Contents lists available at SciVerse ScienceDirect



Journal of Magnetism and Magnetic Materials



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

Dual behaviors of magnetic Co_xFe_{1-x} ($0 \le x \le 1$) nanowires embedded in nanoporous with different diameters

A. Ramazani^{a,b,*}, M. Almasi Kashi^{a,b}, S. Ghanbari^a, F. Eshaghi^a

^a Department of Physics, University of Kashan, Kashan, Iran

^b Institute of Nanoscience & Nanotechnology, University of Kashan, Kashan, Iran

ARTICLE INFO

Article history: Received 21 January 2012 Received in revised form 23 April 2012 Available online 29 May 2012

Keywords: Magnetic model AC electrodeposition Nanowire

ABSTRACT

 $Co_x Fe_{1-x}$ nanowire arrays with various diameters and different composition were fabricated by ac electrodeposition using porous alumina template. Coercivity along the easy axis reaches to a maximum at 2330 Oe, for $Co_x Fe_{1-x}$ nanowires containing about 40 at% Co. The crystalline structure of the nanowires was concentration-independent and shows a bcc structure. The critical diameter for transition from coherent rotation to curling mode is 35 nm for CoFe containing less than 40 at% Co while it is 30 nm for those with more than 40 at% Co. Optimizing the magnetic properties of CoFe with different Co content was seen to be dependent on the diameter of nanowires. For 25 nm diameter, the optimum was shown below 50 at% Co while it was seen above 50 at% for nanowires with 50 nm diameter. The angular dependence of the coercivity with nanowires diameter were also studied.

1. Introduction

Ferromagnetic nanowire arrays have been widely investigated to understand their microstructures, magnetic properties and their applications in microwave circulator [1] recording media [2], magnetic nanodevices [3] and nanosensors [4]. To produce nanowire arrays, advanced lithographic techniques [5], electroless procedures [6] and electrodeposition techniques in nanoporous templates have been developed [7–9]. Among these methods, the electrodeposition in alumina templates which is a simple low-cost technique has been widely used [10,11]. The advantage of the alumina templates over other porous membranes is the possibility to fabricate these ordered nanopores, using pre-patterning [12] or multiple anodization steps [13,14]. Most of the studies have been focused on the fabrication and characterization of magnetic materials such as Fe [15], Co [16] and Ni [17]. Since the shape anisotropy is the dominant mechanism in determining the magnetic properties, high coercivities and large squareness have been obtained in these types of nanostructures.

Recently attention has been shifted towards preparing and characterizing of alloy nanowire arrays such as CoNi [18], FeCo [19–22]. It is easy to change the coercivity and squareness of recording media to reach the requirements of real device by adjusting the components of alloy. CoFe-based alloys have received much attention because of high saturation magnetization and low magnetic crystalline anisotropy and elevated Curie temperature

E-mail address: rmzn@kashanu.ac.ir (A. Ramazani).

which is more suitable for high temperature applications. Since the magnetocrystalline anisotropy of CoFe nanowires is almost negligible, the magnetic properties of these nanowires are mainly predominated by shape anisotropy of the nanowires. It was reported that alloy composition of CoFe nanowires has an effective role to optimize the magnetic properties. In these reports, the magnetic properties of CoFe nanowires with 20 and 50 nm diameters with respect to the Co content was seen to be quite different [23,24]. In our previous work the effect of ac electrodeposition frequency and post annealing on the nanowires with various compositions embedded into the porous alumina with 30 nm pore diameter was investigated [25].

In the present work $Co_x Fe_{1-x}$ ($0 \le x \le 1$) nanowires embedded in porous aluminum oxide with pore diameters ranging between 25 to 50 nm were fabricated. The microstructures and magnetic properties of nanowires were studied and the degree of conformity of the coherent rotation and curling model on the magnetic behavior of CoFe nanowires with different Co content was investigated.

2. Experiments

Highly ordered porous aluminum oxide (PAO) templates with pore diameter of about 25 nm were prepared by two-step anodizing process. The process was carried out in 0.3 M sulfuric acid solution at a constant anodization voltage of 25 V for 5 h. After dissolving the formed alumina, the patterned aluminum substrate was re-anodized under the same conditions as the first step for an anodization time of 30 min. Subsequently the pores of the anodic alumina were widened by immersing the anodized

 $[\]ast$ Corresponding author at: Institute of Nanoscience & Nanotechnology, University of Kashan, Kashan, Iran. Tel./fax: +98 3615552935.

^{0304-8853/\$ -} see front matter \circledcirc 2012 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.jmmm.2012.05.036

templates in 6 wt% phosphoric acid at 30 °C for 4, 8, 16 and 20 min yielding a series of porous alumina templates with different pore diameters. Following the widening process, the voltage was systematically reduced to 8 V to promote thinning of the barrier layer. The samples were then ac electrodeposited in electrolyte with different concentrations of $CoSO_4$ and $FeSO_4$. A 45 g/L boric acid was used as buffer. The electrolyte acidity with the NaHCO₃ solution was adjusted to be at 5. The peak to peak deposition voltage and frequency of the sine waveform were 30 V and 200 Hz, respectively.

The crystal structure of the nanowire arrays was examined by X-ray diffraction (XRD). Scanning electron microscopy (SEM) was used to confirm the morphology of the samples. A vibrating sample magnetometer (VSM) was used to measure the magnetic properties of the samples at room temperature. Energy dispersive X-ray spectroscopy (EDX) was used to determine the composition of samples.

3. Results and discussions

Fig. 1 shows SEM micrographs of top surface of anodized alumina templates after pore widening process. The interpore distance was 65 nm and the pore diameters were 25, 30, 35, 45 and 50 nm for the samples widened at 0, 4, 8, 16 and 20 min, respectively. Here, the electrodeposition velocity of Fe^{2+} was



Fig. 1. SEM micrographs of the top surface of anodized alumina templates after the two-step anodization process, widened at (a) 0, (b) 4, (c) 8, (d) 16, and (e) 20 min.

almost the same as that of Co^{2+} . As seen in Fig. 2, the atomic percent of cobalt nanowires initially is slightly more than that of $Co^{+2}/(Co^{+2}+Fe^{+2})$ percentage in the electrolyte but it decreases slightly for *x* more than 0.2. Based on these values, the component of Co_xFe_{1-x} alloy nanowires can be easily controlled by adjusting the relative concentration of Co^{2+} and Fe^{2+} in electrolyte. These results are consistent with those reported by Qin et al. [24].

The hysteresis loops for Co_{0.18}Fe_{0.82} and Co_{0.43}Fe_{0.57} in 25 nm diameter are shown in Fig. 3(a)-(d), with the applied field parallel and perpendicular to the wire's axis. The hysteresis loop (parallel to the wire's axis) of the nanowires with 25 nm pore diameter is evidently different from that of 50 nm (see Fig. 3a, c, e and g). For nanowire arrays with 25 nm diameter, a square hysteresis loop with high coercivity and large squareness is observable. Increasing the pores diameter to 50 nm, the squareness and coercivity become comparatively small. Reducing the Co content (Co_{0.18}Fe_{0.82} nanowire) causes a reduction in the coercivity and squareness of the nanowire arrays. In fact the nanowires have grown with axis perpendicular to the sample surface and the easy axis loops was performed with applied field along to the wires axis. On the other hand, since the samples had a circular shape it may be said that the nanowire array is magnetically isotropic in a plane perpendicular to the nanowires axis.

Fig. 4 shows coercivity and squareness as a function of Co content of the $Co_x Fe_{1-x}$ nanowires with different diameters. With an increase in x to 0.18, the obtained coercivity (with the applied field parallel to nanowires axis) initially decreases, reaches a minimum and then almost linearly increases with increasing x to 0.45-0.6 and then reduces and reaches to about 1000 Oe in the case of pure Co. The minimum and maximum squareness of the alloy CoFe (but not pure Co) nanowires with 25 nm diameter is almost 0.9 and 1 while for 50 nm. it is 0.26–0.49, respectively. However, average coercivity and squareness were about 300 Oe and less than 0.1, respectively when the applied field was perpendicular to the nanowires axis (not shown). As shown in these figures, all Co_xFe_{1-x} nanowires containing almost 18 at% Co exhibit fewer coercivity. The maximum coercivity for the nanowires with 25 nm diameter was seen for the 43 at% Co (H_c =2330 Oe) while it was seen at 58 at% Co for the nanowires with 50 nm diameter $(H_c = 1660 \text{ Oe}).$

Crystalline structure of the samples was examined by X-ray analysis. A D5000 X-ray diffractometer was used, which utilizes a standard Cu tube source run at a voltage of 40 kV and filament current of 40 mA. A Cu (K_{α}) radiation with wavelength of 0.1540496 nm is produced by this system. All θ -2 θ scans were



Fig. 2. Co content of CoFe nanowires as a function of $Co^{+2}/(Co^{+2}+Fe^{+2})$ in the electrolyte.



Fig. 3. Hysteresis loops of CoFe nanowires with different Co content. The applied field was parallel to the wires axis in (a), (c), (e) and (g) and perpendicular in (b), (d), (f) and (h).

made from incident beam angles of 35° to around 80° of the surface with detector increments of 0.1° every 20 s. The incident beam to the sample, the diffracted beam from the sample, and the normal to the sample surface were coplanar.

In order to distinguish the peaks of nanowires, the remaining pure aluminum metal was removed from behind the samples. Sample was seated on an amorphous substrate, aluminum was then removed from behind the samples, using a mixture of HCl and saturated CuSO₄. Considering the high X-ray activation volume of alumina, it was expected that the whole nanowire length would be exposed by the X-ray beam applied from behind the samples.

Fig. 5 shows the XRD patterns of the $Co_x Fe_{1-x}$ nanowires with various diameters in which *x* ranging from 0.5 to 0.9. The XRD analysis revealed that they all are body-centered cubic structure



Fig. 4. Coercivity and squareness of CoFe nanowires with different diameters as a function Co content.

and the main diffraction peak can be assigned to be preferential (110) CoFe. It may be said that nanowires diameter and cobalt content have no effect on the crystalline structure of Co_xFe_{1-x} nanowires.

As reported, the CoFe ordered alloys show small magnetocrystalline anisotropy K_1 [26]. The results show crystalline anisotropy in the $Co_x Fe_{1-x}$ nanowires is negligible and can be omitted and could not have a significant effect on the coercivity variations. If any variation occurred in the preferential direction of the bcc structure due to the predomination of shape anisotropy in these nanowires, the variation of the magnetic properties with respect to these crystalline variations was unexpected. It should be noted that nanowires were embedded into the parallel nanopores therefore all are parallel and have the same crystalline orientation. On the other hand although all the X-ray diffraction pattern show preferential (110) orientation, it is not possible to say those are single crystals. Many reports confirmed ac electrodeposited nanowires formed with polycrystalline structure [27,28]. The rapid change in coercivity of the samples containing more than 85 at% Co might be associated with the transition in the crystalline structure from cubic to hcp lattices. This conclusion is supported by the abrupt change in squareness of the samples containing more than 85 at% Co.

A nanowire with a high aspect ratio (an aspect ratio m=c/a < 10) can be considered as a prolate spheroid. In this case, according to the following equations [29]:

$$N_{a} = N_{b} = 4\pi \frac{m}{2(m^{2} - 1)} \times \left[m - \frac{1}{2\sqrt{m^{2} - 1}} \times \ln\left(\frac{m + \sqrt{m^{2} - 1}}{m - \sqrt{m^{2} - 1}}\right) \right]$$
$$N_{c} = 4\pi \frac{1}{(m^{2} - 1)} \times \left[\frac{m}{2\sqrt{m^{2} - 1}} \times \ln\left(\frac{m + \sqrt{m^{2} - 1}}{m - \sqrt{m^{2} - 1}}\right) - 1 \right]$$

the demagnetization factor along the hard axis (N_a and N_b), is equal to 2π , while it is equal to 0 along the easy axis N_c . As shown in Fig. 6 the length of the wires is almost 700 nm and the wires diameter is ranging between 25 and 50 nm. The aspect ratio of prepared nanowires then changes from 28 to 14. Since the infinitely long cylinder approximation can be used for nanowires having an aspect ratio greater than about 10, the shape anisotropy has the same effect on the magnetic properties of our prepared nanowires. The variations of magnetic properties then could be due to magnetostatic interaction between the nanowires and/or be because of appearance of incoherent effects in the nanowires with larger diameter (transition from coherent to curling mode).

Coercivity of $Co_x Fe_{1-x}$ nanowires with various diameters shows dual behavior (see Fig. 4); they almost follow the coherent rotation and curling models. The coercivity variation of the CoFe nanowires containing more than 40 at% Co is negligible when the diameter of the nanowires increases from 25 to 35 nm, while it is considerable for those nanowires containing less than 40 at% Co. It is seen that the coercivity of the CoFe nanowires with 43 at% Co, changed from 2330 to 2280 Oe (almost 2 at% reduction) when the diameter increased from 25 to 35 nm while with the same variation of the diameter, it increases from 1950 to 2165 Oe and then reduces to 1740 Oe for CoFe nanowires containing 25 at% Co. It may therefore be said that the small change in coercivity due to change in diameter of the nanowires with more than 40 at% Co, is in agreement with coherent model in which the coercivity is diameter independent [29] while in those containing less than 40 at% Co, a considerable reduction of coercivity due to diameter is an indication of greater consistency of the curling model with the magnetic behavior of these alloys [30]. It should be noted that the coercivity of nanowires which almost follows the curling model inversely changes with diameter square.



Fig. 5. XRD patterns of the CoFe nanowires with various diameters containing (a) 81, (b) 58 and (c) 43 at% Co.

For more clarification, the effect of diameter on the coercivity of $Co_{18}Fe_{82}$ and $Co_{50}Fe_{50}$ nanowires is displayed in Fig. 7. As shown in Fig. 7(a) the coercivity of $Co_{18}Fe_{82}$ nanowires are well fitted with radial inverse square curve to 0.00111 nm⁻² (diameter=30 nm), while in Fig. 7(b) the fitted curve include less points and approaches to 0.00111 nm⁻² (diameter=35 nm), for the $Co_{50}Fe_{50}$ nanowires. As a rule of thumb it may be said that the coercivity of nanowires which initially is independent of the diameter, decreases with further increase in diameter according to radial inverse-square law [30]. With an increase in the Fe content, the transition from coercivity independency to the radial inverse-square dependency occurs for the nanowires with larger diameters. Anyway, the experimental data of Fig. 4 represent the magnetic behavior of all CoFe nanowires with more than 35 nm diameter is more consistent with curling model.

The coercivity reduction with increase in diameter may have another source. As reported by Chen and Qin the squareness of nanowire arrays with 20 and 50 nm diameter and interpore distance of 60 and 100 nm was almost 1 while it was about



Fig. 6. Cross section SEM micrograph of FeCo nanowire arrays embedded in AAO template.



Fig. 7. Coercivity of (a) $Co_{18}Fe_{82}$ nanowires and (b) $Co_{50}Fe_{50}$ nanowires as a function of $1/D_p^2$ along with fitted radial inverse square curve.

0.98 and 0.49 for our nanowires with 25 and 50 nm diameters and same interpore distances of 65 nm, respectively. The difference between our results and what was reported by Chen and Qin may be a direct consequence of magnetostatic interaction between nanowires. The diameter to interpore distance ratio of nanowire arrays reported by Chen and Qin is 0.33 and 0.5, which is an indication of low magnetostatic interaction between nanowires. In the present work, this ratio varies from 0.38 to 0.76 for 25 to 50 nm diameters, respectively. In comparison, the former (0.38) is almost the same as what is reported by them while the later is almost twice than what they reported and implies a large interwire magnetostatic interaction resulting in a 50 at% reduction in squareness.



Fig. 8. Angular dependence of the coercivity to diameter of CoFe nanowires, containing different amounts of Co.

For more investigation the angular dependence of the coercivity with diameter for CoFe nanowires with various Co concentrations were studied and shown in Fig. 8. It can be clearly seen that no matter how the Co content changes, the coercivity with the angle (the angle between applied field and wires axis) decreases with almost the same slope if the angle is less than 45°, but it drastically reduces with increase in angle after 45°, for that prepared with 30 nm diameter. On the other hand, as the diameter increases to 50 nm, the coercivity decreases rather steeply with increase in angle between 45° and 77°, while the slope remarkably decreases with increase in the angle more than 80°. This behavior is in agreement with obtained results by Cheng-Zhang and Lodder [31] in which the angular dependence of the coercivity of Fe nanowire with respect to the packing density was studied. In the present work increasing the diameter from 30 to 50 nm increases the packing density about 2.7 times. Therefore it may be said that the coercivity treatment with the angle is almost the same for the Fe and CoFe nanowires.

4. Conclusions

By anodizing aluminum in sulfuric acid and immersing template into phosphoric acid for different widening times, the diameters of the subsequently deposited nanowires were varied.

Highly ordered $C_{0x}F_{1-x}$ alloy nanowire arrays were produced in anodic aluminum templates. Coercivity and squareness of the CoFe alloy nanowires are improved over the properties of similar nanostructures composed of pure Co and Fe. The crystalline structure of the nanowires is concentration independent and shows a bcc structure for Co_xFe_{1-x} nanowires containing only a small amount of Co. Coercivity of deposited nanowires as a function of diameter has shown that the coherent model was established in CoFe nanowires containing more than 40 at% Co having less than 40 nm diameter, while curling model has shown greater consistency with the behavior of nanowires (with a wide range of diameters) with less than 40 at% Co. Maximum coercivity for the nanowires with 25 nm diameter was seen in $Co_{0.43}Fe_{0.57}$, while it was seen for nanowire with 50 nm diameter $Co_{0.58}Fe_{0.42}$. The study of angular dependence of the coercivity with diameter CoFe nanowires shows similar treatment with angular dependence of the coercivity with packing density of Fe nanowires.

References

- M. Darques, J.De. La, T. Medina, L. Piraux, L. Cagnon, I. Huynen, Nanotechnology 21 (2010) 145208.
- [2] G.H. Yue, X. Wang, L.S. Wang, P. Chang, R.T. Wen, Y.Z. Chen, D.L. Peng, Electrochimica Acta 54 (2009) 6543.
- [3] B. Yang, B. Aksak, Q. Lin, M. Sitti, Sensors and Actuators B: Chemical 114 (2006) 254.
- [4] M. Almasi Kashi, A. Ramazania, H. Abbasian, A. Khayyatiana, Sensors and Actuators A 174 (2012) 69.
- [5] D.B. Seley, D.A. Dissing, A.V. Sumant, R. Divan, S. Miller, O. Auciello, L.A. Lepak, E.A. Terrell, T.J. Shogren, D.A. Fahrner, J.P. Hamilton, M.P. Zach, ACS Applied Materials and Interfaces 3 (2011) 925.
- [6] Z. Zhang, S. Dai, D.A. Blom, J. Shen, Chemistry of Materials 14 (2002) 965.
- [7] C.T. Sousa, A. Apolinario, D.C. Leitao, A.M. Pereira, J. Ventura, J.P. Araujo, Journal of Materials Chemistry 22 (2012) 3110.
- [8] R. Lavin, J.C. Denardin, A.P. Espejo, A. Corts, H. Gómez, Journal of Applied Physics 107 (2010) 09B504.
- [9] N. Dadvand, G.J. Kipouros, Journal of Nanomaterials 2007 (2007) 46919.
- [10] A.S. Samardak, E.V. Sukovatitsina, A.V. Ognev, L.A. Chebotkevich, R. Mahmoodi, S.M. Peighambari, M.G. Hosseini, F. Nasirpouri, Sensors and Actuators A 174 (2012) 69.
- [11] S. Song, G. Bohuslav, A. Capitano, J. Du, K. Taniguchi, Z. Cai, L. Sun, Journal of Applied Physics 111 (2012) 056103.
- [12] H. Masuda, H. Yamada, M. Satoh, H. Asoh, M. Nakao, H. Tamamura, Applied Physics Letters 71 (1997) 2770.
- [13] H. Masuda, K. Fukuda, Science 268 (1995) 1466.
- [14] H. Zeng, M. Zheng, R. Skomski, D.J. Sellmyer, Y. Liu, L. Menon, S. Bandyopadhyay, Journal of Applied Physics 87 (2000) 4718.
- [15] J.M. Baik, M. Schierhorn, M. Moskovits, Journal of Physical Chemistry C 112 (2008) 2252.
- [16] H. Pan, B. Liu, J. Yi, C. Poh, S. Lim, J. Ding, Y. Feng, C.H.A. Huan, J. Lin, Journal of Physical Chemistry B 109 (2005) 3094.
- [17] D. Laroze, P. Vargas, D. Altbir, M. Vazquez, Brazilian Journal of Physics 36 (2006) 3B.
- [18] Y. Rheem, B.Y. Yoo1, W.P. Beyermann, N.V. Myung, Nanotechnology 18 (2007) 125204.
- [19] R. Zhao, J.J. Gu, L.H. Liu, Q. Xu, N. Cai, H.Y. Sun, Acta Physica Sinica 61 (2012) 027504.
- [20] X. Lin, G. Ji, T. Gao, X. Chang, Y. Liu, H. Zhang, Y. Du, Solid State Communications 151 (2011) 1708.
- [21] H.R. Khan, K. Petrikowski, Journal of Magnetism and Magnetic Materials 249 (2002) 458.
- [22] G.H. Yue, X. Wang, L.S. Wang, P. Chang, R.T. Wen, Y.Z. Chen, D.L. Peng, Electrochimica Acta 54 (2009) 6543.
- [23] W. Chen, S. Tang, M. Lu, Y. Du, Journal of Physics: Condensed Matter 15 (2003) 4623.
- [24] D.H. Qin, Y. Peng, L. Cao, H.L. Li, Chemical Physics Letters 37 (2003) 4661.
- [25] M. AlmasiKashi, A. Ramazani, F. Es'hagh, S. Ghanbari, A.S. Esmaeily, Physica B 405 (2010) 2620.
- [26] R.M. Bozorth, Ferromagnetism, IEEE, New York, 1991.
- [27] R.E. Benfield, D. Grandjean, J.C. Dore, Z. Wu, M. Kroll, T. Sawitowski, G. Schmid, European Physical Journal D 16 (2001) 399.
- [28] N.J. Gerein, J.A. Haber, Journal of Physical Chemistry B 109 (2005) 17372.
- [29] L. Sun, Y. Hao, C.L. Chien, P.C. Searson, IBM Journal of Research and
- Development 49 (2005) 79. [30] A. Aharoni, Journal of Applied Physics 82 (1997) 1281.
- [31] L. Cheng-Zhang, J.C. Lodder, Journal of Magnetism and Magnetic Materials 88 (1990) 236.