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Hydrothermal formation of Ni-Zn ferrite from heavy metal co-precipitates

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The hydrothermal synthesis of Ni-Zn ferrite from simulated wastewater containing Ni^{2+} and Zn^{2+} ions has been studied. The influence of co-precipitation order, the existence of Na^+ in suspension, the hydrothermal reaction time and temperature on the composition, morphology and saturation magnetization (σ_s) of the hydrothermal products is reported. Adding the simulated wastewater to the NaOH solution can prevent the formation of α-Fe_2O_3 in the Ni-Zn ferrite. Increasing the hydrothermal reaction time improved the magnetization of the Ni-Zn ferrite, while the influence of temperature, stirring intensity and Na^+ in suspension on the hydrothermal formation of ferrite were not obvious. Thermodynamic calculation indicated that under hydrothermal conditions (180–240°C), the order of chemical stability is as follows: $NiFe_2O_4 > Fe_2O_3 > Na_2Fe_2O_4$. The high Gibbs formation energy of $Na_2Fe_2O_4$ prevented the incorporation of Na^+ into the ferrite lattice.

1. Introduction

Ferrites are a group of technologically important materials that are used in magnetic, electronic and microwave fields. Spinel-type ferrites can be prepared by a variety of methods. For the synthesis of Ni-Zn soft ferrite ($Ni_xZn_{1-x}Fe_2O_4$), the conventional way is through the solid-state reaction of a mixture of oxides, carbonates, and hydroxides of Ni, Zn and Fe at elevated temperature [1]. The disadvantages of the high reaction temperature and the need to mill have led to this method being replaced by the hydrothermal method. It has been reported that uniform ferrite particles with controlled size, shape and stoichiometry can be produced by controlling the hydrothermal conditions. However, commercial magnetic ferrites are produced from pure chemical reagents [2, 3], and little attention has been paid to the synthesis of magnetic ferrite from metal containing wastewater.

The need to purify wastewater containing metal ions arises from their toxicity and non-biodegradable nature, which may pose serious ecological problems [4, 5]. The ferrite method for toxic metal removal from wastewater consists of the precipitation of cations from an alkaline aqueous solution containing ferrous or ferrite ions. The magnetic ferrites are usually formed by oxidation in air or neutralization of the solution at a temperature above 50°C, and a variety of heavy metals in wastewater can be simultaneously and effectively removed. However, the ferrite procedures are in principle rather costly for implementation on a large scale due to the comparatively high temperatures involved. Another problem is that most of the ferrite sludge is not recycled; it is either disposed of directly or sintered at high temperature and then used as landfill material.

The purpose of the present work was to investigate the possibility of synthesizing Ni-Zn ferrite from simulated wastewater via neutralization followed by hydrothermal treatment. The relationships between the process parameters, composition and magnetic properties of the hydrothermal products are discussed.

2. Experiment

Simulated wastewater containing known concentrations of heavy metal ions (Ni^{2+} and Zn^{2+}) was mixed with appropriate quantities of Fe^{3+} ions in a glass beaker. The concentrations of Ni^{2+}, Zn^{2+} and Fe^{3+} in the resulting solution were 0.1 mol/L, 0.1 mol/L and 0.4 mol/L, respectively. The co-precipitation process was performed by adding the simulated wastewater to NaOH solution (2 mol/L) whilst stirring at 25°C until the pH reached 11, then the suspension was stirred for a further hour. After co-precipitation, 60 ml of the suspension was transferred to a stainless autoclave (model WDF, Wei Hai Automatic Control Reactor Company) with an inner volume of 100 ml. It was treated in the temperature range 180–240°C for 1–8 hours under saturated steam pressure. To study the influence of co-precipitation order on the formation of Ni-Zn ferrites, further experiments were performed at 25°C in which the NaOH was added to the wastewater. The deposits formed were then treated at 200°C for 4 hours.

After hydrothermal treatment, the autoclave was cooled to room temperature, the solids were separated from the liquid by filtration and washed with distilled water several times. Then the solids were desiccated at 80°C for 12 hours, pulverized in a ceramic mortar and stored in plastic tubes for subsequent study.

The particle morphology was observed using scanning electron microscopy (SEM). The crystalline phases in the products were identified by X-ray diffraction analysis (XRD). The saturation magnetization was determined using a vibrating sample magnetometer (VSM).

3. Results and discussion

3.1. Effect of co-precipitation order

XRD and VSM analysis indicated that the neutralization precipitates formed at 25°C were amorphous materials with no magnetization, which implied that metal hydroxides rather than ferrites formed in the co-precipitation process. SEM observation indicated that the precipitates formed in both cases were spherical particles with an average diameter of about 40 nm. Uniform Ni-Zn ferrite spherical particles with diameter of about 70 nm were formed after hydrothermal treatment at 200°C for 4 hours.

Fig. 1 shows the influence of co-precipitation order on the composition of the hydrothermal products. Compared with the conventional mixing method (adding NaOH to wastewater), the inverse way (adding wastewater to NaOH) seems more suitable for the formation of Ni-Zn ferrite since the formation of α-Fe_2O_3 in Ni-Zn ferrite was prevented effectively. The reason for this may be attributed to the different dissolution constants of the corresponding hydroxides. As shown in Table I, the theoretical pH values at which the hydroxides begin to occur are 2.2, 7.2 and 6.6 for $Fe(OH)_3$, $Ni(OH)_2$ and $Zn(OH)_2$, respectively. The lower the precipitation pH, the easier it is for the metal hydroxide to form. In the inverse mixing way (adding wastewater to NaOH), the whole precipitation process was carried out in a strong alkaline solution ($pH \geq 11$), which resulted in the simultaneous precipitation of Fe^{3+}, Ni^{2+} and Zn^{2+} ions. In the conventional co-precipitation way (adding NaOH to the simulated wastewater), the pH value in suspension increases gradually from about 2.0 to 11.0 as the NaOH is added. Therefore, Fe^{3+} ion was precipitated first as the pH reached 2.1; Ni^{2+} and Zn^{2+} ions were then precipitated almost simultaneously at $pH \geq 6.6$ due to the small difference in their precipitation pH. The non-uniform distribution of metal hydroxides would lead to the comparatively high local Fe^{3+} concentration after dissolution at the hydrothermal condition, which led to the formation of Fe_2O_3.

TABLE I Dissolution constant and precipitation pH of metal hydroxides

	$Fe(OH)_3$	$Ni(OH)_2$	$Zn(OH)_2$
K_{sp}	1.1×10^{-36}	2.0×10^{-15}	1.66×10^{-16}
pH*	2.15	7.15	6.61

pH*: pH at which metal hydroxide precipitations begins.
Condition for calculation: $[Fe^{3+}] = 0.4$ mol/L, $[Ni^{2+}] = [Zn^{2+}] = 0.1$ mol/L.

3.2. Effect of hydrothermal parameters

The effect of hydrothermal parameters such as reaction time, temperature and stirring intensity on the composition and magnetic properties of the hydrothermal products were investigated and the corresponding experimental results are summarized in Table II. In general, the hydrothermal treatment converted the deposits consisting of metal hydroxides with no magnetism to Ni-Zn ferrite with saturation magnetizations (σ_s) of 48.4–59.5 emu/g. The increase in hydrothermal reaction time from 1 hour to 8 hours increased the σ_s values of Ni-Zn ferrites from 48.4 emu/g to 57.0 emu/g. On the other hand, the increase of hydrothermal reaction temperature from 180°C to 240°C led to a loss of σ_s values from 56.2 emu/g to 53.4 emu/g.

3.3. Effect of $[Na^+]$ in suspension

Lin [6] showed that the existence of Na^+ in the crystal lattice of ferrite would decrease the magnetic properties of ferrite powder. Two experiments, removing (washing) the Na^+ from the deposits before or after the hydrothermal treatment, were carried out to investigate the effect of Na^+ in suspension on the hydrothermal formation of ferrites since Na^+ was un-avoid in the starting material (NaOH solution). The concentration of Na^+ in the suspension without washing before hydrothermal treatment was about 0.86 mol/L, while almost no Na^+ was detected in the washed deposit suspension. The results in Fig. 2 show that the XRD patterns for the

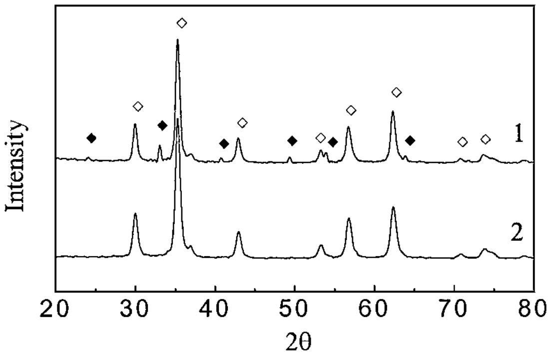

Figure 1 XRD patterns of hydrothermal products formed via different co-precipitation orders. Adding NaOH to wastewater (1) and vice versa (2). ◇: $Ni_xZn_{1-x}Fe_2O_4$, ◆: α-Fe_2O_3.

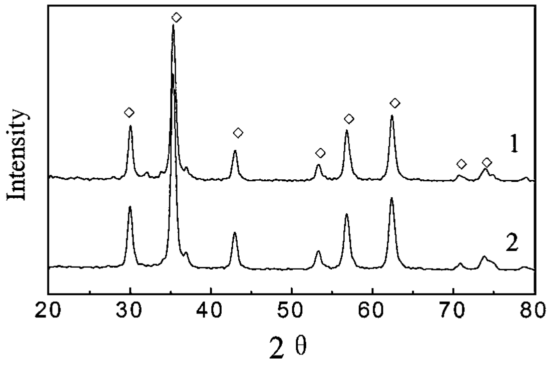

Figure 2 XRD patterns of hydrothermal products formed by removing Na^+ before (1) or after (2) hydrothermal treatment. ◇: $Ni_xZn_{1-x}Fe_2O_4$.

TABLE II Influence of hydrothermal parameters on σ_s of Ni-Zn ferrites

	Hydrothermal parameters											
	Time (hr)				Temperature (°C)				Stirring speed (rpm)			
	1	2	4	8	180	200	220	240	0	150	300	450
σ_s (emu/g)	48.4	51.8	55.0	57.0	56.2	50.6	54.7	53.4	58.0	54.7	57.9	59.5

hydrothermal products formed in both cases were the same and that no compounds except Ni-Zn ferrite were detected, which implies that the existence of Na^+ in suspension had little influence on the hydrothermal formation of Ni-Zn ferrite. The reason for this is explored further in the thermodynamic analysis.

3.4. Thermodynamic equilibrium analysis

According to Mandaokar [5], the hydrothermal synthesis of ferrites from co-precipitates involves dispersion, dissolution, precipitation, growth and structural ordering. The precipitation of ferrite from solution might depend on two factors: the evaporation of water from solution and the difference in the solubility between the products and reactants. The evaporation of water in the closed autoclave was calculated from the Redlich-Kwong equation [7]:

$$P = \frac{RT}{V - b} - \frac{a}{T^{0.5}V(V + b)}$$

where P: vapor pressure, Pa' V: volume of vapor, m^3, T: temperature, K, R: constant of ideal gas, 8.314 $\text{Pa} \cdot \text{m}^3/(\text{mol} \cdot \text{K})$, a: constant, $0.42748R^2T_c^{2.5}/P_c$, b: constant, $0.08664\, RT_c/P_c$, T_c: super-critical temperature of water, 647.3 K, P_c: super-critical pressure of water, 22.048 MPa.

Fig. 3 shows that under the experimental conditions (water occupying 60% of the total inner volume of the autoclave, temperature in the range 160–240°C), less than 2.3% of the water was vapor in the closed hydrothermal system. The concentrations of the soluble species should increase only slightly with the evaporation of water. So it seems that the hydrothermal formation of Ni-Zn ferrite had little connection with the variation of the solubility of species at different temperatures.

Thermodynamic equilibrium calculations were performed to investigate the thermodynamic stability of related species under hydrothermal conditions. It is worth noting that the Ni^{2+}-Fe^{3+} aqueous system, rather than Ni^{2+}-Zn^{2+}-Fe^{3+} aqueous system, was considered due to the shortage of basic thermodynamic data for Ni-Zn ferrite. Following Yang [8], the influence of pressure at different temperatures was also neglected. The thermodynamic trends deduced from the Ni^{2+}-Fe^{3+} aqueous system may be used as indicative of the Ni^{2+}-Zn^{2+}-Fe^{3+} aqueous system.

Based on previous results [5] and the present work, two routes for the formation of ferrite were considered. In one route, the metal hydroxides dissolved as the temperature increased, then the reaction of the soluble ions led to the formation of ferrite. Another possibility was that after the dissolution of the metal hydroxides, Fe_2O_3 was formed, then Fe_2O_3 reacted with the soluble metal ions to form ferrite.

On the basis of the above assumption, the related reactions in the Ni^{2+}-Fe^{3+} aqueous system were listed as follows:

$$2Fe^{3+} + 6OH^- \rightarrow Fe_2O_3 + 3H_2O \quad (1)$$

$$Fe_2O_3 + 2Na^+ + 2OH^- \rightarrow Na_2Fe_2O_4 + H_2O \quad (2)$$

$$Fe_2O_3 + Ni^{2+} + 2OH^- \rightarrow NiFe_2O_4 + H_2O \quad (3)$$

$$2Fe^{3+} + 2Na^+ + 8OH^- \rightarrow Na_2Fe_2O_4 + 4H_2O \quad (4)$$

$$2Fe^{3+} + Ni^{2+} + 8OH^- \rightarrow NiFe_2O_4 + 4H_2O \quad (5)$$

$$\Delta G^o = \sum \nu_i G_i^o$$

where ΔG^o: standard Gibbs formation free energy of reactions (1) to (5), G_i^o: standard Gibbs free energy of spices, γ_i: stoichiometric coefficient.

Fig. 4 shows the variation of ΔG^o with temperature. From the thermodynamic viewpoint, a low ΔG^o value

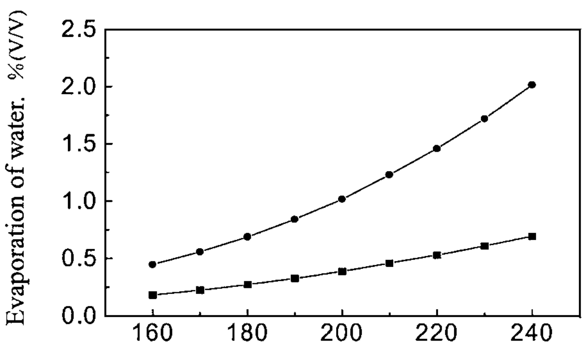

Figure 3 Vaporization of water under hydrothermal condition. Percent of water volume: ■: 40%, ●: 60%.

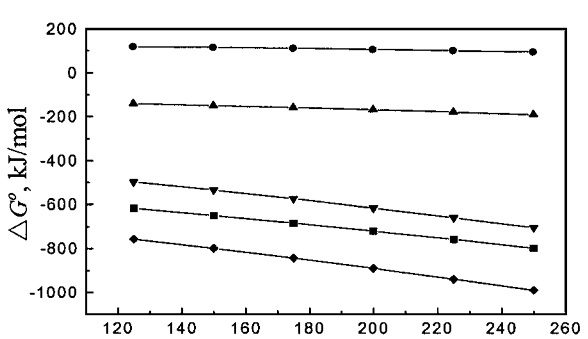

Figure 4 Variation of ΔG^o with temperature for different reactions. ■: (1), ●: (2), ▲: (3), ▼: (4), ♦: (5).

of a reaction corresponds to a high thermodynamic likelihood of the reaction happening. The ΔG^o values of reaction (4) and (5) were much lower than those of (2) and (3), which indicates that the hydrothermal formation route of ferrite may be via the reactions of soluble ions rather than the precipitation of Fe_2O_3 followed by the reaction of Fe_2O_3 and metal ions. According to the ΔG^o values in Fig. 4, the thermodynamic stability of species in the temperature range 180–240°C was as follows: $NiFe_2O_4 > Fe_2O_3 > Na_2Fe_2O_4$. The high Gibbs formation energy of $Na_2Fe_2O_4$ may have prevented the incorporation of Na^+ into the ferrite lattice.

4. Conclusion

Ferrite with a saturation magnetization of more than 50 emu/g can be synthesized from simulated wastewater via co-precipitation followed by hydrothermal treatment. Metal hydroxides were formed in the co-precipitation process and converted to magnetic ferrite after hydrothermal treatment.

Adding the simulated wastewater to the NaOH solution, seems to prevent the formation of α-Fe_2O_3 in Ni-Zn ferrite. The conventional mixing way (adding NaOH solution to the simulated wastewater) resulted in the separate precipitation of Fe^{3+}, Ni^{2+} and Zn^{2+} ions, which caused a comparatively high local Fe^{3+} concentration in the following hydrothermal dissolution-precipitation process and hence accelerated the formation of α-Fe_2O_3 in Ni-Zn ferrite.

Increasing the hydrothermal reaction time improved the saturation magnetization of the Ni-Zn ferrite, while the influences of temperature, stirring intensity and Na^+ in suspension on the hydrothermal formation of ferrite were not obvious. In the temperature range 180–240°C, the thermodynamic stability was: $NiFe_2O_4 > Fe_2O_3 > Na_2Fe_2O_4$. From the thermodynamic viewpoint, the high Gibbs formation free energy of $Na_2Fe_2O_4$ under hydrothermal conditions may prevent the incorporation of Na^+ into the spinel structure of ferrite.

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