

CONTROL OF PARTICLE SIZE AND MORPHOLOGY OF COBALT-FERRITE NANOPARTICLES BY SALT-MATRIX DURING ANNEALING

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Salt-matrix annealing of mechanically alloyed Co-ferrite nanopowder was used to modify its particle size and morphology. Efficiency improvement due to suppression of sintering and growth resulted in reduction of average particle size from ~100nm for salt-less to ~40nm for salt-full annealing procedure. Nanosized single-phase cobalt-ferrite particles were observed after 2h annealing at 750°C in the samples milled for 20 hours both with and without NaCl. NaCl:CoFe₂O₄ ratio of 10:1 resulted in cabbage-like clusters containing particles smaller than ~50 nm.

Keywords: Salt-matrix annealing; Growth suppression; Cobalt-ferrite nanopowder

1. Introduction

Spinel ferrites are represented by the formula unit AB₂O₄. Most of the spinel ferrites form cubic spinel structure. Anions (O²⁻) accommodate themselves in the fcc lattice sites, while cations sit in the tetrahedral and octahedral coordinated interstitial positions to form the A and B sublattices.¹ Among the family of ferrite materials, cobalt ferrite (CoFe₂O₄) is of the most important and abundant magnetic substance found. CoFe₂O₄ is well known

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to have large magnetic anisotropy, moderate saturation magnetization, remarkable chemical stability and mechanical hardness. These properties make it a desirable candidate for utilization in the recording media.²

Nano-size ferrites have been produced by various methods such as chemical co-precipitation,³ sol-gel procedure,⁴ aerosol route,⁵ microwave processing⁶ and shock wave stimulation.⁷

High-energy ball milling of metallic oxides is a simple solid-state technique for production of nanosized ferrite powder exhibiting unusual properties.⁸⁻¹⁰ During MA, some magnetic properties can be improved, while the others deteriorate due to stress, strain and defects introduced by milling of the sample. Residual stress/strain elimination by annealing is required to improve the magnetic properties.¹¹ But, the heat treatment leads to grain growth and sintering of the nanoparticles.

Results of recent studies on salt-matrix annealing of the cobalt-ferrite synthesized by mechanical alloying are presented in this paper. NaCl salt was employed as an annealing growth-preventive-medium. Its utilization was shown to have great impact on the morphology and particle size of cobalt-ferrite nanopowders.

2. Experimental Procedure

Highly pure Fe₂O₃ and Co₃O₄ powders supplied by Merck (GmbH) having the molar ratio of 1:1 were milled together in a vial containing hardened steel balls using a RETSCH PM4000 high-energy ball-milling machine for 20 h with running speed of 350 rpm. Ball to powder weight ratio (BPR) was 20:1. Direction of the rotation in MA process was changed each 2 h.

The as-milled CoFe₂O₄ nanoparticles were mixed with NaCl powders. Sodium chloride (NaCl) was chemically stable and highly soluble in water. It was added to prevent CoFe₂O₄ from growing into large crystals during annealing. The mixture was annealed under Ar (99.9999%) for 2 h. The powder was then washed with deionized water and centrifuged repeatedly to remove all NaCl which might be remained.

The effect of the NaCl-to-CoFe₂O₄ weight ratio on morphology and particle size was rigorously investigated in detail. The phases in the milled/annealed powders were characterized by X-ray powder diffraction (XRD, Philips PW 3710, Netherlands) having Cu-K_α radiation. Morphology and size of the particles were determined by scanning electron microscope (SEM, Philips XL30, Netherlands) and transmission electron microscope (TEM, CM120, Philips, Netherlands).

3. Results and Discussion

X-ray diffraction patterns of different samples produced in this research are comparatively plotted in Fig. 1. As indicated in the figure, all samples have diffraction peaks related to spinel structure of CoFe₂O₄. Fig. 1a illustrates the XRD pattern of single phase spinel cobalt-ferrite that was achieved after 20 milling hours. Significant peak broadening could be attributed to the formation of nanocrystalline structure and build-up

of the induced milling strain. Notice that annealing resulted in narrowing, sharpening and intensification of the diffracted peaks due to the release of the internal strains and growth of the particles as indicated in Fig. 1b and 1d.

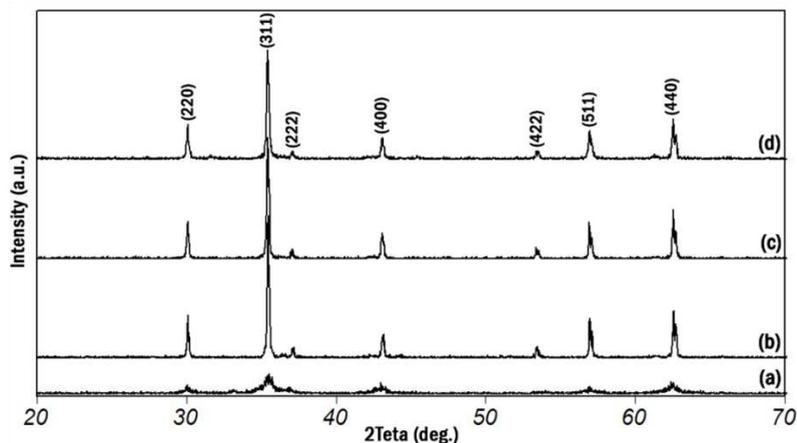


Fig. 1. X-ray diffraction pattern of the samples: (a) milled for 20h, (b) milled for 20h then annealed at 750°C for 2h, (c) milled for 20h then annealed at 750°C for 2h with NaCl:CoFe₂O₄ ratio of 4:1 and (d) milled for 20h then annealed at 750°C for 2h with NaCl:CoFe₂O₄ ratio of 10:1.

Fig. 1a illustrates the XRD pattern of single phase spinel cobalt-ferrite that was achieved after 20 h milling. Significant peak broadening could be attributed to the formation of nanocrystalline structure and build-up of the induced milling strain. Notice that annealing resulted in narrowing, sharpening and intensification of the diffracted peaks due to the release of the internal strains and growth of the particles as indicated in Fig. 1b and 1d. From the XRD patterns, no peaks of NaCl were found. This indicated that the NaCl salt was not left after washing the mixture with the distilled water.

Fig. 2 shows SEM micrographs of the milled powders before and after annealing at different conditions. Large agglomerations of very fine CoFe_2O_4 particles produced after 20 hours milling are observable in Fig. 2a. Heat treatments has been mentioned necessary after mechanical alloying to synthesize magnetic nanoparticles with strong magnetic properties [11,12]. Heat treatment leads, on the other hand, to growth and sintering of the nanoparticles. As a case in point, Fig. 2b shows significant growth of CoFe_2O_4 particles after 2 h annealing at 750°C.

The average size of the particles is above 100 nm. In this experiment, NaCl was used to prevent particle growth due to the annealing treatment. As is clearly seen in Fig. 2c&d, an increase in the NaCl-to- CoFe_2O_4 ratio, culminated more growing prevention. Success in obtaining finer particles at the same annealing conditions was, hence, achievable. The average size of the particles was under 50 nm, when the samples were annealed at 750°C for 2 h with NaCl:CoFe₂O₄ ratio of 10:1. Fig. 2d revealed cabbage-like growth of particulate clusters in the samples.

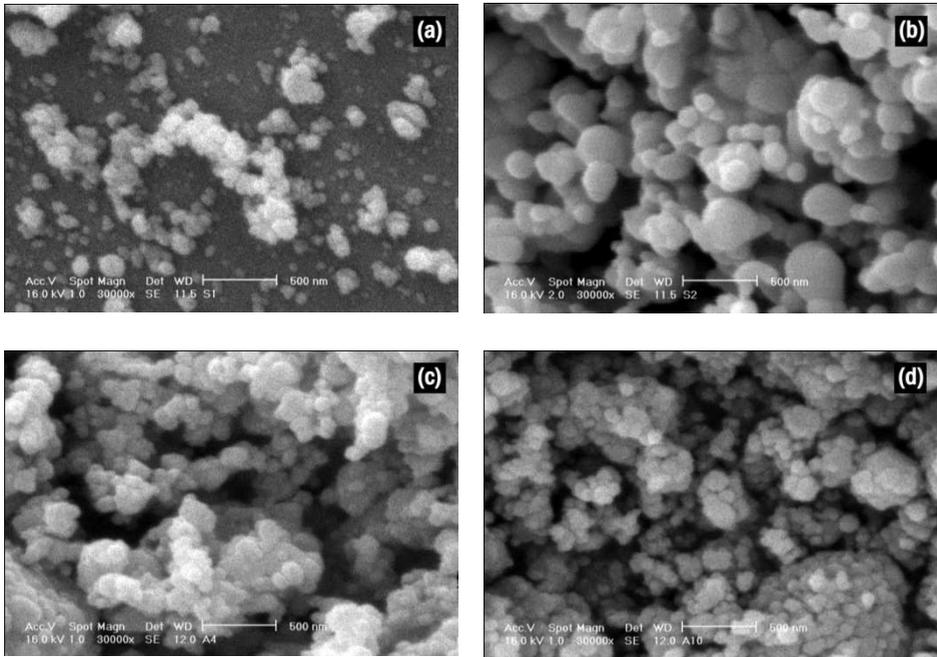


Fig. 2. SEM images of the samples: (a) milled for 20 h, (b) milled for 20 h then annealed at 750°C for 2 h, (c) milled for 20 h then annealed at 750°C for 2 h with NaCl:CoFe₂O₄ ratio of 4:1 and (d) milled for 20 h then annealed at 750°C for 2 h with NaCl:CoFe₂O₄ ratio of 10:1.

Fig. 3 compares the TEM images of the ball-milled samples with ball-milled and then annealed at 750°C for 2 h with NaCl:CoFe₂O₄ ratio of 10:1. Large surface free energy of the ball-milled particles having ~20nm diameter resulted in intense agglomeration of the particles seen in Fig. 3a. TEM image of the sample shown in Fig. 3b indicated that cabbage-like colony of three clusters were produced by gathering of the fine particles together when the powders were annealed. A comparison of the images illustrated in Figs. 2d and 3b confirmed that the average size of the particles was around 40 nm.

4. Conclusion

Single phase nanosized CoFe₂O₄ powder was synthesized by 20 hours ball milling of pure Fe₂O₃ and Co₃O₄ powders with weight ratio of 20. The results showed that annealing of the as-milled powder mixture relaxed the induced strains and stimulated the growth of the particles. Using NaCl as a preventive medium (matrix) proved, however, an appropriate method for diminution of the particle growth and controlling of the size of the particulates. Nanosized particulates embedded in cabbage-like colony of cobalt-ferrite clusters were obtained by the procedure exercised in this research.

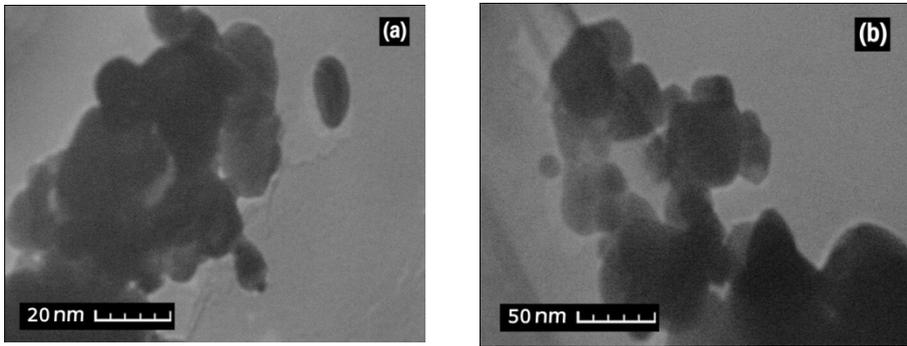


Fig. 3. TEM images of the samples: (a) milled for 20 h, (b) milled for 20 h then annealed at 750°C for 2 h with NaCl: CoFe_2O_4 ratio of 10:1.

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