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Aluminium-Bearing Ferrite Formation from γ-FeOOH in an Aqueous Suspension

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Synopsis. Stoichiometric Al-bearing ferrites[$Al_xFe_{3-x}O_4$ (x=0.05—0.46)] are formed by a transformation reaction from γ-FeOOH in an aqueous suspension. The transformation reaction proceeds in a suspension containing γ-FeOOH, Fe(II) and Al ions without oxidation at 25 °C and a pH of 9.5—11.0.

We recently found that γ-FeOOH is transformed to Fe_3O_4 in the presence of Fe(II) ion in an aqueous suspension at 25 °C and pH 7.0—11.0.[1] In the presence of Fe(II) and Zn(II) ions, γ-FeOOH is transformed to stoichiometric Zn(II)-bearing ferrites at 25 °C and pH 7.5—11.4.[2] In the case of the Mg(II) ion, stoichiometric Mg(II)-bearing ferrites were formed under the same conditions.[3] In the case of Cd(II), nonstoichiometric Cd(II)-bearing ferrites were formed at 25 °C and a pH of 7.5—10.5.[3] Since all of these cases involved divalent metal ions, in this study we considered the Al ion as being a trivalent metal ion. We investigated the formation of the Al-bearing ferrites from γ-FeOOH in the presence of the Al and Fe(II) ions at 25 °C. Here, we briefly discuss the mechanism for the formation of metal ion-bearing ferrites in terms of an air oxidation reaction.

Experimental

Chemicals. All of the chemicals used in the present work were of analytical grade, and the chemical solutions were prepared with distilled water. A NaOH solution was prepared with distilled water through which nitrogen gas had been passed in order to remove any dissolved oxygen. The γ-FeOOH was prepared according to a method described previously.[1]

Apparatus. The reaction vessel, which was reported in a previous paper, was adopted.[1]

Procedure. After adding an $AlCl_3$ solution (0.02 dm^3, 0—0.27 mol dm^{-3}, pH 3.0) into a γ-FeOOH suspension (0.75 dm^3, pH 4.0), nitrogen gas was passed through the solution for 2 hours in order to remove any dissolved oxygen and carbon dioxide. A $FeCl_2$ solution (0.02 dm^3, 0.54 mol dm^{-3}, pH 3.0) was added into the suspension, and the pH was increased to the desired level by adding an alkaline solution. When the pH reached 8.0—11.0, the reaction was initiated and the reaction pH became lower. The reaction pH was kept constant by adding an alkaline solution. During the reaction nitrogen gas was passed through the suspension in order to prevent an oxidation reaction. After the reaction was continued for 60 hours (25 °C) the reaction suspension was centrifuged at 4000 rpm under a nitrogen atmosphere. The precipitate was washed with an acetate buffer solution (pH 4.1, 0.05 mol dm^{-3}) to isolate the products, by dissolving the unreacted Fe(II), and washed with a NaOH solution (pH 11.2) to remove the unreacted Al ions. The precipitate was then washed with distilled water, followed successively with acetone to remove water as completely as possible. The washing water and acetone had been previously deaerated by passing nitrogen gas through it to prevent oxidation. Finally, the precipitate was dried under a nitrogen atmosphere (room temperature). The products, thus obtained, were examined by powder X-ray diffractometry and IR spsectroscopy.

Chemical Analysis. The Fe(II) and Fe_{total} concentrations were determined by the 2,2′-bipyridyl method.[4] When the Fe_{total} was determined, Fe(III) ions were reduced to Fe(II) ions with hydroxylamine. The Al concentration was determined by spectrophotometry with 8-quinolinol.

Results and Discussion

Figure 1 gives a ternary diagram (Fe^{2+}, Fe^{3+}, Al^{3+}) showing the chemical composition of the products obtained by increasing the pH for the reaction suspension [the mixture of γ-FeOOH, $Al(OH)_3$ and $Fe(OH)_2$] to pH 10.5 and allowing it to stand for 60 hours. In this study, the mole ratio of Fe(II) ion to Fe(III) of γ-FeOOH in the reaction suspension (Fe(II) : γ-FeOOH) was fixed to 2 : 1, and the mole ratio of Al ion to Fe(II) of γ-FeOOH (Al : γ-FeOOH) varied from 0—4 : 1. The straight line in Fig. 1 connecting the chemical compositions corresponds to the Fe_3O_4 transformation to Al_2FeO_4 (Al-bearing ferrite) and shows the chemical compositions of the intermediate

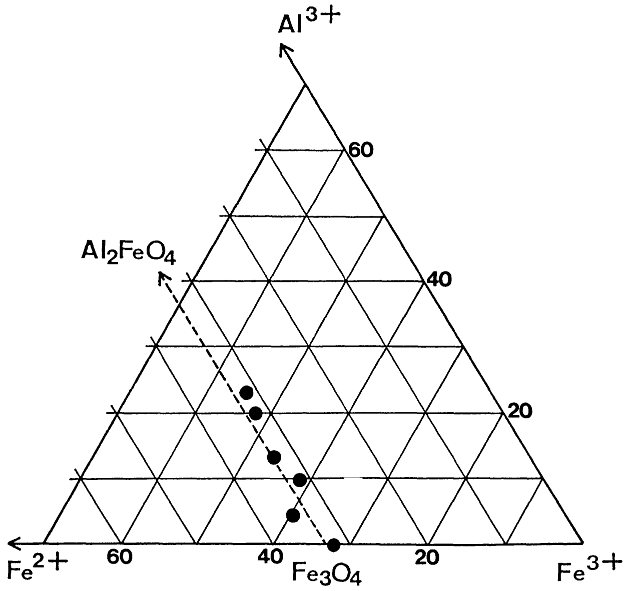

Fig. 1. Ternary diagram showing chemical compositions of the products. Broken line shows stoichiometric compositions of Al-bearing ferrites.

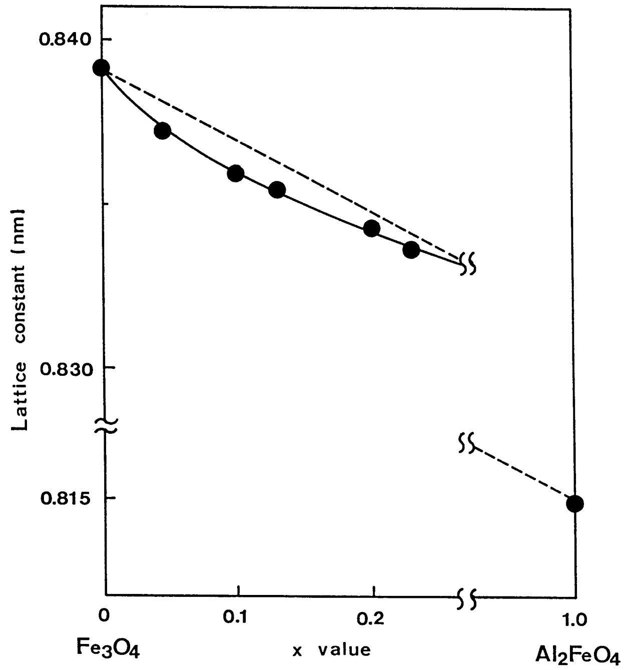

Fig. 2. Relationship between lattice constants of products and Al contents. The x values represent the mole ratio of Al_2FeO_4 to (Al_2FeO_4+Fe_3O_4).

stoichiometric solid solutions. As can be seen from Fig. 1, the chemical compositions of all the products are nearly equal of those of the stoichiometric Al-bearing ferrite. The aluminium contents of the products were 0—0.75:1 at a mole ratio of Al:Fe_{total}. About 25 per cent of the Al ions in each product. In the X-ray diffraction patterns for the products, only the peaks of the spinel-type compound appeared. In the IR spectra, no bands of γ-FeOOH or other iron(III) oxides were observed. These results suggest that the products are virtually stoichiometric Al-bearing ferrites. The slight deviation from stoichiometry seems to be due to an incomplete reaction, whereby a very small amount of Fe(III) remained unreacted.

Figure 2 shows the relationship between the Al content of the products and the lattice constants. The Al content of the products is represented by the Al_2FeO_4 mole percent of a solid solution between Fe_3O_4 and Al_2FeO_4 assuming that the products are Al-bearing ferrites, whose Al, Fe(II) and Fe(III) ion compositions are given in Fig. 1. The lattice constants of the products decreased with increasing Al content in the products, indicating that Al ions in the products were incorporated into an Al-bearing ferrite spinel structure.5) In the IR spectra of products containing a higher Al content, the band characteristics of the spinel ferrites appeared near 510 cm^{-1}, and all of the bands were shifted toward high frequencies, compared with those of Fe_3O_4. These shifts were due to the incorporation of Al ions into the spinel structure of Fe_3O_4.6)

We next examined the effect of the pH on the γ-FeOOH transformation reaction to the Al-bearing ferrite at Al:γ-FeOOH=1:1. When the reaction pH was 8.0, no ferrites were formed from γ-FeOOH in 60 h (25 °C). However, at pH 9.5—11.0, all of the γ-FeOOH transformed to Al-bearing ferrites. The same results were obtained for the Al-bearing ferrite formation reaction by an air oxidation of an $Fe(OH)_2$ suspension containing Al ions.5) In a previous paper3) we proposed that under air oxidation metal ion-bearing ferrites are formed from the γ-FeOOH which is formed as an intermediate by the air oxidation of Fe(II) ions in the reaction suspension. The results of the present experiments are consistent with the reaction mechanism which we have proposed.

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