Aluminium Substituted Magnetite by Wet Method

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Abstract. Aluminium substituted magnetite particles with Al^{3+} content in the range from 0.7 to 4.0wt% were synthesized by the hydrothermal oxidation reaction. It was found that the mixing procedure was critical to prepare single-phase ferrite particles: it was required that Al ions were neutralized before the precipitation of Fe ions. As the aluminium content increases, the magnetization of the obtained particles decreased in the range from 86 to 60emu/g. The lattice constant also decreased from 0.840 to 0.836nm. XPS analysis indicated that aluminium in the obtained particles was both in hydroxide and oxide states, and that the molar fraction of them was approximately 20% and 80%, respectively. The lattice constant was in good agreement with the calculated value using the Vegard's law in Fe_3O_4 - $\gamma\text{-Fe}_2\text{O}_3$ - FeAl_2O_4 solid solution and taking into account of the existence of aluminium hydroxide.

1. INTRODUCTION

Ferrite has been widely used in many application such as electromagnetic devices and magnetic inks. The electric and magnetic properties of ferrite depend on the cation configuration in the spinel lattice, which consists of tetrahedral and octahedral interstitial sites. The cation distribution in the spinel lattice is controlled by many factors such as the kind of the cation, the ionic radius and the valence state. In addition, the cation distribution is not always in thermal equilibrium state, therefore, it depends on the sample preparation route. From this point of view, it is expected that hydrothermal-synthesized ferrite possesses unique property in comparison with ferrite prepared by ceramic method[1,2,3]. In this paper, we've investigated the method for synthesis of the aluminium substituted magnetite particles by the aerial oxidation, and then briefly discussed the stoichiometry and the aluminium distribution in the obtained particles.

2. EXPERIMENTAL PROCEDURE

The following three mixing methods of aluminium sulfate, ferrous sulfate and sodium hydroxide solutions were employed. In the first case, after ferrous sulfate solution was mixed with sodium hydroxide solution, aluminium sulfate solution was added in the suspension of ferrous hydroxide (this denotes method A). In the second case, aluminium sulfate solution was mixed with sodium hydroxide solution, and then ferrous sulfate solution was added in the mixed solution (method B). In the last case, the mixed solution of aluminium sulfate and ferrous sulfate was added in a sodium hydroxide solution (method C). These mixing procedure were carried out at 90°C under N_2 -bubbling to avoid the oxidation of ferrous ion during the mixing. The $\text{Al}^{3+}/\text{Fe}^{2+}$ ratio in the initial hydroxide suspensions was adjusted from 0.05 to 0.33, and the total amount of Al^{3+} and Fe^{2+} was kept constant at 0.8 mol/dm³.

The air-flow was put through the above hydroxide suspensions under mechanical stirring, where the temperature of the suspensions were kept at approximately 90°C. The pH value during the oxidation reaction was kept at approximately 10.5 with the titration of diluted sodium hydroxide solution. After the completion of the oxidation, the pH value of the obtained suspension was adjusted to approximately 11.5 with diluted sodium hydroxide solution in order to remove unreacted aluminium ions. Then the precipitates were filtrated, washed with distilled water and dried in air at 60°C.

3. RESULTS AND DISCUSSION

The method B provided only granular particles, the X-ray diffraction pattern of which showed only spinel structure. In the cases of the method A and C, granular particles were formed with irregular-shaped particles. X-ray diffraction patterns for these products indicated the mixture of the spinel phase and a small amount of α -ferric oxyhydroxide, and that the fraction of α -ferric oxyhydroxide prepared by the method C was less than that by the method A. Therefore, it is found that the method B is the most suitable mixing procedure for synthesis of aluminium substituted magnetite particles.

Next, we discuss the properties of the aluminium substituted magnetite particles synthesized by the method B. The magnetization decreased in the range from 86 to 60emu/g with an increase in Al^{3+} content from 0.70 to 4.0wt%. The decrease of the magnetization can be explained by the substitution of diamagnetic Al^{3+} for Fe^{3+} in octahedral site. The lattice constant of the obtained spinel phase decreased from 0.840 to 0.836nm with an increase of the Al^{3+} content with the above range, as expected from the ionic radius difference between Fe^{3+} (0.79Å) and Al^{3+} (0.68Å). But the lattice constant variation deviated from the simple Vegard's law, in which the obtained particles were assumed to be $\text{Fe}_{3-x}\text{Al}_x\text{O}_4$.

In order to clarify the reason for the deviation from the simple Vegard's law, we performed X-ray photoelectron spectroscopic measurement of Al(2p). First, we measured the Al(2p) spectra of aluminium hydroxide and aluminium substituted magnetite prepared by conventional ceramic technique. The spectra was numerically fitted to Lorentzian functions : center at 76.2eV and a width of 2.1eV for aluminium hydroxide, center at 75.0eV and a width of 2.0eV for aluminium substituted magnetite. Then, the XPS spectra for the obtained particles with Al^{3+} content of 3.5wt% were measured. Figure 1 indicates that the XPS spectrum of Al(2p) consisted of a broad signal. It was reproduced by the superposition of the above two Lorentzian functions, and the chemical states of Al were determined by their percentages in the various states. The Al percentage in oxide state was approximately 80% and that in hydroxide state was approximately 20%. It implies that a part of aluminium are not incorporated into the spinel lattice but precipitated out of the ferrite particles, probably at grain boundary and particle surface. It may be attributed to the difference of hydrolytic precipitation rate between Fe and Al ions.

Fig.1 XPS spectrum of Al(2p) in the obtained particles.

Fig.2 The measured lattice constant versus the lattice constant calculated from the Vegard's law

Detail discussion on the lattice constant variation of the obtained spinel phase needs the corrected Al content which is estimated by subtraction of Al content in hydroxide state from the total Al content. Furthermore, the ferrous content deviated from the stoichiometric value because of some oxidation degree during drying process. Therefore, it is considered that the spinel phase is $\text{Fe}_3\text{O}_4 - \gamma\text{-Fe}_2\text{O}_3 - \text{FeAl}_2\text{O}_4$ solid solution. Figure 2 shows the measured lattice constant versus the lattice constant calculated from the Vegard's law, in which the obtained particles assumed to be composed of aluminium hydroxide and the above mentioned solid solution. The values of 0.8397, 0.8350 and 0.8146nm were used as the lattice constant of Fe_3O_4 , $\gamma\text{-Fe}_2\text{O}_3$ and FeAl_2O_4 , respectively. A dashed line represents the values calculated using the Vegard's law. From this figure, it is seen that the lattice constant is in good agreement with those calculated using the Vegard's law. Accordingly, the deviation from the simple Vegard's law is attributed to the existence of aluminium hydroxide and $\gamma\text{-Fe}_2\text{O}_3$ which is formed during drying process.

4. CONCLUSION

The aluminium substituted magnetite particles with Al^{3+} content up to 4.0wt% were synthesized by the hydrothermal oxidation reaction of aqueous suspensions. It was found that the mixing procedure was critical to prepare single-phase ferrite particles : it was required that Al ions were neutralized before the precipitation of Fe ions. It is clarified that the obtained particles have non-uniform aluminium distribution : a part of aluminium are precipitated as hydroxide state at grain boundary and particle surface. Consequently, the measured lattice constant is in good agreement with the lattice constant calculated from the Vegard's law, considering that the obtained particles consists of aluminium hydroxide and $\text{Fe}_3\text{O}_4 - \gamma\text{-Fe}_2\text{O}_3 - \text{FeAl}_2\text{O}_4$ solid solution.

References

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