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Influence of aspect ratio and anisotropy distribution in ordered CoNi nanowire arrays

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ABSTRACT

The size effects on magnetic properties of nanowires arrays were studied varying the nanowires diameter and maintaining the same periodicity among them, for two different nominal compositions of Co and Ni in the alloy form. The competition among magnetocrystalline and shape anisotropies changes drastically from smallest to biggest diameters altering the easy axis direction. In the case of 75% of Co in alloy, experimental values of the effective anisotropy constant (K_{eff}) vary from positive to negative depending on the diameter, which means a reversal of the easy axis direction. For 50% of Co the shape anisotropy dominates over the magnetocrystalline for all studied diameters.

1. Introduction

Low-dimensional cylindrical nanowires are nearly ideal systems for theoretical [1–3] study in nanomagnetism since they can be considered as model systems to investigate the interaction processes and magnetic reversal mechanism. Also, among magnetic nanostructures, ordered arrays of nanowires are considered of great interest due to their novel properties compared to bulk materials, leading to a wide range of potential technological applications from high-density magnetic storage media, to sensors other devices [4,5].

Despite the production of a number of nanostructures have been performed by various lithography techniques [6], a much less expensive method, based on electrochemical route, is increasingly being used to prepare magnetic nanowires and their arrays.

Particularly, magnetic properties of Ni, Fe, Co nanowires and their alloys, electroplated in alumina porous template have been extensively studied for different groups around the world [7–10]. It is well established that Ni and Fe nanowires present easy axes along the wire axis due to the predominant shape anisotropy contribution [11,12]. However, the case of Co is especially interesting due to its large magnetocrystalline anisotropy that favors in many cases a perpendicular-to-the-axis easy magnetization axis for the hcp equilibrium phase [13–15]. Bulk hcp cobalt presents crystalline anisotropy constant $K_1 = 4.5 \times 10^6$ erg/cm^3 at room temperature. Such perpendicular-to-the-axis anisotropy nearly balances the shape anisotropy contribution, $K_s = 6.35 \times 10^6$ erg/cm^3 [16]. The competition between both contributions determines the easy axis direction and the magnetization reversal process.

The study of the angular dependence of coercivity allows us to obtain interesting information about the dominant mechanism that is followed by the reversing magnetization that could be either coherent rotational mode or magnetization curling [17]. For example, Rheem et al. have reported this angular dependence of coercivity in CoNi nanowires, where the content of Ni is higher than the Co one [18] and attributed to curling mode for the magnetization reversal in the considered samples. Also Vivas et al. have discussed the problem of the magnetic anisotropy in CoNi nanowires, but in their case the samples used had one fixed diameter and also presented Co and Ni and segregated phases, as seen by XRD [19].

In this paper, we investigate the effect of different nanowire aspect ratios on the magnetic properties of $Co_{50}Ni_{50}$ and $Co_{75}Ni_{25}$ arrays electrodeposited into the porous of an anodic alumina membranes (AAMs) used as templates. We found that the actual mode of magnetization reversal is influenced by the nanowires diameter, which actually determine the anisotropy strength and the magnetization easy axis orientation.

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2. Experimental procedures

The fabrication method is based on the two-step anodization process [20] where we have used sulphuric acid solution, at 2 °C, with 25 V of anodization potential. Under these conditions, 2.5 μm thick AAM have been prepared with self-assembled pores characterized by 25 nm in diameter and 65 nm pore-to-pore distances in a hexagonal arrangement. Subsequently, we have widened the pores diameters by controlled chemical etching using a solution of H_3PO_4 (5 wt%) with different exposure times at 35 °C. The final diameter of pores is thus 25, 35 and 45 nm. Notice that after this chemical etching the pore-to-pore distance remains constant for all samples.

Such AAM have been used as templates for electrodeposition [21,22] of $Co_{50}Ni_{50}$ and $Co_{75}Ni_{25}$ nanowires arrays. They have been fabricated by filling up the pores using pulsed electrodeposition from two distinct solutions as given in Table 1. The average length of nanowires is evaluated to be 2.5 μm from the duration of electroplating (average growth rate=5 μm/h) for which we obtain length to diameter aspect ratio of 100, 71.4 and 55.5 corresponding to 25, 35 and 45 nm diameters, respectively. During this process, the electrolyte was kept at constant temperature of 65 °C for both solutions to avoid precipitations of Co salts. Both electrolytes were prepared to match pH=4.

3. Results and discussion

Fig. 1 shows SEM images of electrodeposited CoNi nanowires into an AAM where the hexagonal well-ordered periodicity (65 nm) is observed in both samples. Also, the figures show that the pulsed electrodepositions successfully fill the AAM pores after 30 min of electroplating. Brighter spots seen in this figure represent the CoNi nanowires contrast and the darker areas are the AAM pores where the electrodeposition process was not able to fill them completely. Nevertheless, the average nanowires length is about the expected 2.5 μm.

Fig. 2 shows the XRD pattern for both compositions that were measured using the incident Cu K_α line (1.54 Å). Fig. 2 (a and b) depicted on top (blue line) show the expected relative intensities lines corresponding to (a) $Co_{75}Ni_{25}$ and (b) $Co_{50}Ni_{50}$ XRD patterns, which are related to CoNi alloys. At the lower part, experimental XRD patterns are shown for each sample, (c) $Co_{75}Ni_{25}$ and (d) $Co_{50}Ni_{50}$. From the observed peaks in the XRD patterns, we can confirm the composition of both CoNi alloys. The XRD data show some textured growth driven by the electrodeposition method and indicate that some of the peaks, at specific crystallographic directions, do not present a significant intensity over the measured patterns. Such textured growth will affect the magnetic properties as discussed ahead. Also, the constant temperature of 65 °C has ensured the deposition of CoNi alloys instead of Co and Ni segregated phases.

Table 1
Solutions for electrodeposition of CoNi alloys.

Electrolyte composition (g/l)		
Salts	$Co_{50}Ni_{50}$ (g)	$Co_{75}Ni_{25}$ (g)
$CoSO_4 \cdot 7H_2O$	30	150
$NiSO_4 \cdot 7H_2O$	300	150
$CoCl_2 \cdot 7H_2O$	0	22.5
$NiCl_2 \cdot 7H_2O$	50	22.5
H_3BO_3	30	45

Magnetic measurements were performed in a Vibrating Sample Magnetometer (VSM) under a maximum applied field of 18 kOe. Particularly, hysteresis loops and their main parameters (i.e., coercivity and remanence) were determined as a function of the angle between applied field and the nanowires orientation. Fig. 3 shows the angular dependence of coercivity and reduced remanence, where 0° means the magnetic field applied parallel to nanowires and 90° perpendicular (in-plane orientation, considering the AAM surface) to them.

Different behavior was observed depending on the diameter (see data set presented with different symbols in Fig. 3) and composition of the nanowires. Firstly, we observe that the highest coercivity value is often reached when the applied magnetic field is parallel to the nanowires axis. It is remarkable that in some specific samples ($Co_{75}Ni_{25}$ and $Co_{50}Ni_{50}$ nanowires with 25 nm diameter) the coercivity barely changes respect to the applied field orientation. Such behavior can be correlated to a transition of reversal mechanisms, from coherent rotation to curling [23]. For a better understanding, the reversal mode is defined by the competition between the demagnetization and exchange energies. In other words, increasing the aspect ratio the curling mode is favorable whereas decreasing it the coherent rotation is likely to happen. A critical diameter (cm) can be estimated when the magnetization easy axis is aligned to the applied field defined by [24].

$$r_c = 2q\left(\frac{2}{N_a}\right)^{1/2}\frac{A^{1/2}}{M_s}, \tag{1}$$

where q is related to the aspect ratio of a prolate spheroid (1.8412 for a cylinder), N_a is the demagnetization factor (2π for a cylinder), A is the exchange stiffness constant (erg/cm) and M_S is the saturation magnetization (emu/cm^3). Taking into account all these variables we were able to estimate these critical diameters for each composition, which are 27.2 nm ($Co_{75}Ni_{25}$) and 31.3 nm ($Co_{50}Ni_{50}$). Looking to the estimation our explanation is that for diameter below to the critical diameter value the curling mode should be expected whereas above such value is likely to be coherent rotation mode.

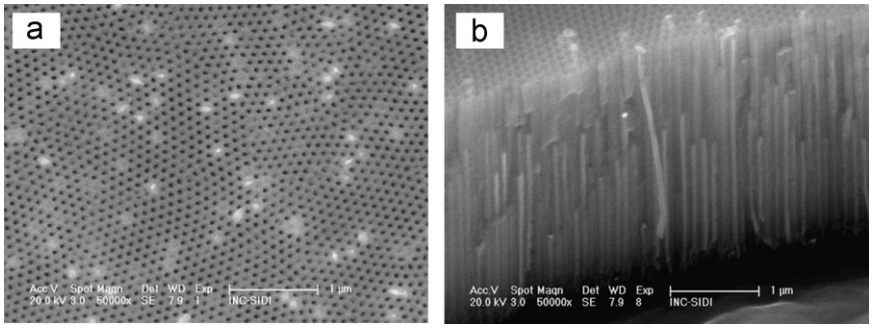

Fig. 1. SEM images of CoNi nanowire arrays with 25 nm of diameter and 65 nm of pore-to-pore distance.

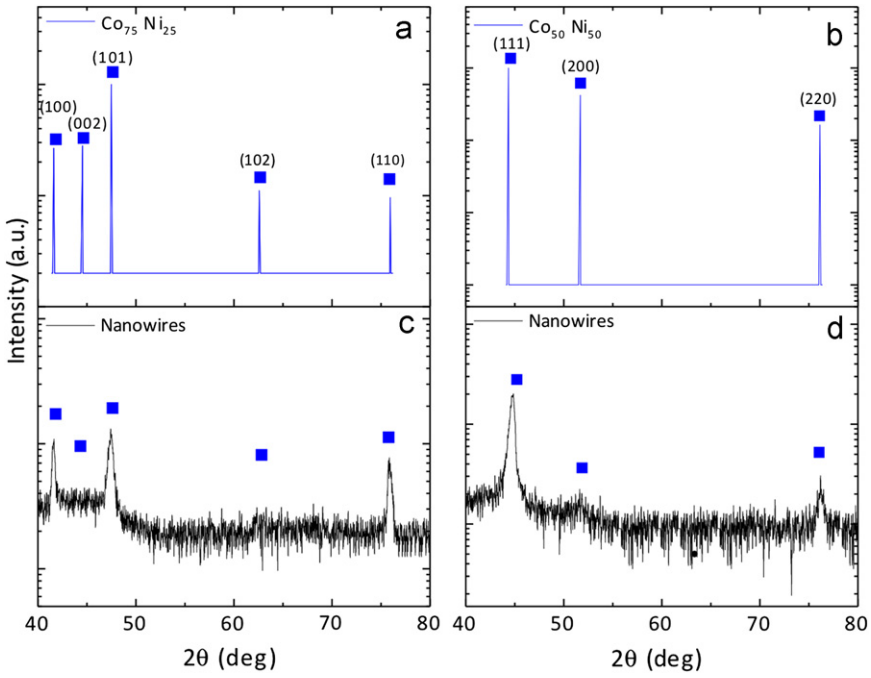

Fig. 2. (a and b) Expected and (c and d) measured XRD patterns for $Co_{75}Ni_{25}$ and $Co_{50}Ni_{50}$ nanowires. Both nanowire samples have 25 nm diameter (aspect ratio = 100).

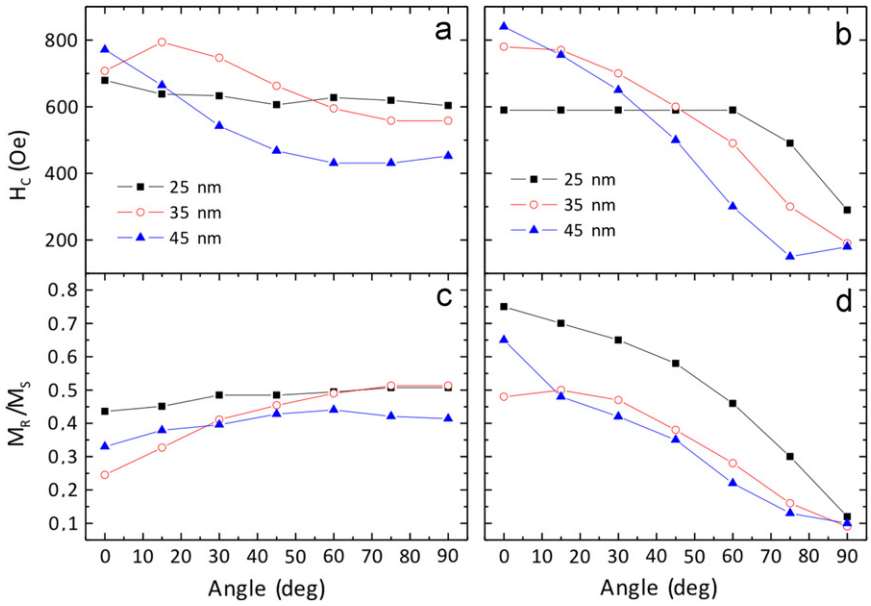

Fig. 3. (a and b) Coercivity and (c and d) reduced remanence variation with applied magnetic field angle for the samples $Co_{75}Ni_{25}$ (a and c) and $Co_{50}Ni_{50}$ (b and d).

For the majority nanowires sets the reversal mechanism corresponds to a coherent rotation mechanism, i.e., for diameter over 30 nm both CoNi alloys show a reversal mechanism dominated by coherent rotations. The curling mode is only expected in nanowires that present 25 nm diameters.

Assuming an axial magnetization easy axis, curling mode reversal process is characterized by an increase of coercivity with angle, while the opposite holds for coherent rotation [25]. On the other hand, curling is expected for smaller diameters (i.e., higher aspect ratio) while coherent rotation holds for larger diameters (i.e., reduced aspect ratio). In the present case, for $Co_{75}Ni_{25}$ nanowires a nearly balanced angular dependence is observed indicating apparently a compensation of anisotropies with axial and transverse easy axis similarly to the case of pure Co nanowires. Similar result is obtained for $Co_{50}Ni_{50}$ nanowires with small diameter in a wide angular range, while in the case of nanowires with highest diameter (i.e., smaller aspect ratio) the reversal mode resembles that of coherent rotation as expected.

Fig. 3 (c and d) show the evolution of the reduced remanence with the applied field angle. For $Co_{75}Ni_{25}$ nanowires, the reduced remanence shows a modest increase on its value when increasing the applied field angle, indicating a growth in strength of transverse magnetic anisotropy. This can be ascribed to the important hcp crystalline contribution having the *c*-axis nearly transversely oriented [13]. In summary, only 25% of Ni content is not able to reduce drastically the contribution of magnetocrystalline anisotropy. In the case of $Co_{50}Ni_{50}$ nanowires, the easy axis is clearly identified and pointing into the axial orientation. That is also connected with the fcc crystalline structure of $Co_{50}Ni_{50}$ nanowires that reduces the magnetocrystalline anisotropy. It

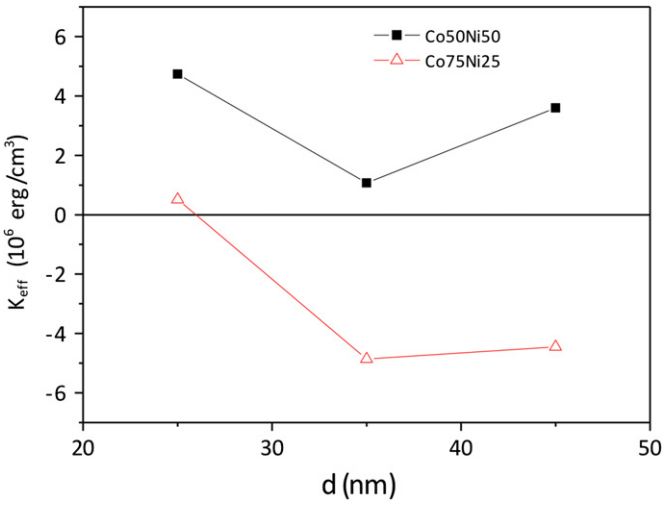

Fig. 4. Evolution of the effective anisotropy constant with the diameter.

allows us to conclude that, at least, 50% Ni in the nanowire is enough to determine a dominant axial anisotropy.

Quantitative evaluation of the effective anisotropy constant, K_{eff}, can be achieved from the experimental hysteresis loops as a difference between the magnetic fields necessary to saturate the sample in parallel and perpendicular directions, which can be expressed as [26].

$$K_{eff} = 2\pi M_S(H^{\perp} - H^{//}), \quad (2)$$

where M_S is the saturation magnetization, $H^{\perp}$ and $H^{//}$ denote the saturation fields along perpendicular and parallel orientations, respectively. Fig. 4 shows the variation of K_{eff} as a function of pore diameter. In the case of $Co_{75}Ni_{25}$, the nanowire array with smaller diameter presents slightly positive values of K_{eff}, meaning a magnetization easy axis parallel to the nanowires. However, it is important to observe that K_{eff} for $Co_{75}Ni_{25}$ is always more negative than for $Co_{50}Ni_{50}$. The change of sign of K_{eff}, denotes the modification of easy magnetization direction from axial to perpendicular to the nanowires. It is important to note that this is only due to the balance between the shape and magnetocrystalline anisotropies.

Finally, note that the effective anisotropy for the $Co_{50}Ni_{50}$ is always positive, indicating that for this sample the shape anisotropy is dominant and then, the magnetization easy axis is in the axial direction.

4. Conclusions

We have investigated the influence of the geometric parameters and composition in the magnetic behavior of CoNi nanowires. XRD patterns show two different crystallographic symmetries (hcp and fcc) regarding the composition of the nanowires. $Co_{75}Ni_{25}$ nanowires present hcp symmetry, that give rise to a competition between shape and magnetocrystalline anisotropies, which determines the direction of the easy magnetization axis. For $Co_{50}Ni_{50}$, with fcc symmetry, the shape anisotropy is the most important one. Moreover, the analysis of the K_{eff} gives us information respect to the easy axis modification that is complete dependent on the diameter size and composition of samples.

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