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Ceramics International 36 (2010) 2241–2245
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Short communication

Effects of annealing on phase evolution, microstructure and magnetic properties of mechanically synthesized nickel-ferrite

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Received 2 March 2010; received in revised form 6 March 2010; accepted 26 April 2010
Available online 25 June 2010

Abstract

The influence of milling and subsequent annealing on nickel-ferrite phase formation was investigated by X-ray diffraction (XRD). Microstructure and magnetic properties of $NiFe_2O_4$ were determined by field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM) and vibration sample magnetometry (VSM). Single phase nanosized nickel-ferrite was obtained by 30 h mechanical alloying (MA) and subsequent annealing at 600 °C for 1 h. Magnetic properties of the milled powder were extensively affected by the annealing temperature. Considerable growth of the particles and necking by sintering resulted from annealing at 1000 °C.

Keywords: A. Powders: solid state reaction; C. Magnetic properties; D. Ferrites; E. Soft magnets

1. Introduction

Synthesis of ultrafine nickel-ferrite ($NiFe_2O_4$) particles has been extensively investigated during recent years [1–5]. Nickel-ferrite nanoparticles present a wide range of applications requiring low microwave-number and from low to high permeability such as electronic devices [6], ferrofluids [7], magnetic drug delivery [8] and high density information storage [9]. Magnetic properties depend substantially on the synthesis route of nickel-ferrite. Production of $NiFe_2O_4$ nanoparticles has been practiced via several techniques like chemical co-precipitation [10], sol–gel [11], shock wave [12], microwave processing [13] and aerosolization [14].

High-energy ball milling of metallic oxides is a simple solid state technique for the production of nanosized ferrite powder exhibiting unusual properties [15–19]. During MA, some magnetic properties can be improved, while others deteriorate due to stress, strain and defects introduced by milling. Residual stress/strain elimination by annealing is required to improve the magnetic properties [18,20].

In this study, the effect of annealing temperature on phase evolution, morphology, particle size and magnetic properties of nano-sized nickel-ferrite powders synthesized by mechanical alloying at room temperature have been investigated.

2. Materials and experimental procedure

Pure powders of Fe_2O_3 (Merck, Gmbh, 99 wt%) and NiO (Sigma, USA, 99.99 wt%) were mixed at a molar ratio of 1:1. The mixture was loaded into a steel vial together with steel balls of 10 and 15 mm diameters. Ball to powder weight ratio (BPR) was 15:1. Milling was continued for up to 30 h with running speed of 300 rpm. The as-milled sample was annealed at different temperatures according to: (1) heating up to various temperatures with a rate of 10 °C/min in air, (2) dwelling for 1 h within the furnace, (3) cooling inside the furnace to a lower temperature (~400 °C) and (4) cooling down to room temperature. Phase characterization of the milled/annealed powder was determined by X-ray powder diffraction analysis (XRD, Philips, PW 3710) with Cu-Ka radiation. Morphology and size of the particles were determined by field emission

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0272-8842/$36.00
doi:10.1016/j.ceramint.2010.06.004

scanning electron microscopy (FESEM, Hitachi, S-4160) and transmission electron microscopy (TEM, Philips, CM200). Magnetic properties were measured by vibration sample magnetometer (VSM, I.R. Iran).

3. Results and discussion

The XRD patterns of the as-milled (10 and 30 h) and milled (30 h) and then annealed samples are shown in Fig. 1. Phase evaluation of the 10 h milled sample shows the start of nickel-ferrite phase formation. Diffracted peaks related to remnant hematite and nickel oxide phases are also observed in the same XRD pattern (Fig. 1). In fact, mechanical alloying provides the activation energy needed to overcome the kinetic barrier for solid state reaction between iron and nickel oxides according to the following reaction [21]:

$$Fe_2O_3(s) + NiO(s) \rightarrow NiFe_2O_4(s), \quad \Delta G_{298} = -18.3 \text{ kJ/mol} \tag{1}$$

From Fig. 1 (curve b), it can be inferred that the formation of nickel-ferrite does not complete by milling for 30 h; while raw materials partially remain in the sample. Although NiO peaks are not easily distinguishable from the other overlapping peaks, their ~43.3° and 37.3° peak intensities reduce while ~35.7° peak intensity increases due to 600 °C annealing. This effect can be attributed to consumption of NiO during the annealing. The Fe_2O_3 partial-peaks can also be seen at about 33.2° and 54.1°, while its other peaks may overlap with the major peaks of nickel-ferrite. Significant peak broadening could be pertinent to the formation of nanocrystalline structure and build-up of the induced milling strains.

Single phase nickel-ferrite spinel was achieved after 30 h milling and annealing at 600 °C (Fig. 1c). Increasing of annealing temperature results in narrowing, sharpening and intensification of the diffracted peaks due to release of the internal strains and growth of the particles as indicated in Fig. 2c–e.

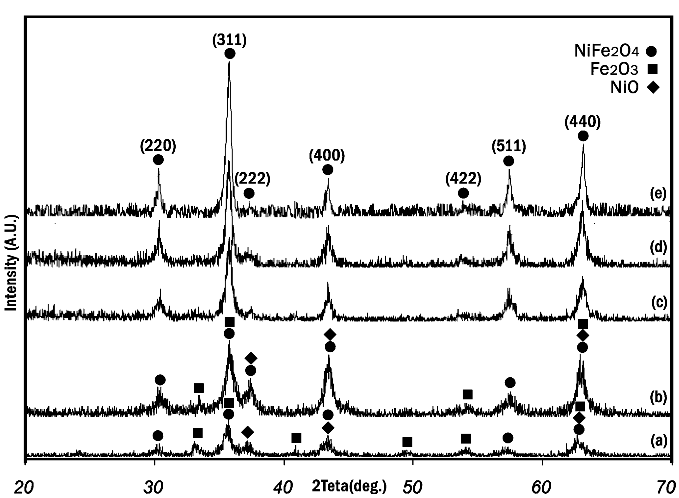

Fig. 1. X-ray diffraction pattern of the samples: (a) milled for 10 h, (b) milled for 30 h, (c) milled for 30 h then annealed at 600 °C for 1 h, (d) milled for 30 h then annealed at 800 °C for 1 h and (e) milled for 30 h then annealed at 1000 °C for 1 h.

Fig. 2 shows SEM micrographs of the milled powders before and after annealing at different temperatures. Large agglomeration of very fine nickel-ferrite particles is observed for the samples milled for 10 h (Fig. 2a). After 30 h, the agglomerated clusters are smaller (Fig. 2b). This means that the speed of fracturing is greater than that of the cold welding at $t = 30$ h.

SEM images of the samples annealed at 600 and 800 °C for 1 h show (1) slight particle growth and (2) increase in the agglomerate volume ratio. After annealing at 1000 °C, significant particle growth and necking by sintering occurs (Fig. 2e). The average size of the particles is about 800 nm.

Fig. 3 compares TEM images of a milled and a milled-annealed sample. Agglomeration of the particles during annealing clearly resulted in the increase of the average nickel-ferrite particle size from less than 50 to ~70 nm. Slight particle growth due to 600 °C annealing can also be inferred from the figure.

Saturation magnetization and coercivity of the samples measured by a vibration sample magnetometer at room temperature are plotted in Figs. 4 and 5, respectively. Variations of coercivity with particle growth could be described by magnetic domain theory [22]. During the annealing, particle growth and recovery of the strains induced by milling are carried out at the same time. Coercivity of the samples can also be affected by the residual strain and many other complex factors mentioned by previous authors [22]. Annealing at 600 °C increases the coercivity of the as-milled powder from 54.5 to 217.8 Oe. It shows that the effect of the particle size on coercivity of the sample is greater than that of the residual strain. Annealing at 600 °C causes the transfer of the single magnetic domain of the as-milled particles into pseudo single-domain of the annealed particles. High-temperature annealing of the as-milled powder results in decreasing of the coercivity from 217.8 to 70.1 Oe at 800 °C and to 47.2 Oe at 1000 °C. This effect can result from transition of the magnetic single-domain to magnetic multi-domain during growth of the particles [22].

Production method affects the magnetic saturation of ferrites. The magnetic saturation of the as-milled nickel-ferrite powders produced in this research (11.4 emu/g) is considerably lower, for example, than that of the powders produced by Sepelak et al. [23] (54.5 emu/g). This decrease can be attributed to the spin canting that dominates over the effect of site exchange of cations in the surface induced from the mechanical milling of the powder [23–25]. Annealing can significantly improve the crystallinity of the powder synthesized by high-energy ball milling and change its magnetic properties. The annealing of as-milled powder at different temperatures leads to gradual increase of the magnetization saturation from 11.4 (for as-milled) to 37.2 emu/g (for $T = 1000$ °C). This is due to the non-equilibrium cation distribution and the canted spin arrangement resulting from the mechanical alloying and the relaxation towards the equilibrium configuration. Heating results in relaxation of the mechanically synthesized nickel-

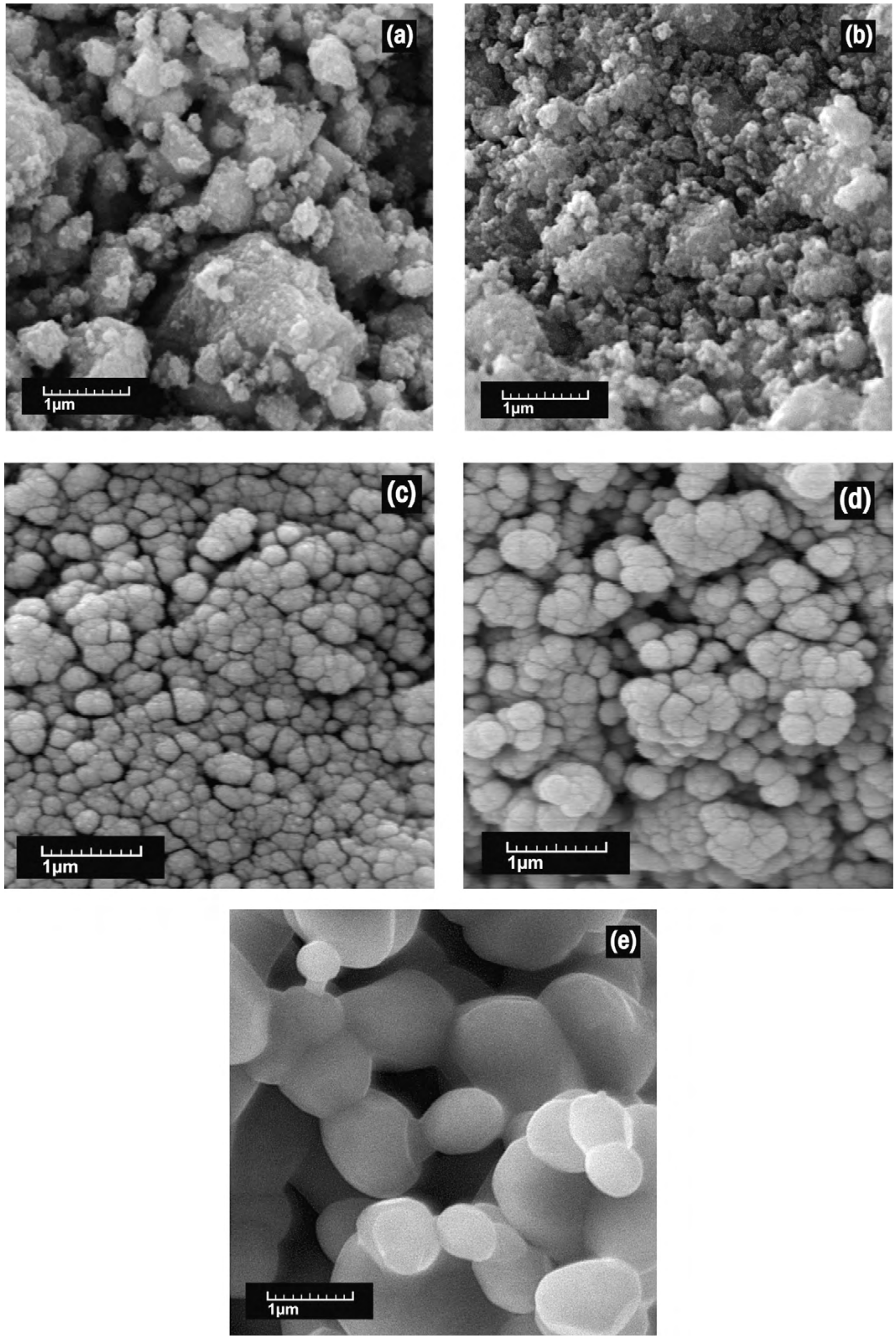

Fig. 2. FESEM images of the samples: (a) milled for 10 h, (b) milled for 30 h, (c) 30 h milled and then 1 h annealed at 600 °C, (d) 30 h milled and then 1 h annealed at 800 °C and (e) 30 h milled and then 1 h annealed at 1000 °C.

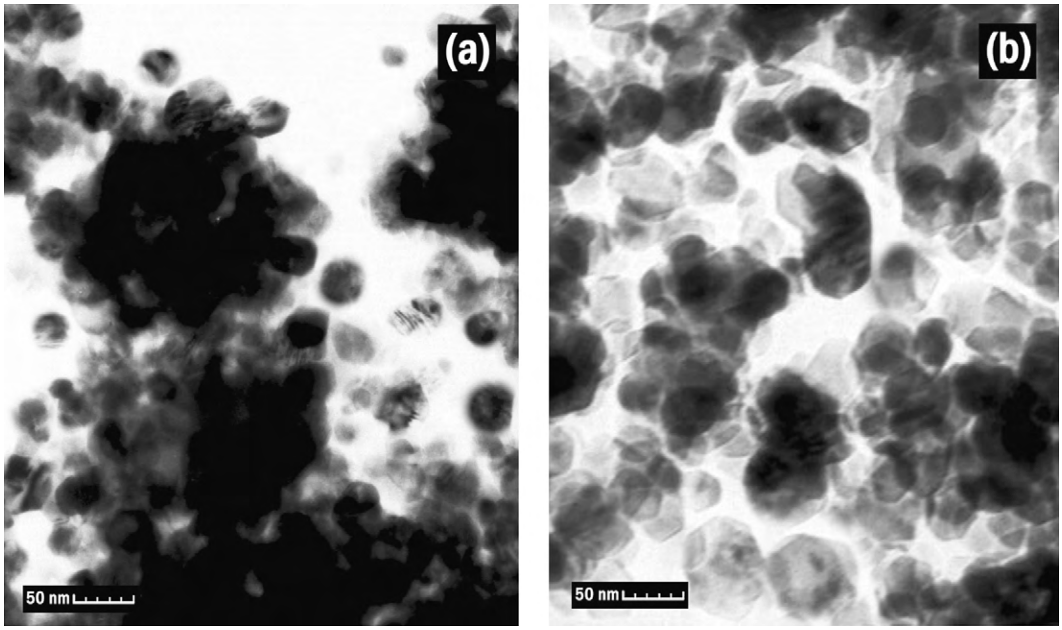

Fig. 3. TEM image of the sample milled for 30 h: (a) before annealing and (b) after annealing at 600 °C.

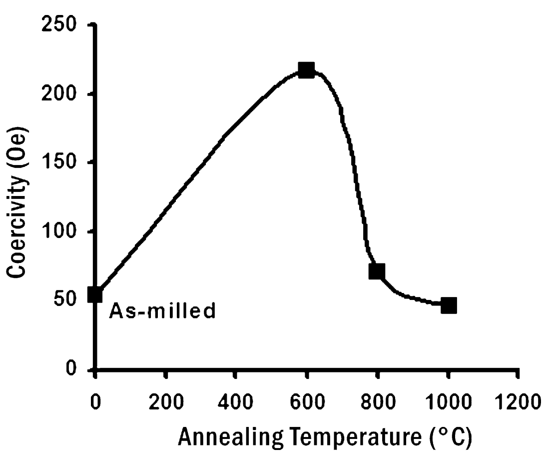

Fig. 4. Effect of annealing temperature on coercivity of nickel-ferrite samples.

ferrite towards a structural and magnetic state which is similar to that of the bulk [23]. The considerable particle growth by annealing in temperature more than 1000 °C can deteriorate some magnetic properties of the particles, because the particles evolved from nano- to microstructure.

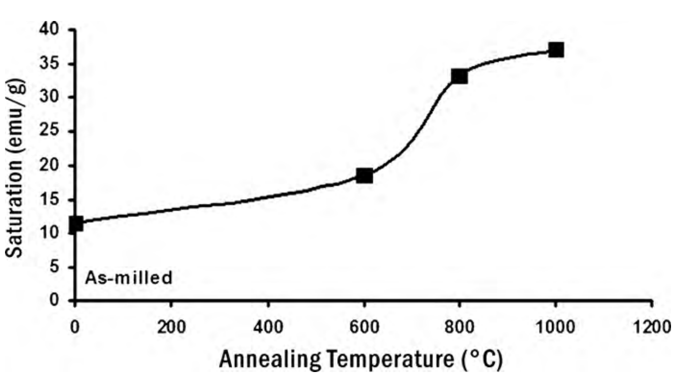

Fig. 5. Magnetization saturation versus annealing temperature.

4. Conclusions

Single phase nanosized nickel-ferrite powder was synthesized by 30 h ball milling and annealing at 600 °C. Annealing of the as-milled powder frees strain induced by milling, improves the crystallinity of the powder and promotes particle growth. Magnetic properties of the powders extensively change with annealing temperature. Coercivity of the annealed powder changes due to the transformation of magnetic single-domain into magnetic multi-domain of the particles. Magnetization saturation increases with annealing temperature because of relaxation from the non-equilibrium cation distribution and the canted spin arrangement resulting from the mechanical alloying synthesis.

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