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Fabrication and characterization of $\text{Co}_{1-x}\text{Fe}_x$ alloy nanowires

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$\text{Co}_{1-x}\text{Fe}_x$ alloy nanowires with 40 nm diam and $x=0-1.0$ were fabricated by electrodeposition in nanopores of alumina templates. The crystalline structure of the nanowires is concentration dependent and shows a transition from the cobalt hexagonal-closed-packed structure (hcp) to a face-centered-cubic structure (fcc) in the concentration range $0 < x < 0.1$. For an iron content greater than 15 at % the structure becomes body-centered-cubic (bcc). The nanowires with an aspect ratio of about 8 show a highly anisotropic magnetization with the easy axis along the length of the wire. The squareness of the hysteresis loops is between 72% and 93% for magnetic fields parallel to the wires while the squareness is less than 13% for fields perpendicular to the wires. The coercivity along the easy axis reaches a maximum of 2150 Oe for $x=0.55$ and is almost concentration independent for $0.5 < x < 0.6$. © 2002 American Institute of Physics. [DOI: 10.1063/1.1449450]

I. INTRODUCTION

Many of the magnetic devices used in today's technologies are based on the magnetic properties of thin films or bulk materials. With the advent of nanofabrication processes, opportunities to use the unique properties associated with nanostructured materials exist that were not previously thought possible. However, conventional technologies used to obtain nanostructures, such as e-beam lithography, x-ray lithography, and scanning probe-based lithography are very expensive and not always suitable for commercial applications.

A less expensive alternative for the production of nanostructures is the electrodeposition of various materials in nanoporous membranes. Examples of nanoporous membranes that have been used for electrodeposition include polycarbonate membranes created by etching damage tracks of high-energy particles and alumina membranes produced by the anodic oxidation of aluminum.¹ The advantage of the alumina templates over other porous membranes is the possibility of obtaining them with ordered nanopores using pre patterning² or multiple anodization steps.³⁻⁶

The magnetic properties of transition metals electrodeposited in alumina templates have been studied by several groups.^{4,7-10} High coercivities and large values for the squareness have been measured parallel to the wire axis in these types of nanostructures with shape anisotropy being found to be the dominant mechanism in determining the magnetic properties. In the present study we have investigated the crystallographic and magnetic properties for various concentrations of $\text{Co}_{1-x}\text{Fe}_x$ alloys deposited in the pores of an alumina matrix produced by anodization in oxalic acid.

II. EXPERIMENTS

High-purity 99.997% Al strips ($6 \times 20 \times 0.25$ mm³) were used as the starting material. The strips were ultrasonically cleaned for 15 min in acetone and then annealed in air at 500 °C for 2 h in order to increase the size of the crystalline grains and remove any mechanical stress induced in the samples during the cutting process of the strips. The samples

were then electropolished in a solution of perchloric acid, ethanol, and 2-butoxyethanol at a current density >500 mA/cm² and a temperature of 5 °C. To obtain highly ordered pores a two-step anodization process was employed. In the first anodization step the Al strips were anodized at 40 V in 0.3 M oxalic acid at 5 °C for 2 h. The aluminum oxide was then stripped off in a 0.6 M chromic acid and 0.4 M phosphoric acid solution at 60 °C. Subsequently, the sample was reanodized for 30 min using the same anodization conditions as in the first step. A nonequilibrium anodization process in which the voltage was reduced to about 8 V followed the second anodization. This led to a reduction of the barrier layer that formed between the porous alumina and the Al substrate, thus facilitating the electrodeposition of the metals. The $\text{Co}_{1-x}\text{Fe}_x$ alloy was then electrodeposited in the synthesized template from a concentrated Watts-type electrolyte containing 45 g/l boric acid and CoSO_4 , CoCl_2 , and FeSO_4 salts in different ratios depending on the composition desired for the final alloy. The electrodeposition was carried out at 37 °C with an ac voltage of 8 V_{rms} and a frequency of 60 Hz using a graphite counterelectrode.

Scanning electron microscopy (SEM) was used to study the morphology of the alumina templates. The crystalline properties of the nanowires were investigated using x-ray diffraction (XRD) after the Al substrate of the samples was dissolved using a saturated solution of mercury chloride. The composition of the nanowires was determined by energy dispersive spectroscopy (EDS) and the magnetic properties were measured using a Quantum Design SQUID magnetometer.

III. RESULTS AND DISCUSSION

Figure 1 shows a SEM micrograph of the top surface of an anodized alumina template after the two-step anodization process. The average pore diameter is 40 nm while the interpore distance is 95 nm. The pores are parallel with each other through the entire thickness of the alumina layer and form a hexagonally ordered array with typical ordered domain size of 1 μm. The length of the electrodeposited nanowires is determined from cross-sectional SEM to be 290 nm

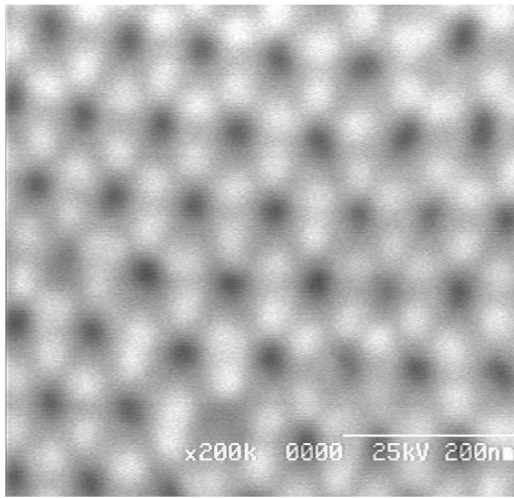


FIG. 1. SEM top view of a nanopore array in anodic alumina prepared by a two-step anodization in 0.3 M oxalic acid. The average pore diameter and inter pore distance are 40 nm and 95 nm, respectively.

± 20 nm. The x-ray diffraction pattern for the Co nanowires shows a hexagonal-closed-packed (hcp) structure with a $(10\bar{1}0)$ texture as shown in Fig. 2. As the concentration of Fe increases there are two crystallographic transitions. The first one occurs in the $0 < x < 0.1$ range where a mixed state between the hcp and fcc (γ) phases exists. For $x = 0.1$ the mixing ratio of hcp:fcc is about 7:3. For an iron content greater than 15 at% the only stable phase is the α phase (body-centered-cubic) with the lattice parameter being the same as that for pure iron.

Typical hysteresis loops for the $\text{Co}_x\text{Fe}_{1-x}$ nanowires are shown in Fig. 3(a) with the easy magnetization axis being along the length of the wires for all the samples. The value of the coercivity field for the pure Co nanowires is 1400 Oe, about 30% less than previous results for Co nanowires having a larger aspect ratio.¹¹ As the Fe content increases, the coercivity rapidly increases reaching essentially a concentration independent plateau of approximately 2150 Oe in the $0.5 < x < 0.6$ range before decreasing to a value of 1750 Oe

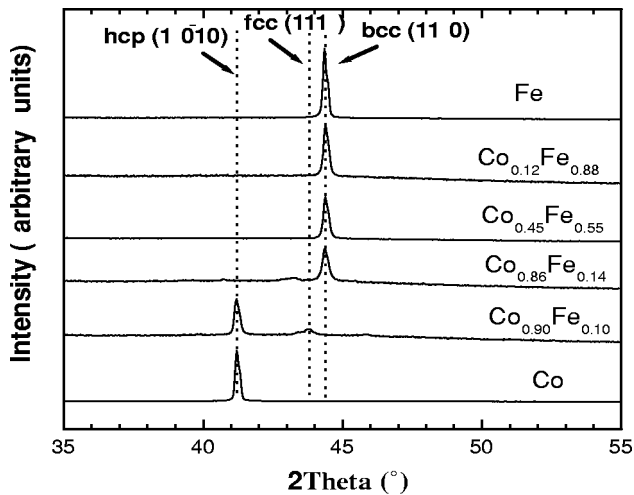
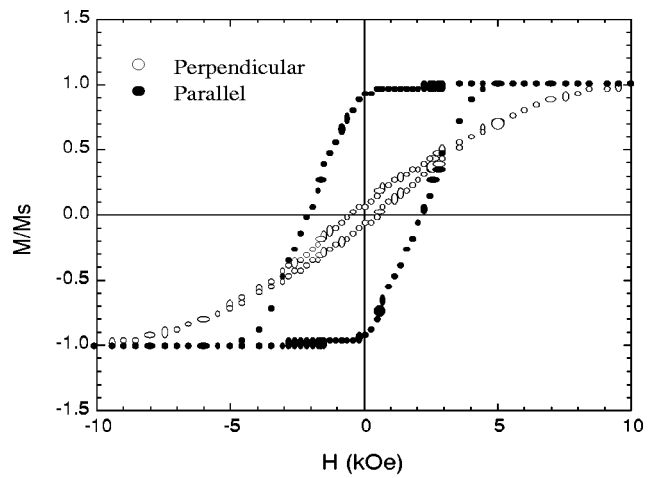
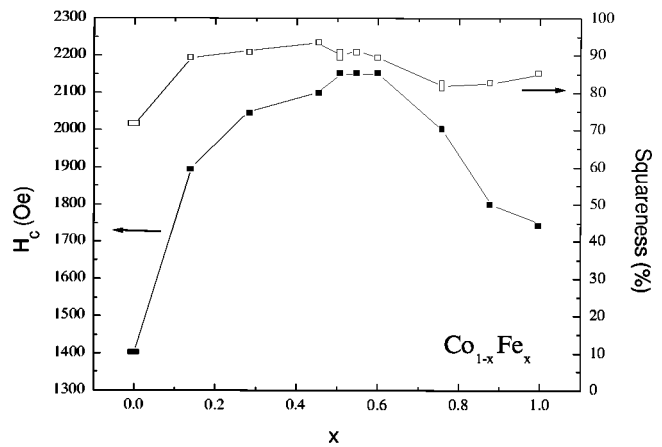


FIG. 2. X-ray diffraction pattern for $\text{Co}_{1-x}\text{Fe}_x$ nanowires arrays after removing the Al substrate.



(a)



(b)

FIG. 3. (a) Hysteresis curves for a $\text{Co}_{0.45}\text{Fe}_{0.55}$ nanowire array with fields oriented perpendicular (○) and parallel (●) with respect with the nanowire axis. (b) Concentration dependence of the coercivity field H_c (■) and squareness (□) along the nanowire axis.

for the pure Fe nanowires as shown in Fig. 3(b). This maximum coercivity value is also about 30% smaller than coercivities found in previous studies on Co–Fe nanowires having larger aspect ratios.¹² The abrupt change in coercivity with a small addition of iron might be associated with the transition in the crystalline structure from the highly anisotropic hcp lattice to cubic lattices with higher symmetry. This conclusion is supported by the change in squareness along the wire length, from 72% for the Co nanowire sample to values larger than 80% for the other CoFe nanowire samples as also seen in Fig. 3(b). For fields normal to the wires, the squareness is less than 13% for the $\text{Co}_{1-x}\text{Fe}_x$ nanowires while the coercivities range between 450 and 750 Oe.

Measurements of the crystalline anisotropy in $\text{Co}_{1-x}\text{Fe}_x$ bulk alloys indicate that for $x = 0.55$ the crystalline anisotropy is zero.¹³ Thus the $\text{Co}_{0.45}\text{Fe}_{0.55}$ ensemble of nanowires should be an ideal system to study how the magnetic properties of our nanowire arrays are governed by the shape anisotropy. Approximating the cylindrical nanowires as prolate ellipsoids with an aspect ratio of 8, the theoretical coercivity

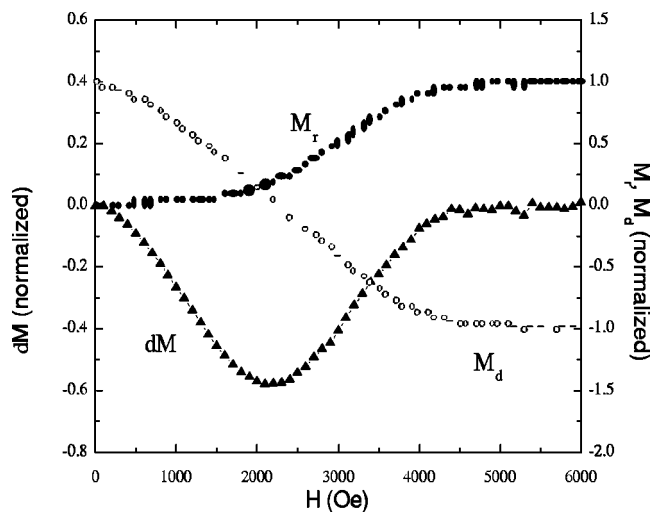


FIG. 4. Henkel plot for alumina sample filled with electrodeposited $\text{Co}_{0.45}\text{Fe}_{0.55}$. δM is defined as $\delta M = M_d - (1 - 2M_r)$, where M_d is the reduced dc demagnetization remanence and M_r is the normalized isothermal remanence.

based solely on shape anisotropy would be 11 kOe ($= (N_x - N_z)M_s$) using the bulk value for the saturation magnetization of 1923 G.¹⁴ This large overestimation of H_c as compared to the measured value of 2150 Oe suggests other mechanisms are also present. The reduction in the coercivity might be due to nonuniform growth of the nanowires and to concentration inhomogeneities that formed in the individual nanowires during the electrodeposition process and give rise to local composition variations as compared to the average determined by EDS. Also the presence of any magnetostatic interaction between the nanowires may have a significant effect on the estimated coercivity force. Dipolar stray fields from adjacent nanowires will oppose the magnetization of its neighbors and thus reduce the applied field necessary to reverse their magnetization. To investigate whether any interactions between the nanowires were present, modified Henkel plots¹⁵ (δM as a function of the applied field) derived from the isothermal remanent magnetization $M_r(H)$ and dc demagnetization remanence $M_d(H)$ curves can be used.

Negative values in δM are typically associated with magnetostatic interactions that tend to destabilize the magnetized state, while positive values indicate the existence of exchange interactions between the individual particles. For the $\text{Co}_{0.45}\text{Fe}_{0.55}$ nanowires, δM takes only negative values with a peak at 2100 Oe (see Fig. 4) suggesting magnetostatic interactions dominate.

In conclusion, highly ordered $\text{Co}_{1-x}\text{Fe}_x$ alloy nanowire arrays have been produced in anodic alumina templates. The magnetic properties—coercivities and squareness of hysteresis loops—of the CoFe alloy nanowires are improved over the properties of similar nanostructures composed of pure Co and Fe. The concentration dependence of the coercivity force along the nanowire axis appears to be related to the crystalline structure of the nanowires and the coercivity reaches a maximum in the range in which the nanowires crystallize in the body-centered-cubic structure.

ACKNOWLEDGMENT

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