Bi-magnetic microwires: a novel family of materials with controlled magnetic behavior

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Abstract

A novel technique involving combined sputtering and electroplating procedures has been recently developed to deposit metallic (magnetic or not) nano and microlayer tubes onto glass-coated amorphous magnetic microwires to enable the tailoring of their magnetic behavior. Here, after introducing the general aspects of that technique, we present the latest results on a new family of two-phase magnetic samples: bi-magnetic multilayer microwires. They consist of a magnetically soft nucleus (typically a Fe or Co base amorphous microwire, coated by Pyrex layer) onto which a 30 nm thick Au layer is first sputtered followed by the electroplating of a harder microlayer, namely $Co_xNi_{(1-x)}$ layer, with x controlled by the current density during electrodeposition whose micrometric thickness is also controlled by plating time. The hysteresis loops present a two-step reversal process typical of two-phase magnetic material. The magnetization reversal of the soft nucleus and the harder layer takes place at around 1 Oe and up to about 200 Oe, respectively. The presence of sputtered and electroplated layers induces significant stresses in the soft magnetic nucleus that modify its magnetization easy axis. This technique allowing us the tailoring of the magnetic behavior of multilayer magnetic microwires opens new possibilities for applying these novel materials as sensing elements in various devices.

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1. Magnetic microwires: the state of the art

Magnetic microwires can be considered as one of the families of particular interest for research in the area of technical magnetism. First of all their cylindrical symmetry converts them into suitable materials for given technological applications (e.g., studies on technical problems with cylindrical symmetry, local field sensing, axial magnetic or electrical transport, etc.). To this geometry characteristic determining a strong longitudinal magnetic shape anisotropy, one should add the magnetic properties that derive from composition and structure giving rise to crystalline and magnetoelastic anisotropies, respectively. While polycrystalline wires exhibit let us say conventional properties, in the last decade a number of studies were reported on a couple of families of magnetic microwires with amorphous structure prepared by rapid solidification methods, namely, in rotating water [1] or by quenching and drawing technique [2]. These microwires, amorphous in nature,

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lack magnetocrystalline anisotropy but undergo strong mechanical stresses frozen-in during the quenching fabrication process. Particularly, the quenching and drawing technique allows one to fabricate composite magnetic microwires consisting of a metallic amorphous nucleus, a few microns in diameter, covered by micrometric Pyrex-like insulating coating. Some review papers have been reported on these materials [3,4], but let us remember here an important point: the cover confers very outstanding properties for electrical insulation and corrosion protection, and also induces additional stresses in the nucleus. These additional stresses firstly depend on the metallic to total diameter ratio (obviously the thicker the coating, the stronger the stresses [5]). But they also change with temperature as they rise from the different thermal expansion coefficients of nucleus and coating, as it has been recently confirmed and analyzed [6]. The total stresses couple with magnetostriction, determined by the alloy composition, to result in a strong magnetoelastic anisotropy. Finally, this magnetoelastic anisotropy together with shape anisotropy determines the magnetic behavior of the microwire. In the case of Fe-based microwires with positive magnetostriction, its nearly single-domain structure with longitudinal easy axis determines a magnetization process by depinning and propagation of a single wall resulting in a squared hysteresis loop. Negative magnetostriction Co-base microwires exhibit a circumferential transverse easy axis and their nearly non-hysteretic loop is characterized by nearly constant permeability practically until approaching magnetic saturation. Finally, non-magnetostrictive CoFe-base microwires exhibit ultralarge initial permeability with very reduced coercivity, and they are well known to exhibit giant magnetoimpedance effect [7].

Following previous studies concerning the role of the coating, a new family of composite microwires has been recently reported [8]. The main idea in that work was to introduce novel multilayered microwires each layer conferring a specific magnetic contribution, either by their own magnetic character or just through the mechanical stresses induced in the nucleus of the multicomposite microwire. In fact, electroplating of a magnetic CoP microlayer onto Cu microwire was previously introduced to prepare bi-layer microwires [9]. But in the case of taking the glass-coated microwires as starting material a problem arose from the difficulty to deposite a new layer due to the insulating character of the coating [10]. A solution was found in sputtering a tiny nanolayer onto the Pyrex cover that would subsequently serve as a substrate electrode where an additional layer whose thickness and composition were further controlled was electrodeposited. This final metallic electroplated layer can either have or not have a magnetic character [11]. And when magnetic, it could be magnetically harder or softer than the precursor microwire so as to, open a new family of magnetic materials with particular geometry and magnetic single or multi-magnetic character, and consequently novel applications. Here, we will restrict our disussion only to the case of multilayer microwires with one or two magnetic phases.

2. Fabrication of multilayer microwires

Glass-coated amorphous microwires have been produced in the laboratory by the quenching and drawing technique [2-3,12]. This is based on direct casting from the melt, and a few grams of the desired master alloy is placed into a Pyrex-like glass tube inside a HF inductor heater. The alloy and the tube are heated up to the metal melting point so as to soften the glass material adjacent to the melting alloy. A glass capillary is then drawn from the soft glass portion and wound on a rotating coil. At appropriate drawing conditions, the molten metal fills the glass capillary and so a microwire is formed with the metal core completely coated by a glass shell.

This technique allows the fabrication of continuous microwires, typically a km long. Typical metallic nucleus diameter is in the range 1–30 μm, while thickness of the glass coating is between 2 and 15 μm. With respect to the metallic composition, besides pure metallic elements, e.g., Cu, alloys of magnetic metals Fe, Ni and Co are employed together with metalloids such as Si, C, or B that enable the amorphicity of the samples.

For this review manuscript we have selected results on microwires with alloy compositions of typical magnetic behavior: Fe-base alloys with positive magnetostriction, $\lambda = 3 \times 10^{-5}$, and CoFe-base alloys with vanishing magnetostriction, $\lambda = 0.2 \times 10^{-6}$. Pyrex-coated Cu microwire has also been produced to study the properties of electroplated magnetic layers.

The process of fabrication of multilayer microwires consists first in the sputtering of a tiny metallic nanolayer of elements such as Ag, Au or Ti on the Pyrex surface. Full details of this sputtering procedure can be found elsewhere [8]. The thickness of the sputtered layer (up to 700 nm) can be carefully controlled by checking the technical parameters of sputtering. For the cases of subsequent electroplating, the sputtered layer thickness was fixed at 30 nm, its uniformity and homogeneity being verified by nano indentation with a tolerance in the order of 10%.

In order to proceed with electrodeposition of an additional layer, a chamber was specially designed for this purpose in our laboratory. This cell consists of a closed-bottom Pyrex cylinder 2 cm in diameter inside which a tubular platinum electrode net is placed. The sputter-coated microwire was vertically placed at the center of the cell, maintained straight by an inert platinum weight hanging on the wire and electrically isolated from the sputtered coat. Afterwards, the cell was filled with a suitable electrolytic bath selected according to the metal to be electrodeposited. Electrodeposition of various metallic non-magnetic, e.g., Ag, and magnetic, pure elements, Ni, and alloys, CoNi, have been performed using the above-described cell. The thickness of electroplated layers can be tailored by isochronal electroplating at increasing current density or, alternatively, by increasing the electroplating time at constant current density. Fig. 1a shows the thickness of the electrodeposited CoNi layer as a function of electroplating time at constant current and of the current density for 15 min. The bath used to deposit the CoNi alloy is composed of $NiCl_2$ (45 g/l), $NiSO_4$ (300 g/l), H_3BO_3 (45 g/l), $CoCl_2$ (45 g/l), $CoSO_4$ (300 g/l). A nearly linear dependence on both parameters is found. Fig. 1b shows the linear correlation between 15 min isochronal plating and $Co_{(100-x)}Ni_x$ alloy composition checked by glow discharge optical emission spectroscopy (GDOES) technique. The composition is nearly non-dependent on plating time. All the magnetic measurements were done in a VSM magnetometer at room temperature.

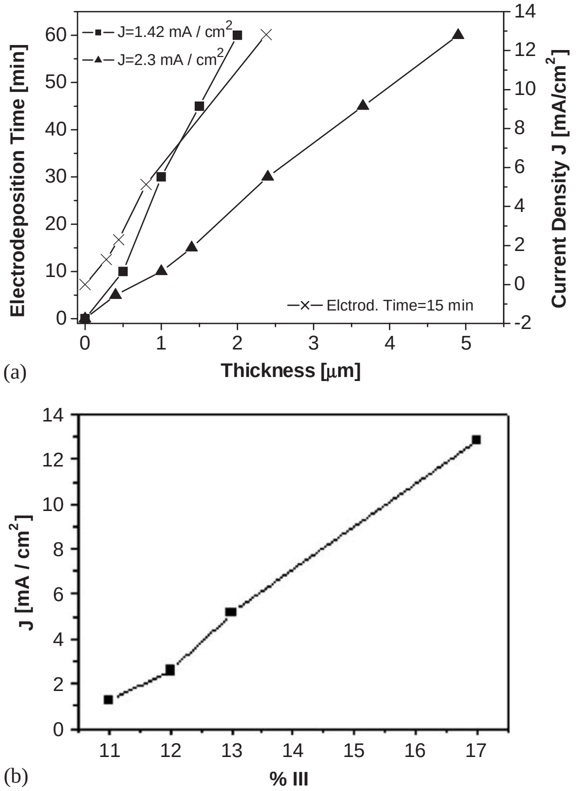

Fig. 1. (a) The thickness of electroplated CoNi layer as a function of electrodeposition time and current density. (b) Dependence of alloy composition $Co_xNi_{(100-x)}$ with current density for isochronal electroplating.

3. Single magnetic-phase multilayer microwires

Ti and Au thin layers have been sputtered on the surfaces of the glass-coated microwires as previously described. In spite of their nanometric thickness, sputtered layers by themselves can induce very noticeable changes in the magnetic behavior of the microwires. Fig. 2 shows the results for a non-magnetostrictive $(CoFeNi)_{75}Si_{15}B_{10}$ glass-coated microwire before and after sputtering a 100 nm thick Ti layer. The as-prepared microwire exhibits a loop denoting a transverse magnetic anisotropy with anisotropy field, H_K, of around 12 Oe. As introduced previously, this anisotropy comes from the coupling between magnetostriction, λ_s, and the internal stresses, σ, frozen-in during the quenching fabrication. But, after sputtering the Ti nanolayer, a square shaped bi-stable hysteresis loop is observed denoting now the existence of a single domain structure with longitudinal easy magnetisation direction. Consequently, the Ti layer induces quite a noticeable longitudinal magnetic anisotropy (estimated to be 1.0 kJ/m^3). But the most important point is that the easy magnetization direction qualitative changes from transverse to longitudinal direction. Even if not mentioned, a sputtering process of a 30 nm thick Au layer has been performed in all the microwires.

In a similar way, the electrodeposition of a metallic non-magnetic layer onto the sputtered nanolayer gives rise to additional significant changes in the hysteresis loops. As deduced from loops in Fig. 3, now the sputtered-Au layer enhances the longitudinal magnetic anisotropy, while the Ag-plated microlayer induces a change in the magnetization easy axis towards a transverse direction. In both cases, changes in the hysteresis loops and of the magnetization easy axes should be ascribed to the additional stresses induced in

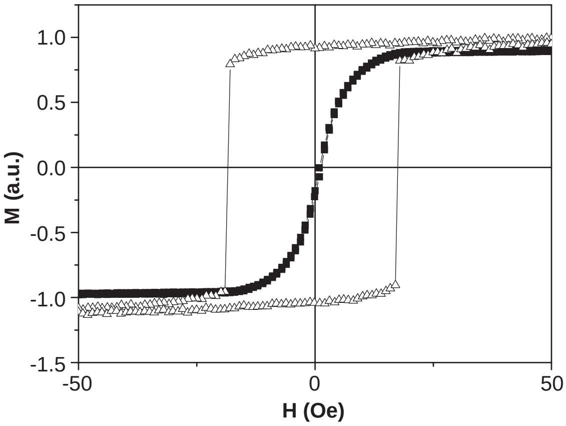

Fig. 2. Hysteresis loops of a $(CoFeNi)_{75}B_{15}Si_{10}$ glass-coated microwire (8.0 and 30.0 µm, metallic nucleus and total diameters, respectively) before (■) and after (△) sputtering a 100 nm thick Ti nanolayer.

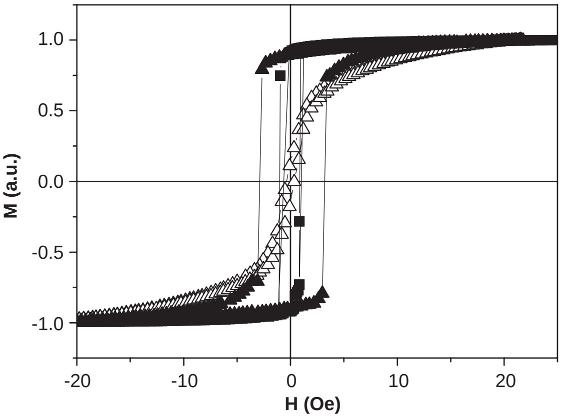

Fig. 3. Hysteresis loops of a $Fe_{72.5}Si_{12.5}B_{15}$ glass-coated microwire (21.4 and 34.0 μm, metallic nucleus and total diameters, respectively), in its as-prepared state (■), after sputtering a 30 nm thick Au nanolayer (▲), and after a subsequent electroplating of a 14 μm thick Ag microlayer (△).

the magnetic nucleus by the sputtered and electroplated layers.

4. Bi-magnetic multilayer microwires

The most interesting possibility is the electroplating of a magnetic microlayer with different hardness in comparison with the soft nucleus. Here, we introduce results for the case of a relatively harder outer CoNi microlayer. Two alloys have been selected as starting glass-coated microwires: FeSiB ($Fe_{74}B_{10}Si_{11}C_5$) alloy exhibiting positive magnetostriction, $\lambda = 32 \times 10^{-6}$, and CoFe ($Co_{67.06}Fe_{3.84}Ni_{1.44}B_{11.53}Si_{14.47}Mo_{1.66}$) alloy with very reduced magnetostriction, $\lambda = 0.2 \times 10^{-6}$. Two series of electroplating experiments have been performed: (i) at constant current density, $j = 2.30\,\mathrm{mA/cm^2}$, for a range of increasing plating time (up to 60 min), and (ii) isochronal (15 min) plating at different current density (up to 12 mA/cm^2). Summarized results can be observed in Fig. 4 for magnetostrictive and non-magnetostrictive glass-coated microwires. Most important characteristics in both series of results is that hysteresis loops correspond to typical two-phase magnetic materials composed an ultrasoft phase with effective coercivity, H_{c1}, and a medium-hard phase with large Barkhausen jumps occuring at fields, H_{c2}, of the order up to 200 Oe.

The soft phase, ascribed to the inner microwire, contributes with a fixed magnetic moment, while the contribution of the harder CoNi shell increases, as expected, with electroplating time and current. Coercivity of the nucleus, H_{c1}, is of the order of 1–3 Oe for as-prepared glass-coated microwires, and increases notably upon electroplating the CoNi microlayer. Also, the low-field permeability decreases indicating as in previous cases that transverse anisotropy is induced by the plated layer (see Fig. 5).

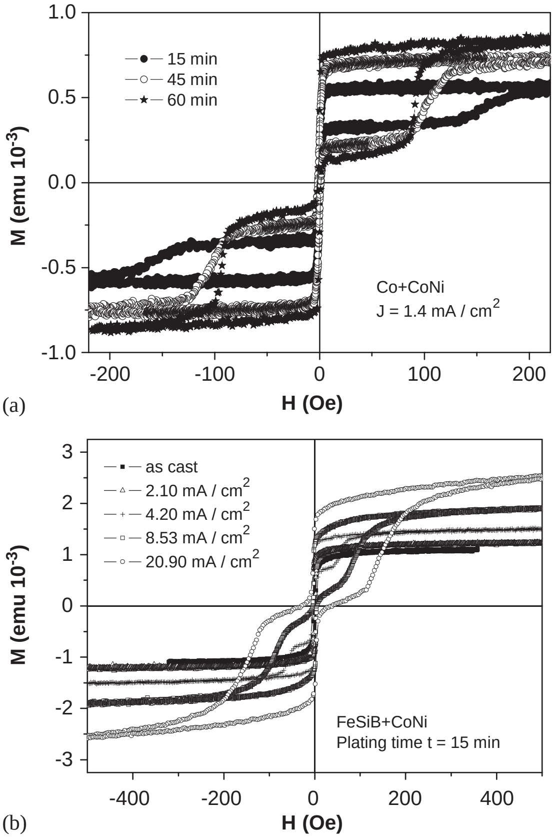

Fig. 4. (a) Hysteresis loops of a non-magnetostrictive CoFe-base glass-coated microwire for a range of CoNi layers with increasing plating time for given density of current ($j = 1.4\,\mathrm{mA/cm^2}$). (b) Loops of a magnetostrictive Fe base glass-coated microwire for a range of CoNi layers with increasing plating current density for given plating time of 15 min.

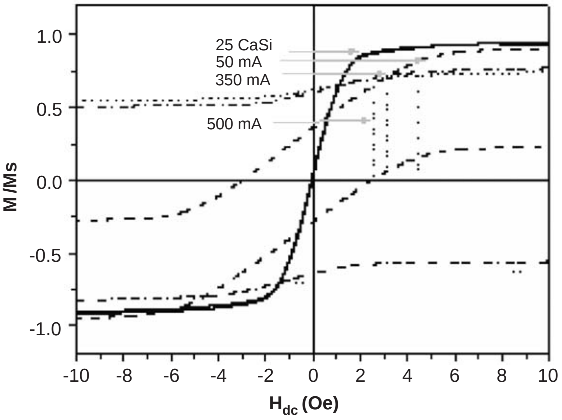

Fig. 5. Low-field region of loops shown in Fig. 5a.

Fig. 6 shows the dependence of coercive fields H_{c1} and H_{c2} as a function of the electroplating parameters. As observed in Fig. 6a, H_{c2} increases monotonically with the current density. The magnetization reversals occurring at high fields are not so abrupt as for the soft inner microwire. According to Fig. 6a, the increase in coercivity H_{c2} with current density must be connected not only with an increase in the CoNi microlayer thickness but also with the modification of the magnetic hardness induced by the change of composition (increase of Ni content). A different behavior is observed in Fig. 6b, where after an initial increase in H_{c2} at low current density, it progressively decreases for longer plating times. This reduction should be ascribed to the increased thickness of the CoNi microlayer as its composition remains nearly constant.

Additional measurements on the giant magnetoimpedance, GMI, effect (1 mA AC current at 1 MHz) have been performed in bi-magnetic multilayers whose nucleus is composed of non-magnetostrictive material ($Co_{67.06}Fe_{3.84}Ni_{1.44}B_{11.53}Si_{14.47}Mo_{1.66}$) after plating a CoNi layer at various current densities. As observed in Fig. 7, a four-peak response appears instead of the common two-peaks behavior. Peaks at the larger field seem to be connected with the transverse anisotropy induced by the CoNi microlayer, while the two peaks at the lower field should be connected with irreversibilities in the magnetization process. Even though the origin of this behavior must be rigorously justified in further studies, we can state that a new circumferential element has been induced by the outer CoNi layer, and that sources such as stresses and magnetic interactions are being considered to better understand the observed response including its reduced [13] GMI amplitude.

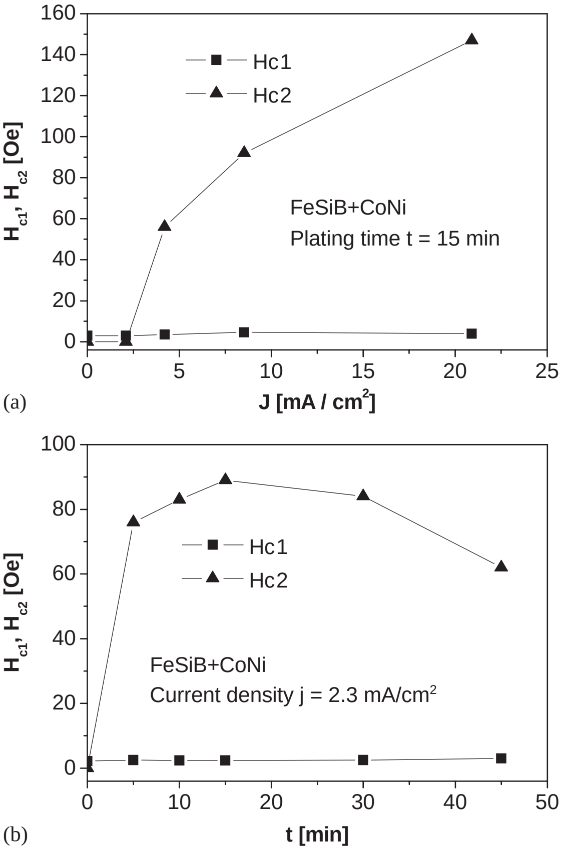

Fig. 6. Dependence of fields H_{c1} and H_{c2} on parameters of electroplating: (a) electrodeposition keeping the plating time constant in 15 min and varying the current density; (b) keeping the deposition current density constant at 2.3 mA/cm^2 and varying the deposition time.

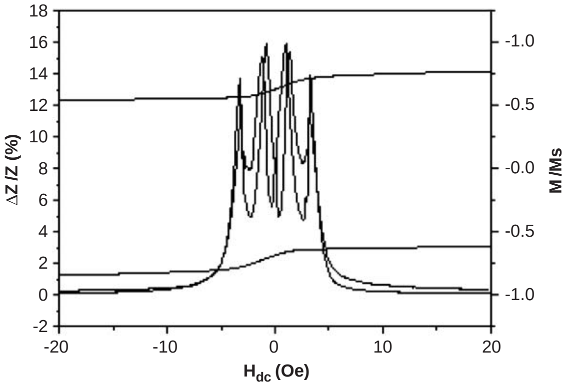

Fig. 7. GMI response of a Co-base microwire coated with a 500 mA CoNi layer. The low-field hysteresis loop is also shown.

Finally, to have a deeper information on the magnetic role played by the electroplated CoNi microlayer, additional experiments have been done by plating CoNi layers onto glass-coated Cu microwires. Fig. 8 shows an

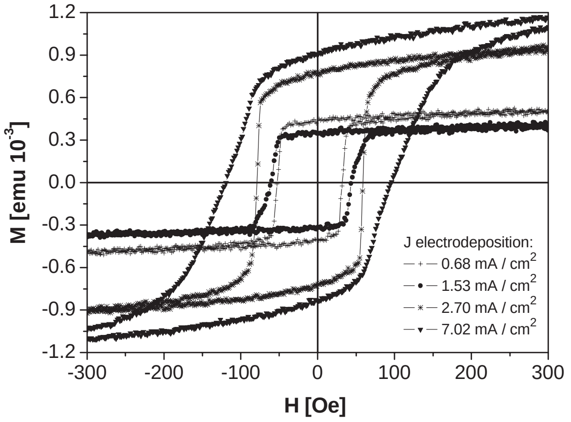

Fig. 8. Hysteresis loops of the CoNi microlayers electroplated onto Cu glass-coated microwire for a range of plating current density during 15 min.

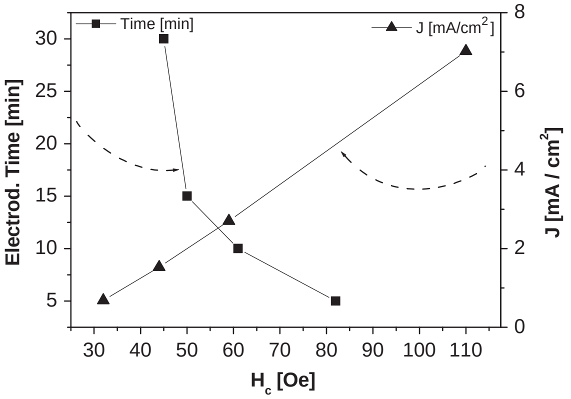

Fig. 9. Hystereris loops of CoFe-base microwires coated with CoNi in the low-field region. Electrodepostion current density appears as a parameter.

example corresponding to the case of isochronal electroplating under different current densities. Now, only one large Barkhausen jump is observed and the saturation magnetic moment increases with current density or equivalently with thickness of the microlayer.

Coercivity increases with current density indicating an increasing magnetic hardening of the electroplated microlayer, which is consistent with the results of Fig. 4a. But, again, a different result is obtained for the case of electroplating under constant current density for increasing plating time. Fig. 9 summarizes the dependence of coercivity on current density and plating time from results in Fig. 8. While a linear increase in current density is observed, coercivity is nearly proportional to the inverse electroplating time.

5. Conclusions

A novel method consisting of combined sputtering and electroplating techniques has been developed for preparing multilayer single and bi-magnetic microwires by sputtering and electroplating techniques. The magnetic character can be tailored by a suitable choice of the magnetostrictive amorphous metallic nucleus, together with the specific stresses induced by the deposited layers. In this way, the preparation of multilayer microwires characterized either by square-shaped hysteresis loops (typical of magnetically bi-stable microwires with longitudinal easy axes), or by nearly non-hysteretic loops (for those microwires with circumferential or radial magnetization easy axes), can be achieved.

Soft/hard bi-magnetic behavior can be tailored by proper selection of inner microwire and electroplated magnetic layer. Here we have introduced soft magnetic amorphous nucleus and medium-hard CoNi outer layer, but a number of other materials can be considered. Thickness and composition of the electroplated layer determine the relative weight of the harder phase as well as its coercivity. Both are finally determined by the electroplating time and current density. The thickness increases with time and current density, while the latter additionally induces a notable change in the composition.

It is worth noting that huge differences in the hysteresis loops should be finally ascribed to the stresses induced by the sputtered and electroplated layers, although additionally magnetostatic interactions between magnetic layers are also to be considered.

The novelty of the method for preparing bi-magnetic multilayer microwires opens new opportunities to develop very promising magnetic materials that can be employed in different technological applications, and mainly as sensing elements in various devices (magnetic field and magnetoelastic sensors).

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