Influence of the Surfactant and Annealing Rate on the Morphology, Magnetic and Structural Characteristics of Co₂FeAl Nanoparticles

Zahra Pezeshki-Nejad^a, Abdolali Ramazani^{a,b}, Sima Alikhanzadeh-Arani^a, Mohammad Almasi-Kashi^{a,b}, Masoud Salavati-Niasari^{*a}

^a *Institute of Nano Science and Nano Technology, University of Kashan, Kashan, P. O. Box. 87317–51167, I. R. Iran*

^b *Department of Physics, University of Kashan, Kashan 87317-51167, Iran*

*Corresponding author: Tel.: +98 31 5591 2383, E-Mail address: salavati@kashanu.ac.ir.

Abstract

This research focuses on the synthesis and characterization of the attractive magnetic alloys, full-Heusler Co₂FeAl nanoparticles. A modified co-precipitation method has been developed in a template of chitosan biopolymer. XRD pattern of the product confirmed the high crystalline quality of the L2₁-ordered nanoparticles, refined by *Rietveld* analysis. It was found that using different annealing rates can be surprisingly effective to achieve different morphologies from granular microstructure to fibrous-shaped nanostructure. Based on the obtained results of the high resolution TEM image, the presence of both populations of large single crystal grains and polycrystalline clusters containing several small particles (about 10 nm) can be found in the sample annealed up to 700 °C with 5 °C/min. This particle size distribution led to the co-existence of high and low coercive-field phases in the related FORC diagram. Major hysteresis loops showed that the using of chitosan biopolymer resulted in a smaller magnetic saturation compared to that of the control sample, probably due to presence of the oxide shell around the surface of nanoparticles when exposed to air.

Keywords: Co₂FeAl; Nanostructures; Chitosan template; Magnetic interaction

1. Introduction

Magnetic nanostructures are attractive scientific objects with many present and emerging applications, such as permanent and soft magnets, sensors, and spintronic devices. One of the most interesting magnetic materials, owing to their possible applications, are ternary Heusler alloys with the general formula X_2YZ (full-Heusler) or XYZ (half-Heusler), where X and Y are usually transition elements such as Ni, Co, Fe, Pd, Cr, and Z is an *sp* element such as Si, Al, Ge [1-3]. So far, several reports on the use of half-metallic Co-based full-Heusler alloy electrodes in magnetic tunnel junctions have been presented [4], synthesizing by different techniques, including conventional dc sputtering [5], ion beam sputtering [6], low-temperature molecular beam epitaxy [7], electrodeposition [8], arc melting method [9, 10] and melt-spinning process [11]. Recently, Wang et al [12] synthesized Co_2FeGa nanoparticles by a chemical silica-assisted approach. In the other work, the mechanical alloying route has been utilized for fabrication of Co_2CrAl nanocrystalline [13]. Du et al [14] reported that the higher annealing temperature and the longer annealing time leads to the better crystallinity of Co_2FeAl nanoparticles.

In this study, we synthesized Co_2FeAl (CFA) nanostructures through the simple and low-cost co-precipitation method mediated by the excellent template of biopolymer chitosan. Chitosan is a unique fat-absorbing dietary fiber that inhibits the absorption of dietary fat during digestion, and it has a number of commercial and possible biomedical uses. The control sample was also synthesized under identical conditions but in the absence of the polymer matrix in order to clarify and discuss the role of the chitosan on the properties. It is well-known that the nanocrystalline magnetic alloys have promising applications in indifferent fields such as hyperthermia, catalysis, drug delivery, magnetic based sensors and microwave applications, owing to the fact that the magnetic transition temperatures, rate of catalyzing and microwave absorbance characteristics vary with particle size [15]. The effect of the grain size and morphology on the magnetic properties has already been investigated using the major hysteresis curve measurements [16, 17],

which provide an average magnetic behavior. Recently, the highly sensitive and accurate method based on high-resolution measurements of first-order reversal curves (FORC) was used for study the effect of size and morphology on magnetic properties of iron oxide nanoparticles [18, 19]. This technique can provide the detailed information about the magnetization behavior of a sample, magnetic phases, interaction and coercive field distributions. FORC analysis has been widely used for characterization of the various types of the materials such as spin crossover nanoparticles [20], magnetic nanowires [21], spin transition microparticles [22], and so on. Herein, the dependence of magnetic interaction and coercivity field distributions on the morphology and grain size of Co_2FeAl nanostructures was studied by FORC diagrams.

2. Experimental

The metal nitrates, cobalt(II) acetate tetrahydrate ($\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, 99.9% pure, Merck), aluminum(III) nitrate nonahydrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 98.5% pure, Merck) and iron(III) nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 99% pure, Merck), and biopolymer chitosan (99% pure, Merck), used in our experiments were used as received without further purification. Firstly, the three metal nitrates with Co:Fe:Al in a 2:1:1 atomic ratio were dissolved at room temperature in a little distilled water individually, and then added together to obtain the solution of metals. Then, 1.5 gr of biopolymer chitosan was dissolved in 70 ml of distilled water containing acetic acid (with pH of about 3) to obtain clear chitosan solution. The prepared solution of metal salts was slowly added into the polymer solution under stirring to produce precursor solution. 0.57 gr of NaOH was dissolved in 80 ml deionized water, and then was dropped in above solution until a white precipitation appeared in solution. At this time, the pH value of solution was about 7. Then, the solution was filtered, and the obtained precipitation was washed with distilled water and subsequently dried at 80°C in a vacuum oven. Finally, the obtained powder was annealed up to 700°C for 2 h with a heating rate of $5^\circ\text{C}/\text{min}$ under Ar/H_2 atmosphere. To investigate the effect of heating rate on the morphology and magnetic properties of the products, the heating rate was enhanced to 10 and $15^\circ\text{C}/\text{min}$ in the other prepared samples.

Control sample of Co₂FeAl was also prepared as above (with a rate of 15 °C/min), but in the absence of chitosan. The magnetic properties of the samples were detected at room temperature using a vibrating sample magnetometer (VSM, Meghnatis Kavir Kashan Co., Kashan, Iran).

3. Results and Discussion

The structure refinement for the X-ray pattern was carried out using a FULL PROF code [23] based on the *Rietveld* analysis. Well-defined peaks ((111), (200), (220), (311), (400), (422)) can be observed in the XRD pattern of the prepared sample in Fig. 1. The presence of the (111), (311) and (200) superlattice reflections in addition to fundamental peaks such as (220) reflection confirm the L2₁-ordered structure of CFA alloy (space group *Fm3m*) consisting of four face centered cubic (fcc) sublattices [24, 25]. It is well-known that the disordering on the Co-site leads to a reduction of the intensity I(200), while the disordering between the Fe- and Al-sites leads to a reduction of I(111) [26]. The lattice parameter was determined to be $a=b=c=5.672(6)$ Å. The shoulder of the (220) reflection seen at $2\Theta = 44.3^\circ$ can be related to (1 1 1) reflection of the pure Co grain growth.

The composition of the synthesized powder of Co₂FeAl Heusler alloy was estimated to be in accordance with Co:Fe:Al = 2:1:1 from EDX spectrum without any impurity, as shown in Fig. 2a.

Fig. 2b shows the FT-IR spectra of sample before and after annealing. It can be seen that the absorption peaks at 2923.5 cm⁻¹ (C–H stretching vibration), 1087 cm⁻¹ (C–O stretching vibration), 1634.7 cm⁻¹ (amid I), due to the existence of chitosan [27, 28], and also the vibrations of the nitrate groups at 1383.5 and 895.2 cm⁻¹ observed before annealing disappear after annealing up to 700 °C. The broad peaks in the wavenumber about 3436 and 1630 cm⁻¹ are caused by the OH stretching and bending vibrations, respectively, of the water molecules absorbed on the surface of the particles [29]. The absorption weak bond at low frequency (~ 600 cm⁻¹) is due to the metal-oxide vibrations of the oxidized surface of particles on the exposure to air. So, the spectra indicated that the utilized precursors and chitosan were completely decomposed in the final product.

The observed variation of grain size and morphology with the annealing rate were interesting, as illustrated in the scanning electron microscopy (SEM) in Fig. 4. That sample annealed with 5 °C/min is composed of tiny particles sticking together to form the compacted grains with a non-uniform grain size distribution (Fig. 3a), while by increasing the heating rate to 10 °C/min, the morphology of the product is deformed to nanofibers (Fig. 3b) with a diameter in the range of 40 to 50 nm. But we can see that with further increasing to 15 °C/min, the sample consists of both nanoparticles and nanofibers merged into each other, as shown in Fig. 3c. There are two key factors for growth of the grains: magnetic interactions between single atoms and the stability of fibrous structure of the chitosan matrix on the heating process. According to the report [30], chitosan chains crystallize in an orthorhombic unit cell that retain in the precursor up to 500 °C [27]. On the other hand, magnetic nanoparticles tend to come together and form short chains, rings or close-packed aggregates owing to the magnetic dipole-directed self-assembly [31]. Balance between these two factors can provide a clue for the formation mechanism. Here, the prepared isolated nanoparticles at a slow heating rate (5 °C/min) have opportunity to come together as much as possible, due to a strong magnetic interaction, to minimize the magnetic energy and produce a magnetic moment of zero, resulting in the aggregated grains. By increasing the heating rate, the fiber network of chitosan matrix directs and controls the growth process of the produced nanoparticles in the form of long nanofibers. It was clear that the heating rate of 10 °C/min leads to the more uniform and homogenous nanofibers compared to the higher rate of 15 °C/min. In order to study the effect of chitosan on the morphology, the SEM image of the control sample in the absence of chitosan annealed with 15 °C/min is represented in Fig. 3d. Irregularly shaped particles of CFA from nano- to multimicro-meter size are observed in this sample. Compared to Fig. 3c, it is obvious that the nanoparticles can grow in the chitosan matrix and produce the smaller grains than that obtained without chitosan.

Further transmission electron microscopy (TEM) observations of the sample annealed with 5 °C/min confirmed the presence of almost large grains (more than 100 nm) ordered like beads chain (Fig. 4a), and spotty rings in SEAD pattern in Fig. 4b indicated a polycrystalline structure of the Heusler alloy. The magnified TEM image (Fig. 4c) showed an assembly of nanoparticles with an average diameter of about 10 nm, as shown in high-resolution TEM image in Fig. 4d, while the average crystallite size of this sample was estimated to be 18 nm using the Scherrer equation. The inset pattern illustrated the polycrystalline nature of these clusters, while Fig. 4e confirmed that each larger grain is a single-crystal CFA grain, as the lattice fringes with a spacing of 0.29 nm are related to (200) plan of the Housler alloy. So, two different particle sizes were detected in the sample. Fig. 4f shows the TEM image of the sample annealed with 10 °C/min. It can be seen that the fibers shown in Fig. 3b consist of nanorods with different lengths and a diameter of 30 to 70 nm. Therefore, the effect of the heating rate on the size and morphology of the samples annealed with different rates was emphasizes by TEM images.

The magnetic measurement was carried out on a vibrating sample magnetometer (VSM) (Magnetic DaneshPajoh Inst.). Magnetic hysteresis loops in Fig. 5a showed that the synthesized samples are ferromagnetic at room temperature. We can see that the loops for the samples synthesized in the presence of chitosan with different rates have similar shape with a small difference in the values of H_c and M_s (Table 1). This means that the overall magnetic behavior of the nanoparticles is not very affected by changing the heating rate during annealing process in the present study. While the maximum magnetization (~ 30 emu/g) of the sample synthesized with 15 °C/min is significantly degraded relative to that of the control Co_2FeAl sample (~ 53 emu/g) heated with the same rate, probably owing to the formation of an oxide shell around the surface of nanoparticles when exposed to air which leads to a reduction in M_s value [32]. On the other hand, the presence of chitosan between the magnetic nanoparticles decreases the magnetic interaction, resulting in a larger coercive field.

In order to study the magnetic characteristic of this system in more detail, first order reversal curves (FORCs) were recorded for all samples. The FORC measurement was carried out on a VSM instrument equipped with the special software. A field of 4 kOe was applied to saturate the sample, and then it was decreased to a reversal field (H_a). Finally, it was reversed to its saturation amount (4kOe). FORC distribution function is defined as [33, 34]:

$$\rho(H_a, H_b) \equiv - \frac{\partial^2 M(H_a, H_b)}{\partial H_a \partial H_b},$$

in which $M(H_a, H_b)$ is the magnetization measured at (H_a, H_b) . A FORC diagram is a counter plot of the obtained $\rho(H_a, H_b)$ along axes of the interaction field $H_u = -(H_a + H_b)/2$ and the coercive field $H_c = (H_a - H_b)/2$.

Fig. 5b shows, for example, the FORC measurement for the sample synthesized at the lowest heating rate. The related FORC diagrams are shown in Fig. 6. The presence of the closed contours around the $H_u = 0$ axis with large spread in this direction, due to the interacting single-domain particles [35], is detectable in all diagrams (region indicated by A). In addition, we can see the second peak near the origin of the FORC diagrams (indicated by B), suggesting the behavior of the soft-magnetic particles with a lost coercivity. The prepared samples therefore contain a mixture of the hard and soft phases. The contours are highly elongated in the H_c direction, indicating the presence of an assemblage of the different grain sizes in our samples. It was in agreement with the TEM images in Fig. 4, which detect a particle size distribution from about 10 nm to more than 100 nm.

Fig. 7a shows the coercivity distribution along the H_c axis that presents a log-normal function distribution of the hard phase particles and also a small peak close to the zero due to the soft phase particles. FORC diagrams revealed that the density of these phase components changes by changing the heating rate, as by increasing the heating rate, the peak of the soft phase becomes stronger. As expected, values of the FORC coercivity peak (H_c^{FORC}) of the hard phase for all samples are clearly lower than the related values

given by the major hysteresis loops (see Table 1) owing to the effect of the soft phase and its interaction on the hard phase. It is notable that the distribution of the hard phase in the samples annealed with 10 °C/min is more elongated to the higher H_c with a larger H_c^{FORC} value rather than the others. It can be related to the effect of the shape anisotropy due to the special morphology of this sample (Fig. 4f); however the randomly oriented nanorods, without a considerable inert anisotropy, would not affect the major hysteresis loop.

Furthermore, the control sample has a stronger peak of the hard phase and a weaker peak of the soft phase particles in compared with the samples synthesized in the presence of chitosan with the same rate (15 °C/min). This suggested the presence of the larger grains in the control sample, in agreement with the SEM images. The co-existence of large grains and some isolated nanoparticles in the TEM images are responsible for the two-phase behavior. A lower concentration of such isolated particles in the TEM images resulted in a slight appearance of the soft phase component in the FORC diagram.

Furthermore, the spread of distribution of the hard phase along the H_u axis is considerable, as a result of the interaction between hard-phase particles. The cross-sections of the high-field peak along the H_u axis compare the interaction distribution of the samples in Fig. 7b. In contrast to Preisach assumption, the distribution of the interaction fields did not completely correspond with a Gaussian distribution. In addition to a strong peak (I) near the $H_u = 0$ axis, there are also two weak peaks (II) and (III) in $H_u < 0$ region with a positive and negative values of the distribution ρ , respectively. Peak (II) appears as a distortion of the outer contours at negative H_u values of the FORC diagrams, especially in Figs. 6b and c, while peak (III) creates a negative feature as a dark blue area indicated by the black arrows. These peaks can originate from the interaction between the soft and hard phases, known as interference region. A small negative displacement of the distribution peak (I) can be a result of a positive mean-field interaction between the particles of a magnetizing system [36]. In the other hand, the full width at half maximum (FWHM) of the cross-section curve for the control sample is the largest among the products, indicating a more interaction between the

grains. This is reasonable because the larger grains with little void spaces in this sample create a more interaction.

The interactions between the hard particles and also between the hard and soft phases are responsible for the characteristics of the FORC diagrams. It was found that unlike the results obtained from the major hysteresis loops, which are highly similar for the samples annealed with different rates, the FORC data detected the differences in the amount of the corecivity distribution and particle interaction in three annealing rates. These differences help to understand the effect of heating rate on the magnetic properties of the products and so develop the relationship between the morphology and magnetic properties.

4. Conclusions

In the present study, Co_2FeAl Heusler alloys were prepared by the co-precipitation method and effect of annealing rate on the morphology, size and magnetic properties was also investigated. We found that changing the annealing rate is an important factor during the synthesizing process, which changes the morphology from granular to fibrous. In spite of the major hysteresis loops, which measure the average magnetic properties, the first-order reversal curves (FORC) provided more detailed information about the magnetic characteristics and confirmed the dependence of the magnetic properties on the annealing rate. Indeed, no special effect was observed on the behavior of the hysteresis loops of the nanoparticles when different annealing rates are used. Furthermore, the results showed that the presence of chitosan biopolymer plays an important role on the characteristics of the products. *Rietveld* analysis of XRD data indicated that the single phase of the L2_1 -ordered structure was synthesized after annealing to 700°C for 2 h. The presence of two hard and soft phases was detected by the FORC diagrams, in agreement with the SEM and TEM images.

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Table 1: Measurements obtained for the synthesized Co₂FeAl alloys with different annealing rates.

Annealing rate (°C/min)	H_c^{FORC} (Oe)		H_c hysteresis loop (Oe)	M_r (emu/gr)	Morphology and Particle size
	Soft phase	Hard phase			
5	~ 0	932	592	30.00	granular (large grains > 100 nm & nanoparticles of about 10 nm)
10	~ 0	980	658	30.02	Fibrous (30-70 nm in diameter)
15	~ 0	1030	681	30.09	granular & fibrous
15 (control sample)	~ 0	782	520	53.12	irregular shape with a wide size distribution

Figure captions:

Fig. 1. Fitting of the XRD pattern of Co_2FeAl alloy using the Rietveld method.

Fig. 2. (a) EDX spectrum, and (b) FT-IR spectra before (up) and after annealing (down) of the synthesized CFA alloy.

Fig. 3. SEM images of the annealed samples in the presence of the chitosan with a heating rate of (a) 5, (b) 10 and (c) 15 °C/min, and (d) image of the control sample annealed with 15 °C/min.

Fig. 4. (a)-(e) TEM, HRTEM image and SEAD pattern of the sample annealed with 5 °C/min, and (f) TEM image of the of the sample annealed with 10 °C/min.

Fig. 5. (a) Hysteresis loops of the Co_2FeAl samples annealed at 700 °C, and (b) typical FORC measured for the sample at 5 °C/min.

Fig. 6. FORC diagrams for the synthesized Co_2FeAl alloy with a heating rate of: (a) 5, (b) 10, (c) 15 °C/min, and (d) for the control sample with 15 °C/min ($\text{SF} = 2$).

Fig. 7. Cross sectional cuts of the FORC distribution (ρ) of the synthesized samples, evaluated at: (a) $H_u = 0$, and (b) H_c^{FORC} (hard phase).

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