

Investigation on the Effects of Milling Atmosphere on Synthesis of Barium Ferrite/Magnetite Nanocomposite

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Abstract In this research, barium ferrite /magnetite nanocomposites synthesized via a mechano-chemical route. Graphite was used in order to reduce hematite content of barium ferrite to magnetite to produce a magnetic nanocomposite. The effects of processing conditions on the powder characteristics were investigated by XRD, VSM, and HRTEM techniques. XRD results revealed that milling under air and argon atmospheres resulted in the appearance of Fe_3O_4 peaks beside $\text{BaFe}_{12}\text{O}_{19}$ peaks after 15 and 20 hrs milling, respectively. The intensity of Fe_3O_4 peaks in the XRD patterns increased by increasing the milling time. VSM studies revealed that saturation magnetization of the 40-hrs milled samples under air and argon atmospheres was 31.25 and 36.42 emu/g, respectively. This difference might be due to more Fe_3O_4 content in the latter sample. By annealing of the 40-hrs milled sample in air, saturation magnetization increased to 139.12 emu/g.

Keywords Barium ferrite · magnetic nanocomposite · ball milling · milling atmosphere

1 Introduction

Synthesis of nanosize magnetic powders has received great attention for application in recording media, magnetic fluids etc. Barium ferrite ($\text{BaFe}_{12}\text{O}_{19}$) shows potential for application in perpendicular recording media applications. Hexagonal platelet shape with easy axis normal to plane, moderate coercivity, chemical stability and high Curie temperature are some of the advantages of barium ferrite which makes it suitable for these applications. In addition, development of wireless and radar electronics needs low loss magnetic microwave devices and barium ferrite is a suitable candidate for microwave device applications [1–6]. There have been attempts for production of nanoparticles of barium ferrite in recent years using methods such as sol-gel [7, 8], microwave-assisted sol-gel auto-combustion [9], auto-combustion [10], hydrothermal [11], co-precipitation [12], self-propagation high-temperature synthesis [13], carbon combustion [14], spray pyrolysis [15], aerosol [16] and molten salt [17].

Mechanical milling method is widely used for mechanical assisted reactions and powder particle refinement [18]. This method has also been used for producing wide range of nanostructured materials and magnetic powders [19–22].

Barium and strontium ferrites can be heat treated in the atmosphere of gases such as nitrogen, hydrogen, carbon containing gases or a mixture of these gases to change the structural composition and hence the magnetic properties. Lower coercivity of resulted structure is suitable property for magnetic recording media that need easy re-writing characteristics [23–26].

The goal of current research was to replace the heat-treatment process under the atmospheres mentioned with a novel mechano-chemical technique to produce a magnetic nanocomposite of $\text{BaFe}_{12}\text{O}_{19}/\text{Fe}_3\text{O}_4$. In this manner

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graphite was used in order to reduce iron oxide content of barium ferrite during mechanical milling under air and argon atmospheres. The effects of the milling atmosphere on the powder particle characteristics were investigated.

2 Experimental Procedure

A mixture of barium ferrite, $\text{BaO} \cdot 6(\text{Fe}_2\text{O}_3)$ (Sigma-Aldrich, particle size $\leq 44 \mu\text{m}$) and graphite (Sigma-Aldrich, particle size $\leq 20 \mu\text{m}$) was treated mechano-chemically in a high energy planetary ball mill for 10, 15, 20 and 40 hours under air and argon atmosphere. Ball to powder mass ratio and rotating speed were 35 and 300 rpm, respectively. The molar ratio of graphite to barium ferrite was considered as C:O=1.1. 40-hrs milled samples under air and argon atmospheres were subjected to vacuum heat treatment at 800°C for 10 min.

A Bruker D8 advance diffractometer equipped with a high-resolution, highly sensitive Lynx Eye Detector, with $\text{Co-K}\alpha$ radiation was used for XRD analysis. The step size of 0.02 degrees and mean time of 1 sec per step was used for XRD measurements. Crystallite size of the milled samples calculated via the Williamson-Hall [27] method, based on the widening of three strongest peaks of a certain phase. The magnetic-property measurements carried out by a LakeShore Model 7307 vibrating sample magnetometer (VSM) at room temperature. Particle size and morphology was investigated with a monochromated FEI Tecnai F20ST/STEM-FEG transmission electron microscope. TEM samples were prepared by suspending a few mg of the sample in ethanol. After shaking the suspension in an ultrasonic bath, it was brought on a carbon support film on a Cu grid. The absorbed gas on graphite (C) would be CO and CO_2 gases which is indicated as $\text{C}(\text{CO})$ and $\text{C}(\text{CO}_2)$ hereafter, respectively.

3 Results and Discussion

Figure 1 shows the XRD patterns of barium ferrite and graphite mixtures milled for different times under air and argon atmospheres. Analysis of the XRD patterns revealed that Fe_3O_4 phase starts to form after 15 hrs of milling in both samples. As the milling time increases, Fe_3O_4 peaks become stronger and those of barium ferrite weaken in both atmospheres. After 40 hrs of milling in argon atmosphere peaks of FeO can be detected, while reduction process cannot proceed further than Fe_3O_4 in air atmosphere. Carbon peaks disappeared before 15 hrs of milling in both samples. This is because of softer nature of graphite in the mixture. Milling conditions and impact forces of balls has a stronger effect on graphite than barium ferrite and results in amorphization of this phase after a few hours of milling. Reduction of Fe_2O_3 with graphite in the mechanical milling medium has been reported earlier [28].

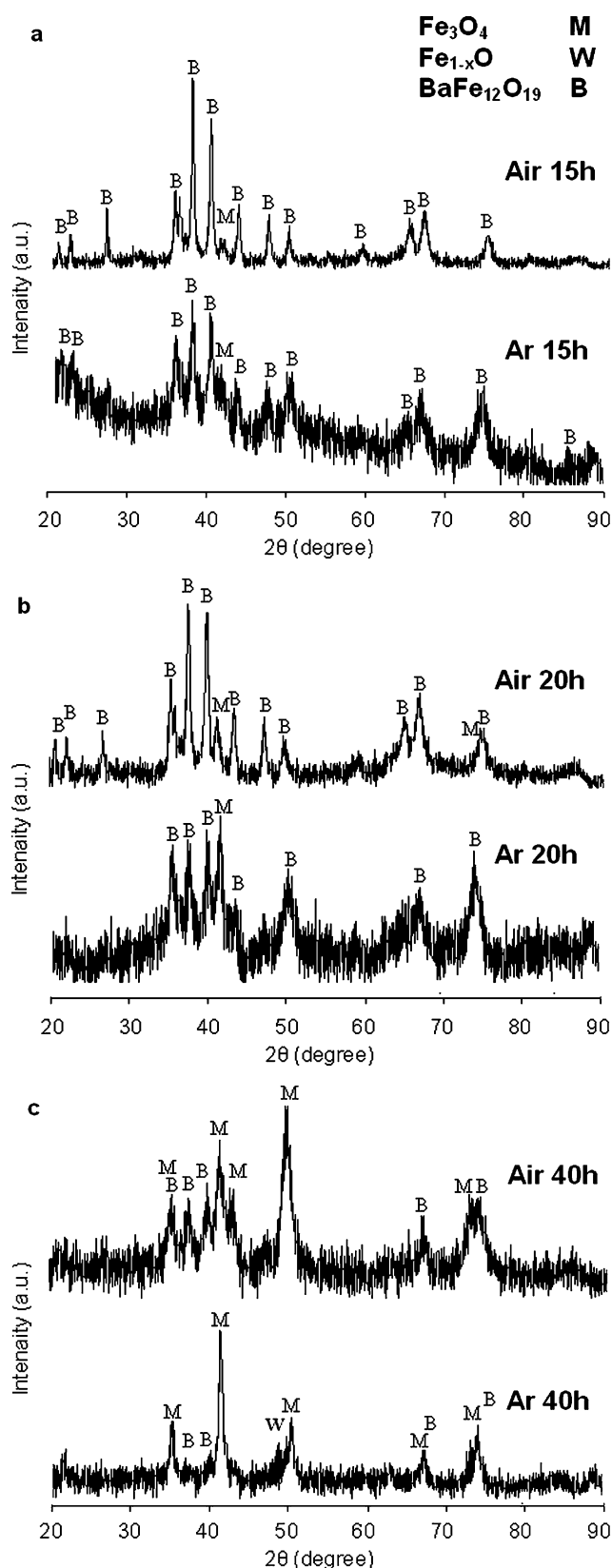


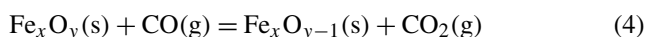
Fig. 1 XRD patterns of barium ferrite and graphite mixture milled for 15, 20 and 40 hrs in air and argon atmosphere: (a) 15 h, (b) 20 h, (c) 40 h

Milling under air atmosphere postpones the reduction process. In fact by milling in air atmosphere, the reduced species which have an activated surface due to the absorbed energy in the milling medium are in contact with oxygen in air. Therefore, the reduced species might re-oxidize again.

Reduction of iron oxide is a heterogeneous reaction and several simultaneous reactions can occur [29]. However, for Fe_2O_3 powder which is milled in air atmosphere the following consecutive reactions with solid carbon can occur [30]:

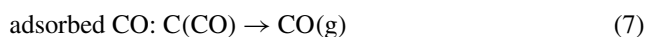


In addition two other reactions which can take place for iron oxides in contact with gas are



The reactions between Fe_2O_3 in barium ferrite and graphite can occur easily in the solid state; since in the milling medium there is intimate contact between reactant phases due to high pressure of the balls impact force.

Milling of Fe_2O_3 and graphite under argon atmosphere revealed that CO_2 can be detected in short milling times (about 1 hr milling) and in higher milling times CO is detected [31]. There might be three different states for adsorbed gas on activated carbon with dangling bonds:



At the beginning of milling, the dominant adsorbed gas on graphite (C) would be CO and CO_2 gases on dangling bonds of activated carbon. During higher milling times the crystal structure of soft graphite would be broken and in this case the situation similar to gasification reaction takes place, i.e., $\text{C} + \text{CO}_2 \rightarrow 2\text{CO}$ where the carbon atom moves to gas phase from solid state [31].

In addition, transformation of Fe_2O_3 to Fe_3O_4 depends also on the manner which the milling is performed. Frequent opening of the vial of the ball mill will prevent aforementioned transformation. It has been reported that a closed vial lid results in complete transformation of Fe_2O_3 to Fe_3O_4 [32]. Furthermore, the reverse reaction of formed Fe_3O_4 may happen in milling medium. Hence, oxygen partial pressure is an important and dominant parameter in controlling of iron oxides transformations.

The mean crystallite size variations of barium ferrite in the milled samples are shown in Table 1. It can be seen that

Table 1 Mean crystallite size (nm) of barium ferrite in the milled samples under air and argon atmosphere

Milling time (h)	10	15	20	40
Air	43	28	17	–
Argon	39	25	19	9

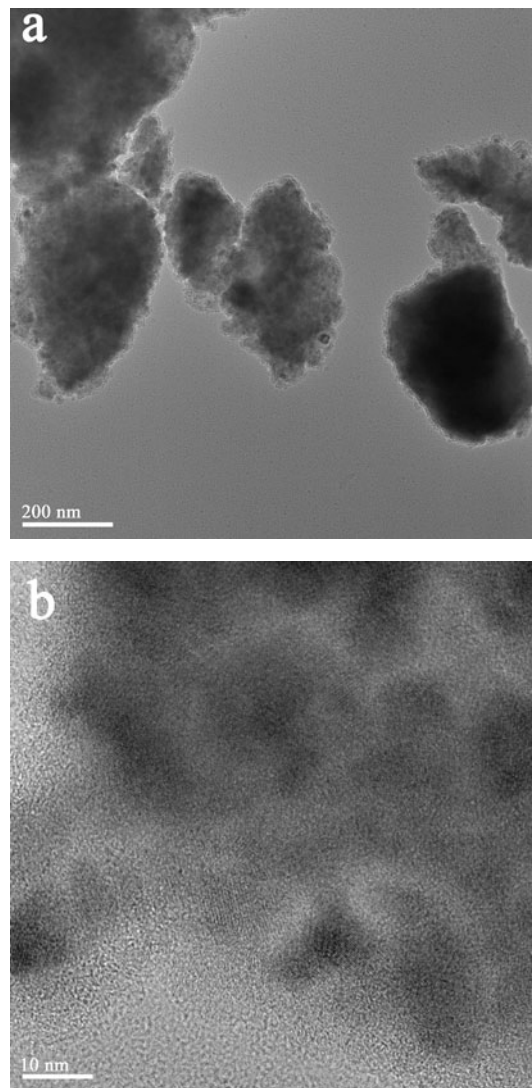


Fig. 2 TEM images of 40-hrs milled sample under air atmosphere: (a) agglomerates of nano-particles, (b) agglomerates at higher magnification

increasing milling time decreases the crystallite size. The decreasing trend in mean crystallite size is faster in shorter milling times and becomes slower in longer milling times. This behavior is more evident in sample which is milled under argon atmosphere.

Figure 2 shows TEM images of milled sample under air atmosphere for 40 hrs. Figure 2a shows agglomerates of fine particles. Higher magnification of these agglomerates

in Fig. 2b, illustrates nano crystallites with mean diameter of 10 nm with a standard deviation of ~ 2 nm. This is in consistence with crystallite size calculations of XRD results mentioned earlier.

Figure 3 shows XRD patterns of 40-hrs milled samples in air and argon atmospheres heat treated under vacuum at 800 °C. As can be seen, Fe/Fe₃O₄ composite form in both samples. Heat treatment at high temperature and residual of remained carbon in the milled sample accelerate the reduction process to FeO and then to Fe. Iron and magnetite are dominant phases in the composition of these samples as can be concluded from the relative intensity of the reflections in the XRD patterns.

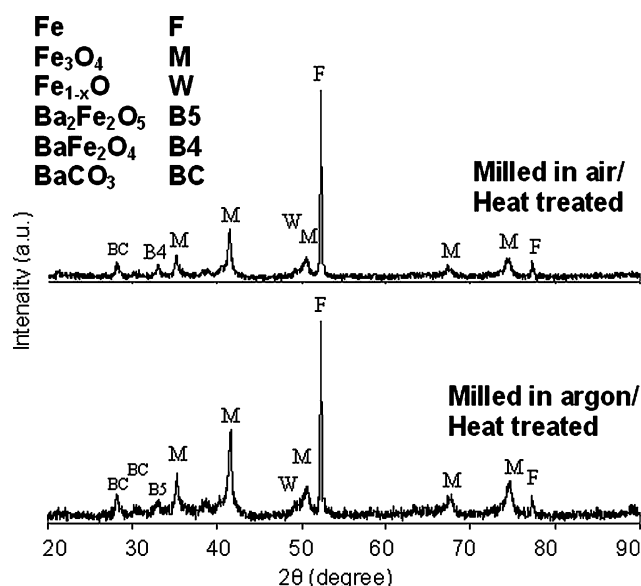


Fig. 3 XRD patterns of 40-hrs milled samples in air and argon atmospheres, heat treated under vacuum at 800 °C

Fig. 4 Magnetic hysteresis loops of 40-hrs milled samples in air and argon atmospheres before and after heat treatment under vacuum at 800 °C

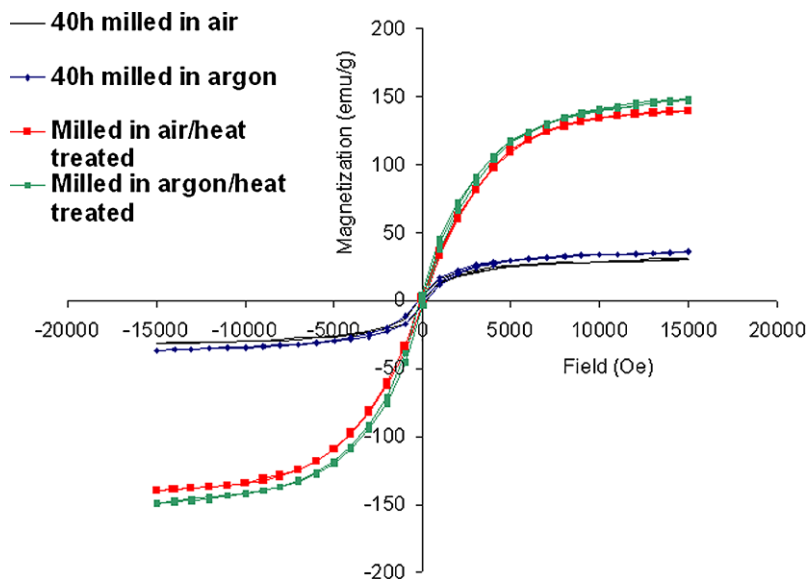


Figure 4 is the hysteresis loops of milled samples for 40 hrs under different atmospheres and samples which are 40 hrs milled and then heat treated at 800 °C. It can be seen that sample milled under argon atmosphere has a higher saturation magnetization (36.42 emu/g) in comparison to sample milled under air atmosphere (31.25 emu/g). The higher value of saturation magnetization for sample milled under argon might be due to a higher amount of Fe₃O₄ in this sample, as can be observed in the XRD patterns in Fig. 1.

Coercivity values are 232.22 and 180.74 Oe for samples milled in air and argon, respectively. Heat treatment of the 40-hrs milled samples at 800 °C resulted in an increase in saturation magnetization and decrease in coercivity values. The saturation magnetization of the 40-hrs milled samples in air and argon atmospheres increases to 139.12 and 145.07 emu/g after heat treatment at 800 °C, respectively. The coercivity value of the above samples decreases to 112.50 and 93.20 Oe, respectively. The alteration in magnetic properties in heat-treated samples is mainly due to the formation of magnetically soft α -Fe phase and removal of residual carbon by its oxidation. These results show that the milling atmosphere has a negligible effect on the magnetic properties of heat-treated samples.

4 Conclusions

Barium ferrite and graphite were mechanically milled in air and argon atmosphere, and the following conclusion can be drawn:

1. In the milling medium, hematite content of barium ferrite reduced and Fe₃O₄ formed beside remained barium ferrite which resulted in the formation of BaFe₁₂O₁₉/Fe₃O₄ nanocomposites. The crystallite size of barium ferrite

was 17 and 19 nm after 20 hrs milling under air and argon atmospheres, respectively.

2. In argon atmosphere the reduction process proceeded to FeO after 40 hrs milling, while this phase was not detected by 40 hrs milling under air atmosphere. The reduction process proceeded faster under argon atmosphere. This is attributed to the possibility of re-oxidizing of reduced species in air.
3. Saturation magnetization for samples that were milled under argon and air atmospheres was 36.42 and 31.25 emu/g, respectively. Higher saturation magnetization for the sample milled under argon atmosphere was attributed to the more Fe₃O₄ formed in this sample.
4. Heat treatment of the 40-hrs milled samples in air and argon atmospheres under vacuum at 800 °C increases the saturation magnetization to 139.12 and 145.07 emu/g, respectively.
5. TEM images of the sample milled 40 hrs under air atmosphere confirmed the nanometric structure of the sample. The mean crystallite size in this sample was as small as 10 nm.

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