Formation of a Chromium-bearing Ferrite, $Cr_{0.42}Fe_{2.56}O_{4.00}$, in Aqueous Suspension by Nitrate Oxidation

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The title ferrite has been obtained by nitrate oxidation of an aqueous suspension containing a Cr^{3+} : Fe_{total} ratio of 0.16 : 1.00 and an optimum sulphate concentration (SO_4^{2-} : Cr^{3+} = 1.0 : 1.0) at pH 7.0 and 80 °C. When the sulphate concentration in the initial suspension is low or high (SO_4^{2-} : Cr^{3+} = 0.2 or 5.0 : 1.0), the incorporation of Cr^{3+} into the spinel-type ferrite is suppressed (Cr^{3+} : Fe_{total} = 0.01 : 1.00 to 0.03 : 1.00). The ferrite is formed *via* an intermediate compound which is a complex of chromium(III) and iron(II) hydroxides and SO_4^{2-}.

THE formation of Fe_3O_4 or metal-bearing ferrites by air oxidation in aqueous suspensions (the 'ferrite process ') has been investigated, and it has been reported that Mg-, Cd-, Ti-, Pb-, and V-bearing ferrites are formed at 65 °C and pH 9—12.[1-5] The ferrite process is influenced by substances present in the reaction medium and by the conditions, *e.g.* PO_4^{3-} is a strong inhibitor of the formation of Fe_3O_4.[6,7] Tamaura *et al.*[8] suggested that pure Fe_3O_4 is obtained when a dispersing reagent, *e.g.* sucrose, is present in the reaction medium. Kiyama[9] has established the range of temperature and alkalinity of the aqueous suspension over which Fe_3O_4 is formed as a stable species. At certain concentration ranges of Mg^{2+}, Cd^{2+}, Pb^{2+}, or V^{4+} in the initial solution before air oxidation, by-products such as α-FeO(OH) or hydroxides of the above ions are formed together with ferrites.[1,2,4,5]

In this study, the formation of chromium-bearing ferrites was investigated under conditions in which NO_3^- is present in the reaction medium, and the effect of SO_4^{2-} on the incorporation of Cr^{3+} into the ferrite was determined. At an early stage we found that the incorporation of Cr^{3+} into the ferrite is suppressed by SO_4^{2-} which is strongly co-ordinated with Cr^{3+}.[10] We did not employ air oxidation since the suspensions of $Fe[OH]_2$ are oxidised by the NO_3^- present.

EXPERIMENTAL

Analytical grade chemicals were used. A solution (3 mol dm^{-3}) of Na[OH] was prepared by dissolving the solid in distilled water freed from carbon dioxide and oxygen. Two reaction vessels used in previous studies[3-5] were employed.

Procedure.—To each reaction vessel (vessels 1 and 2) was added distilled water (0.7 dm^3). Carbon dioxide-free nitrogen gas was then bubbled through the water for *ca.* 1 h at 65 °C to remove the oxygen present. At the end of this process with nitrogen still passing, $Fe[SO_4]\cdot 7H_2O$ (14.4 g) was added to vessel 1. The pH value of the solution was adjusted to 9.0 (at 65 °C). The suspension was then allowed to stand for 2 h, before centrifugation in the absence of air. The residue was washed several times with oxygen-free distilled water and centrifuged, to remove as much of the SO_4^{2-} as possible. The $Fe[OH]_2$ precipitate thus obtained was transferred to the distilled water in vessel 2, and the temperature was raised to 80 °C. The suspension was allowed to stand for 2 h, while still passing the nitrogen gas. Then, a chromium(III) nitrate solution (0.02 dm^3) containing a known amount of $Cr[NO_3]_3\cdot 9H_2O$ (Cr^{3+} : Fe_{total} = 0.16 : 1) was added to initiate oxidation of Fe^{2+} [equation (1)].[11] The resulting suspension is

$$3Fe^{2+} + NO_3^- + 4H^+ \longrightarrow 3Fe^{3+} + NO + 2H_2O \quad (1)$$

designated the ' initial ' suspension. On addition of the chromium(III) nitrate solution the pH of the reaction solution decreased to *ca.* 4. The pH was adjusted to 7.0 by adding sodium hydroxide solution.

After standing for 1—12 h (the ' oxidation ' time) in the nitrogen atmosphere at pH 7.0 and 80 °C, vessel 2 was cooled to room temperature, and the suspension was centrifuged at 1 200 revolutions min^{-1} in a nitrogen atmosphere. The residue thus obtained we designate precipitate A. Approximately half of this was washed several times with sulphuric acid solution (pH 1.2) by centrifuging in a nitrogen atmosphere. The residue obtained is designated precipitate B. Precipitate A was washed several times with acetone to remove as much of the water as possible; B was washed several times with distilled water and acetone. The residues were dried at room temperature *in vacuo*, then analyzed chemically to determine the Fe^{2+}, Fe^{3+}, and Cr^{3+} contents, and subjected to *X*-ray diffractometry and i.r. and Mössbauer spectroscopy. The 2θ angles of the diffraction peaks were calibrated against silicon powder using manganese-filtered Fe-K_α radiation. The Mössbauer spectrum was recorded at room temperature, the i.r. spectrum by the KBr-disc technique.

Addition of SO_4^{2-} *to the* $Fe[OH]_2$ *suspension in vessel* 2. In some experiments, after transferring the $Fe[OH]_2$ precipitate to vessel 2, a $Na_2[SO_4]$ solution (0.02 dm^3) containing a known amount of SO_4^{2-} was added to give eventual SO_4^{2-} : Cr^{3+} ratios of 0.2 : 1.0, 1.0 : 1.0, and 5.0 : 1.0.

Chemical analysis. Each dried precipitate (*ca.* 80—100 mg) was dissolved in hot H_2SO_4 solution (0.02 dm^3) (1 : 1). To determine the amount of Fe^{2+}, the solution was cooled then titrated with $\frac{5}{6} \times 10^{-2}$ mol dm^{-3} standard $K_2[Cr_2O_7]$ solution using 5,6-phenanthroline as indicator. The (total) iron in the solution was reduced with bismuth amalgam using apparatus devised by Iwasaki *et al.*,[12] and then determined by titration with the standard $K_2[Cr_2O_7]$ solution.

For the analysis of Cr^{3+} content, the precipitate was completely dissolved in the sulphuric acid solution, and the resulting solution was diluted to 0.13 dm^3 with distilled water. Then, 0.1 mol dm^{-3} $Ag[NO_3]$ solution (0.01 dm^3) and ammonium disulphate (15 wt. %, 0.02 dm^3) were added. Excess of ammonium disulphate was completely decomposed by gently boiling the solution for 20 min. After cooling to room temperature, HCl solution (0.1 mol dm^{-3}, 0.02—0.04 dm^3) was added, and the resulting solution titrated with 0.025 mol dm^{-3} standard Fe[SO$_4$] solution using diphenylamine as indicator.

RESULTS AND DISCUSSION

Characterization of Precipitates A and B.—*X*-ray diffraction patterns of A and B (oxidation time 1 h) obtained at a Cr^{3+} : Fe_{total} ratio of 0.16 : 1.00 and at an optimum sulphate concentration (SO_4^{2-} : Cr^{3+} ratio = 1.0 : 1.0) in the ' initial ' suspension gave only peaks for a spinel-type compound. Chemical analyses showed that all the Cr^{3+} and iron in the ' initial ' suspension were incorporated in A. However, after washing this precipitate, *ca.* 40% of the Cr^{3+} and iron ions were removed. Almost all iron lost was in the form Fe^{2+}. This indicates that precipitate A, which is soluble in the acidic washing solution, is composed of Cr^{3+} and Fe^{2+}, which might be hydrolyzed. The Fe^{2+}, Fe^{3+}, and Cr^{3+} contents of precipitate B (94.45 mg) were 0.357, 0.618, and 0.160 mmol respectively. We can thus estimate the chemical formula to be $0.080Cr_2O_3{\cdot}0.357FeO{\cdot}0.309Fe_2O_3$ ($= Cr_{0.42}Fe_{2.56}O_{4.00}$), provided that the precipitate is composed of only a spinel-type compound. The weight evaluated from the chemical formula is 93.86 mg.

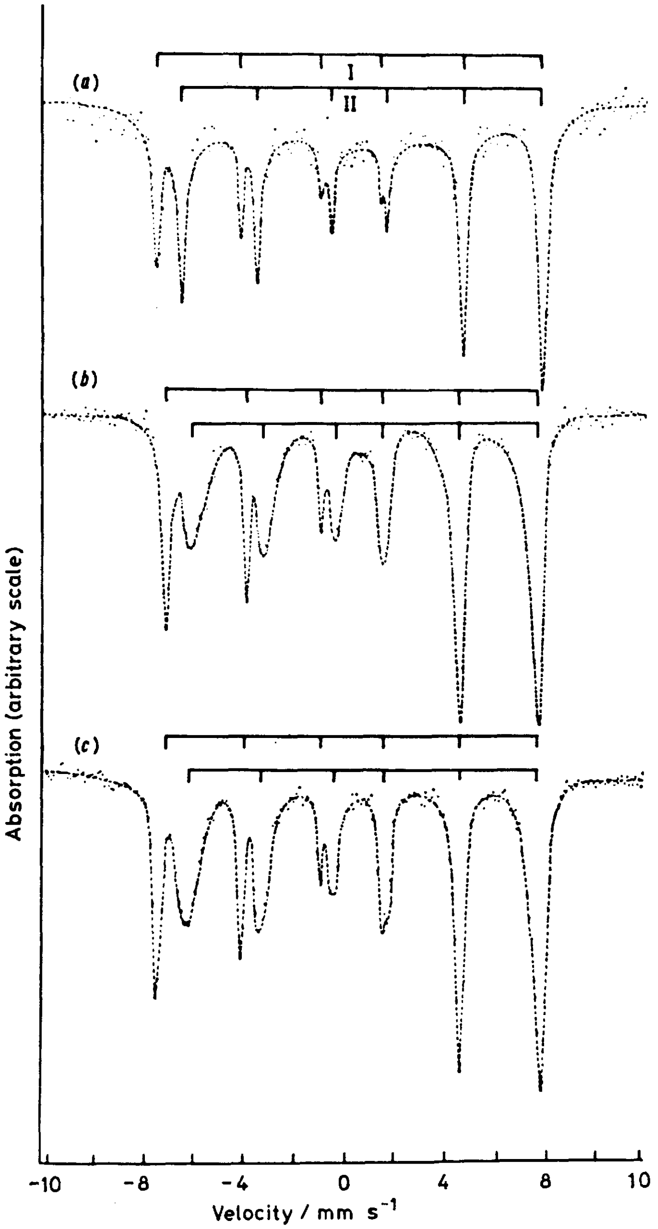

FIGURE 1 Mössbauer spectra of (*a*) the Fe_3O_4 obtained by nitrate oxidation in solution, (*b*) precipitate B obtained at Cr^{3+} : Fe_{total} = 0.16 : 1 and SO_4^{2-} : Cr^{3+} = 1.01 : 1, and (*c*) chromium ferrite ($Cr_{0.44}Fe_{2.56}O_{4.00}$) obtained by the solid-state reaction

The Mössbauer spectrum of precipitate B is given in Figure 1(*b*). All peaks are assigned to a spinel-type compound [peaks I to tetrahedral iron ions (A site), peaks II to octahedral iron ions (B site)]. The peaks for the B site are broadened. This is in contrast to Figure 1(*a*), where the peaks for the B site of Fe_3O_4, obtained by nitrate oxidation at a Cr^{3+}: Fe_{total} mol ratio of 0 : 1.00 in the initial suspension, are not broadened. Figure 1(*c*) shows the Mössbauer spectrum of a chromium ferrite ($Cr_{0.44}Fe_{2.56}O_{4.00}$) obtained by solid-state reaction at 1 200 °C according to the method of Katsura *et al.*[13] The peaks for the B site are again broadened. This broadening of the peaks for the B site of precipitate B and the chromium ferrite shows that charge hopping between Fe^{2+} and Fe^{3+} is not fast enough to restore the natural peak width. Robbins *et al.*[14] also pointed out such broadening for a chromium ferrite obtained by solid-state reaction. Thus, precipitate B is a chromium ferrite with the spinel-type structure and the Cr^{3+} is incorporated into the B site.

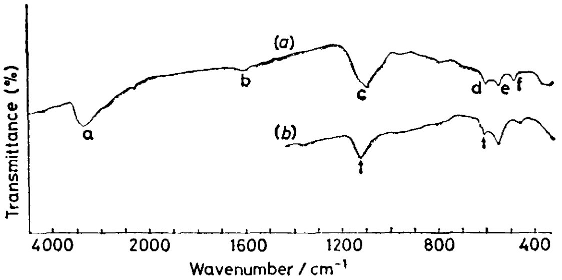

FIGURE 2 Infrared spectra of (*a*) precipitate A obtained at Cr^{3+} : Fe_{total} = 0.16 : 1 and SO_4^{2-} : Cr^{3+} = 1.0 : 1 (oxidation time 1 h), and (*b*) the intermediate compound formed before air oxidation in the formation of a lead ferrite [4]

The Fe_3O_4 obtained by nitrate oxidation in solution gave two bands at 560 and 360 cm^{-1} in the i.r. spectrum. The first band corresponds to vibrations of the oxygen ions along the tetrahedral bond, and the second is due to the motion of the oxygen in a direction almost perpendicular to the former vibrations.[15] The chromium ferrite ($Cr_{0.44}Fe_{2.56}O_{4.00}$) obtained by the solid-state reaction gave a slightly different i.r. spectrum: the band at 560 cm^{-1} is seen but not that at 360 cm^{-1}, and a shoulder at 450 cm^{-1} appears. The i.r. spectrum of precipitate B was very similar.

Intermediate Compound containing SO_4^{2-}.—Figure 2(*a*) shows the i.r. spectrum of the precipitate A (oxidation time 1 h) obtained at a $Cr^{3+}:Fe_{total}$ ratio of 0.16 : 1.00 and at the optimum sulphate concentration ($SO_4^{2-}:Cr^{3+} = 1.0:1.0$) in the 'initial' suspension. The bands a and b (3 400 and 1 625 cm^{-1}) are assigned to H_2O, f(495 cm^{-1}) to $Fe[OH]_2$ and $Cr[OH]_3$, and e(560 cm^{-1}) to chromium ferrite; bands c and d are not assigned to H_2O, $Fe[OH]_2$, or $Cr[OH]_3$. Figure 2(*b*) shows the i.r. spectrum of the intermediate compound in the formation of a lead ferrite ($Pb_{0.19}Fe_{2.75}O_{4.00}$) by air oxidation.[4] The bands of SO_4^{2-} in the intermediate compound appear at 1 130 and 610 cm^{-1} (arrowed).[4] Bands c and d in Figure 2(*a*) are therefore similarly assigned to SO_4^{2-}. When precipitate A was washed with the acidic solution, no SO_4^{2-} was determined in the precipitate (chromium ferrite), only in the washing solution. Thus, precipitate A comprises an intermediate compound containing SO_4^{2-}, which seems to form a complex with the hydroxides of Cr^{3+} and Fe^{2+}, together with the chromium ferrite. This intermediate compound dissolves easily in the acidic washing solution.

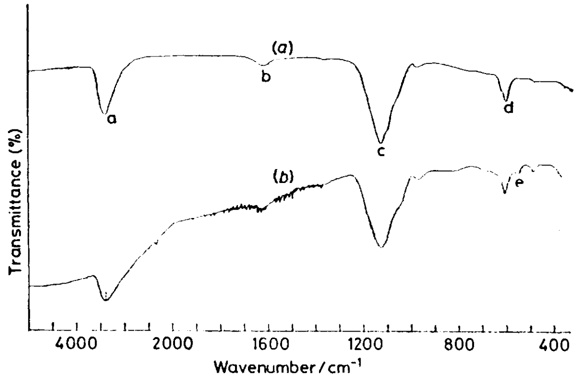

FIGURE 3 Infrared spectra of precipitate A obtained at $Cr^{3+}:Fe_{total} = 0.16:1$ and $SO_4^{2-}:Cr^{3+} = 5.0:1$. Oxidation time: (*a*) 1 h, (*b*) 12 h

Figure 3 shows the i.r. spectra of precipitate A [oxidation time: (*a*) 1 h; (*b*) 12 h] obtained at a $Cr^{3+}:Fe_{total}$ ratio of 0.16 : 1.00 and at a high sulphate concentration ($SO_4^{2-}:Cr^{3+} = 5.0:1.0$). No bands for hydroxide of Cr^{3+} or Fe^{2+} (band f, 495 cm^{-1}) appear in the i.r. spectrum after oxidation for 1 h, only the bands c and d due to SO_4^{2-} in the intermediate compound. This shows that the amount of metal hydroxide is very small, and that an intermediate compound containing SO_4^{2-} is mainly formed. However, after oxidation for 12 h a small peak due to a spinel-type compound (band e, 560 cm^{-1}) appears together with those for SO_4^{2-} in the intermediate compound. In the *X*-ray diffraction patterns of precipitate A, no peaks were seen after oxidation for 1 h, but after 12 h peaks for the spinel-type compound were present. Thus, the intermediate compound containing SO_4^{2-} is gradually transformed to the spinel-type compound by oxidation with NO_3^- in the nitrogen atmosphere. The Cr^{3+} content in the spinel-type compound formed at the high sulphate concentration, as seen later, was very small ($Cr^{3+}:Fe_{total} = 0.01:1.00$).

Figure 4 shows the i.r. spectra of precipitates A (*a*) and B (*b*) obtained after oxidation for 1 h at a $Cr^{3+}:Fe_{total}$ ratio of 0.16 : 1.00 and at a low sulphate concentration ($SO_4^{2-}:Cr^{3+} = 0.2:1.0$) in the initial suspension.

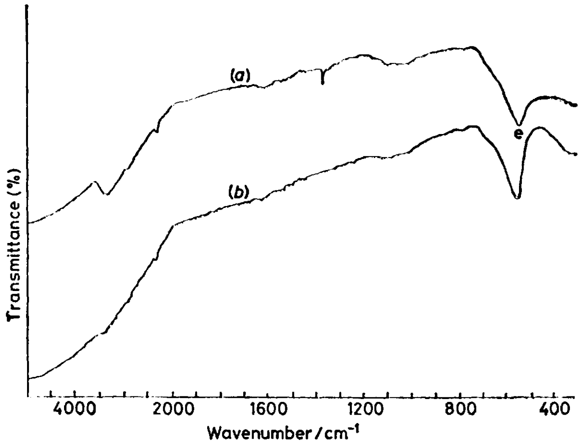

FIGURE 4 Infrared spectra of precipitates A (*a*) and B (*b*) obtained at $Cr^{3+}:Fe_{total} = 0.16:1$ and $SO_4^{2-}:Cr^{3+} = 0.2:1$ (oxidation time 1 h)

No bands due to SO_4^{2-} of the intermediate compound are observed for A, but there is a strong band due to a spinel-type compound (band e, 560 cm^{-1}). However, the absorption at 500 cm^{-1} is stronger than that of precipitate B, due to the presence of chromium(III) hydroxide which has a strong absorption at 500 cm^{-1}. Precipitate B, which was obtained by washing A, shows a typical i.r. pattern of a spinel-type compound. Chemical analyses showed that only 3 mol % iron of precipitate A dissolved in the acidic washing solution, but *ca.* 80 mol % of Cr^{3+}. Thus, when the sulphate concentration in the initial suspension is very low ($SO_4^{2-}:Cr^{3+} = 0.2:1.0$), after oxidation for 1 h, no intermediate compound is formed, only chromium(III) hydroxide and the spinel-type compound. The hydroxide in precipitate A dissolves in the acidic washing solution, and thus precipitate B is of the spinel-type compound. The Cr^{3+} content in the spinel-type compound formed at the low sulphate concentration, as seen later, was very low ($Cr^{3+}:Fe_{total} = 0.03:1.00$).

Effect of SO_4^{2-} *on the Incorporation of* Cr^{3+} *into the Ferrite*.—In precipitate B (oxidation time 1 h) obtained at a $Cr^{3+}:Fe_{total}$ ratio of 0.16 : 1.00 and at $SO_4^{2-}:Cr^{3+}$ ratios of 0.2 and 0.5 : 1.00 in the initial suspension the $Cr^{3+}:Fe_{total}$ ratio was 0.03 and 0.01, respectively. However, at the optimum sulphate concentration ($SO_4^{2-}:Cr^{3+} = 1.0:1.0$), the $Cr^{3+}:Fe_{total}$ ratio was 0.164 : 1.00. Thus, when the sulphate concentration in the initial suspension is low or high ($SO_4^{2-}:Cr^{3+} = 0.2$ or $5.0:1.0$) the incorporation of Cr^{3+} into the chromium ferrite is strongly suppressed. Kaneko and Katsura[1] suggested that the metal ions incorporated into the ferrite are significantly hydrolyzed; metal ions which are not hydrolyzed cannot be incorporated. The greater co-ordinating ability of SO_4^{2-} for Cr^{3+} (SO_4^{2-} may displace bridging OH of hydrolyzed Cr^{3+}) [10] seems to be the cause of the suppression of the incorporation of Cr^{3+} into the ferrite at the high sulphate concentration.

When the sulphate concentration is very low or absent, polymerization of Cr^{3+} takes place preferentially. Once Cr^{3+} is highly polymerized *via* bridging OH it becomes inert, and the interaction between the hydroxides of Cr^{3+} and Fe^{2+} is difficult. [Chromium(III) complexes, like those of Co^{3+}, are inert, *i.e.* their rates of ligand exchange are generally low.[10]] This seems to be the cause of the marked reduction of the incorporation of Cr^{3+} into the ferrite at low sulphate concentration in the initial suspension.

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