Chemical Physics Letters 670 (2017) 1–4

Contents lists available at ScienceDirect

Chemical Physics Letters

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

Research paper

The influence of pH value and composition on the microstructure, magnetic properties of Co-Fe-Al Heusler nanoparticles

F.J. Yang, J.J. Min, Z.W. Kang, S.Y. Tu, H.B. Chen, D.G. Liu, W.J. Li, X.Q. Chen *, C.P. Yang

Hubei Collaborative Innovation Center for Advanced Organic Chemical, Faculty of Physics and Electronic Science, Key Laboratory of Ferro- and Piezo-electric Materials and Devices, Hubei University, Wuhan 430062, PR China

A R T I C L E I N F O

Article history:
Received 29 October 2016
Revised 20 December 2016
In final form 29 December 2016
Available online 31 December 2016

Keywords:
Co-Fe-Al
Half-metallicity
Heusler alloy
Nanoparticles

A B S T R A C T

Co-Fe-Al nanoparticles were synthesized by using a simple solution reduction method. The effects of pH value and atomic composition on the morphology, microstructure and magnetic properties of the prepared Co-Fe-Al nanoparticles were investigated. It was found that pure Co-Fe-Al phase with small particle size can be obtained at pH = 7.0 which have high saturation magnetization and low coercivity. Furthermore, the defects will increase with the increasing of Co composition in Co-Fe-Al nanoparticles which induce the deterioration of the *B*2 ordering, the abrupt decrease of magnetic moment and the abrupt increase of coercivity.

1. Introduction

Experimentally, after the first observation of the tunnel magnetoresistance (TMR) for a magnetic tunnel junction (MTJ) using a $Co_2Cr_{0.6}Fe_{0.4}Al$ Heusler alloy [1], the relatively large TMR at room temperature has been reported in MTJs using Co-based full-Heusler alloy electrodes such as Co_2FeAl [2], $Co_2FeAl_{0.5}Si_{0.5}$ [3], $Co_2Cr_{0.6}Fe_{0.4}Al$ [4], Co_2FeSi [5] and Co_2MnSi [6]. Since the density of states contains only one direction of spin-polarized sub-bands at Fermi level based on theoretical calculation [7], Co-based full-Heusler alloys can provide near 100% spin-polarized current. So Co-based full-Heusler alloys such as Co_2MnSi [6], Co_2MnAl [8], Co_2MnGe [9], Co_2FeSi [10], and Co_2FeAl [2,11,12] have been studied widely. Among Co-based full-Heusler alloys, Co_2FeAl has attracted much attentions because it was demonstrated to provide not only giant TMR effects in MTJs [2,11], but also a very low Gilbert damping constant [12].

Due to their small particle size and high surface to volume ratio, nanoscale magnetic particles exhibit many novel physical and chemical properties. Hence magnetic nanoparticles have gained a wide interest for their potential applications in various fields, such as data storage devices, catalysis, drug delivery and biomedical imaging [13–15]. Most of magnetic nanoparticles synthesized up to now are based on binary compounds and alloys [13,16]. However, the ternary Co-based magnetic nanoparticles were thought to be a breakthrough from the viewpoint of materials design [17]. Various physical methods including magnetron sputtering [2,11,12], molecular beam epitaxy [18] and arc melting [19] are commonly used to prepare Co_2FeAl Heusler alloys. However, up to now, there are very few studies on the synthesis of Co_2FeAl Heusler alloys using the chemical methods. Sapkota et al. synthesized Heusler alloy Co_2FeAl nanowires by using electrospinning method with the existence of polymer [20]. Almasi-Kashi et al. prepared Co_2FeAl nanoparticles by using co-precipitation method with the existence of polymer [21,22]. Kumar et al. prepared Co_2FeAl nanoparticles by reducing a methanol impregnated mixture of metal salts [23]. These methods inevitably used other solvents except for metal salts and de-ionized water. Du et al. synthesized Co_2FeAl nanoparticles by using only de-ionized water as the reaction medium [24]. However, they only confirmed the corresponding annealing conditions which were required to prepare pure Co_2FeAl nanoparticles. Moreover, all these studies fixed the atomic ratio of Co:Fe:Al around 2.0:1.0:1.0 and less information on the Co-Fe-Al Heusler nanoparticles is available in the literature.

So in this work, we adjusted the experimental parameters such as annealing temperature, atomic composition and pH value systematically. The change of microstructure and magnetic properties of Co-Fe-Al Heusler nanoparticles with these experimental parameters were thoroughly investigated.

2. Materials and methods

The Co-Fe-Al nanoparticles used in this work were synthesized as follows. The precursor solution of $CoCl_2·6H_2O$, $Fe(NO_3)_3·9H_2O$ and $Al_2(SO_4)_3·18H_2O$ was dissolved in 900 ml de-ionized water.

* Corresponding author.
E-mail address: chxq@hubu.edu.cn (X.Q. Chen).

http://dx.doi.org/10.1016/j.cplett.2016.12.062

Then, NaOH solution was slowly dropped into these precursor solutions with stirring by a glass rod. After the complete settling of Co, Fe and Al ions, the precipitation was obtained by filtering the solution. (1) To check the influence of pH value, appropriate amounts of $CoCl_2·6H_2O$ (2.855 g), $Fe(NO_3)_3·9H_2O$ (2.424 g) and $Al_2(SO_4)_3·18H_2O$ (1.999 g) were dissolved. Different pH values (from 5.0 to 11.0) of the precursor solution were obtained by adjusting the input of the NaOH solution. (2) To prepare Co-Fe-Al nanoparticles with different atomic composition, the weight of $CoCl_2·6H_2O$ and the pH value were fixed at 2.855 g and 7.0. Moreover, the weight of $Fe(NO_3)_3·9H_2O$ and $Al_2(SO_4)_3·18H_2O$ were changed. All chemicals, $CoCl_2·6H_2O$ (>99%), $Fe(NO_3)_3·9H_2O$ (>99%), $Al_2(SO_4)_3·18H_2O$ (>99%) and NaOH (>99%) were purchased from SY Technology Instrument and were used without any further purification. Then, the obtained precipitations were dried at 80 °C and annealed at various temperatures (from 650 to 850 °C). The annealing process was performed in high purity Ar with 10% hydrogen gas mixture. Finally, the composition of the obtained Co-Fe-Al nanoparticles was characterized by using an X-ray fluorescence (XRF-1800) instruments. The crystal structure of the samples was characterized by powder X-ray diffraction (XRD, Bruker advanced D8) using Cu Kα radiation. The morphology of the samples was determined by scanning electron microscopy (SEM, JSM 7100) fitted with energy dispersive X-ray spectroscopy (EDX). The static magnetic properties were characterized by using a vibrating sample magnetometer (VSM, Lakeshore 7304).

3. Results and discussion

The XRD patterns of Co-Fe-Al nanoparticles prepared under different pH values are shown in Fig. 1. When Co-Fe-Al nanoparticles were prepared at pH = 5.0, except obvious reflections belonging to Co-Fe-Al, strong $FeAlO_3$ (113), $FeAl_2O_4$ (311) and weak $FeAl_2O_4$ (511) peaks at 35.7°, 36.5° and 58.7° were observed. Compared with $Co(OH)_2$, $Fe(OH)_3$ and $Al(OH)_3$ are much easier to precipitate at low pH value. So after partial oxidation, Fe-Al ferrite diffraction peaks were observed. With the increasing of pH value to 7.0, the amount of $Co(OH)_2$ precipitation increased so that the Fe-Al ferrite diffraction peaks disappeared. With further increasing the pH value to 9.0, due to the increasing of Co concentration in Co-Fe-Al Heusler alloy, the weak reflections of Co_3O_4 (220) and Co (200) were observed. Since the $Al(OH)_3$ precipitation can be dissolved in strong alkali condition, the formation of Co-Fe-Al Heusler nanoparticles was depressed when pH = 11.0 which induced the disappearance of (200) and the weakening of (220), (400) and (422) peaks. Furthermore, the positions of (220), (400) and (422) peaks of Co-Fe-Al nanoparticles monotonically shift toward higher angle with the increasing of pH value which can be clearly seen in the inset of Fig. 1. Since the atomic radius of Co is smaller than those of Fe and Al. The shift might be due to the fact that the increasing of Co composition in the lattice of Co-Fe-Al, which leads to the contraction of the unit cell. The increasing of Co composition and decreasing of Fe and Al composition in Co-Fe-Al nanoparticles with increasing pH value from 5.0 to 11.0 were confirmed in corresponding XRF and EDX measurements.

The hysteresis loops of Co-Fe-Al nanoparticles prepared at different pH values are shown in Fig. 2. The inset shows the saturation magnetization (M_s) and the coercivity (H_c) of Co-Fe-Al nanoparticles as functions of pH value. When the pH value was 5.0, the M_s (29.7 emu/g) was small, which might be due to the lack of Co atoms and the existence of Fe-Al ferrite. With increasing pH value to 7.0, the increase of Co composition and the disappearance of Fe-Al ferrite induce a large M_s (103.7 emu/g). With further increasing pH value to 9.0, the appearance of a little elemental Co causes the increasing of M_s to 113.3 emu/g. The high M_s of the samples with pH value at 7.0 and 9.0 could be a consequence of the relatively pure Co-Fe-Al phase as evidenced from the XRD results. The variation of H_c with pH value is also due to the variation of amount of Co-Fe-Al phase.

The SEM images of Co-Fe-Al nanoparticles without annealing prepared at different pH values are shown in Fig. 3. When the pH value increase from 5.0 to 7.0, the Co-Fe-Al nanoparticles become less defective because of the enhancement of nucleation density at higher pH values [25]. The decreasing of defects and Fe-Al ferrite induced small and uniform Co-Fe-Al particles. The average particle size was estimated to be about 100 nm. With further increasing pH value from 7.0 to 9.0, the formation of large particles might be due to the aggregation of small particles, which is induced by the strong magnetic interaction between magnetic atoms (Fe or Co) containing in Co-Fe-Al grains [26,27]. When further increasing pH value to 11.0, much larger particles were observed because of the much more obvious aggregation of small particles which was due to the increasing of Co composition and decreasing of Al composition.

The XRD patterns of $Co_{2(1+x)}Fe_{1-x}Al_{1-x}$ nanoparticles annealed at 850 °C with different x (x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5) are shown in Fig. 4. The diffraction peaks at 31.8°, 45.1°, 65.6° and 83.1° correspond to (200), (220), (400) and (422) plane of Co-Fe-Al respectively. When x = 0.0, the (200), (220), (400) and (422) diffraction peaks of Co-Fe-Al nanoparticles can be clearly seen. With increasing Co composition from x = 0.0 to x = 0.3, the intensity of Co (111) diffraction peak became much stronger. The intensity ratio of (002) super-lattice peak to (004) fundamental peak

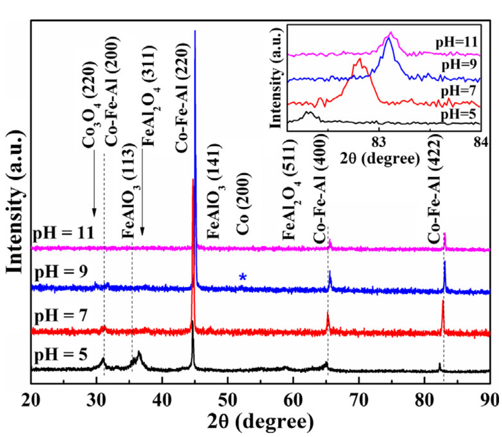

Fig. 1. The XRD patterns of Co-Fe-Al nanoparticles with different pH values annealed at 850 °C for 15 h under Ar, H_2 gas mixture.

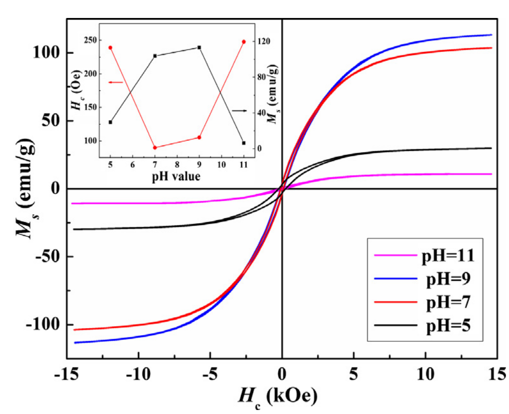

Fig. 2. The room temperature hysteresis loops of Co-Fe-Al nanoparticles with different pH values annealed at 850 °C for 15 h under Ar, H_2 gas mixture. The inset shows the M_s and H_c as functions of pH value.