2nd International Conference on
Ultrafine Grained and Nanostructured Materials
Center of Excellence For High Performance Materials
School of Metallurgy and Materials Engineering
University College of Engineering, University of Tehran
Tehran, Iran. 14-15 Nov. 2009

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

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Received 30 September 2009
Revised Day Month Day

Effect of milling and subsequent salt-matrix annealing on morphology and particle size of cobalt-ferrite was investigated. X-ray diffraction (XRD) with Cu-K_a radiation was employed for phase identification. Scanning electron microscope (SEM) and transmission electron microscope (TEM) were used to determine the morphology and the size of the particles. Single phase nano-sized cobalt-ferrite was obtained after 20 hours mechanical alloying (MA). Utilization of the Salt-matrix prevented growth of the nanoparticles during annealing.

Keywords: Cobalt-ferrite; Nanoparticles; Mechanical alloying; Annealing; Salt-Matrix.

1. Introduction

Spinel ferrites are represented by the formula unit AB2O4. Most of the spinel ferrites

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form cubic spinel structure. Anions (O^{2-}) 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 ($CoFe_2O_4$) is of the most important and abundant magnetic substance found. $CoFe_2O_4$ is well known 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]

Nanosize ferrites have been produced by various methods such as chemical co-precipitation,[3] sol–gel procedure,[4] aerosol route,[5] microwave processing [6] 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 morphology and cobalt-ferrite nanopowder particle-size.

2. Experimental procedure

Highly pure Fe_2O_3 and Co_3O_4 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 was chemically stabile 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_a 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. Result and discussion

Figure 1 shows X-ray diffraction pattern of the produced samples. As indicated in the figure, all samples have diffraction peaks related to spinel structure of $CoFe_2O_4$.

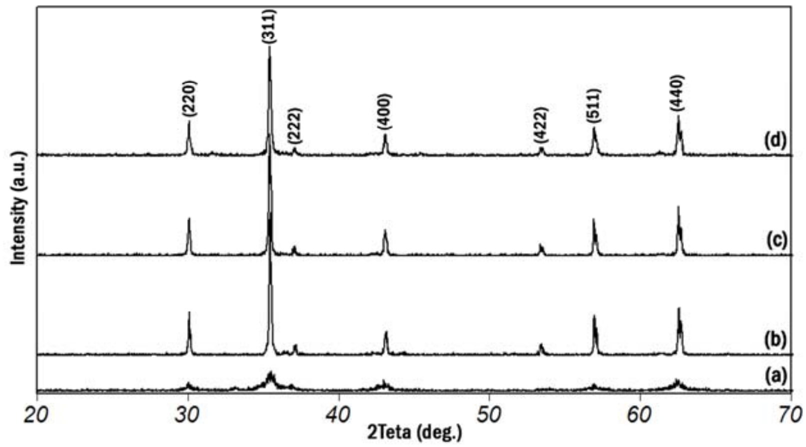

Fig. 1. X-ray diffraction pattern of the samples: (a) milled for 20 h, (b) milled for 20 h then annealed at 750°C for 2 h, (c) milled for 20 h then annealed at 750°C for 2 h with NaCl:$CoFe_2O_4$ ratio of 4:1 and (d) milled for 20 h then annealed at 750°C for 2 h with NaCl:$CoFe_2O_4$ ratio of 10:1.

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 pattern, 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]. 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 annealing tretment. 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:$CoFe_2O_4$ ratio of 10:1. Fig. 2d revealed cabbage-like growth of particulate clusters in the samples.

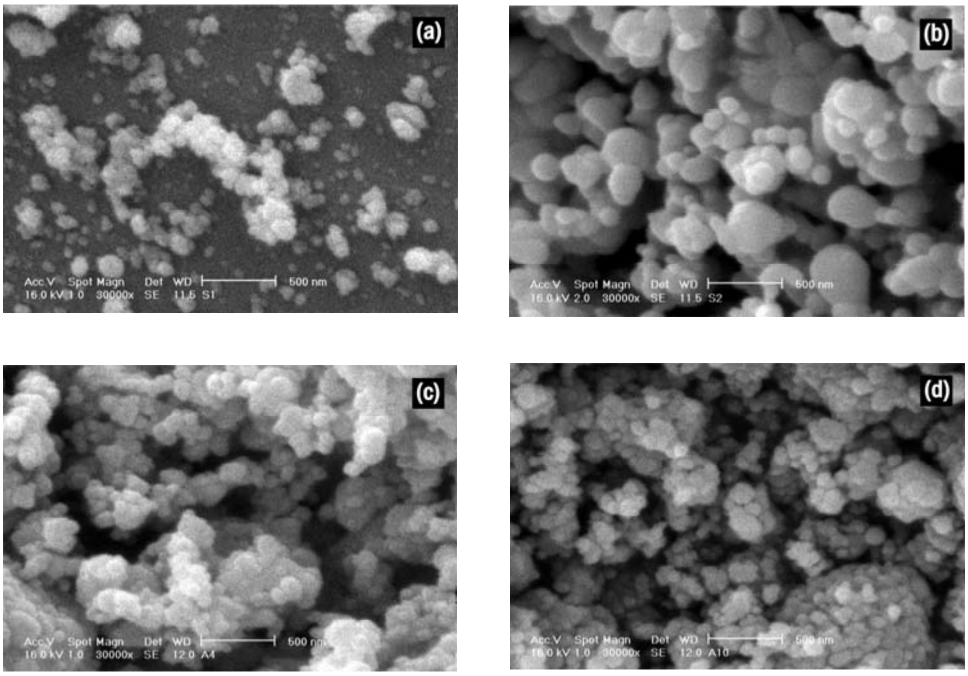

Fig. 2. SEM images of the samples: (a) milled for 20 h, (b) milled for 20 h then annealed at 750°C for 2 h, (c) milled for 20 h then annealed at 750°C for 2 h with NaCl:CoFe2O4 ratio of 4:1 and (d) milled for 20 h then annealed at 750°C for 2 h with NaCl:CoFe2O4 ratio of 10:1.

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:$CoFe_2O_4$ 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 $CoFe_2O_4$ powder was synthesized by 20 hours ball milling of pure Fe_2O_3 and Co_3O_4 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.

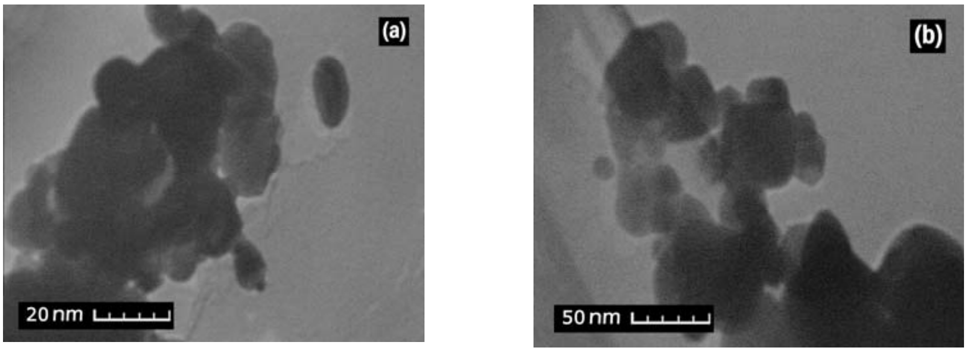

Fig. 3. TEM images of the samples: (a) milled for 20 h, (b) milled for 20 h then annealed at 750°C for 2 h with NaCl: $CoFe_2O_4$ ratio of 10:1.

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