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Role of intensive milling in the processing of barium ferrite/magnetite/iron hybrid magnetic nano-composites via partial reduction of barium ferrite

M.J. Molaei [a,c,*], A. Ataie [b], S. Raygan [b], S.J. Picken [c]

[a] Materials and Energy Research Center, P.O. Box: 31787-316, Karaj, Iran
[b] School of Metallurgy and Materials Engineering, College of Engineering, University of Tehran, P.O. Box: 14395-553, Tehran, Iran
[c] Delft Chem Tech, Faculty of Applied Sciences, Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands

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ABSTRACT

In this research a mixture of barium ferrite and graphite was milled for different periods of time and then heat treated at different temperatures. The effects of milling time and heat treatment temperature on the phase composition, thermal behavior, morphology and magnetic properties of the samples have been investigated using X-ray diffraction, differential thermal analysis, high resolution transmission electron microscopy and vibrating sample magnetometer techniques, respectively. X-ray diffraction results revealed that $BaFe_{12}O_{19}/Fe_3O_4$ nanocomposites form after a 20 h milling due to the partial reduction of $BaFe_{12}O_{19}$. High resolution transmission electron microscope images of a 40 h milled sample showed agglomerated structure consisting of nanoparticles with a mean particle size of 30 nm. Thermal analysis of the samples via differential thermal analysis indicated that for un-milled samples, heat treatment up to 900 °C did not result in α-Fe formation, while for a 20 h milled sample heat treatment at 700 °C resulted in reduction process progress to the formation of α-Fe. Wustite was disappeared in an X-ray diffraction pattern of a heat treated sample at 850 °C, by increasing the milling time from 20 to 40 h. By increasing the milling time, the structure of heat treated samples becomes magnetically softer due to an increase in saturation magnetization and a decrease in coercivity. Saturation magnetization and coercivity of a sample milled for 20 h and heat treated at 850 °C were 126.3 emu/g and 149.5 Oe which by increasing the milling time to 40 h, alter to 169.1 emu/g and 24.3 Oe, respectively. High coercivity values of milled and heat treated samples were attributed to the nano-scale formed iron particles.

1. Introduction

Barium ferrite is a widely used magnetic material as a permanent magnet [1]. Metallic ions relative to oxygen ions in crystal structure of barium ferrite are in such positions that give rise to suitable magnetic properties for this ceramic material. High coercivity, high Curie temperature, good mechanical hardness and chemical resistivity against corrosive environments are some of the reasons for wide application of this material [2,3].

In recent years, some of the researches have focused on production of nanocrystalline powder and films of barium ferrite because of their superior magnetic properties [4–6]. Furthermore, nanocrystalline magnetic powders with increased surface area have lower sintering temperature, less grain growth and increased density of bulk magnetic parts which result in increased magnetic properties [7].

It has been suggested to alter magnetic properties of barium ferrite to make it suitable for some applications such as recording media. In order to decrease the coercivity of this material, substitution of Co–Ti or Co–Zn for some of iron ions in the crystal structure of barium ferrite has been proposed. As a result of this substitution, saturation magnetization decreases [8]. Heat treatment under different gaseous atmospheres is an alternative route to ion substitution methods for altering magnetic properties of barium ferrite. Heat treatment of barium or strontium ferrite under the atmosphere of nitrogen, hydrogen and carbon containing gases (or a mixture of them) gives result in a magnetic material with lower coercivity which makes it suitable for applications that high coercivity of this ceramic material should be avoided. The structure from these heat treatments mostly consists of iron. Gas heat treatment of these ferrites requires high purity gases (H_2, CO, CH_4, N_2, etc.) and treatment at elevated temperatures [9,10].

High energy ball milling is a method for production of nanostructured ceramic or metallic powders [11,12]. We have proposed a mechano-thermal method for partial reduction of barium ferrite by carbon in high energy mechanical milling. Subsequent heat treatment at low

* Corresponding author at: Materials and Energy Research Center, P.O. Box: 31787-316, Karaj, Iran.
E-mail address: mj.molaee@merc.ac.ir (M.J. Molaei).

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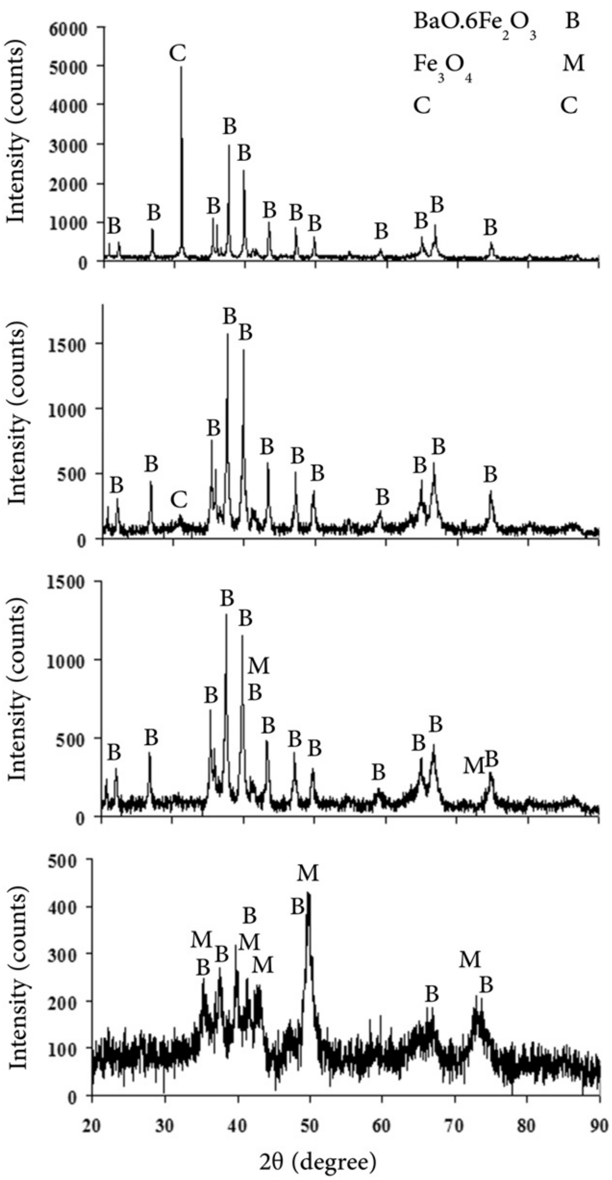

Fig. 1. X-ray diffraction patterns of barium ferrite and graphite mixtures milled for different times.

temperatures, results in a decrease in coercivity and an increase in saturation magnetization toward a soft magnetic structure. In previous works [13–17], magnetic properties of barium ferrite nanocomposites via mechano-thermal treatments were investigated. In this research the effect of high energy ball milling on magnetic properties of heat treated barium ferrite/magnetite nanocomposites has been investigated.

2. Experimental procedure

Barium ferrite, BaO.6(Fe_2O_3) (Sigma-Aldrich, particle size ≤ 44 μm) and graphite (Sigma-Aldrich, particle size ≤ 20 μm) powders with a C:O molar ratio of 1.1 were mixed. A planetary high energy ball mill with a ball to powder mass ratio of 35 and rotating speed of 300 rpm was used for milling of the powder mixtures in air atmosphere. Ball milling container volume was 300 ml. Milled samples were heat treated at different temperatures under vacuum. Phase analysis was performed with a Bruker D8 advance X-ray Diffraction (XRD) machine equipped with a high resolution, high sensitive Lynx Eye Detector, with Co-Kα radiation. The step size of 0.02° and mean time of 1 s per step were used for XRD measurements. Calculation of crystallite size of the milled samples was done using the Williamson–Hall method [18]. Differential Thermal Analysis (DTA) analysis was performed with a TG/DTA-7 Pyris Diamond, PerkinElmer device with a heating rate of 10 °C/min under dynamic atmosphere of nitrogen with flow rate of 30 ml/min. Magnetic properties of milled and heat treated samples were measured by a LakeShore Model 7307 Vibrating Sample Magnetometer (VSM) at room temperature. Particle size and morphology were studied with a monochromated FEI Tecnai F20ST/STEM-FEG High Resolution Transmission Electron Microscope (HRTEM). For preparation of HRTEM samples a few mg of powder was suspended in ethanol and kept in an ultrasonic bath for few minutes and then brought on a carbon support film on a Cu grid.

3. Results and discussion

Fig. 1 shows XRD patterns of milled samples for different periods of time. As can be seen, by increasing milling time to 20 h, magnetite peaks appear and increasing the milling time to 40 h has negligible effect on phase composition. It seems that partial reduction of barium ferrite to its lower oxides results in formation of $BaFe_{12}O_{19}/Fe_3O_4$ nano-composites. Ba containing phase(s) which should result from the reduction reaction might have small amount and are not detected in the XRD peaks. The crystallite size for 20 and 40 h milled samples was 17 and 13 nm, respectively. Reduction of Fe_2O_3 with carbon via high energy milling has been reported before [19].

Fig. 2 shows the HRTEM images and Selected Area Electron Diffraction (SAED) pattern of the 40 h milled sample. As can be seen, the sample is consisted of agglomerated nano-particles with a mean particle

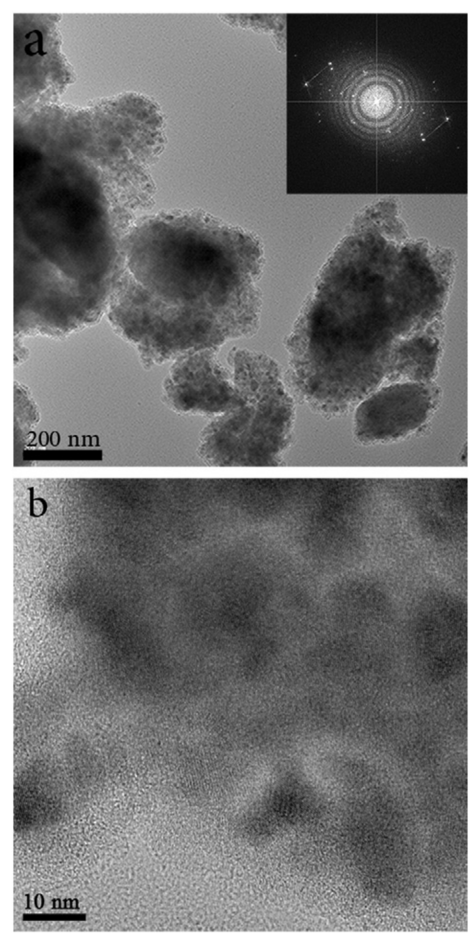

Fig. 2. High resolution transmission electron microscope images of 40 h milled sample; a) agglomerated which is consisted of particle smaller than 30 nm and SAD pattern at the right corner of the image, b) crystallites in higher magnifications.