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Synthesis and Characterization of Nanosized $Mn_xFe_2O_4$ Powders by Glycothermal Process

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ABSTRACT

Nanosized $Mn_xFe_2O_4$ powders were prepared in ethylene glycol solution under mild temperature and pressure conditions by precipitation from metal nitrates with aqueous potassium hydroxide. The average size and distribution of the synthesized $Mn_xFe_2O_4$ powders was about 20 nm and broad, respectively. The phase of synthesized particles was crystalline reacted at 200°C for 6 h. The magnetic properties of the synthesized $Mn_xFe_2O_4$ powders were about 35–60 (emu/g) with superparamagnetic character.

Key words : $Mn_xFe_2O_4$ powders, Glycothermal process, Superparamagnetic character, Nanosize, VSM

1. Introduction

Ferrites are important magnetic materials, which are widely used in many electronic and magnetic applications, such as in transformers, choke coils, high frequency application, data storage, noise filters and recording heads, due to their high magnetic permeabilities and low magnetic losses. Recently, the Magnetic Carrier Technology(MCT) was developed by using magnetic bead coated with bioactive materials for the selective extraction of biological components or delivery of medicine to intended body parts.[1,2] The small sizes and single domain natures of the nanosized ferrite powders give them super paramagnetic properties.[3] As a result of this property, magnetic fluids have been prepared from these ferrites. The magnetic fluids can be used as material separation systems, dynamic loud speakers and acoustic devices.[4] In addition to the magnetic fluid applications such particles can be also used as Giant Magneto Resistant(GMR) materials in magnetic recording heads due to their single particle nature.[5]

Many different ways of producing nanosize ferrite powders are described in the literature such as, sol-gel processing,[6] hydrothermal processing[7,8] and ion exchange resin manufacture methods.[9,10]

In most of the methods listed above, the crystalline phases are frequently developed during calcinations from the amorphous room temperature phases, whereas crystalline phases may be formed during synthesis in the glycothermal technique. It is also easier to produce well-dispersed nanosized particles with a narrow size distribution in solution and also processing costs are cheap compared with other production techniques of nanosized powders.[11] Furthermore, if process conditions such as solute concentration, reaction temperature, reaction time and the type of solvent were carefully controlled, the desired shape and size of the particles can be produced.[12,13] Uniform distribution of the particles is essential for optimal control of grain size and microstructure to maintain high reliability. It has been demonstrated that such powders are composed of much softer agglomerates and have much better sinterability than those prepared by calcination decomposition of the same oxides.[14] These powders could be sintered at low temperature without calcination and milling steps.[15]

The objective of this study is to prepare the nanosized $Mn_xFe_2O_4$ powders with superparamagnetic property by glycothermal process and to investigate the effects of the processing conditions on the formation, morphology and phase of the powders.

2. Experimental Procedure

The preparation sequence of $Mn_xFe_2O_4$ powders is schematically illustrated in Fig. 1. $Mn_xFe_2O_4$ precursors were precipitated from 0.3 M $Mn(NO_3)_2 \cdot 6H_2O$ and 0.3 M $Fe(NO_3)_3 \cdot 9H_2O$ solution by slowly adding 1 M KOH solution with rapid stirring in which the pH of starting solutions varied between 5 and 9. The precipitated $Mn_xFe_2O_4$ precursors were washed by repeated cycles of centrifugation and re-dispersion in water. Washing was performed minimum five times by ethanol. Excess solution was decanted after the final washing and the wet precursor was re-dispersed in 250 ml ethylene glycol under vigorous stirring. The resulting suspension was placed in a 1000 ml stainless steel pressure vessel. The vessel was then heated to the 200–210°C at a rate of 10°C/min. The pressure of the reactor gradually

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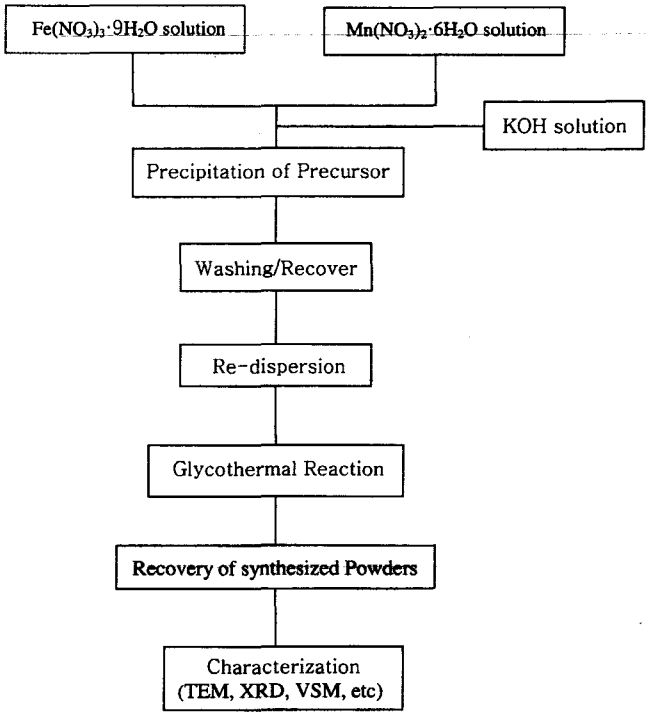

Fig. 1. Experimental flow chart of synthesis of the $Mn_xFe_2O_4$ powders by glycothermal reaction in ethylene glycol solution.

increased about 200 psi and maintained 200 psi during the holding period. The reaction products were washed five times by repeated centrifugation and re-dispersion in ethanol. The recovered powders were analyzed for phase composition using X-ray diffraction (Rigaku, CN 2014) over the 2 theta range from 10–80° at the rate of 2.5°/min. The morphology of the synthesized particles was observed using Transmission Electron Microscopy(TEM, Philips, JEM-200CX). The magnetic property of the powder was measured by VSM(Vibrating Sample Magnetometer VSM-5, Toei Kogyo Co. LTD.,) and the specific surface area was measured by the BET method (Micromeretics ASAP 2000).

3. Results and Discussion

The conditions of glycothermal processing have significant effects on the formation, phase component, morphology and particle size of $Mn_xFe_2O_4$ powders. The pH in the reaction medium affected significantly the formation of $Mn_xFe_2O_4$ powders. The reaction temperature had a great effect on the particle size of the products and the agglomeration among particles.[16] Lowering reacting temperature leads to decreasing grain size and increasing agglomeration among particles.[16] It has been proposed that crystallization under glycothermal conditions proceeds by dissolution-precipitation and structural rearrangement.[17] The reaction time plays an important role in the phase transformation from hydroxide to oxide.

In this study, the reaction temperature was 200°C and

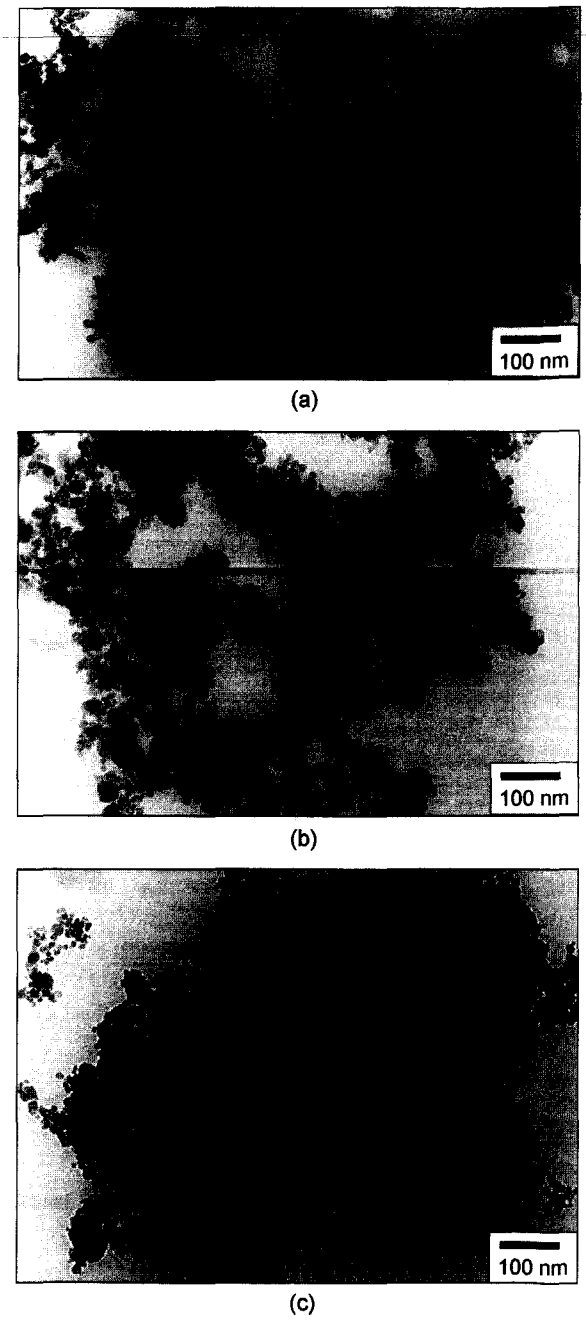

Fig. 2. TEM micrographs of the synthesized $Mn_xFe_2O_4$ powders reaction at 200°C for 6 h as a function of starting solution pH; (a) 5, (b) 7 and (c) 9.

reaction time was 6 h because ethylene glycol boils at 196°C. Fig. 2 shows the transmission electron microscopy of the synthesized particles of the reaction at 200°C for 6 h as a function of pH of starting solution. It has been shown that the average sizes of the synthesized $Mn_xFe_2O_4$ powders are about 20 nm and the size distributions for the $Mn_xFe_2O_4$ powders are more than 15% in the pH range of starting solution of 5 to 9. After glycothermal reaction at pH of starting solution of 5 and 9, the surface area of the synthesized

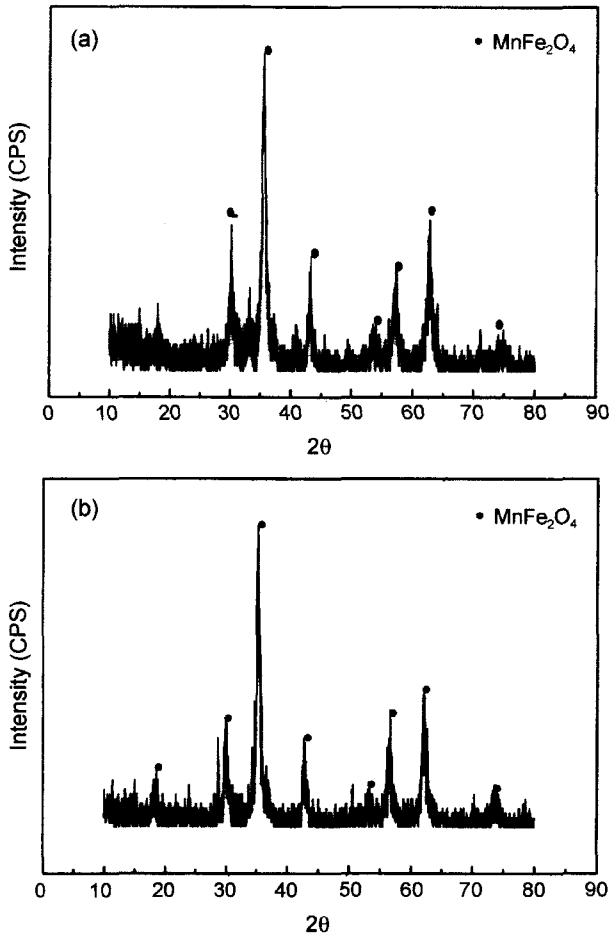

Fig. 3. X-ray diffraction patterns of the synthesized $Mn_xFe_2O_4$ powders reaction at 200°C for 6 h as a function of starting solution pH; (a) 5 and (b) 9.

$Mn_xFe_2O_4$ powders was 75.15 m^2/g and 73.75 m^2/g, respectively. The shapes of the synthesized $Mn_xFe_2O_4$ powders were irregular type at the pH range of starting solution of 5 to 9.

Fig. 3 shows the X-ray diffraction pattern of the $Mn_xFe_2O_4$ powders synthesized in ethylene glycol solution. The X-ray powder diffraction patterns have shown that the synthesized magnetic particles have a single spinel phase of $Mn_xFe_2O_4$.

Fig. 4 shows magnetic properties of the synthesized $Mn_xFe_2O_4$ powders as a function of pH of starting solution. From the VSM analysis, the synthesized nanosized crystalline powder exhibiting superparamagnetic behavior in the pH range of starting solution from 5 to 9. It has shown that the magnetism of the synthesized $Mn_xFe_2O_4$ powders was different with pH variation of starting solution.

The magnetisms of the synthesized $Mn_xFe_2O_4$ powders were about 60 (emu/g), 35 (emu/g), 55 (emu/g) at the pH of starting solution of 5, 7, 9, respectively.

It might be possible that the magnetic nanoparticle could be applicable for drug delivery as nanoparticulate magnetic carrier.

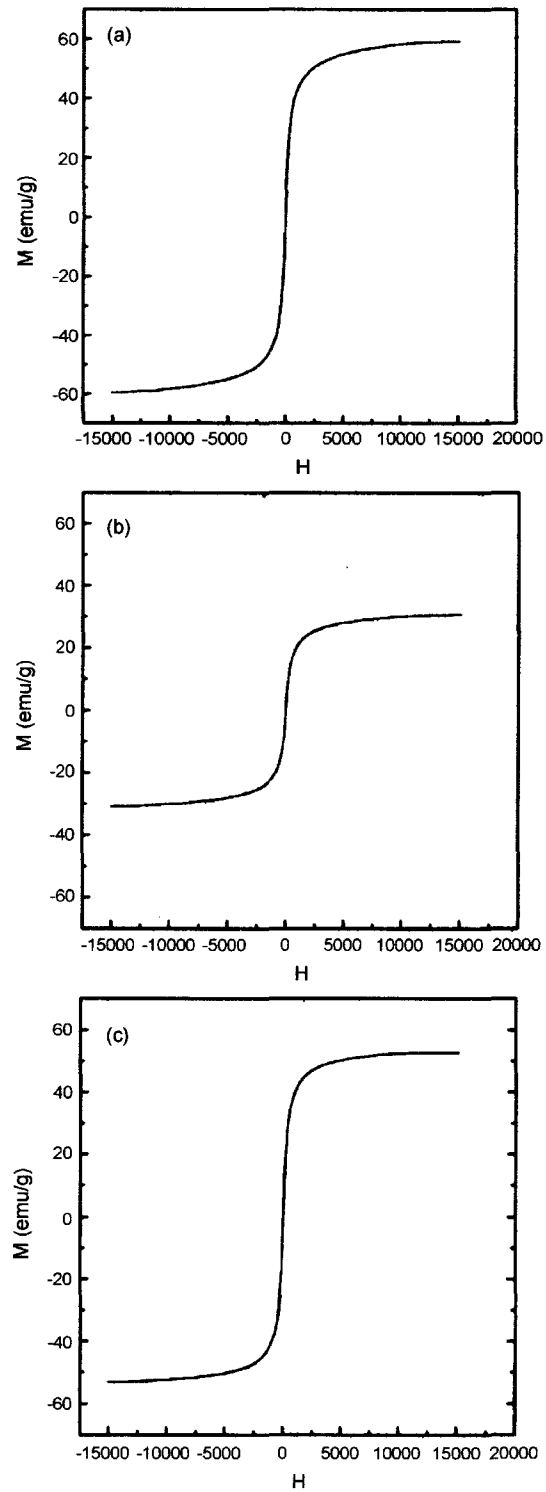

Fig. 4. Magnetic properties of the synthesized $Mn_xFe_2O_4$ powders by glycothermal reaction at 200°C for 6 h as a function of pH; (a) 5, (b) 7 and (c) 9.

4. Conclusion

Nanosized $Mn_xFe_2O_4$ powders were prepared in ethylene glycol solution at 200°C and 100 psi conditions by precipita-

tion from 0.3 M $Mn(NO_3)_2 \cdot 6H_2O$ and 0.3 M $Fe(NO_3)_3 \cdot 9H_2O$ solution with aqueous 1 M KOH. The average size and distribution of the synthesized particles were different as a function of pH of starting solution. The average sizes of the synthesized $Mn_xFe_2O_4$ powders were about 20 nm at the pH range of starting solution of 5 to 9. The surface areas of the synthesized $Mn_xFe_2O_4$ powders were 75.15 m^2/g, 73.75 m^2/g at pH of starting solution of 5, 9, respectively. The crystalline phase of the synthesized powders was $Mn_xFe_2O_4$. Glycothermal synthesis of $Mn_xFe_2O_4$ powders yields a nanosized crystalline powder exhibiting superparamagnetic character. The magnetisms of the synthesized $Mn_xFe_2O_4$ powders were 35–60 (emu/g) in the range of pH of starting solution of 5–9. It is possible to the application of magnetic nanoparticles for drug delivery using nanoparticulate magnetic carrier. If the pH and reaction condition of the solution is carefully controlled, it is possible to control the average size, crystalline phase and magnetic property of the synthesized powders under mild temperature and pressure in ethylene glycol solution.

REFERENCES

1. B. R. Pieters, R. A. Williams and C. Webb, "Magnetic Carrier Technology," pp. 248-86, Colloid and Surface Engineering. Ed. By R. A. Williams, Butterworth-Heinemann, Oxford, 1992.
2. M. Ozaki, "Synthesis of Magnetic Particles," pp. 421-43, Chemical Processing of Ceramics. Ed. By Burtrand I. Lee, Edward J. A. Pope, Marcel Dekker, New York, 1994.
3. M. Rozman and M. Drofenik, "Hydrothermal Synthesis of Manganese Zinc Ferrites," *J. Am. Ceram. Soc.*, **78** [9] 2449-55 (1995).
4. V. E. Fertman, "Magnetic Fluids Guidebook, Properties and Applications," Chp. 3, Hemisphere Publishing Corp. (1990).
5. J. A. Brug, T. C. Anthony and J. H. Nickel, "Magnetic Recording Head Materials," *MRS Bull.*, Sept., 23-7 (1996).
6. M. Seki, J. Sato and S. Usui, "Observations of Ultrafine $ZnFe_2O_4$ Particles with Transmission Electron Microscopy," *J. Appl. Phys.*, **63** [5] 1424-27 (1988).
7. S. Komarneni, E. Freagan, E. Bravel and R. Roy, "Hydrothermal Preparation of Ultrafine Ferrites and Their Sintering," *J. Am. Ceram. Sci.*, **71** [1] C26-C8 (1988).
8. J. R. Ahn, D. S. Bae and J. S. Kim, "CO_2 Decomposition Properties of Ternary Ferrites Synthesized by the Wet Processing," *J. Kor. Ceram. Soc.*, **37** [10] 962-67 (2000).
9. P. Sainamthip and V. R. W. Amarakoon, "Preparation of Manganese Zinc Ferrite Powders by Alcoholic Dehydration of Citrate/Formate Solutions," *J. Am. Ceram. Soc.*, **71** [2] C-92-C-5 (1988).
10. R. F. Ziolo, E. P. Giannelis, B. A. Weinstein, M. P. Ohoro, B. N. Ganguly, V. Mehrotra, M. W. Russell and D. R. Huffman, "Matrix-mediated Synthesis of Nanocrystalline γ-Fe_2O_3: A New Optically Transparent Magnetic Material," *Science*, **257** 219-23 (1992).
11. S. Hirano, "Hydrothermal Processing of Ceramics," *Am. Ceram. Soc. Bull.*, **66** [9] 1342-44 (1987).
12. W. J. Dawson, "Hydrothermal Synthesis of Advanced Ceramic Powders," *Am. Ceram. Soc. Bull.*, **67** [10] 1673-78 (1989).
13. S. B. Cho, S. Venigalla and J. H. Adair, "Morphological Control of α-Al_2O_3 Particles Precipitated from 1,4-butanediol Solution," Sci., Tech., & App., of Colloid. Susp., edited by James H. Adair, Jon A. Casey, Clive A. Randall (Sridhar Venigalla) pp. 139-150 (1995).
14. K. Haberko and W. Pyda, Advances in Ceramics, Vol, 12, Science and Technology of Zirconia II. Edited by N. Claussen, etc, (Am. Ceram. Soc.), pp 774-83 (1984).
15. M. Rozman, M. Drofenik and D. Kolar, "Sintering of Nanosized MnZn Ferrite Powders," *Euro-Ceramics*, **5** 47-54 (1995).
16. H. Cheng, J. Ma, Z. Zhao and L. Qi, "Hydrothermal Preparation of Uniform Nanosize Rutile and Anatase Particles," *Chem. Mater.*, **7** [4] 663-72 (1995).
17. E. Tani, M. Yoshimura and S. Somiya, "Hydrothermal Preparation of Ultrafine Monoclinic ZrO_2 Powders," *J. Am. Ceram. Soc.*, **64** [12] C180-81 (1981).