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Synthesis of Crystalline Ferrites Below 60°C

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Abstract

The ranges of aging temperature and time were determined for the preparation of zinc, cobalt, nickel and iron ferrites in crystalline form by their direct precipitation from aqueous solutions of the corresponding metal chlorides with ammonia below 60°C.

Introduction

In our previous papers,[1,2] it was shown that fine powders of zinc ferrite can be successfully synthesized at a temperature near room temperature. The relatively simple procedure involved addition of either ammonia or hydrazine monohydrate in an aqueous solution of $FeCl_2$ and $ZnCl_2$, followed by aging at a constant temperature within the range 30–60°C. The particles of zinc ferrite obtained were very fine, less than 0·1 μm in size, but had relatively high crystallinity, comparable to that found in powders heated up to 600°C.[1] Using hydrazine monohydrate, the concentration of metal solution had to be low in order to get crystalline powders of zinc ferrite, avoiding the formation of hydrazine complexes of metals.[2]

We have now extended the work to other ferrites, $CoFe_2O_4$, $NiFe_2O_4$ and Fe_3O_4, and determined the conditions for the synthesis of these materials in crystalline form near room temperature.

Experimental Procedure

Experimental procedure was very simple: into the mixed-metal solutions of MCl_2 (M = Ni, Co and Fe) and $FeCl_2$ having the metal ratio M/Fe of 1/2, ammonia was mixed at a constant temperature between 0 and 60°C by shaking. The concentration of each metal in aqueous solution was kept at 0·05 mol/dm^3 and that of ammonia at 15 mol/dm^3. After aging at a constant temperature for 0·5–8 h , the precipitates were collected by filtering and washing using water at room temperature. They were examined by X-ray powder diffractometry and scanning electron microscopy. The detailed experimental procedure was the same as was reported in our previous paper.[1] The temperature of aging was limited to between 0 and 60°C. Below 0°C, the handling of the aqueous solution was not easy and at 80°C it was difficult to keep the conditions of metal concentration because of the evaporation of water.

The formation conditions of the ferrites crystallized in a spinel structure are summarized in Fig. 1 in terms of aging temperature and time. In this figure, the results on zinc ferrite reported before are included for comparison.[1]

$ZnFe_2O_4$

Aging at a temperature between 30 and 60°C for more than 2 h resulted in the formation of a single phase of zinc ferrite in the crystalline state. Below 30°C, an amorphous phase was obtained even after a considerable aging time. This amorphous phase could be changed to spinel structure only by heat treatment above 400°C. Short time aging gave a so-called green-rust phase[3] which was expected to contain Fe^{2+}, Fe^{3+}, Zn^{2+}, OH^- and Cl^-. The representative X-ray powder patterns are shown in Figs 2(a) and (b) for zinc ferrite spinel synthesized by aging at 40°C for 8 h and for the green-rust phase prepared at 0°C for 4 h, respectively. The powder pattern for the green-rust phase is characteristic, with two broad peaks which can be indexed as 003 and 006. The crystallinity of the spinel which was measured by the half width of the 311 diffraction line was found to depend strongly on both aging temperature and time, the half width of the spinel obtained by aging at 60°C for more than 4 h corresponding to that heated up to 600°C. The atomic ratio of Fe/Zn was determined by atomic absorption spectrometry to be 2·2, corresponding to $Zn{:}_{0\cdot 94}Fe_{2\cdot 06}O_4$.

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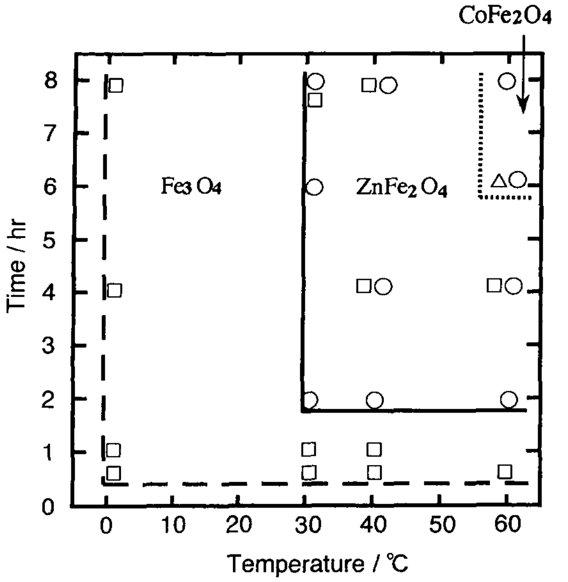

Fig. 1. Formation range of aging temperature and time for the crystalline ferrites. △ $CoFe_2O_4$; ○ $ZnFe_2O_4$; and □ Fe_3O_4.

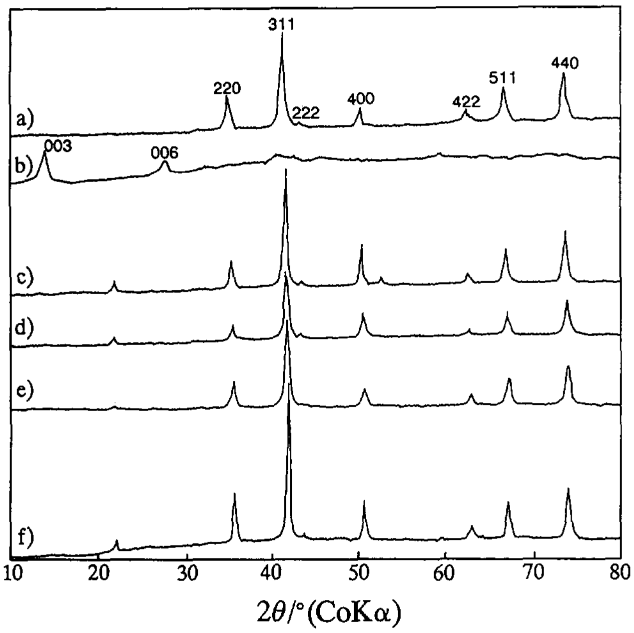

Fig. 2. X-ray powder patterns of the products: (a) $ZnFe_2O_4$; at 40°C for 8 h; (b) green-rust containing Zn^{2+}; at 0°C for 4 h; (c) $CoFe_2O_4$; at 50°C for 6 h; (d) $NiFe_2O_4$; at 40°C for 8 h; (e) (Ni, Zn)Fe_2O_4; at 40°C for 8 h; (f) Fe_3O_4; at 60°C for 0·5 h.

$CoFe_2O_4$

After aging at 60°C for 6 h, a single phase of spinel was obtained. As its X-ray powder pattern in Fig 2(c) shows, it has rather high crystallinity. The atomic ratio of Fe/Co determined was 2·2.

The aging at 60°C for 2 h and also at a temperature below 50°C for 6 h, gave a mixture of the green-rust phase and spinel, the former being the main phase at the low aging temperature.

$NiFe_2O_4$

No single phase of nickel ferrite was synthesized by the present procedure, by aging at temperatures from 0 to 80°C for up to 5 days. In most cases, the green-rust phase coexisted with a spinel having a low crystallinity. By heat treatment of this mixture to 600°C, a well-crystallized nickel ferrite associated with a small amount of Fe_2O_3 was obtained, where the overall ratio of Fe/Ni was 2·2.

Because the green-rust phase was soluble in dilute HCl, the spinel phase could be isolated. One of the powder patterns is shown in Fig 2(d). However, its atomic ratio of Fe/Ni was determined to be 5·0, indicating an Fe-rich composition.

An attempt was made to synthesize the mixed ferrites of zinc and nickel by the present procedure. Only in the mixed-metal solution of Zn/Ni = 4/1 was a single phase of spinel obtained (Fig. 2(e)). The metal composition determined by atomic absorption spectrometry, however, was $(Zn_{0·87}Ni_{0·13})_{0·91}Fe_{2·09}O_4$, namely, a much smaller ratio of Zn/Ni in the precipitates than in the starting metal solution. From the metal solutions containing more nickel ions, the mixture of the spinel and the green-rust phase was always obtained. These results show the difficulty in incorporating nickel ions into the spinel structure by the present procedure.

By solid-state reaction between Fe_2O_3 and NiO, it was reported that spinel formation was so suppressed that a single phase of $NiFe_2O_4$ was not obtained even at 900°C, the single phase being prepared only from a mixture of precursor raw materials ($FeCl_3$ and $NiCl_2$) using ethylene glycol.[4]

Fe_3O_4

At all temperatures examined, Fe_3O_4 with spinel structure (magnetite) is obtained, as shown in Fig. 1. In this case also, the green-rust was formed at short aging times (less than 0·5 h). The structural conversion from the green-rust to spinel was easily followed by observing the color change of the colloidal particles from deep green to black. In the sample synthesized at 0°C, a small amount of FeOOH was detected by X-ray diffraction; this was seen under scanning electron microscopy to have needle-like morphology The powder pattern of the sample after aging at 60°C for 0·5 h is shown in Fig. 2(f). SEM shows that Fe_3O_4 obtained at 60°C was composed of aggregates of minute particles of less than 0·1 μm in size.

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