The Formation of the Cd-bearing Ferrite by the Air Oxidation of an Aqueous Suspension

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When the Cd^{2+}/Fe_{total} ratio in the initial solution is below 0.1, almost all cadmium ions are incorporated into the ferrite with the spinel-type structure by the air oxidation of an aqueous suspension at a pH 9.0 and at 65 °C. The Cd-bearing ferrite thus obtained is a ferromagnet and is oxidized to form a completely oxidized Cd-bearing ferrite at 150 °C in the air; this ferrite is still a ferromagnet and belongs to the Fe_2O_3–$CdFe_2O_4$ binary system, with the same spinel type structure. When the Cd^{2+}/Fe_{total} ratio in the initial solution increases to 0.5, the crystalline phases formed is complicatedly changed; the products are also significantly affected by the pH value of the suspension. The most favorable pH value at 65 °C to form the Cd-bearing ferrite is proposed to be 10.0.

Feitknecht[1] has found that Fe_3O_4 with the spinel-type structure is formed by the air oxidation of the iron(II) hydroxide, $Fe(OH)_2$, in a suspended solution at a pH of about 8.5. Kiyama[2] reported that the temperature increase of the suspension is favorable for the formation of Fe_3O_4. Recently, more favorable conditions for the formation from the suspension have been studied by Tamaura *et al.*[3] by using a dispersing reagent such as sucrose. Ferrite, the solid solution of $(Fe, M)_3O_4$ with a spinel-type structure composed of iron and other metal ions M, was also synthesized at temperature above 60 °C. Yasuoka *et al.*,[4] Hamamura *et al.*,[5] and Kiyama[6] have succeeded in synthesizing Mn- and $ZnFe_2O_4$, $BaFe_2O_4$, and Mn-, Co-ferrites respectively. Katsura *et al.*[7,8] and Kaneko and Katsura[9] have also studied the formation of a solid solution of $FeCr_2O_4$–Fe_3O_4, Fe_2TiO_4–Fe_3O_4, and $MgFe_2O_4$–Fe_3O_4. In their paper, Kaneko and Katsura[9] have clarified that the magnesium ion is incorporated in only a limited amount at 65 °C and pH 9.0, and that no Mg-ferrite is formed at pH values below 8.0. Kiyama[6] has shown that the amount of cobalt ion incorporated into the ferrite structure increases as the R value($NaOH/FeSO_4$) of the suspension increases. The ferrite formation from the suspensions and the content of metals other than iron in the ferrite seem to be influenced by such reaction conditions as the pH value, the temperature, and the metal concentration in the reaction solution.

In this paper, the reaction conditions for the formation of the Cd-bearing ferrite from the suspension are investigated, and the most favorable reaction condition for forming it are discussed. The Cd-bearing ferrite means the ferrite containing the cadmium ions more or less in its crystal structure to form the solid solution between Fe_3O_4 and $CdFe_2O_4$; we will call the Cd-bearing ferrite simply Cd-ferrite; we do not mean the $CdFe_2O_4$ compound.

Experimental

Reagents. Chemical reagents of analytical grades were used. A 2-mol/dm^3 sodium hydroxide solution was prepared by dissolving sodium hydroxide in distilled water free from carbon dioxide and oxygen. A 0.863 mol/dm^3 cadmium sulfate solution was prepared from $CdSO_4 \cdot 7H_2O$.

Apparatus. The reaction vessel of the Dewar type used in this study was the same as that employed in a previous study.[9]

Procedure. After adding the distilled water, cadmium sulfate, and sodium sulfate to the reaction vessel, nitrogen gas was bubbled into the solution while it was being stirred at 1000 r.p.m. for 1 h to remove the dissolved gases of carbon dioxide and oxygen. Then a 12.0-g portion of $FeSO_4 \cdot 7H_2O$ was added to the solution. The resultant volume of the solution was set at 200 cm^3, and the total concentration of the sulfate ion was fixed at 65 mmol/200 cm^3 (we call this solution the initial solution). The subsequent procedures were just the same as those described in the previous paper.[9] The Precipitate A means the product obtained after the air oxidation. The Precipitate B was obtained by lowering the pH value of the suspension containing the Precipitate A to pH 5.0. The procedure was described in detail in the previous report.[9]

Chemical Analysis. The Cd^{2+} content was determined gravimetrically after precipitating bis(8-quinolinolato)Cd(II). The amounts of Fe^{2+} and Fe^{3+} ions were determined by the method described previously.[9]

The Precipitates A and B were examined by the X-ray powder diffraction method by using Fe $K\alpha$ radiation and electron microscopy.

Results and Discussion

The X-Ray Powder Diffraction Data at pH *9.0.* Figure 1 shows the X-ray powder diffraction patterns of the Precipitates A obtained at various concentrations of Cd^{2+} in the initial solutions and at pH 9.0. At the Cd^{2+}/Fe_{total} ratios of 0.03 and 0.1 in the initial solutions, only the peaks corresponding to the compound with the spinel structure are seen (the patterns A and B in Fig. 1). However, at a ratio of 0.2, the peaks of the spinel-type compound become fairly small and the peaks of α-FeOOH are seen (the C pattern in Fig. 1). At a ratio of 0.15 the pattern was the same as that of the ratio of 0.10. At a ratio of 0.30, no peaks were observed in the X-ray powder diffraction pattern; this means that no crystalline compounds are formed. However, at a ratio of 0.40, as may be seen in the D pattern in Fig. 1, cadmium hydroxide was crystallized, together with the spinel-type compound.

Figure 2 shows the X-ray powder diffraction patterns of the Precipitates B. At the ratios of Cd^{2+}/Fe_{total} from

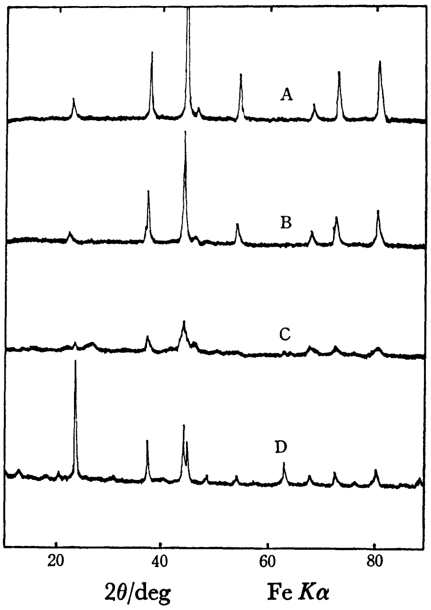

Fig. 1. The X-ray powder diffraction patterns of the Precipitates A obtained at the Cd^{2+}/Fe_{total} molar ratios of 0.03(pattern A), 0.10(pattern B), 0.20(pettarn C), and 0.40(pattern D), respectively.

0.03 to 0.10 in the initial solution, the patterns are similar to those of the Precipitates A (the A and B patterns in Figs. 1 and 2). At the ratio of 0.20, however, the two small peaks due to the presence of the α-FeOOH and the spinel-type compound both seem to be slightly stronger than those of the Precipitate A (the C patterns in Figs. 1 and 2). This indicates that some soluble compounds such as cadmium hydroxide are formed in the Precipitate A, together with α-FeOOH and the spinel-type compounds. At the ratio of 0.40, as may be seen in the D patterns in both Figs. 1 and 2, the cadmium hydroxide in the Precipitate A is completely dissolved by lowering the pH value to 5.0.

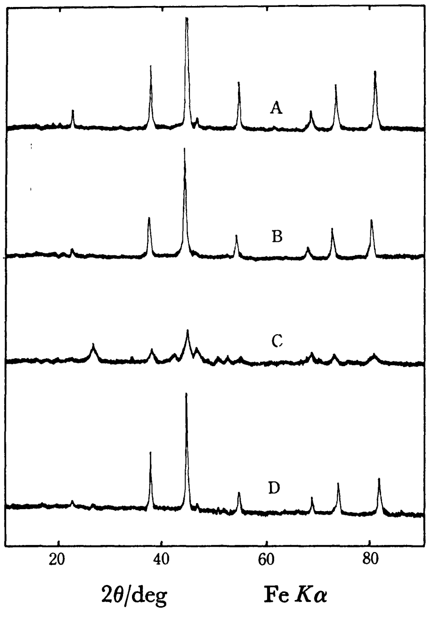

Fig. 2. The X-ray powder diffraction patterns of the Precipitates B obtained at the Cd^{2+}/Fe_{total} molar ratios of 0.03(pattern A), 0.10(pattern B), 0.20(pattern C) and 0.40(pattern D), respectively.

In view of the results presented above, the oxidation reactions of the $Fe(OH)_2$ suspension in the presence of Cd^{2+} at pH 9.0 and at 65 °C may be classified into the four processes: (1) the formation of only the spinel-type compound at the Cd^{2+}/Fe_{total} ratio in the initial solution below 0.10; (2) the formation of α-FeOOH, the spinel compound, and cadmium hydroxide at the ratios from 0.15 to 0.20; (3) the formation of only amorphous materials at the ratio of 0.30, and (4) the formation of the cadmium hydroxide crystal together with the spinel-type compound at the ratios above 0.40.

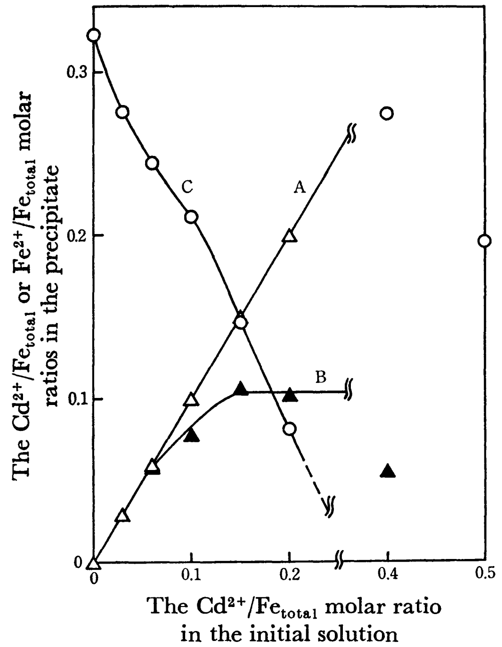

Fig. 3. The relationship between the Cd^{2+}/Fe_{total} molar ratio in the initial solution and the Cd^{2+}/Fe_{total} or the Fe^{2+}/Fe_{total} molar ratio in the Precipitates A and B. The curve A: the Cd^{2+}/Fe_{total} molar ratio in the Precipitate A, the curve B: the Cd^{2+}/Fe_{total} molar ratio in the Precipitate B, the curve C: the Fe^{2+}/Fe_{total} molar ratio in the Precipitate B.

Chemical Composition of the Oxidation Products at pH *9.0.* Figure 3 shows the relationship between the Cd^{2+}/Fe_{total} molar ratio in the initial solution and the Cd^{2+}/Fe_{total} or Fe^{2+}/Fe_{total} molar ratio in the Precipitates A and B. As may be seen in Fig. 3, Curve A, the Cd^{2+} content in the Precipitate A increases linearly with an increase in the Cd^{2+} concentration in the initial solution. The Cd^{2+} in the initial solution was completely extracted by the Precipitate A over the range from 0 to 0.3 of the Cd^{2+}/Fe_{total} ratio in the initial solution.

As may be seen in Curve B, the Cd^{2+} content in the Precipitate B increases with an increase in the Cd^{2+}/Fe_{total} ratio within a limited range from 0 to 0.1, but approaches a constant Cd^{2+}/Fe_{total} ratio, approximately 0.1, in the range from 0.15 to 0.20 in the initial solution. This suggests that all the Cd^{2+} in the initial solution is taken into the Cd-ferrite at ratios below 0.10. This process corresponds to the oxidation reaction (1) in the previous section. At the ratios from 0.15 to 0.20, it is likely that some variable amount of the precipitate of cadmium hydroxide which is soluble at pH 5.0 is formed in the Precipitate A. This corresponds to the oxidation reaction (2). At the ratio of 0.30, we could not obtain a constant content of Cd^{2+} after duplicated analyses of the Precipitate B. This may correspond to the oxidation reaction (3). At the ratio of 0.40, the Cd^{2+}/Fe_{total} ratio in the Precipitate B was 0.057, which is smaller than those at the ratios from 0.05 to 0.20. This indicates that the incorporation of the cadmium ion into the Cd-ferrite is rather reduced at ratios above 0.40. This corresponds to the oxidation reaction (4).

Curve C in Fig. 3 shows the Fe^{2+}/Fe_{total} ratio in the Precipitate B. Since no iron ions were detected in the solutions coexisting with both the Precipitate A and B, the iron oxides formed in the Precipitate A seem hardly to be dissolved at all at pH 5.0. As may be seen in Curve C, the Fe(II) content in the Precipitate B decreases with an increase in the Cd^{2+}/Fe_{total} ratio in the initial solution; this may suggest that the cadmium ion replaces the Fe(II) ion in the spinel-type structure at Cd^{2+}/Fe_{total} ratios from 0 to 0.10 in the initial solution. The further decrease in the Fe^{2+}/Fe_{total} ratio at higher ratios of Cd^{2+}/Fe_{total} in the initial solution (0.10 to 0.20) is due to the gradual formation of α-FeOOH, together with the formation of oxidized Cd-ferrite.

Lattice Constant. Figure 4 shows the relationship between the lattice constant of the Cd-ferrite obtained from the Precipitates B and the Cd^{2+}/Fe_{total} ratio in the initial solution at pH 9.0. As may be seen in Fig. 4, Curve A, the lattice constant of the Precipitate B increases almost linearly with an increase in the amount of Cd^{2+} in the initial solution with the Cd^{2+}/Fe_{total} ratios from 0 to 0.15. This shows that the cadmium ion is incorporated into the ferrite. However, at ratios above 0.15 the lattice constant gives a constant value, 0.8510 nm. Curve B in Fig. 4 shows the relationship between the lattice constant of the completely oxidized-Precipitates B obtained by heating at 150 °C in the air and the Cd^{2+}/Fe_{total} ratio in the initial solution. The X-ray diffraction patterns were identical with those of the Precipitates B, but each peak belonging to the spinel-type structure was shifted to a higher angle. The lattice constant of the oxidized-Precipitates B increases with an increase in the Cd^{2+}/Fe_{total} ratios in the initial solution from 0 to 0.20. As has been mentioned before, at the ratio of 0.30 the Precipitate B was composed of only an amorphous product, and even if we heated this at 150 °C for a day, we could not obtain a crystalline phase. At the ratio of 0.40, the lattice constant of the oxidized-Precipitate B was 0.8429±0.0001 nm. This value is somewhat lower than that at 0.20. At present, we are not able to interpret whether or not this difference is significant.

From these experiments, we may say that the Precipitates B obtained from the initial solutions with the Cd^{2+}/Fe_{total} ratios from 0 to 0.20 comprise a limited solid solution between Fe_3O_4 and $CdFe_2O_4$, that the further $CdFe_2O_4$ component is never incorporated in the spinel structure under the present experimental conditions, that this solid solution is unstable at higher temperatures, say, above 100 °C, in the air, and that it is interestingly oxidized completely to form a limited solid solution between γ-Fe_2O_3 and $CdFe_2O_4$. Figure 5 shows the relationship between the lattice constant and the mole fraction x of the $CdFe_2O_4$ component in the solid solution. The lattice constants of γ-Fe_2O_3 and

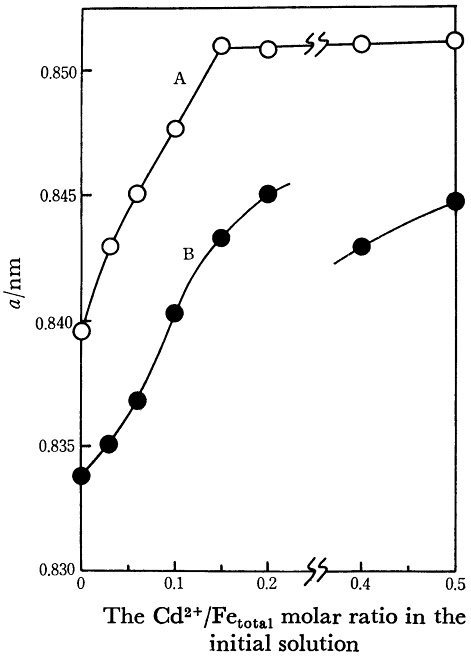

Fig. 4. The relationship between the Cd^{2+}/Fe_{total} molar ratio in the initial solution and the lattice constant of the Precipitate B or the oxidized-Precipitate B. The curve A: Precipitate B, the curve B: the oxidized-Precipitate B. a: Lattice constant.

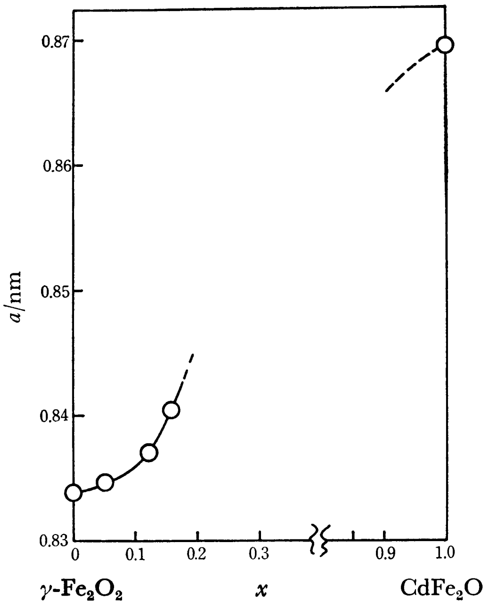

Fig. 5. The relationship between the lattice constant and the x value of the oxidized-Precipitate B. The x represents the molar ratio of $CdFe_2O_4$ to ($CdFe_2O_4$+γ-Fe_2O_3). a: Lattice constant.

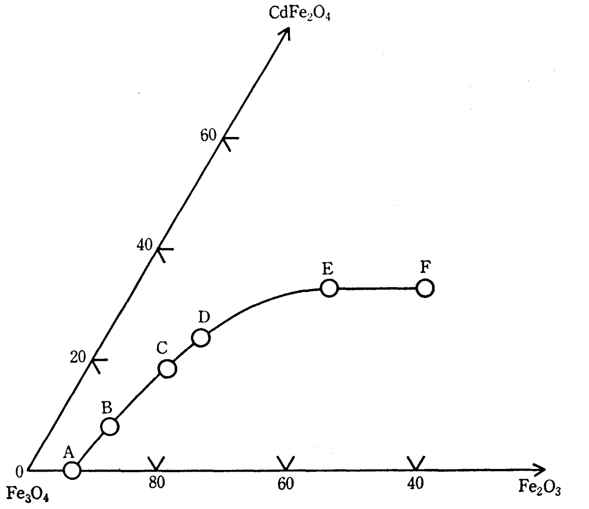

Fig. 6. The chemical compositions of the Precipitate B expressed as the Fe_3O_4–Fe_2O_3–$CdFe_2O_4$ system. Points A, B, C, D, E and F were obtained at the Cd^{2+}/Fe_{total} molar ratios of 0.00, 0.03, 0.06, 0.10, 0.15 and 0.20, respectively.

$CdFe_2O_4$ were determined by Schrader and Buttner[10] and Roberts *et al.*[11] respectively. As may be seen in Fig. 5, the lattice constants of the oxidized-Precipitates B fall between those of γ-Fe_2O_3 and $CdFe_2O_4$.

Composition Diagram for the Precipitates B. Figure 6 shows the composition diagram for the Precipitates B formed at pH 9.0. For convenience, Fe_3O_4, Fe_2O_3 and $CdFe_2O_4$ are selected as the three component systems. As may be seen in Fig. 6, the Precipitates B all significantly deviate from their stoichiometric compositions. Under the present conditions, it seems to be next to impossible to synthesize the stoichiometric solid solution.

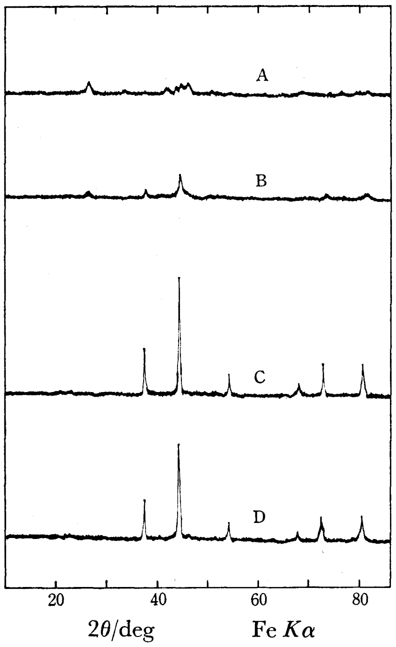

Fig. 7. The X-ray powder diffraction patterns of the Precipitates A obtained at pH 7.0(patternA), 8.0-(pattern B), 10.0(pattern C) and 11.0(pattern D). The Cd^{2+}/Fe_{total} molar ratio was fixed to 0.10.

This was also true for the Fe_3O_4–Fe_2TiO_4 and the Fe_3O_4–$MgFe_2O_4$ systems, which were studied by Katsura *et al.*[8] and by Kaneko and Katsura[9] respectively.

pH *Dependence on the Formation of the Precipitates A and B.* In the preceding section, we discussed the properties of the Precipitates A and B formed at pH 9.0 and at 65 °C. We also studied the pH dependence on the formation of the Precipitates A and B by changing

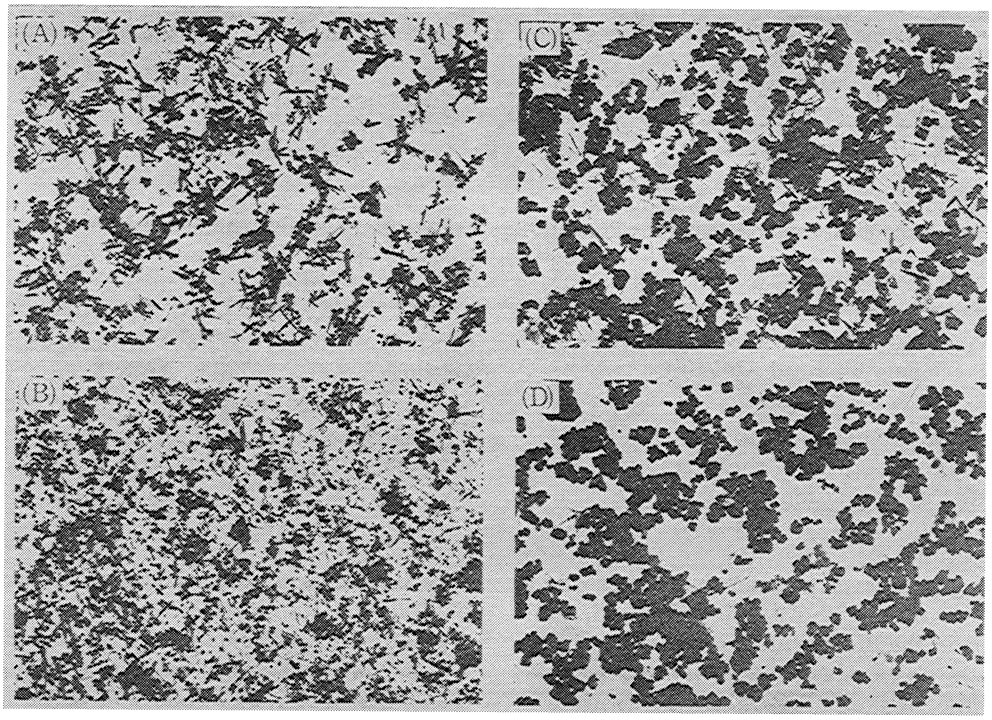

Fig. 8. The electron-micrographs of the Precipitates B obtained at pH 7.0(A), 8.0(B), 10.0(C) and 11.0(D). The Cd^{2+}/Fe_{total} molar ratio was fixed to 0.10.

the pH values from 7.0 to 11.0 at 65 °C. Figure 7 shows the X-ray diffraction patterns of the Precipitates A obtained at pH 7.0, 8.0, 10.0, and 11.0. At pH 9.0 (the patterns B in Fig. 1), 10.0, and 11.0, very sharp peaks caused by the presence of the ferrite structure are seen, while at pH 7.0 and 8.0 the peaks flatten out. It is presumed that the ferrite crystal with a small particle size and the α-FeOOH phase are formed at pH 7.0 and 8.0. The same X-ray patterns were obtained for the Precipitates B. Figure 8 shows the electron micrographs of the Precipitates B obtained at pH 7.0, 8.0, 10.0, and 11.0. As may be seen in Fig. 8, the large-size Cd-ferrite (0.12 μm) is formed together with a little amount of the needle-like crystals. However, the particle of the Cd-ferrite crystal becomes small at pH 7.0 and 8.0, and the amount of the needle-like crystals increases. These needle-like crystals seem to be composed of α-FeOOH. Thus, the results obtained by the electron microscopy agree very well with those obtained from the X-ray diffraction patterns.

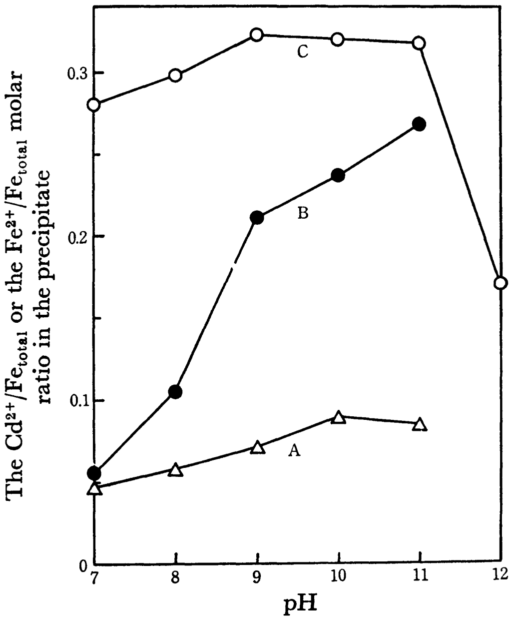

Fig. 9. The relationship between the pH value of the suspension and the chemical composition of the Precipitate B. The Cd^{2+}/Fe_{total} molar ratio in the initial solution is fixed to 0.10. The curve A: the Cd^{2+}/Fe_{total} ratio in the Precipitate B, the curve B: the Fe^{2+}/Fe_{total} ratio in the Precipitate B, the curve C: the Fe^{2+}/Fe_{total} ratio of the Precipitate B formed without Cd^{2+}.

Figure 9 illustrates the relationship between the Cd^{2+}/Fe_{total} or the Fe^{2+}/Fe_{total} ratio in the Precipitate B and the pH value of the suspension. As may be seen in Fig. 9, Curve A, approximately half of the Cd^{2+} added to the initial solution was taken into the Precipitate B at any pH value. However, considering the precision in the present chemical analysis, it is evident that the Cd^{2+}/Fe_{total} ratio in the Precipitate B gives its maximum value at pH 10.0. As seen in Fig. 9, Curve B, the Fe^{2+}/Fe_{total} ratio in the Precipitate B increases abruptly at pH 9.0, and then increases gradually from 9.0 to 11.0. The lower ratio at a lower pH range (from 7.0 to 8.0) is the result of the formation of α-FeOOH, together with the further oxidation of the Cd-ferrite with a small particle size (see Fig. 8). Curve C in Fig. 9 shows the pH dependence of the chemical composition of Fe_3O_4 (Cd=0) for the sake of comparison. As may be seen in Curve C, the Fe^{2+}/Fe_{total} ratios fall in a narrow range from 0.28 to 0.32 (in stoichiometric composition, the ratio is 0.333) at the pH intervals from 7.0 to 11.0. Thus in the presence of Cd^{2+} in the initial solution, α-FeOOH is liable to be formed together with the Cd-ferrite. However, only a small amount of α-FeOOH is crystallized, together with a large amount of the Cd-ferrite, when the pH value increases to 11.0. In addition, we can safely conclude that, at pH 11.0, the cadmium ion intrinsically replaces the Fe(II) ion in the crystal lattice of the spinel-type structure.

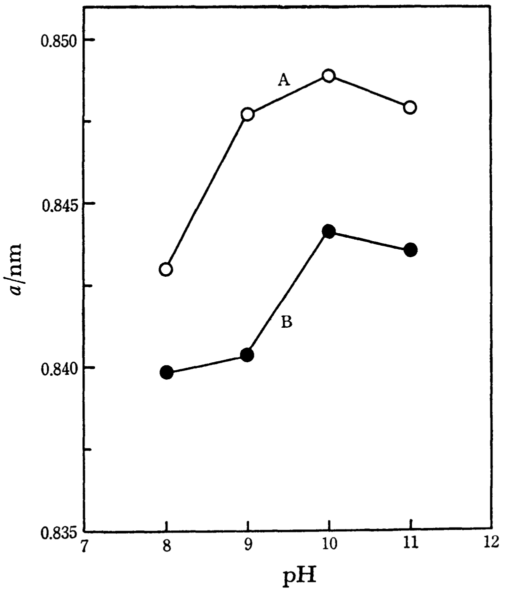

Fig. 10. The relationship between the pH value of the suspension and the lattice constant of the Precipitate B or the oxidized-Precipitate B obtained at the Cd^{2+}/Fe_{total} molar ratio of 0.10. a: Lattice constant.

Figure 10 shows the relationship between the lattice constants of the Precipitate B and the oxidized-Precipitate B and the pH value at which the Precipitate B is formed. As may be seen in Fig. 10, Curve A, the lattice constant of the Precipitate B increases irregularly with an increase in the pH value from 8.0 to 10.0, and attains its maximum value, 0.8489 nm, at pH 10.0. Thereafter, at pH 11.0, the lattice constant decreases slightly. It seems likely that the Cd-ferrite is most favorably formed at pH 10.0, because the more the cadmium ion replaces the Fe(II) ion, the more the lattice constant increases. However, we have to consider also the grades of oxidation of the Cd-ferrite at various pH values in the suspension. As was mentioned in the previous section, the Cd-ferrite formed at low pH values, 7.0 and 8.0, is small in particle size and so is oxidized easily during the air oxidation, while maintaining the spinel-type structure. For example, as may be seen in Fig. 10, the lattice constants of the Cd-ferrites formed at pH 8.0 and 9.0 are quite different from each other (Curve A). We assume that the Cd-ferrite formed at pH 8.0 is oxidized significantly during the air oxidation. As may be seen in Fig. 10, Curve B, the lattice constants of the completely oxidized-Precipitates B at pH 8.0 and 9.0 are nearly the same amount of cadmium ion is incorporated into the ferrite at both pH values. Furthermore, we have confirmed that the pH value of 10.0 is the most favorable for forming the Cd-ferrite at 65 °C. Here, we should emphasize that the formation of the (Fe, M)$_3$O$_4$ type of ferrite is sensitively affected by the pH value in the suspension.

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