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Featured Letter

Magnetization curves of electrodeposited Ni, Fe and Co nanotubes

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ABSTRACT

The formation of ferromagnetic nanotubes (Ni, Fe, Co) and their structural and magnetic properties were investigated. Ferromagnetic behaviors were analyzed by means of magnetization measurements as a function of the applied magnetic field for different orientations. The coercive field values and remanence showed no the predominance of a specific reversal mode for magnetic moments, probably due to the imperfections in the real nanotubes if compared with the ideal conditions for theoretical predictions. For obtaining, the chemical electrodepositing using porous polycarbonate membranes as templates, with "average" pore diameter of 250 nm. A 100 nm gold layer was deposited on the opposite side of membrane, as a cathode and supporting base for nanotubes for the formation of nanotubes with diameter ranging from up to 300 nm.

1. Introduction

One-dimensional systems such as nanowires and nanotubes stand out [1–5]. Porous anodic alumina and track-etched polymer membranes are two of most used membranes [6,7]. The fabrication of nanotubes arrays, based on porous templates can be done by several techniques through the filling of pores with the desired material [8,9]. Among these, electro-deposition is a simple, efficient and low-cost technique [10]. Nanowires and nanotubes are attractive nanomaterials for electronic, optoelectronic and sensor applications [11–13]. The nanowires/nanotubes constituted by ferromagnetic materials have received considerable attention due to applications in high density magnetic recording [14–19]. Studies have shown the possibility to the formation by using a conductive layer of thickness less than the pore diameter, without membranes functionalizing [20,21]. Some papers reported the magnetic behavior of electrodeposited nanowires, specifically the magnetic anisotropy through coercivity and remanence [22,23]. Several methods were used for the fabrication of elongated nanoparticles [24–33]. Studies correlated interesting magnetic properties and the reduced dimensionality for nanotubes [34–39]. Progress using computer simulation and theoretical calculations permitted studying magnetic nanotubes to analyze their properties [35,40–45]. Even so, the doubts about the behavior of real systems are always the ones that will be used in technological applications. Theories are not always able to predict every detail in a real nanometer-scale structure. That is why the work, presents the synthesizing and investigation about magnetic properties of metallic nanotubes composed by Ni, Fe and Co.

2. Experiment

The porous membranes used were polycarbonate (PCT) (Millipore MERCK). The pore diameter specified by the manufacturer is on average 250 nm and the membrane thickness is 25 μm. The porosity of the membrane is 0.138 (13.8%) and pore density is 10^8 cm^{-2}. A gold layer was evaporated on one side of the membrane to serve as a cathode (work electrode) with a thickness of 100 nm. The electrolytic solutions were prepared with sulfates ($NiSO_4{\cdot}6H_2O$, $CoSO_4{\cdot}7H_2O$ and $FeSO_4{\cdot}5H_2O$) 0.4 M in aqueous solution. Boric acid 0.5 M was added and the pH = 3.5.

3. Results and discussions

Deposition was using an Ivium-Stat.XRe potentiostat, at room temperature. The dc electrodeposition was performed in the chrono-amperometric mode for reduction of Ni^{2+} (Co^{2+}) at −1.0 V and Fe^{2+} at −2.0 V. All metallic tubes grow along the pore walls of the membrane on the basis of Au layer [19,20]. Fig. 1a–c shows panoramic micrographs of the with nanotube structures, mean diameter of 265 nm. The diameter of the tubes varies between 235 and 300 nm. It is possible that an increase in the pore diameter of the polycarbonate membrane occurred during deposition.

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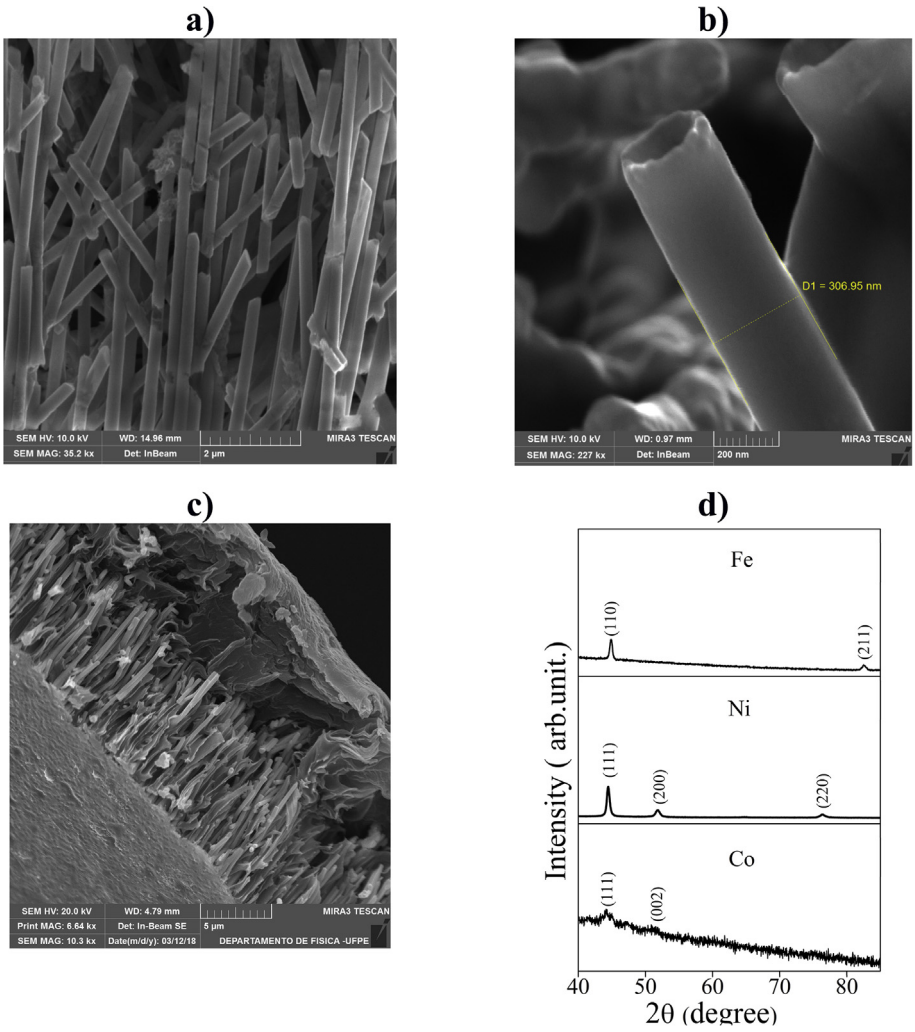

Fig. 1. SEM micrographs of Fe, Co and Ni nanotubes array. a) A close view of electrodeposited nanotubes. b) A nanotube with external diameter of 306 nm and showing the internal side. c) Tubes within the membrane showing that there is good relative parallel orientation therebetween with a typical offset originating from the membrane used as a template and having lengths ranging from 9 to 12 μm. d) X-ray diffraction data of Fe, Ni and Co nanotubes.

Initially the pore diameter varied between 223 and 268 nm with an average of 250 nm.

The formation of tubular nanostructure is demonstrated according to Fig. 1b. In figure is possible to verify in this tube the internal part with wall thickness around 38 nm and internal diameter of 267 nm. Fig. 1c and d show crystalline nanotubes having lengths ranging from 9 to 12 μm. The tubes are not quite parallel and that there is a deviation from the relative parallelism conditioned by the direction of the pores of the polycarbonate membrane. In the rest of the text we shall call the direction parallel to the tube perpendicular to the plane of the arrangement.

For magnetic characterization, measurements of the magnetization, M as a function of the magnetic field, H samples constituted by nanotubes (NT) inside the PCT membrane were performed. The field was applied perpendicular to the plane of the membrane (parallel to the tubes axis $H_{//}$) and parallel to the membrane (perpendicular to the nanotubes axis $H\perp$). We plot the reduced magnetization, M/M_S as a function of H, where M_S is the saturation magnetization. Fig. 2a–c presents the magnetization versus applied field for nanotubes of Ni, Fe and Co.

The initially behavior for all samples is a tendency to saturation for lower fields with parallel field [33,35,38]. For the Ni samples (Fig. 2a), the parallel reduced remanence ($m_r = M_r/M_S$) is $m_{r//} = 0.35$ and the perpendicular $m_r\perp = 0.27$. As reported in studies in the literature [33,35] the values of perpendicular remanence should be very small and smaller than that of parallel remanence. In the Co nanotubes (Fig. 2c) this behavior is similar with values much lower still, thus raising the question about the reasons that give rise to these differences. For nanotubes the anisotropy is strong due to dipolar effects [33]. As shown in Fig. 2a–c, the hysteresis loop is wide at the center for parallel and perpendicular external field. Insets represent XRD data showing crystalline nanotubes of Ni, Fe and Co, respectively. For the Fe nanotubes, the parallel coercivity is $H_{C//} = 84$ Oe and the perpendicular $H_C\perp = 115$ Oe. For the Ni nanotubes, the parallel coercivity is $H_{C//} = 146$ Oe and the perpendicular is $H_C\perp = 161$ Oe, larger than bulk nickel, $H_C = 0.7$ Oe. The increase in coercivity is associated with shape anisotropy (tubular geometry) and magneto-crystalline anisotropy of nanotubes. The interaction between the ferromagnetic surfaces may contribute to the mechanism of this phenomenology. Values in Fig. 2 are in correspondence with the reported for Ni nanotubes of 25 μm in length and 200 nm in diameter [19]. The coercive field values for Co nanotubes are $H_{c//} = 244$ Oe and $H_c\perp = 289$ Oe, larger than Ni, due to the strong magnetic anisotropy of cobalt. For the nickel and cobalt (Fig. 2a and c) it was expected that for perpendicular field narrow hysteresis, in low fields. It is possible that, morphology and defects of sample add pinning centers that directly affect behavior. For iron (Fig. 2b) it seems that there is a higher