Formation of Aluminium-bearing Ferrite in Aqueous Suspension by Air Oxidation

By **Kazuo Ito,* Tadao Kanzaki, Yutaka Tamaura,** and **Takashi Katsura,** Department of Chemistry, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152, Japan

Aluminium-bearing ferrites and Al-bearing goethites are formed by air oxidation of $Fe[OH]_2$ suspensions containing aluminium(III) ions, with the mol ratio, Al^{III} : Fe_{total}(r_{Al}), in the range 0.03—0.40 : 1 at pH 10.5 and 65 °C. The amount of Al-bearing ferrites in the products decreases with increasing r_{Al}, whereas that of the Al-bearing goethites increases. At r_{Al} = 0.60 : 1 only the Al-bearing goethite, $Fe_{0.71}Al_{0.29}O(OH)$, is formed. The chemical composition of the Al-bearing ferrite formed at r_{Al} = 0.03 : 1 is that of the stoicheiometric ferrite ($Fe_{2.95}Al_{0.05}O_{4.00}$). The values of r_{Al} in the Al-bearing ferrites are approximately half of those in the Al-bearing goethites.

THE formation of ferrites by air oxidation of aqueous suspensions has already been investigated in our laboratory, and it has been reported that ferrites bearing magnesium, cadmium, zinc, lead, titanium, and vanadium are formed at 65 °C and pH 8—12.[1-6] Metal (M)-bearing ferrites possess crystal structures comprising solid solutions between Fe_3O_4 and MFe_2O_4 or M_2FeO_4. In the case of Cr^{III}, $Cr_{0.42}Fe_{2.56}O_{4.00}$ is obtained by nitrate oxidation of an aqueous suspension at pH 7.0 and 80 °C.[7] When the concentration of Mg^{II} or Cd^{II} in the initial suspension is low, Mg- or Cd-bearing ferrite is readily formed,[1,2] but when the concentrations of these metals are high, basic magnesium(II) sulphate, cadmium(II) hydroxide, and/or α-FeO(OH) (goethite) are formed with the ferrites.[1,2] Zinc-bearing ferrites are formed at $Zn^{II} : Fe_{total}$ mol ratios of 0—0.5 : 1 (excluding 0.06 : 1) at pH 10.0; at $Zn^{II} : Fe_{total} = 0.06 : 1$, α-FeO(OH) is formed.[3] Zinc-bearing ferrite with a normal spinel structure is formed at $Zn^{II} : Fe_{total} = 0.50 : 1$.[3] At a low lead(II) concentration in the initial suspension, α-FeO(OH) tends to be formed, but at a higher concentration, Pb-bearing ferrite is obtained at pH 12.[4] Titanium-bearing ferrites are formed at $Ti^{II} : Fe_{total}$ mol ratios of 0—0.5 : 1 in the initial suspension at pH 9.0.[5] At low vanadium(IV) concentrations in the initial suspension, stoicheiometric vanadium-bearing ferrites are formed with a higher content of V^{IV}.[6]

In this paper, we report on the formation of aluminium-bearing ferrites and by-products (Al-bearing goethites) by air oxidation of aqueous suspensions. Turnock and Eugster[8] have studied the stoicheiometric Al-bearing ferrites formed by the solid-state reaction, and reported on the relationship between the lattice constants and the chemical compositions of these stoicheiometric ferrites.

EXPERIMENTAL

Reagents.—Chemicals of analytical grade were used. A solution of sodium hydroxide was prepared by dissolving Na[OH] in distilled water free from carbon dioxide and oxygen. A sulphuric acid solution of aluminium(III) sulphate (0.863 mol dm^{-3}) (pH 2) was prepared from $Al_2[SO_4]_3 \cdot 17H_2O$.

Apparatus.—A Dewar-type reaction vessel described previously[1] was used.

Procedure.—Distilled water, aluminium(III) sulphate solution, and sodium sulphate were transferred to the reaction vessel and nitrogen gas bubbled through the rapidly stirred solution for 1 h to remove dissolved CO_2 and oxygen. Iron(II) sulphate heptahydrate (12 g) was then added. The volume of the solution was adjusted to 0.2 dm^{-3} and the total concentration of the sulphate ion fixed (65 mmol). The pH was adjusted to 10.5 by adding sodium hydroxide solution (2 mol dm^{-3}) and the suspension was left to stand for 1 h with stirring under a nitrogen atmosphere at 65 °C (we call this suspension the ' initial suspension '). Subsequent procedures were the same as those described by Kaneko and Katsura.[1]

After completion of the oxidation reaction, the pH of the suspension was raised to 11.4 by adding a sodium hydroxide solution (4 mol dm^{-3}), left to stand for 1 h, and then washed three times with distilled water by centrifugation. The precipitate thus obtained is referred to as ' the product '. At this pH (11.4), aluminium(III) hydroxide can be dissolved completely.

The products were examined by *X*-ray powder diffraction with Fe-K_α radiation, electron microscopy, Mössbauer spectroscopy at room temperature, and Curie-point measurement *in vacuo*.

Preliminary experiments were carried out in order to establish the pH value of the reaction suspension from which the Al-bearing ferrites were readily obtained. At lower pH values (<11.0), formation of the Al-bearing ferrites was suppressed and the product was mostly α-FeO(OH) at pH 8.0. At pH >11.0, however, almost all the aluminium(III) ions remained in the supernatant. In this study, therefore, the oxidation reaction was carried out at pH 10.5.

Chemical Analysis.—The aluminium(III) content was determined by spectrophotometry with 8-hydroxyquinoline. Iron(II) and iron(III) ions were determined by the method of Kaneko and Katsura.[1]

RESULTS AND DISCUSSION

Formation of Al-bearing Ferrites and Al-bearing Goethites.—Figure 1 shows the electron micrographs of the products obtained by the air oxidation of the $Fe[OH]_2$ suspension containing aluminium(III) ions with Al^{III} : Fe_{total} in the range 0.00—0.60 : 1 at pH 10.5 and 65 °C. When no aluminium(III) ions were present in the initial suspension [$r_{Al} = 0.00$, Figure 1(*a*)], only cubic particles were observed. These were identified as Fe_3O_4 by *X*-ray diffractometry, Mössbauer spectroscopy, and chemical analysis. However, when Al^{III} : Fe_{total} in the initial suspension was in the range 0.06—0.40 : 1, needle-shaped

[Figure 1(*b*)] and spindle-like [Figure 1(*c*)] particles appeared together with cubic particles. At $r_{Al} = 0.60:1$ [Figure 1(*d*)], only irregularly shaped particles were observed.

When r_{Al} of 0.06—0.40 : 1, diffraction peaks and absorption lines due to α-FeO(OH) and a spinel-type compound were observed in the *X*-ray powder patterns and Mössbauer spectra of the products, while at $r_{Al} = 0.60:1$ only those for α-FeO(OH) were present. Chemical analysis showed that the $Fe^{II}:Fe_{total}$ mol ratio of the products decreased with increasing r_{Al} value and that no iron(II) ions were found at $r_{Al} = 0.60:1$. Hence, we concluded that the ' needles ', ' spindles ', and irregularly shaped particles were α-FeO(OH).

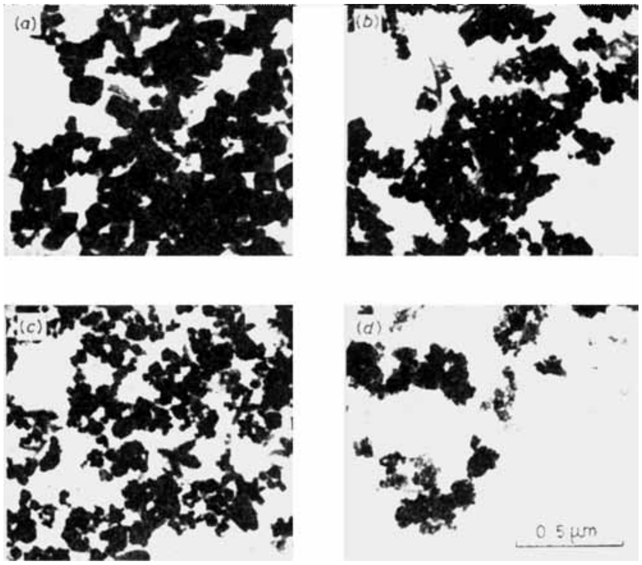

FIGURE 1 Electron micrographs of the products obtained at $Al^{III}:Fe_{total}$ mol ratios of 0.00 (*a*), 0.06 (*b*), 0.20 (*c*), and 0.60 : 1 (*d*)

The relationship between the relative amounts of the spinel-type compounds and α-FeO(OH) in the products and the concentration of Al^{III} in the initial suspensions (r_{Al}) is given by Figure 2. The iron contents of these two compounds were estimated from the peak area of the hyperfine absorption pattern (spinel-type compound) and of the quadrupole-split lines [α-FeO(OH)] in the Mössbauer spectra. The broken line in the lower r_{Al} range in Figure 2 indicates that the amount of α-FeO(OH) was too small to be estimated. It can be seen that the amount of α-FeO(OH) in the products increases almost linearly with increasing r_{Al}, whereas that of the spinel-type compound decreases.

The *X*-ray powder diffraction spacing, d_{110}, of α-FeO(OH) at $r_{Al} = 0.60:1$ was 0.414 nm, a different value to that of pure α-FeO(OH) (0.418 nm).[9] Taylor and Schwertmann[10] studied the formation of Al-bearing goethites by air oxidation of $Fe[OH]_2$ suspensions containing aluminium(III) ions at pH 5—7 (20 °C), and suggested that d_{110} of the Al-bearing goethites decreased with increasing concentration Al^{III} in the goethite. In the present study, the d_{110} values of α-FeO(OH) of the products gradually decreased with increasing r_{Al} value. Taylor and Schwertmann[10] also reported that the particle shape of the Al-bearing goethites changed from needles to small non-needle-like particles, on increasing the concentration of Al^{III}. As shown in Figure 1(*b*)—1(*d*), a similar change in the particle shape of α-FeO(OH) is observed here. Hence, under the present experimental conditions, both the formation of spinel-type compounds and the formation of Al-bearing goethites take place over a range of r_{Al} of 0.03—0.40 : 1. At $r_{Al} = 0.60:1$, only Al-bearing goethite was formed.

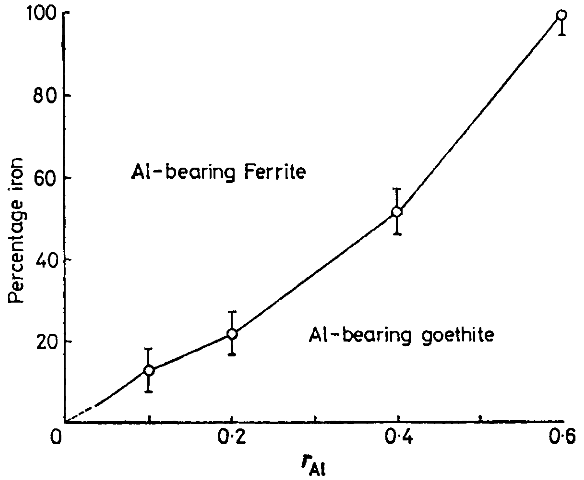

FIGURE 2 Relationship between the relative amounts of iron in the spinel-type compounds and the Al-bearing goethites in the products and the $Al^{III}:Fe_{total}$ mol ratio (r_{Al}) of the initial suspension

Figures 3 and 4 show the changes in the values of the lattice constant, a_0, and the Curie point of the spinel-type products respectively at $r_{Al} = 0.00—0.40:1$ and at pH 10.5 (65 °C). Both parameters decreased linearly

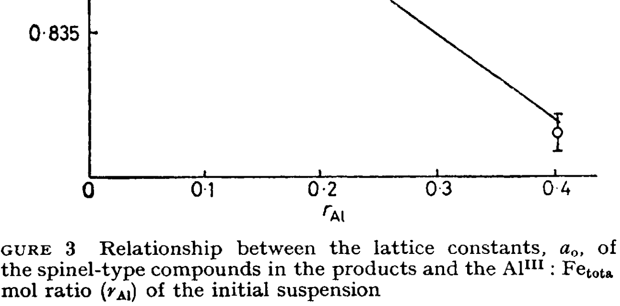

FIGURE 3 Relationship between the lattice constants, a_0, of the spinel-type compounds in the products and the $Al^{III}:Fe_{total}$ mol ratio (r_{Al}) of the initial suspension

Distribution of Al^{III} between the Al-bearing ferrites and goethites

r_{Al}		Al-bearing ferrites		Al-bearing goethites	
Initial suspension	Products	r_{Al}	Chemical composition	r_{Al}	Chemical composition
0.03	0.017	0.017	$Fe_{2.95}Al_{0.05}O_{4.00}$		
0.06	0.034	0.029	$Fe_{2.92}Al_{0.08}O_{4.00}$	0.074	$Fe_{0.93}Al_{0.07}O(OH)$
0.10	0.060	0.045	$Fe_{2.87}Al_{0.13}O_{4.00}$	0.111	$Fe_{0.90}Al_{0.10}O(OH)$
0.20	0.122	0.087	$Fe_{2.77}Al_{0.23}O_{4.00}$	0.176	$Fe_{0.85}Al_{0.15}O(OH)$
0.60	0.408			0.408	$Fe_{0.71}Al_{0.29}O(OH)$

with increasing r_{Al}. Turnock and Eugster[8] have reported that the values of a_0 of the stoicheiometric Al-bearing ferrites [$Fe_{3-x}Al_xO_4$ ($x \leqslant 2$)] from the solid-state reaction decrease linearly with increasing value of x.

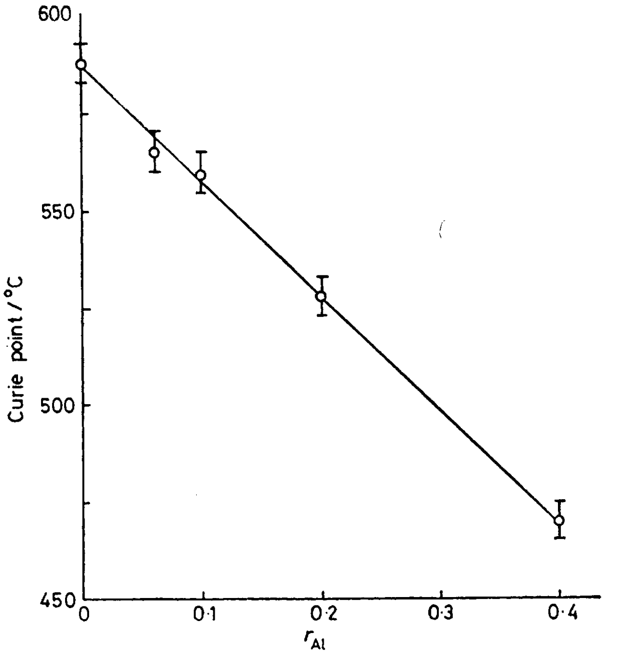

FIGURE 4 Relationship between the Curie point of the spinel-type compounds in the products and the Al^{III} : Fe_{total} mol ratio (r_{Al}) of the initial suspension

Moreover, Pickart and Turnock[11] have reported that the Curie points of the Al-bearing ferrites decrease linearly with increasing x in the range 0—0.4. These results suggest that the spinel-type compounds in the products are the Al-bearing ferrites.

Distribution of Aluminium(III) *between the Al-bearing Ferrite and Al-bearing Goethite.*—The aluminium(III) contents of the products determined by chemical analysis are given in the Table. These values are *ca.* 60% of those of the initial suspensions. Thus, 60% of the aluminium(III) ions in the initial suspensions were incorporated into the Al-bearing ferrites and/or goethites in the products.

The aluminium(III) contents and the chemical compositions of the Al-bearing ferrites were estimated from the lattice constants of the ferrites in the products, assuming that the chemical compositions were stoicheiometric.[10] At $r_{Al} = 0.03 : 1$, the aluminium(III) content of the Al-bearing ferrite is the same as that of the products determined by chemical analysis. This shows that a stoicheiometric Al-bearing ferrite ($Fe_{2.95}Al_{0.05}O_{4.00}$) is formed at $r_{Al} = 0.03 : 1$, although a very small amount of Al-bearing goethite was also formed. The aluminium(III) contents and the chemical compositions of the Al-bearing goethites were estimated from the chemical compositions of the Al-bearing ferrites and those of the products.

The aluminium(III) contents of the Al-bearing ferrites and Al-bearing goethites increase with r_{Al}, those for the ferrites being approximately half of those for the goethites at each r_{Al} value. This suggests that the reaction mechanisms for the formation of the Al-bearing ferrites and goethites are not affected by the concentration of Al^{III} in the initial suspensions. However, as mentioned in the previous section, the formation of the Al-bearing ferrites is suppressed while that of the Al-bearing goethites is increased at higher concentrations of Al^{III}, indicating that the reaction rates for the formation of the two compounds are different; the rate for the formation of the Al-bearing ferrites is reduced at higher aluminium(III) concentrations.

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