Tuning the magnetization reversal process of FeCoCu nanowire arrays by thermal annealing

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(Received 26 June 2013; accepted 8 July 2013; published online 25 July 2013)

Arrays of hexagonally ordered Fe₂₈Co₆₇Cu₅ nanowires with tailored diameter from 18 to 27 nm were prepared by electroplating into anodic alumina templates and annealed in the temperature range of 300–600 °C, preserving but refining their *bcc* crystal structure. Despite the partial reduction of saturation magnetization and corresponding shape anisotropy after annealing at 500 °C, larger coercivity, 0.36 T, and squareness ratio, $M_r/M_s = 0.98$, were obtained. This unexpected behavior is interpreted through micromagnetic simulations where the magnetic hardening is associated with the transition from vortex to transverse domain-wall reversal modes connected with the reduction of saturation magnetization. Simulations also predict a significant coercivity increase with decreasing nanowires diameter which agrees with experimental data in the overlapping diameter range. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4816479>]

I. INTRODUCTION

Nanoscaled magnetic arrays receive nowadays considerable attention motivated not only by fundamental interests but also by their potential applications in magnetic memory, spintronics, and sensor devices.^{1–3} Electrochemical route to prepare ordered arrays of magnetic nanowires is attracting increasing interest. In this technique, magnetic nanowire arrays are produced by template-assisted electrodeposition into self-assembled anodic alumina pores, in which geometrical parameters as pore diameters, length, and center to center spacing between the pores can be easily controlled by varying the anodic electrochemical parameters. Highly ordered nanoporous alumina templates with pore diameters ranging from around 15 to 200 nm and lengths from 100 nm up to 50 μm can thus be obtained.

In the last years, studies on ferromagnetic-nonmagnetic multilayer nanowire arrays and binary systems, including CoCu, FeAg, CoAg, CoPd, and CoPt, have been reported in the literature^{4–7} due to their interesting magnetic and magnetotransport properties.

From the large variety of magnetic systems, FeCo nanowires exhibit the necessary capability to be employed in novel generation of rare-earth-free permanent magnets due to their high Curie temperature, large saturation magnetization, and high shape anisotropy. Magnetic properties of FeCo alloys nanowires can be tuned by adjusting the alloy composition or adding other elements^{8–10} or by suitable thermal treatments.¹¹ Particularly, high values of coercivity and remanence have been measured when the magnetic field is applied parallel to the nanowires and have been attributed mainly to the magnetic shape anisotropy.^{12,13}

The aim of this investigation was to find the conditions under which enhanced magnetic hardening of FeCo nanowires was achieved with a final objective to search for their potential applications in novel family of rare-earth free permanent magnets. In this paper, we report on tailoring of the magnetic properties (i.e., coercivity and remanence) in arrays of FeCoCu magnetic nanowires by suitable thermal treatments as well as by adjusting the nanowires diameters. While in previous studies on FeCo nanowires,¹⁴ the hardening after annealing was also observed, in the present case, the effect is larger probably due to the presence of Cu atoms. A modest reduction of saturation magnetization of nanowires is observed after thermal treatment which, in spite of the corresponding reduction of shape anisotropy, results in increased coercivity. The coercivity mechanism has been studied considering micromagnetic simulations to interpret the experimentally observed variation of coercivity with thermal treatments for wires with different diameters. We conclude a change of the magnetization reversal mechanism from vortex domain wall (VDW) to transverse domain wall (TDW) mode with annealing.

II. SAMPLE PREPARATION AND STRUCTURAL CHARACTERIZATION

The nanowires were grown inside anodic alumina oxide (AAO) templates. These ordered AAO membranes were synthesized by two-step anodization process on 99.999% Al foils in H₂SO₄ aqueous solution (20 wt. %) by applying a constant voltage of 20 V and keeping the temperature between 0 and 2 °C. The first anodization was performed for 16 h and the second one was lasted for about 3 h to ensure a thickness of nanoporous alumina template (i.e., pore length) of about 40 μm. Moreover, the pore diameter was tuned through a widening process by immersing the anodized membranes into phosphoric acid for different periods of time.

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FeCo nanowires with different compositions were prepared and investigated recently,¹⁴ while in the present study, we focus on FeCoCu nanowires with reduced Cu content. They were grown into the pores of the AAO templates by electrodeposition from a sulfate-based electrolyte containing $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ (35 g/l), $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (2 g/l), $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (15 g/l), H_3BO_3 (10 g/l), and ascorbic acid (10 g/l). The pH value of the electrolyte was maintained at about 3.0. The composition of the nanowires alloy, $\text{Fe}_{28}\text{Co}_{67}\text{Cu}_5$, was checked by Energy-Dispersive X-ray spectroscopy (EDX). These nanowires, hereafter referred to as FeCoCu nanowires, were submitted to controlled thermal treatments in the temperature range from 300 to 600 °C under Ar atmosphere for 2 h.

The geometrical parameters of the nanowire arrays have been controlled by varying the electrochemical conditions. Scanning Electron Microscopy (SEM) imaging allowed us to evaluate the nanowires length, their diameter, as well as the interwire distance. Sets of arrays of 8 μm long FeCoCu nanowires with diameter, D_w , from 18 to 27 nm were fabricated. Figure 1(a) shows the cross-section SEM image of FeCoCu nanowires embedded into the nanoporous alumina matrix which top-view image is presented in the inset. The cylindrical shape, the high aspect ratio, and the high diameter uniformity of the nanowires are clearly visible.

The samples were structurally characterized with CuK_α X-ray diffraction (XRD) on a PANalytical X'pert Pro in Bragg-Bretano geometry. The XRD spectra of the FeCoCu nanowires ($D_w = 18\text{ nm}$) embedded into the alumina template, in two different states (as-deposited and annealed at 500 °C), are shown in Fig. 1(b). The XRD pattern of as-prepared FeCoCu nanowires shows that the wires crystallize in body centered cubic (*bcc*) FeCo phase with [110] texture. It must be noted that the broad diffraction peak around $2\theta = 30^\circ$ is due to the amorphous alumina. It is also worth to mention that there are no additional XRD peaks in as-deposited samples corresponding to Fe, Co, or Cu oxides. In the sample annealed at 500 °C, the *bcc* crystal structure is preserved with significant increase in intensity of (110) peak

denoting an enhancement of [110] texture. The additional smaller diffraction peak (marked by an arrow in Fig. 1(b)) can be assigned to (440) $\gamma\text{-Fe}_2\text{O}_3$ phase. However, although not detected by XRD, some other oxides may be present in the sample after annealing.

The magnetic properties of the nanowire arrays, particularly, the hysteresis loops and their parameters, were measured in a Vibrating Sample Magnetometer (VSM) in the temperature range between 10 K and 300 K (RT) under a maximum field of $\pm 2\text{ T}$ applied parallel and perpendicular to the nanowires axis.

III. RESULTS AND DISCUSSIONS

A. Experimental results

The evolution of coercivity, measured at room temperature (RT) with the field parallel to the nanowires, versus annealing temperature is presented in Fig. 2(a) for the arrays of nanowires with diameters of 18 and 22 nm. As observed, the coercivity increases with annealing temperature and reaches a maximum at 500 °C, then it decreases by increasing further the annealing temperature. The loops squareness (i.e., remanence to saturation magnetization ratio) of all annealed samples was around 0.95. Saturation magnetization (i.e., the value measured under 2 T applied field) takes values of 2.0 T and 1.7 T for as-deposited and 500 °C annealed samples, respectively. This reduction has been ascribed to a partial oxidation of the nanowires due to the own O_2 contained inside the AAO template.^{15,16}

Figs. 2(b) and 2(c) show the parallel and perpendicular hysteresis loops for the 18 nm diameter nanowire array in as-deposited and 500 °C annealed states, respectively. In both cases, it can be deduced that the magnetization easy axis lies along the nanowires axis (i.e., perpendicular to the membrane plane). In as prepared state, and for field applied parallel to the wires, the coercivity and squareness ratio take values of 0.26 T and 0.94, respectively, while after annealing at 500 °C those values increase up to 0.36 T and 0.98,

FIG. 1. SEM top view image of the template (inset) and SEM cross-sectional view of FeCoCu nanowires with 18 nm in diameter, interwire distance of 55 nm, and around 8 μm in length (a). XRD spectra of the sample in its as prepared state and after annealing at 500 °C (b).

FIG. 2. (a) Experimental (filled symbols) RT evolution of coercivity with the annealing temperature for FeCoCu nanowires of indicated diameter, D_w , and corresponding simulations for a single nanowire (lines) and for an array of 7 nanowires (dashed line). Experimental hysteresis loops for the 18 nm diameter FeCoCu nanowires array in as-prepared (b) and after annealing at 500 °C (c) states, where insets (upper left sides) show 3D images of the simulated magnetization distribution in respective vortex (b) and transverse (c) domain wall (see text). The insets in right sides show the magnetic moment configuration of vortex (b) and transverse (c) domain wall in nanowire cross-section.

respectively. When the applied field is oriented perpendicularly to the nanowire axis, the hysteresis loops are sheared and the coercivity and the squareness are less than 0.05 T and 0.04, respectively.

The modification of the anisotropy field induced during annealing can be roughly estimated from the measured loops. From the perpendicular hysteresis loops, an effective parallel anisotropy field of around 0.90 T and 0.98 T can be evaluated for the as-deposited and annealed samples, respectively.

Considering these anisotropy fields and the mentioned change of saturation magnetization with annealing temperature, we can simply derive a change of induced anisotropy during annealing of 1.4×10^5 J/m³. Such induced anisotropy is much smaller than the shape anisotropy of individual nanowires (1.60×10^6 and 1.16×10^6 J/m³ before and after annealing at 500 °C), and denotes that the magnetization process is mainly determined by the cylindrical geometry of the nanowires. The origin of the anisotropy modification during annealing can have multiple reasons. Apart from the mentioned partial oxidation, other microstructural features could have an influence such as stress relaxation, structure ordering, and grain size. Thermal annealing has been widely reported in the literature to produce a higher degree of crystallinity.^{9,17}

We should also keep in mind that the heating of the nanowires is performed under geometrical confinement which can lead on one hand to relief of stresses accumulated during electroplating but also can give rise to a net magnetostrictive anisotropic effect owing to a mismatch between the thermal expansion coefficients (α) of FeCo alloys ($\alpha = 14 \times 10^{-6}$ K⁻¹) and alumina ($\alpha = 6 \times 10^{-6}$ K⁻¹) which will produce an expansion of the alloy along the nanowire axis.¹⁸ We should finally mention that when annealed above 550 °C

the substrate becomes mechanically very soft likely introducing distortion of the pores parallelism which seemingly reduces the axial anisotropy resulting in a reduction of coercivity and squareness.¹⁷

The temperature dependence of hysteresis loops, recorded along the parallel direction to the nanowires axis, has been measured for nanowire samples in the range of 10 K to 300 K. Fig. 3 shows the coercivity as a function of the measuring temperature of 18 nm diameter FeCoCu nanowire array in the as-prepared and annealed at 500 °C states. While M_r/M_s stays almost constant at around 0.98 during the entire temperature range, the coercivity increases with decreasing of temperature as expected. In the case of the sample annealed at 500 °C, the coercivity increase is more pronounced at low temperature.

FIG. 3. Coercivity, measured parallel to the nanowires, versus measuring temperature, in as-prepared and annealed sample.

By decreasing the temperature, the thermal fluctuations are reduced and the coercivity increases. The increase of effective magnetocrystalline anisotropy together with the influence of induced stresses through the coupling between the ceramic alumina matrix and the metallic nanowires can also contribute to a larger value of coercivity with decreasing temperature.¹⁸

B. Micromagnetic simulations

For a better understanding of the magnetization reversal process, micromagnetic simulations using Magpar package¹⁹ with finite element discretization have been performed. For the simulations, we considered a polycrystalline structure of FeCoCu nanowires with [110] textured *bcc* phase in agreement with XRD studies (Fig. 1(b)). For a FeCo nanowire with given composition, typical exchange, and magnetocrystalline constants are, respectively, $A = 10.7 \times 10^{-12}$ J/m, $K = 10^4$ J/m³,^{20–22} while the values of the saturation magnetization, M_s , as a function of annealing temperature have been extracted from the experimental measurements. We have assumed that the wires microstructure consists of grains with [110] direction parallel to the nanowires axis and random in-plane easy axis components.

Simulations have been performed for nanowires whose diameter was varied between 8 nm and 22 nm and the length was fixed at 2 μ m (keeping the high aspect ratio of nanowires). The demagnetization process was simulated for an individual nanowire, as well as for hexagonally ordered arrays of 7 nanowires with the distance between wires of 55 nm. Fig. 2(a) presents a comparison between simulated and experimental data for the annealing temperature evolution of coercivity. Owing to a nearly negligible contribution of magnetocrystalline anisotropy, we can expect the magnetic properties of our system to depend on the shape anisotropy proportional to an effective demagnetizing factor and finally to the square saturation magnetization.^{23,24} Note that the coercivity, being proportional to the shape anisotropy, would decrease as saturation magnetization does after annealing if a coherent rotation magnetization reversal mode is assumed. Contrarily to this expected behavior, the experiment reveals a non-monotonic behavior. The measured coercivity increases as a function of the annealing temperature up to $T = 500$ °C which cannot be explained using the simple shape anisotropy concept.

After the magnetic field is applied parallel to the nanowire axis, at the remanence state, our simulations indicate

the presence of a single domain structure practically along the whole nanowires length with longitudinal magnetization for nanowires with diameter in the range $D_w = 8$ –22 nm. At both nanowire ends, open vortex structures appear that minimize the magnetostatic energy. The magnetization reversal occurs by propagation of a DW which structure, either TDW or VDW mode, appears to be strongly dependent on the saturation magnetization value, for fixed wire diameter. TDW and VDW can be distinguished by the behavior of magnetic moments projected to the NW cross-sectional plane. For TDW all magnetization components are parallel in this plane (Fig. 2(b), right side inset) while for the VDW they form a flux closure circular magnetic configuration (Fig. 2(c), right side inset).

Upon decrease of the saturation magnetization value in the range from 2.0 T to 1.7 T, a significant effect occurs, namely, a transition from VDW to TDW mode (see the corresponding Figs. 2(b) and 2(c) left sides insets) owing to the change of the magnetic correlation length.

The coercivity value for the transverse wall reversal mode is known to be always larger than that for the vortex wall mode,^{25–28} and thus, during the transition between the two DW types, the coercivity increases. Consequently, the experimentally observed enhanced coercivity after annealing can be understood in terms of the transition between VDW propagation for as prepared nanowires and TDW propagation for the annealed nanowires. We should also emphasize that we have checked in the micromagnetic simulations that a change in the intrinsic anisotropy value of the order of the induced anisotropy estimated experimentally does not produce any significant difference in the simulated coercive field.

On the other hand, micromagnetic simulations predict a significant increase of coercivity as the nanowires diameter is reduced (see Fig. 4(a)). Particularly, simulations for individual wires show that coercivity significantly increases (up to 8 kOe) for nanowires with diameter less than 10 nm. Figure 4(b) shows the dependence of experimental coercivity on nanowires diameter in agreement with simulated results for the overlapping range of diameters (simulations are for a wider range of diameters).

Figure 4(b) also includes the variation of squareness (M_r/M_s) as a function of nanowire diameter, D_w , showing a parallel evolution as that of coercivity. The significant reduction of the remanence with increasing nanowire diameter can be attributed to the enhanced magnetostatic interactions as the wires get closer, while the decrease of the coercivity is mainly due to the nanowires “shape anisotropy” effect.^{29,30}

FIG. 4. Simulated coercivity data for individual nanowires as a function of their diameters (a), and experimental data for coercivity (filled symbols) and squareness (open symbols) as a function of diameters for as-deposited nanowire arrays (b).

Finally, we should mention that experimental coercivity values in Fig. 2(a) are typically smaller than those found in the simulations. In this regard, we should note that simulations were performed without consideration of possible influence of thermal fluctuations, that is, the possibility of thermal DW nucleation is not taken into account.

When cooling down to 10 K, the thermal fluctuations are reduced significantly and the experimental value of coercivity increases, approaching the simulated data.

IV. CONCLUSIONS

The magnetic behavior of electrodeposited FeCoCu nanowires with different diameter has been investigated after being annealed in a wide range of temperatures where *bcc* crystalline structure along (110) direction was found according to XRD characterization.

In spite of a partial reduction of the saturation magnetization observed after annealing at 500 °C (and subsequent decrease of longitudinal shape anisotropy), it is experimentally found that coercivity and squareness increase and reach a maximum after annealing. Maximum coercivity (measured at 10 K) as high as 0.47 T and squareness of about 0.98 are obtained after annealing at 500 °C the 18 nm diameter FeCoCu nanowires.

That unexpected behavior has been interpreted through micromagnetic simulation analysis. Simulations of coercivity for hexagonally ordered array of 7 nanowires are very close to the experimental results especially for low temperature measurements. The magnetic hardening observed after annealing is associated with the transition from vortex to transverse domain wall reversal modes in connection with the reduction of saturation magnetization.

Micromagnetic simulations also predict a significant increase of coercivity with decreasing nanowires diameter which are in agreement with experimental values in the overlapping diameter range.

Present results are useful for the design of applications of the nanowires.

ACKNOWLEDGMENTS

This work was supported by the European Community's 7th Framework Program under Project No. REFREPERMAG, Grant Agreement No. 280670, by the Spanish Ministerio de Economía y Competitividad under Project Nos. MAT2010-0278-C05-01 and 04, and FIS2010-20979-C02-02, and by the Regional Government of Madrid,

under Project No. S2009MAT-1726. J. García thanks FICYT for the Severo Ochoa grant.

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