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Formation of Zn-bearing Ferrite by Air Oxidation of Aqueous Suspension

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Zn-bearing spinel ferrites were obtained by air oxidation of the iron(II) hydroxide suspension of the mole fraction Zn(II) to [Zn(II)+$\mathrm{Fe_{total}}$], r_{Zn}, ranging from 0.029 to 0.33 (except for 0.057) at pH 10.0 and 65 °C, but at $r_{\mathrm{Zn}}=0.057$ only α-FeOOH was formed. The Zn-bearing spinel ferrite obtained at $r_{\mathrm{Zn}}=0.33$ has the normal spinel structure. At pH 8.0, the Zn-bearing spinel ferrite is obtained at $r_{\mathrm{Zn}}=0.057$, but the spinel ferrite is slightly oxidized to γ-Fe_2O_3.

Recently, the conditions for the formation of spinel ferrite from aqueous iron(II) hydroxide suspensions containing other metal ions have been investigated in detail by several workers.[1—4] Kiyama[1] investigated the formation of Mn- and Co-bearing spinel ferrites and reported that, in alkaline suspensions, all the metal ions were incorporated into the spinel ferrites. Katsura *et al.*[2] reported that the oxidized Fe_3O_4–Fe_2TiO_4 solid solution with spinel structure was obtained from the suspension containing titanium(IV) ions. Kaneko *et al.* investigated the formation of Mg-[3] and Cd-[4] bearing spinel ferrites. When the mole fraction of Mg(II) to [Mg(II)+$\mathrm{Fe_{total}}$] or Cd(II) to [Cd(II)+$\mathrm{Fe_{total}}$] in the suspension is below 0.091, almost all the metal ions are incorporated into the spinel ferrite by an oxidation reaction at pH 9.0. When the mole fraction is above 0.091, the excess magnesium(II) produces a basic magnesium(II) sulfate, and the crystalline phases formed from the suspension containing cadmium(II) ion are changed in a complicated way.

In this paper, the reaction conditions for the formation of Zn-bearing spinel ferrite from the suspension containing zinc(II) ion are investigated.

Experimental

Reagents. Chemical reagents of analytical grade were used. A 2 mol/dm³ sodium hydroxide solution was prepared by dissolving sodium hydroxide in distilled water free from carbon dioxide and oxygen. A sulfuric acid solution of 0.856 mol/dm³ zinc(II) sulfate (pH≅3) was prepared from zinc(II) sulfate heptahydrate.

Apparatus. The reaction vessel of the Dewar type used in this study was the same as that employed previously by Kaneko and Katsura.[3]

Procedure. After adding distilled water, zinc(II) sulfate solution, and sodium sulfate to the reaction vessel, nitrogen gas was bubbled into the solution while it was being stirred at 1000 $\mathrm{min^{-1}}$ for 1 h to remove the dissolved gases of carbon dioxide and oxygen. Then 12 g of iron(II) sulfate heptahydrate was added to the solution. The resultant volume of the solution was set to 200 cm³, and the total concentration of the sulfate ion was fixed to 65 mmol/200 cm³. pH values were adjusted by using 2 mol/dm³ sodium hydroxide solution and the suspension was let stand for 1 h with stirring under nitrogen at 65 °C (we call this suspension the "initial suspension"). The subsequent procedures were the same as those described by Kaneko and Katsura.[3] The precipitate in this paper means the product obtained by lowering the pH value of the suspension to pH 4.0 with 0.5 mol/dm³ sulfuric acid after the air oxidation. At this pH value, zinc(II) hydroxides and iron(II) hydroxides dissolve completely.

Chemical Analysis. The zinc(II) content was determined by atomic absorption spectrometry after the extraction of an iron with diisopropyl ether. The amounts of iron(II) and iron(III) were determined by the method described by Kaneko and Katsura.[3]

The precipitates were examined by the X-ray powder diffraction method with Fe *Kα* radiation, the electron microscopy, and the Mössbauer spectra measurement at room temperature.

Titration curves were obtained as follows. A sulfuric acid solution containing zinc(II) and/or iron(II) sulfates was titrated with 2 mol/dm³ sodium hydroxide solution at 65 °C. Nitrogen gas was bubbled into the solution during the titration and the values of pH were measured at each point 10 min after the addition of the sodium hydroxide solution.

Results and Discussion

X-Ray Powder Diffraction Patterns, Electron Micrograph, Chemical Composition, and Mössbauer Spectra of the Precipitate obtained by Air Oxidation at pH 10.0. In the X-ray powder diffraction patterns of the precipitate obtained from the suspension of the r_{Zn} values (the r_{Zn} value means the mole fraction of Zn(II) to [Zn(II)+$\mathrm{Fe_{total}}$] in the initial suspension) ranging from 0.029 to 0.33 (except for 0.057), only the peaks for spinel type structure were seen, while at $r_{\mathrm{Zn}}=0.057$, only the peaks for α-FeOOH were observed. The electron micrographs of the precipitate showed the formation of a spherical or cubic particle of spinel ferrite, except for a needle-like crystal of α-FeOOH for $r_{\mathrm{Zn}}=0.057$. Lattice constants a_0 of the spinel ferrites are plotted against the r_{Zn} values in Fig. 1 (curve A). The lattice constants of completely oxidized samples with spinel type structure are also plotted (curve B). The oxidation of the spinel ferrites was performed by heating at 180 °C in air for 6 h. In the X-ray powder diffraction patterns of the oxidized samples, only the peaks for the spinel type structure were seen. Chemical analyses showed that there was no detectable amount of iron(II) in the oxidized samples. As seen from the curves A and B in Fig. 1, the lattice constants of the spinel ferrites and those of completely oxidized samples increase with increasing the r_{Zn} values. This shows that Fe^{2+} in the spinel ferrite is replaced by Zn^{2+}, and that the amount of Zn^{2+} on the lattice points increases with increasing the r_{Zn} values. Chemical analyses showed that, at the r_{Zn} values ranging from 0.029 to 0.33 (except for 0.057), almost all zinc(II) ions in the initial suspension

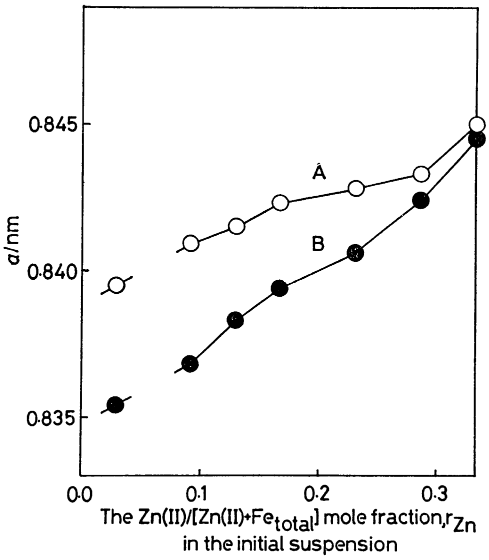

Fig. 1. The relationship between the Zn(II)/[Zn(II)+Fe$_{\rm total}$] mole fraction in the initial suspension and the lattice constants of the spinel ferrite obtained at pH 10.0 or those of the completely oxidized sample with spinel type structure. The curve A: the spinel ferrite, the curve B: the completely oxidized sample, a: the lattice constant.

($>$92%) were taken into the precipitate. The mole fractions of [Zn(II)+Fe(II)] to [Zn(II)+Fe$_{\rm total}$] in the precipitate were 0.30—0.35. These values are close to those of stoichiometric spinel ferrite Fe_3O_4–$ZnFe_2O_4$ (0.333). The lattice constant of the Zn-bearing spinel ferrite at $r_{\rm Zn}=0.33$ (Fig. 1) is very close to that of zinc spinel ferrite $ZnFe_2O_4$ synthesized by the solid state reaction (0.8441 nm).[5]

The Mössbauer spectrum at room temperature of the precipitate obtained at $r_{\rm Zn}=0.33$ showed a quadrupole-split pattern. The isomer shift relative to metallic iron estimated from the quadrupole-split spectrum (0.030 cm s^{-1}) is in good agreement with that of zinc spinel ferrite synthesized by solid state reaction (0.0358 cm s^{-1})[6] within our experimental errors ($\pm$0.008 cm s^{-1} as stand. dev.). Thus, the Zn-bearing spinel ferrite obtained at $r_{\rm Zn}=0.33$ and pH 10.0 is concluded to be the zinc spinel ferrite which has the normal spinel structure.

pH *Dependence on the Formation of the Precipitate for* $r_{\rm Zn}=0.091$. In the X-ray powder diffraction patterns of the precipitate obtained by air oxidation of the suspension of $r_{\rm Zn}=0.091$ at pH values ranging from 7.0 to 10.0, only the peaks for spinel type structure were seen, while at pH 11.0 only the peaks for α-FeOOH were observed. The electron micrographs of the precipitate showed the formation of a spherical or cubic particle of spinel ferrite, except for a needle-like crystal of α-FeOOH at pH 11.0. Figure 2 shows the lattice constants a_0 of the spinel ferrites obtained at pH ranging from 7.0 to 10.0 (curve A) and those of the completely oxidized samples with spinel type structure (curve B). As seen from curve B, the lattice constants of the completely oxidized samples are constant within our experimental errors. Chemical analyses showed that almost all zinc(II) ions in the initial suspension ($>$92%) were taken into the precipitate at the pH values ranging from 7.0 to 10.0, but at pH 11.0, only about 40% of zinc(II) ions were taken in. These results show that, at these pH values, Zn-bearing spinel ferrites which have a constant amount of Zn^{2+} on the lattice points are formed. The mole fractions of [Zn(II)+Fe(II)] to [Zn(II)+Fe$_{\rm total}$] in the precipitate decreased from 0.31 to 0.26 upon decreasing the pH values from 10.0 to 7.0. The lattice constants of the Zn-bearing spinel ferrites obtained at lower pH values, as shown by curve A in Fig. 2, are smaller than those of the spinel ferrites obtained at a higher pH value. These suggest that a Zn-bearing spinel ferrite which is slightly oxidized to γ-Fe_2O_3 is formed at lower pH values. From the electron micrographs, it was shown that the particle size of the Zn-bearing spinel ferrites becomes small at a lower pH value (0.1 and 0.2 μm at pH 7.0 and 10.0, respectively), which seems to cause further oxidation of the spinel ferrites at this lower pH value.

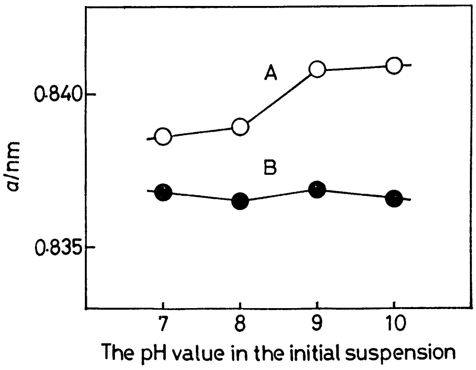

Fig. 2. The relationship between the pH value in the initial suspension and the lattice constants of the spinel ferrite obtained at the Zn(II)/[Zn(II)+Fe$_{\rm total}$] mole fraction of 0.091 in the initial suspension or those of the completely oxidized sample with spinel type structure. The curve A: the spinel ferrite, the curve B: the completely oxidized sample, a: the lattice constant.

Depression of the Formation of Zn-bearing Spinel Ferrite. As mentioned in a previous section, at $r_{\rm Zn}=0.057$ and pH 10.0 the formation of Zn-bearing spinel ferrite is depressed and α-FeOOH is formed. The depression of the Zn-bearing spinel ferrite was, however, restored, when the pH value in the initial suspension was lowered to pH 8.0, that is, only the peaks for the spinel type structure were seen in the X-ray powder diffraction pattern of the precipitate.

Figure 3 shows the titration curves of the solutions of iron(II) sulfate (curve A), zinc(II) sulfate (curve B) and the mixed solution of zinc(II) and iron(II) sulfates (curve C). Iron(II) sulfate is titrated at pH values around 6.7—8.0 (curve A). However, zinc(II) sulfate is titrated first at pH around 5.5—6.0 (region a—b in curve B), and then around 7.4 (region c—d in curve B). During the titration of zinc(II) sulfate, in the region a—c in curve B, a basic zinc(II) sulfate seems to precipitate, and then in the region c—d, the basic zinc(II) sulfate is converted into $Zn(OH)_2$. The

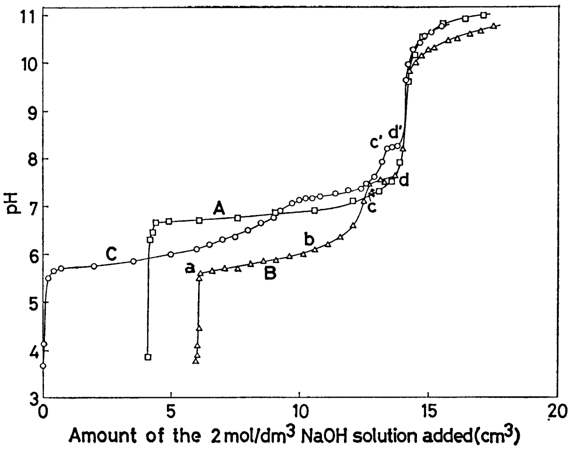

Fig. 3. The titration curves of Fe(II), Zn(II), and Zn(II)+Fe(II) sulfate solutions by 2 mol/dm^3 NaOH. The curve A: 1.08×10^{-2} mol Fe(II), the curve B: 8.56×10^{-3} mol Zn(II), the curve C: 8.56×10^{-3} mol Zn(II)+8.53×10^{-3} mol Fe(II). The titration curves of Fe(II) and Zn(II) sulfate solutions are shown from titer of 4.10 cm^3 and 6.00 cm^3, respectively to compare with that of Zn(II)+Fe(II) sulfate solution. The initial volume of the solutions was fixed to 200 cm^3.

point c in curve B represents the addition of 1.5 moles of sodium hydroxide per atom of zinc. Therefore, we can estimate the chemical formula of the hydrolyzed species at this point to be $Zn(OH)_{1.5}(SO_4)_{0.25}$[7] by assuming that the sulfate ion is coprecipitated. In the case of the mixed solution of zinc(II) and iron(II) sulfates, as seen by curve C (Fig. 3), the conversion reaction of the basic zinc(II) sulfate into $Zn(OH)_2$ occurs also at pH around 8.3 (region c'—d' in curve C).

Thus, at pH 8.0 where the depression of the Zn-bearing spinel ferrite formation is restored, the basic zinc(II) sulfate is precipitated in the suspension before air oxidation.

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