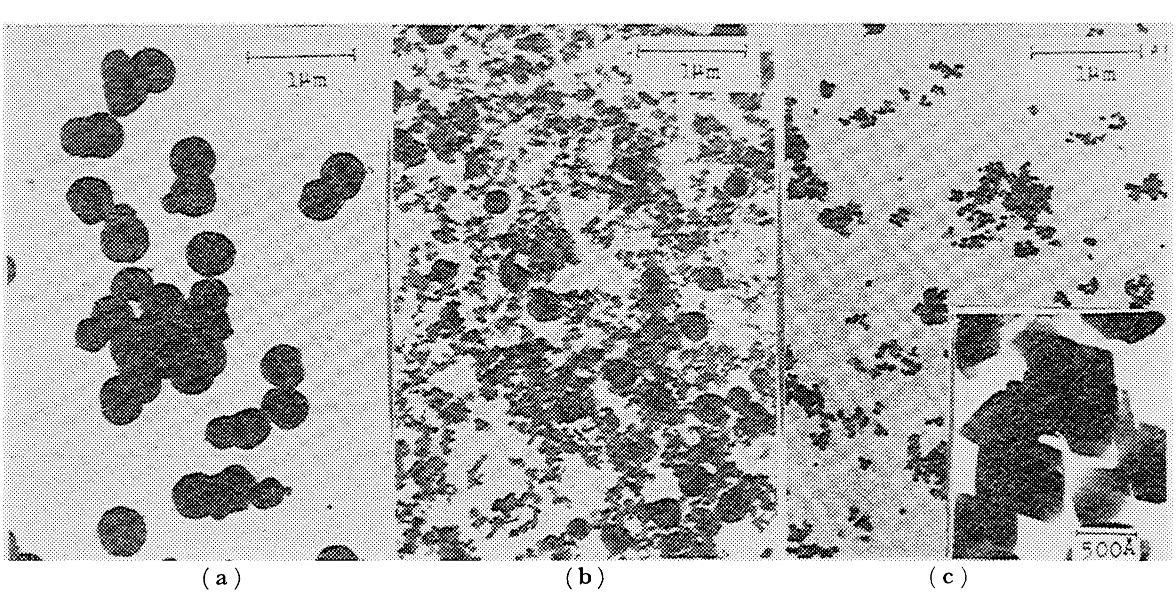

Fig. 3. Electronmicrographs of $Co_xFe_{3-x}O_4$ precipitates with $x=1.4$(a), 1.7(b), and 2.4(c).

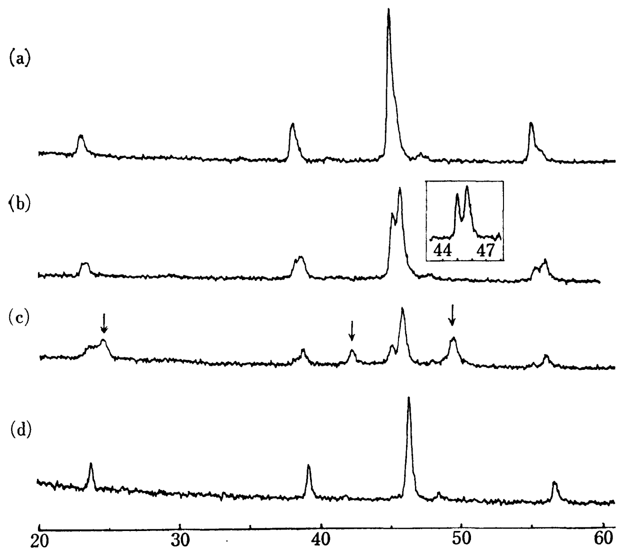

Fig. 4. X-Ray diffraction patterns of $Co_xFe_{3-x}O_4$ precipitates with $x=1.4$(a), 1.7(b), 2.0(c), and 2.4(d) prepared at $R=1.1$. The inset denotes a pattern of a ferrite with $x=1.7$ prepared from the suspension with $R=2.0$. Arrows in (c) indicate the peaks caused by the presence of a solid solution of hydroxides.

at room temperature. The nonferromanetic products with $2.2 \leq x \leq 2.5$ were amorphous, and the products with $x \geq 2.6$ had the same crystal structure as that of Co_3O_4.[14]

$Co_xFe_{3-x}O_4$ samples with 0.1—0.2 μm in r were chosen from the products prepared from the alkaline suspensions, and their demagnetization curves at room temperature were obtained after their saturation magnetization, σ_s, had been measured as has been described previously.[15] The increase in x from 0 to 0.8 caused a slight decrease in σ_s. A further increase in x from 1.4 caused a remarkable decrease in σ_s. The coercive force, $_iH_c$, increases with x and reaches 1.3 kOe for $x \geq 1.2$(Fig. 5). The magnetic properties of each sample which had been subjected to heating *in vacuo* at 350 °C for 5 h were measured. The shape and size of particles in the sample were found by microscopic examination to remain almost unchanged in spite of the heat treatment. The difference in the magnetic properties before and after the heat treatment is dependent on x (Fig. 5). The change in the magnetic properties by heat treatment must be caused by the diffusion of the metal ions within each particle in the $Co_xFe_{3-x}O_4$ samples as well as in the $Mn_xFe_{3-x}O_4$ samples.

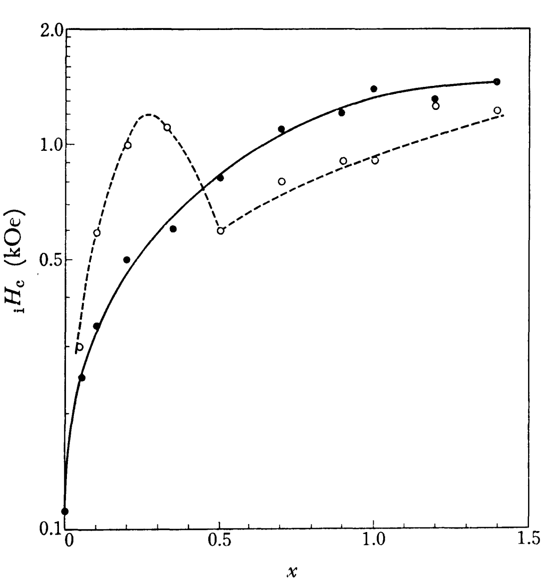

Fig. 5. Coercive force $_iH_c$ plotted against x in Co_x-$Fe_{3-x}O_4$ precipitates before (●) and after(○) heat treatment at 350 °C *in vacuo*.

Mechanism of Ferrite Formation. As has been mentioned above, the solid solution, $M_{x/3}Fe_{1-x/3}(OH)_2$ (M=Mn or Co), with $1.4 \leq x \leq 2.4$ in the starting suspension was transformed into a mixture of two kinds of ferrites, the content of each in the final oxidation product for a given value of x depending on the excess NaOH concentration. After the ferromagnetic ferrite(A), corresponding to $x \leq 1.3$, had been formed, the transformation of the remaining solid solution, $M_{x/3}$-$Fe_{1-x/3}(OH)_2$(M=Mn or Co), into the other ferrite(B) took place and proceeded gradually. It can be deduced from this finding that the content of the Mn or Co ion in the remaining solid solution increases with the progress of the formation of ferrite(A) caused by oxidation.

As has been generally known, the dissolution rate of ferrite into an acidic solution is extremely small as compared with that of the solid solution of hydroxides. By making use of this fact, the changes in the composition of ferrite and the solid solution with the time lapse of oxidation were studied. Several suspensions, each containing 0.36 mol/l of $M_{x/3}Fe_{1-x/3}(OH)_2$(M=Mn or Co) and either 0.11 or 0.95 M excess NaOH($R=1.1$ or 2.3), were subjected to oxidation at 70 °C for 20 h. In the course of oxidation, 200-ml samples of each suspension were taken out after 2, 5, 8, and 20 h. The particle size of ferrite(A) was found by microscopic examination to become greater with the progress of the formation of ferrite(A) by oxidation. The precipitate in each 200-ml suspension, separated from the alkaline solution by filtration, was added to acetic acid (10 wt%). The alkaline filtrate was found to contain a trace of the metal ions. The acidic suspension with pH=4 containing acetic acid was left standing at room temperature for 10—30 min with occasional stirring. The remaining precipitate was separated from the acidic solution with pH=4 by filtration. The precipitate treated with acetic acid was found by X-ray analysis to consist of ferrites with no hydroxides.

The contents of Mn or Co in the remaining solid solution and in the ferrite formed were estimated from the amounts of the metal ions in the acidic filtrate and in the precipitate obtained by treatment with acetic acid respectively. These results are given in Table 3. The Mn or Co content, both in the solid solution and in ferrite (A), becomes greater as the formation of ferrite (A) proceeds by oxidation, and the formation of ferrite (B) begins when x in the solid solution becomes greater than 2. An increase in the concentration of excess NaOH accelerates the particle growth of ferrite (A) and retards the rate of increase in x in both the

Table 3. Relative change in the composition(x) of the remaining solid solution, $M_{x/3}Fe_{1-x/3}(OH)_2$ (M=Mn or Co), and of the ferrite, $M_xFe_{3-x}O_4$, in the course of oxidation at 70 °C

R	Oxidation time (h)								
	0	2	5	8	20	2	5	8	20
	$Mn_{x/3}Fe_{1-x/3}(OH)_2$					$Mn_xFe_{3-x}O_4$			
1.1	1.04	1.30	1.53	—	—	0.66	0.89	1.05	1.05
1.1	1.50	1.96	2.32	—	—	1.30	1.39	1.46	1.46
1.1	2.08	—	2.45	2.50	—	—	1.66[a]	1.91[a]	2.05[a]
2.3	1.50	1.71	1.99	2.57	—	1.03	1.31	1.45	1.46[a]
	$Co_{x/3}Fe_{1-x/3}(OH)_2$					$Co_xFe_{3-x}O_4$			
1.1	1.56	1.91	1.94	2.13	—	1.36	1.38	1.44	1.56[a]
2.3	1.56	—	1.73	1.78	2.62	—	1.37	1.43	1.57[a]

a) Consisting of a mixture of ferrites (A) and (B).

solid solution and ferrite (A) in the course of oxidation.

The change in the size and shape of the particles before and after the transformation into ferrites suggests that the transformation takes place in the suspension medium by the same mechanism as that described for the formation of Fe_3O_4.[6] The suspension medium is saturated with respect to the solid solution of $M_{x/3}Fe_{1-x/3}(OH)_2$(M=Mn or Co). When the suspension is subjected to oxidation with air, the bivalent metal ions (probably hydroxo complexes) in the suspension medium react with the dissolved oxygen. The relative redox potential of each metal ion between bivalent and trivalent states in the suspension medium has been known to decrease in the order of Co>Mn>Fe.[16] This probably causes the predominant formation of an iron(III) hydroxo complex(probably polynuclear). It is considered that the polynuclear complex reacts with the hydroxo complexes of bivalent metal ions of Fe^{2+} and Mn^{2+} or Co^{2+} to form the nuclei of ferrite (A). The hydroxo complexes consumed by the ferrite formation may be incessantly replenished by the dissolution of the particles of the solid solution into the suspension medium.

The nuclei of ferrite(A) might, therefore, grow on epitaxially by the slow coprecipitation of the hydroxo complexes of bivalent metal ions with the polynuclear complex formed by oxidation. As the growth of the particles of ferrite(A) proceeds, x in the remaining solid solution becomes greater and x in each particle of ferrite(A) increases until the epitaxial reaction of its surface with the complexes has been stopped. Thus, the rate of the increase in x of each particle of ferrite(A) during the growth period, which is influenced by the oxidation conditions, will determine the inhomogeneity in the composition of each particle in the samples with $x \leq 1.3$.

Table 2 indicates that, in spite of the decrease in cation vacancies, the a_0 of the samples of manganese ferrite decreases only slightly with an increase in the r. It can be inferred from these results that the Mn concentration increases continuously from the central to the sub-surface portion of each particle, and that both the difference in the concentration between the two portions and the concentration gradient within the particle depend on the r of the sample with a given value of x. The inhomogeneity in the composition of the individual Mn ferrite particles described above will hold true of the particles in the samples of $Co_xFe_{3-x}O_4$ with $x \leq 1.3$.

In conclusion, the anomalous magnetic behavior of the ferrite(A) prepared from the suspension by oxidation must inevitably be associated with its unique structural properties, differing from those of ferrite with the same composition prepared by the solid-state reaction.

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