

Preparation and Magnetic Properties of Zn-Doped Fe₃O₄ Magnetic Colloid

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Abstract. Fe₃O₄ magnetic colloids were produced by co-precipitating a Fe²⁺, Fe³⁺, and Zn²⁺ containing solution with a NaOH solution at 70°C. Analyses results indicated that the Zn content of the Fe₃O₄ colloids was always less than the solution's Zn content. The difference was found to be the smallest when the colloid was precipitated at pH=10. The σ_s values of the Fe₃O₄ colloid significantly improved by adding an appropriate amount of Zn ions and precipitating it at an optimum pH value, pH=10. The optimum Zn ion content was 6.18 at%, which corresponded to Zn_{0.1854}Fe_{2.8145}Fe₂O₄. At this composition the colloid's σ_s value was 94 emu/g, and increased by more than 34% of pure Fe₃O₄ colloid's σ value. By theoretical calculation the σ_s should increase 27.8%.

INTRODUCTION

Investigators have synthesized magnetite colloid by the chemical coprecipitation method to prepare magnetic fluid since 1966[1-3]. An appropriate amount Zn ion in the colloids may increase the colloid's σ_s value because adding Zn ion increases the unbalanced magnetic moment between the spinel's A site and the B site. In this study, we investigate the effects of Zn ion on the σ_s value of Fe₃O₄ magnetic colloids to test whether or not adding Zn ions can increase the colloid's magnetic properties and what the optimum amount of Zn ion is.

EXPERIMENTAL

Fe₃O₄:Zn magnetic colloids were produced by the chemical co-precipitation method, i.e. mixing an acidic solution containing 0.1 M FeCl₂·4H₂O, 0.2 M FeCl₃·6H₂O, an appropriate amount of ZnCl₂·4H₂O, with a sufficient volume of 0.1 M NaOH alkali solution at 70°C, and then centrifuging them from the mixed solution. TEM, XRD, EDX, and VSM analyses were performed to measure the particle size, structure, chemical composition, and magnetic properties of the Fe₃O₄:Zn magnetic colloids.

RESULTS AND DISCUSSION

X-ray diffraction analysis results in Figure 1 reveal that a high pH value of the co-precipitated solution favored the formation of Fe₃O₄ colloids. At pH=10, well crystallized spinel phase was formed and no other phase was detected. Zn ion formed a solid solution with Fe₃O₄. EDX analysis of Zn ion content in Fe₃O₄ colloids (Figure 2) reveals that Zn ion content in Fe₃O₄ colloid was always less than in the original solution because Zn has a higher solubility in this pH range than either Fe²⁺ or Fe³⁺ ions. For an initially fixed Zn ion content of 6.91 at% (8 wt%) in the solution, the Zn ion content in the Fe₃O₄ colloids ranged from 2.87 at% at pH=5 to a maximum value of 6.71 wt% at pH=10. Later, it gradually declined to 6.32 wt% at pH=12. The difference between the Zn ion in the colloid and in the original solution was the smallest at pH=10 because of the Zn ion's amphibious property. At a fixed pH=10 in the precipitated solution, Figure 3 shows the relationship between Zn content in the solution before co-precipitation and Zn content in the Fe₃O₄ colloid. Zn ion content in the Fe₃O₄ colloid is always less than that in the original solution. Electron micrographs reveal that the colloid particles were spherical with a diameter less than 100Å.

Because the σ_s value of $Fe_3O_4:Zn$ colloids was found to be optimal when they were produced at pH=10, $Fe_3O_4:Zn$ colloids were produced at pH=10 for various Zn contents. Figure 4 reveals that the σ_s values of the Fe_3O_4 colloids significantly improved by adding an appropriate amount of Zn ions, e.g. ranging from 70 emu/g at Zn=0 at% to a maximum of 94 emu/g at Zn=6.18 at%. Later they reduced to 70 emu/g at Zn=10.97 at%. The optimal Zn content of the $Fe_3O_4:Zn$ colloid is Zn=6.18 at% where the σ_s value of the colloid is 34% more than the σ_s values of the colloids without adding the Zn ion.

6.18 at% of Zn ion in the $Fe_3O_4:Zn$ colloid implies that, initially, Fe^{2+} is 31.27 at% and Fe^{3+} is 62.55 at% in this colloid. However, adding Zn^{2+} ion replaces Fe^{2+} ion and causes a 6.18 at% surplus of Fe^{2+} in the spinel structure. The fact that x-ray analysis in Figure 1 indicates that the $Fe_3O_4:Zn$ colloid is a single phase solid solution; suggests that the surplus Fe^{2+} must be somewhere in the spinel structure. The Fe^{2+} was apparently oxidized to Fe^{3+} by dissolving oxygen in the solution and became part of the spinel because, at pH=10, free Fe^{2+} is unstable and quite easily oxidized. If such a fact is true, the subsequent spinel formula of the $Fe_3O_4:6.18$ at% Zn colloid is as follows: $(Zn_{0.1854}Fe_{2.8146})_A(Fe_{3.8146}^{3+}Fe_{0.1854}^{2+})_B O_4$. This formula's net magnetic moment, as calculated from its individual magnetic moments, is 5.112μ ; meanwhile, the net magnetic moment of pure Fe_3O_4 is 4μ . Adding 6.18 at% Zn ion to Fe_3O_4 increases the σ_s value of Fe_3O_4 by 27.8%, which is slightly different from the experimental value of 34%. The optimum σ_s value of $Fe_3O_4:Zn$ colloid is that the spinel's A site is occupied by 18.54 at% of Zn ion, which is quite different from the other members of the ferrite family where the optimum σ_s value occurs when the spinel's A site is occupied by 50 at% of Zn ion. Some Hc values were found in the $Fe_3O_4:Zn$ colloids (Figure 4), implying that the colloids contain some larger particles which are beyond superparamagnetic range and are therefore ferrimagnetic. Moreover, Figure 4 indicates that the Hc value of the $Fe_3O_4:Zn$ colloids gradually decrease with the Zn ion content.

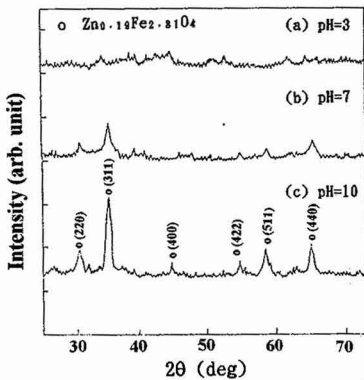


Figure 1 X-ray diffraction patterns (Cu $K\alpha$) of colloids precipitated at various pH values

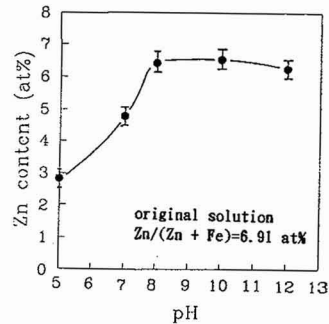


Figure 2 Zn content of colloids precipitated at various pH values

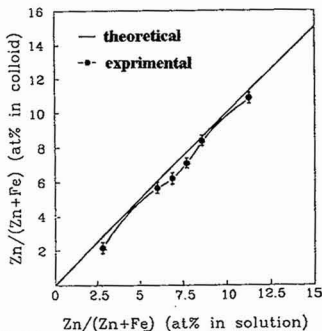


Figure 3 Relationship of Zn content in the original solution and in the precipitated colloid

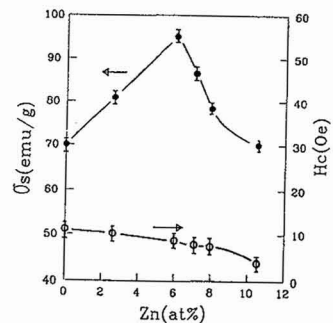


Figure 4 Magnetic properties of colloids at various Zn contents

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