Formation of Zinc(II)-bearing Ferrites from γ-FeO(OH)

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Stoicheiometric zinc(II)-bearing ferrites were formed by increasing the reaction pH of a mixture of γ-FeO(OH), Fe^{II}, and Zn^{II} ions to 9.0 (25 °C) and allowing it to stand for 60 h. This reaction is initiated by the adsorption of the Fe^{II} ion on γ-FeO(OH).

The formation of Fe_3O_4 (magnetite) and metal ion-bearing ferrites in solution by air oxidation of a $Fe(OH)_2$ suspension in the presence and absence of other metal ions at temperatures above 60 °C have been studied.[1-10] Tamaura *et al.*[11] reported that γ-FeO(OH) is transformed to stoicheiometric Fe_3O_4 in the presence of Fe^{II} ion. The transformation reaction of γ-FeO(OH) to Fe_3O_4 is triggered by the adsorption of the Fe^{II} ion on γ-FeO(OH) at room temperature. The resultant intermediate is subsequently transformed to Fe_3O_4. It seems that when another metal ion such as Zn^{II} is adsorbed on γ-FeO(OH), the ion will be incorporated into the lattice structure of the ferrites, during the course of the transformation reaction.

In the present paper, we have studied the formation of zinc(II)-bearing ferrites by the transformation reaction of γ-FeO(OH) in the presence of Fe^{II} and Zn^{II} ions.

Experimental

Chemicals.—All chemicals were analytical grade and distilled water was used for the preparation of the chemical solutions. Sodium hydroxide solutions were prepared by dissolving NaOH in distilled water through which nitrogen gas had been passed to remove dissolved oxygen. The compound γ-FeO(OH) was prepared according to the method described in the previous paper.[11]

Apparatus.—The reaction vessel used previously was adopted.[2-5]

Procedure.—After adding Zn^{II} ion solution (0.02 dm^3, 0—0.54 mol dm^{-3}, pH 3.0) into a γ-FeO(OH) suspension (0.75 dm^3, pH 5.0), nitrogen gas was passed through for 2 h to remove dissolved oxygen and carbon dioxide. An $FeCl_2$ solution (0.02 dm^3, 0.54 mol dm^{-3}, pH 3.0) was added into the suspension, and the pH increased to 9.0. The suspension thus obtained will be referred to as ' the reaction suspension '. At pH 9.0 the reaction was initiated and the reaction pH became lower. To maintain the pH of the reaction suspension at 9.0, an alkaline solution was added during the course of the reaction using a pH-stat instrument. After allowing the reaction suspension to stand for 60 h at pH 9.0 (25 °C) with the passage of nitrogen gas, the mixture was centrifuged at 4 000 r.p.m. under a nitrogen atmosphere. The precipitate obtained was washed with an acetate buffer solution (pH 4.1, 0.05 mol dm^{-3}) to isolate the products (Zn^{II}-bearing ferrites) by dissolving the unreacted Fe^{II} and Zn^{II} ions. The precipitate was washed further with distilled water and successively with acetone to remove water as completely as possible. [The water and acetone had been deaerated by the passage of nitrogen gas to prevent oxidation of the ferrites formed.] Finally, the precipitate was dried under a nitrogen atmosphere (room temperature) and subsequently examined by *X*-ray diffractometry and Mössbauer spectroscopy.

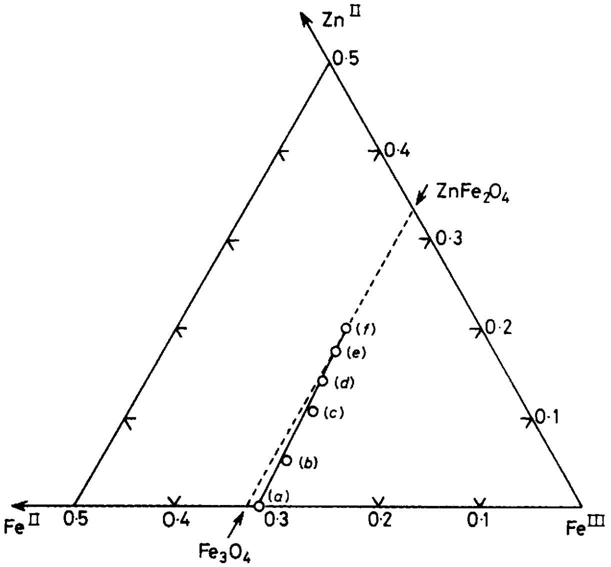

Figure 1. Ternary diagram showing the chemical compositions of the products. The mol ratio of Fe^{II} to the Fe^{III} of γ-FeO(OH) in the reaction suspension was 0.5 : 1. The mol ratios of Zn^{II} to the Fe^{III} of γ-FeO(OH) in the reaction suspension were 0 (*a*), 0.1 (*b*), 0.2 (*c*), 0.3 (*d*), 0.4 (*e*) and 0.5 (*f*), respectively

In studies to investigate the formation of the Zn^{II}-bearing ferrites by the adsorption of the Fe^{II} ion, the concentration of the Fe^{II} ion in the reaction suspension was lowered to 8×10^{-4} mol dm^{-3}.

Chemical Analysis.—The Fe^{II} and $Fe_{tot.}$ concentrations were determined by the 2,2′-bipyridyl method.[12] For the determination of $Fe_{tot.}$ the Fe^{III} ion was reduced to Fe^{II} with hydroxylamine. The Zn^{II} ion concentration was determined by an atomic absorption method.

Results and Discussion

Formation of Stoicheiometric Zn^{II}*-bearing Ferrites.*—Figure 1 gives the ternary diagram (Fe^{II}, Fe^{III}, and Zn^{II}) showing the chemical compositions of the products obtained by increasing the pH of the reaction suspension [reaction mixture of γ-FeO(OH), $Zn(OH)_2$, and $Fe(OH)_2$] to pH 9.0 and allowing it to stand for 60 h. In this study, the mol ratio of Fe^{II} to the Fe^{III} of γ-FeO(OH) in the reaction suspension was fixed at 0.5 : 1, and the mol ratio of Zn^{II} to the Fe^{III} of γ-FeO(OH) varied from 0 to 0.5 : 1.

The straight line (Figure 1) connecting the chemical compositions corresponds to the transformation of Fe_3O_4 to $ZnFe_2O_4$ (Zn^{II}-bearing ferrite) and shows the chemical compositions of the intermediate stoicheiometric solid solutions. The chemical compositions of the products are nearly

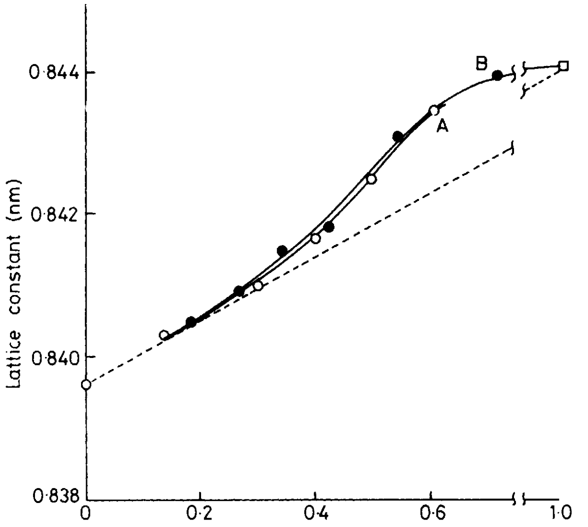

Figure 2. The relationship between the Zn^{II} content of the Zn^{II}-bearing ferrites and the lattice constants. Products formed at 1.4×10^{-2} mol dm^{-3} (curve A) and at 8×10^{-4} mol dm^{-3} (curve B)

equal to those of the stoicheiometric Zn^{II}-bearing ferrites over the mol ratio range of Zn^{II} to Fe^{III} of γ-FeO(OH) in the reaction suspensions of 0—0.5 : 1. In the *X*-ray diffraction patterns of the products, only the peaks of the spinel-type compound appeared. In the i.r. spectra, no bands of γ-FeO(OH) or other iron(III) oxides were observed. These results suggest that the products are virtually stoicheiometric Zn^{II}-bearing ferrites. The slight deviation from stoicheiometry at low Zn^{II} ion concentration was due to a little incompletion of the reaction; a very small amount of Fe^{II} remained unreacted.

Curve A of Figure 2 shows the relationship between the Zn^{II} content of the products and the lattice constants. The chemical compositions are represented by the value of x in $Zn_xFe_{3-x}O_4$, assuming that the products are Zn^{II}-bearing ferrites whose chemical compositions of the Zn^{II}, Fe^{II}, and Fe^{III} ions are given by Figure 1. The lattice constant at $x = 1$ is that of $ZnFe_2O_4$ which is obtained by a solid-state reaction at high temperature.[13] The lattice constants of the products increased with increasing Zn^{II} content in the products which suggests that the Zn^{II} in the products is incorporated into the spinel structure of the Zn^{II}-bearing ferrites. In the Mössbauer spectra of the products containing the higher content of Zn^{II}, split lines due to quadrupole splitting on the octahedral site of the normal spinel ferrite appeared.[14] In the i.r. spectra of the products containing the higher content of Zn^{II}, an increase in the band intensity was observed at its characteristic wavenumber of 405 cm^{-1} owing to a motion of the oxygen ions in a direction almost perpendicular to the tetrahedral bond directions, along which the oxygen ions vibrate.[15] These results also indicate the formation of Zn^{II}-bearing ferrites.

The broken line in Figure 2 is that obtained by connecting the lattice constants of the stoicheiometric Fe_3O_4 and $ZnFe_2O_4$, assuming that the lattice constants of the Zn^{II}-bearing ferrites increase linearly with increasing Zn^{II} content in the ferrites. However, as seen here, the lattice constants of the Zn^{II}-bearing ferrites do not increase linearly. When *ca.* 70 mol% of the Fe^{II} is substituted by Zn^{II}, the lattice constant attains nearly that of stoicheiometric $ZnFe_2O_4$.

Table. The relationship between the Zn^{II} ion concentration in the reaction suspension and the amount of Zn^{II} in the Zn^{II}-bearing ferrites. The values indicate the mol ratio of the metal ions to the Fe^{III} of γ-FeO(OH)

Expt.	Amount of Zn in the reaction suspension before the reaction	Amount of Zn incorporated into the ferrites	Amount of Fe in the reaction suspension after the reaction
1	0	0	0.03
2	0.10	0.072	0.11
3	0.20	0.15	0.19
4	0.30	0.20	0.22
5	0.40	0.26	0.27
6	0.50	0.30	0.30

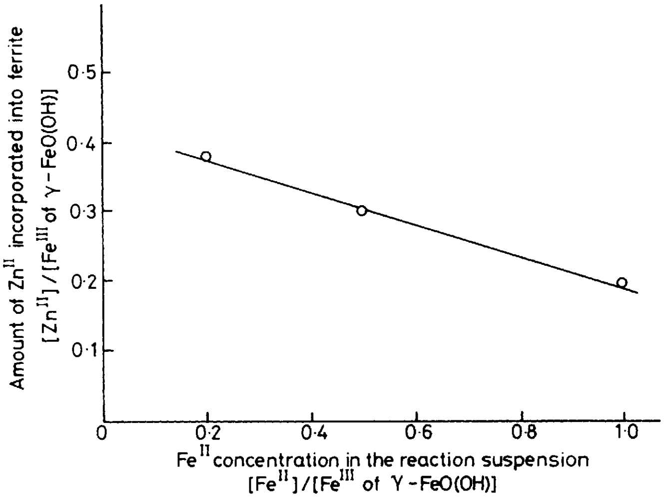

Figure 3. The relationship between the Zn^{II} content in the Zn^{II}-bearing ferrites and the Fe^{II} ion concentration in the reaction suspension

The relationship between the Zn^{II} ion concentration in the reaction suspension and the amount of Zn^{II} in the Zn^{II}-bearing ferrites is given in the Table. The mol ratio of Fe^{II} to the Fe^{III} of γ-FeO(OH) in the reaction suspension was fixed at 0.5 : 1. The amount of Fe^{II}, which was not incorporated into the ferrites, is given in the last column of the Table. Figure 3 shows the effect of the Fe^{II} ion concentration on the amount of Zn^{II} incorporated into the ferrites, where the mol ratio of Zn^{II} to the Fe^{III} of γ-FeO(OH) in the reaction suspension was fixed at 0.5 : 1. As can be seen from the Table and Figure 3 the Zn^{II} and Fe^{II} ions compete for incorporation into the ferrites.

Formation of Zn^{II}*-bearing Ferrites by the Adsorption of* Fe^{II} *on* γ-FeO(OH).—No transformation reaction took place either in the absence of Fe^{II} in the reaction suspension at pH 9.0, or in the presence of Fe^{II} at pH 5.0. In general, the adsorption reaction of the metal ions on the iron oxides takes place when the pH is increased.[16] It seems that the formation of the Zn^{II}-bearing ferrites from γ-FeO(OH) is triggered by the adsorption of the Fe^{II} ion on γ-FeO(OH).

To determine whether or not the Zn^{II}-bearing ferrites are formed by the adsorption of the Fe^{II} ion on γ-FeO(OH), the experiment was carried out at a lower Fe^{II} ion concentration (8×10^{-4} mol dm^{-3}), where the Fe^{II} ion is not precipitated at pH 9.0, but all of the Fe^{II} is adsorbed on the γ-FeO(OH).[11] Here, the mol ratio of Fe^{II} to the Fe^{III} of γ-FeO(OH) in the reaction suspension was fixed at 0.5 : 1, and that of Zn^{II} to the Fe^{III} of γ-FeO(OH) varied from 0 to 0.5 : 1. In the *X*-ray diffraction patterns of the products, which were obtained by increasing the pH to 9.0 and allowing the mixture to stand for 60 h, only the peaks of the spinel-type compounds appeared. The relationship between the lattice constants of the products and the Zn^{II} content in the products is given by curve B in Figure 2. As seen here, curve B is well fitted to curve A, suggesting that the products obtained at the lower Fe^{II} ion concentration are the stoicheiometric Zn^{II}-bearing ferrites. Thus, the Zn^{II}-bearing ferrites are formed by the adsorption of Fe^{II} on γ-FeO(OH).

As mentioned in the previous paper,[11] the transformation reaction of γ-FeO(OH) to Fe_3O_4 proceeds *via* a dissolution–precipitation process after the adsorption step of Fe^{II} ion on γ-FeO(OH). The Zn^{II} ion is adsorbed on the iron oxides at a pH above 5—6,[17] therefore the Zn^{II} ion would be completely adsorbed on γ-FeO(OH) at pH 9.0. It seems that the Zn^{II} ion is adsorbed on γ-FeO(OH) and will be subsequently incorporated into the spinel structure during the course of the transformation of γ-FeO(OH) to Zn^{II}-bearing ferrites. Kaneko and Katsura [1] suggested the importance of the hydrolysis of the metal ions for their incorporation into the spinel structure in the ferrite formation by aerial oxidation of the $Fe(OH)_2$ suspension containing the metal ions. In general, the hydrolysis takes place on the surface of the oxides, when the metal ions are adsorbed on them.[16] The requirement of hydrolysis of the metal ions for the incorporation into the lattice structure would be related to the adsorption of the metal ions on the surface of the iron oxides. Tamaura *et al.*[8] suggested that the Fe^{II} ion is adsorbed on the iron oxides and then oxidized on the surface, when the ferrites are formed by the air oxidation of the $Fe(OH)_2$ suspension at a pH above 9.0 and at 65 °C. They also suggested that a γ-FeO(OH) layer is formed on the iron oxides when the adsorbed Fe^{II} ion is oxidized. In the reaction of the ferrite formation by air oxidation of the $Fe(OH)_2$ suspension containing other metal ions at a pH above 9.0 and at 65 °C, the Fe^{II} ion would be adsorbed along with the metal ions on the γ-FeO(OH) layer, the γ-FeO(OH) being transformed to the metal ion-bearing ferrites on the surface of the iron oxides.

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