Journal of Alloys and Compounds 591 (2014) 58–64

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jalcom

Structural, magnetic, and electronic properties of high moment FeCo nanoparticles

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ARTICLE INFO

Article history:
Received 7 October 2013
Received in revised form 26 November 2013
Accepted 27 November 2013
Available online 16 December 2013

Keywords:
Polyol synthesis
Structural and magnetic properties
Random magnetic anisotropy
Electronic structure calculations

ABSTRACT

Soft-magnetic $Fe_{55}Co_{45}$ alloy nanoparticles have been successfully synthesized by the polyol reduction process followed by annealing under argon. The diethylene glycol (DEG) was used as solvent and reducing agent simultaneously in this process. The synthesized samples of nanoparticles were annealed at 873 K for different times. The alloy formation processes, the evolution of the microstructure, the magnetic properties, and the DOS calculation have been investigated before and after samples annealing. The X-ray diffraction of the synthesized product before annealing shows that a cobalt ferrite is spinel structure of crystallite size of about 10 nm. X-ray diffraction analysis of the samples annealed at 873 K for different times also shows that of the FeCo alloy has been obtained by reducing the cobalt ferrite. It has been confirmed the formation of a body-centered-cubic (bcc) single phase structure where the wt.% increases with annealing times leading to a pure phase after annealing during 4 h. These results are confirmed by transmission electron microscopy study. The saturation magnetization of the Fe–Co alloys increases with annealing time, indicating an increasing homogeneity in composition and the single bcc FeCo phase formation. The highest saturation magnetization of 235 emu $g^{-1}$with a low coercivity of 76 Oe was obtained for the $Fe_{55}Co_{45}$nanoparticles annealed during 4 h. The local random anisotropy constant K_L has been extracted. This work presents also detailed information about total, and atom projected density of state functions, as well as the magnetic moment for different atoms in $Fe_{55}Co_{45}$ alloys and cobalt ferrite.

1. Introduction

The nanocrystalline ferromagnetic materials exhibit interesting magnetic properties from the point of view of fundamental research up to applications. These materials have taken a privileged place in the research of new soft magnetic materials [1,2]. Recently, several researches have been made on the study of the FeCo soft magnetic nanomaterials [3,4].

These materials are interesting for various applications. Because of their unique magnetic properties (high saturation magnetization, large permeability, low coercivity and ferromagnetic behavior up to 1073 K), they are used in transformer cores, electrical generators, electrical motors, pole pieces and for hyperthermia-based therapy [5–7]. The optimization of the structure and microstructure represents the key of success to develop the magnetic properties of these samples. They may be synthesized by high energy milling or chemical route [8–10].

Poudyal et al. have prepared FeCo nanomaterials by surfactants-assisted ball milling; they have found that saturation magnetization of FeCo (obtained by ball milling for 1 h) is 209 emu g^{-1} with 23 nm of nanoparticles size [8]. Zamanpour et al. were able to synthesize FeCo nanoparticles by polyol using ethylene glycol (EG) as solvent; they obtained a saturation magnetization of 200 emu g^{-1} for nanoparticles size of 30 nm [4]. Hiyama et al. were also able to prepare a FeCo alloy in the polyol medium (using EG as solvent), followed by annealing under hydrogen but the particle size and the saturation magnetization were 8 μm and 220 emu g^{-1} respectively [10].

In this paper, we present high magnetic moment $Fe_{1-x}Co_x$ ($x = 0.45$) nanoparticles synthesized by a novel route – the polyol process – followed with annealing under argon. We have carried out structural investigation by careful powder X-ray diffraction (XRD) analysis with Rietveld refinements[14], transmision electron microscopy coupled with energy dispersive spectroscopy (EDS) analysis, and measurement hysteresis loop. In addition to the experiments, the random magnetic anisotropiy (RMA), and a theoretical investigation by density functional theory (DFT) were achieved.

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http://dx.doi.org/10.1016/j.jallcom.2013.11.208

2. Experimental studies

The powders of $Fe_{55}Co_{45}$ nanoparticles were synthesized by reduction polyol method [4,11,12].

High purity analytical grade cobalt acetate anhydrous ($Co(Ac)_2$), iron chloride tertra hydrate ($FeCl_2{\cdot}4H_2O$), diethylene glycol (DEG), sodium hydroxide (NaOH) and ruthenium chloride ($Ru(Cl_2)$) were used in synthetic reaction without any further treatment.

The first step of the synthesis of metal nanoparticles is to process spinels $CoFe_2O_4$ nanoparticles via forced hydrolysis in a polyol medium [13]. The second step is to reduce them by argon gas at 873 K. $CoFe_2O_4$ was synthesized, starting from an amount precursor salts of 100 mmol of $FeCl_2{\cdot}4\,H_2O$ and 80 mmol of cobalt acetate $Co(CH_3COO)_2{\cdot}4H_2O$. The acetate ratio defined as $\frac{[M]}{[OAc]}$ (M stands for the total amount of metallic elements), was fixed to 2.2. The total volume of the DEG is 200 ml. We have dissolved also 5 mmol of ruthenium chloride and 1.26 M of sodium hydroxide. The mixture was then heated at 418 K for 2 h with a rate of 5 K min^{-1}. After completion of the reaction the produced powder was filtered, washed with ethanol and acetone, and dried at 353 K.

After polyol synthesis, the nanopowder wrapped in tantalum foils were annealed in a sealed silica tube under argon gas (350 Torr) at 873 K during 30 min, 1, 2, and 4 h.

The structural properties of the samples obtained before and after annealing were characterized by the powder X-ray diffraction using the BRUKER diffractometer with Cu Kα target ($\lambda = 1.5406$ Å) to determine the crystallographic structure and to identify phases. The intensities were measured at angles from $2\theta = 20^\circ$ to 90° with a step size 0.02°. The structure refinement for the X-ray pattern was carried out using MAUD computer code based on Rietveld analysis [14]. Transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) were performed using a JEOL 2010 FEG microscope operating at 200 kV. The chemical composition of the grains was determined by energy dispersive spectroscopy. The magnetic measurements of the samples were measured using a Physical Properties Measurement System (PPMS9 Quantum Design) under an applied field up to 3 T.

3. Results and discussion

3.1. Structure analysis

Fig. 1 shows typical X-ray diffraction patterns of the FeCo nanoparticles as-synthesized and after annealing at 873 K for distinct durations. The annealing of the powders is accompanied by a decrease of the intensities of Co ferrite peaks and the apparition of FeCo ones. However, the cobalt ferrite phase doesn't exist in samples annealed for 4 h.

Fig. 2 presents, as an example the Rietveld analysis results of XRD pattern of FeCo sample before and after annealing for 4 h at 873 K. The refinement performed for the as-synthesized sample shows the presence of a main phase of $CoFe_2O_4$with spinel structure (space group Fd-3m). The unit cell parameter a is equal to 8.4087 Å.

Three characteristic peaks of FeCo phase corresponding to the crystal planes of (1 1 0), (2 0 0) and (2 1 1) were observed for all annealed samples. The relative contribution of the two crystalline phases given by the Rietveld analysis varies with annealing time for a given temperature 873 K. With increasing the duration of annealing, the proportion of $Fe_{55}Co_{45}$ phase increases from 64.28% to 98.89% for 30 min and 4 h respectively. After an annealing during 4 h the structure refinement shows a main phase of $Fe_{55}Co_{45}$with body centered cubic structure (bcc). The lattice parameter is $a = 2.8539$ Å. No additionnals peaks such as $Co(OH)_2$, $Fe(OH)_2$, are observed in XRD pattern which indicates the high purity of prepared sample. These results provide that increasing the annealing time is important for co-reduction of metal ions (Co^{2+} and Fe^{3+}) and favors the formation of alloy phase. The experimental conditions and structural characterization for all samples are summarized in Table 1.

The grain size and the strain of the nanoparticles was calculated using the Williamson–Hall equation [15]:

$$B\cos(\theta) = \frac{k\lambda}{D} + 4\epsilon\sin(\theta) \quad (1)$$

which D is the grain size, B is the full width at half maximum intensity of the peak, k is the sheerer's constant (0.90), λ is the X-ray wavelength and θ is the Bragg angle. Plots are drawn with $4\sin\theta$ along the x-axis and $B\cos\theta$ along the y-axis for all annealed FeCo samples as shown in Fig. 2. From the linear fit of the data, the auto-coherent diffraction domain size was estimated from the y-intercept, and the strain ϵ, from the slope of the fit.

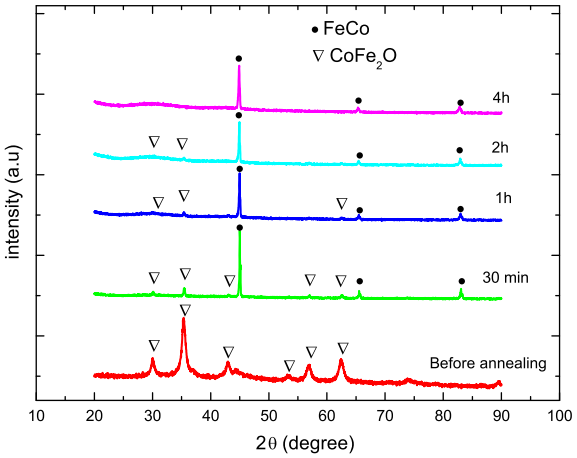

Fig. 1. XRD pattern of the $Fe_{55}Co_{45}$ as-synthesized and annealed samples at 873 K during 30 min, 1 h, 2 h and 4 h.

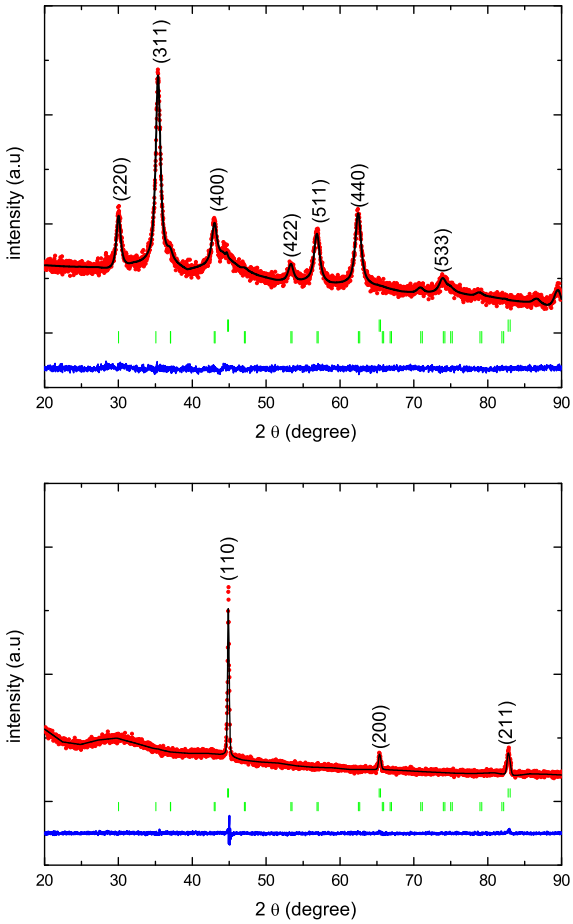

Fig. 2. Rietveld analysis for X-ray diffraction pattern of FeCo as-synthesized (above) and annealed at 873 K for 4 h (below).