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Preparation of Electrodeposited Cobalt Nanowires

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Nanostructured magnetic materials have great interest because of their applications in high-density magnetic information storage and for magnetic sensors. The electrodeposition of materials into porous alumina arrays is a suitable technique to produce nanomaterials, since highly ordered uniform nanomaterials can be obtained simply and cheaply. In this work, template-assisted Co nanowire arrays were prepared by electrodeposition into nanometer-sized pores of an alumite film using a two-electrode electrochemical cell. The Co nanowires were electrodeposited from a solution of 400 g/L of $CoSO_4.7H_2O$ and 40 g/L of H_3BO_3. The morphology of the samples was investigated by means of TEM and AFM. The structural characteristic of the samples was examined using XRD, EDX and FTIR, which confirm the cobalt nanowire formation.

Keywords: *electrodeposition*

1. Introduction

Recently there has been great interest in the synthesis and characterization of one-dimensional materials as nanotubes, nanobelts and nanowires. A variety of materials can be obtained in the form of nanowires with a diameter in the range of nm and lengths going up to several micra[1-4].

In order to produce the nanowires, both physical (thermal plasma and laser ablation) and chemical methods (hydrothermal and carbothermal reductions) have been employed[5,6].

In this work, we have used the template method (Figure 1) to prepare the cobalt nanowires.

Generally, the templates can be nanoscale channels in self-organized anodic alumina membranes (AAM) or polycarbonate membranes[1-3], whose pores can be filled by the metal obtained by electrochemical reduction. These obtained nanostructures can be used in interesting magnetic recording, electronic and electro-optical devices[1-3].

In this work, we have prepared the cobalt nanowires within alumina templates produced by two-step anodization. The morphology of the nanowires was investigated by Atomic Force Microscopy (AFM) and Transmission Electron Microscopy (TEM). X ray diffraction (XRD), Energy Dispersive X ray Spectroscopy (EDX) and Fourier Transform Infrared Spectroscopy (FTIR) were used to investigate the phase structure of the nanomaterials.

2. Materials and Methods

By optimization of the electrodeposition parameters (such as the solution concentration, electrolyte, pH, and the deposition potential/time) highly crystalline cobalt nanowires were obtained. The best condition was: 99.997% pure Al sheet (Vetec S.A.) was pretreated in a 5% NaOH solution at 60 °C for 60 seconds, neutralized in 1 M HNO_3 for 30 seconds, washed in purified Milli-Q water and etching in HNO_3. The electrolyte for anodization was 15% H_2SO_4[2-4].

Since aluminum oxide was slightly soluble in this electrolyte, the reaction product at the polished Al sheet anode was aluminum oxide, according to Equations 1 and 2:

$$\text{ANODE: } 2\,Al\,(s) + 3\,H_2O \rightarrow \alpha\text{-}Al_2O_3\,(s) + 6H^+\,(aq) + 6\,e^- \quad (1)$$

$$\text{CATHODE: } 6\,H^+(1\,M) + 6\,e^- \rightarrow 3\,H_2\,(g) \quad (2)$$

The polished Al sheet was anodized at 10 V for 10 minutes and the formed oxide film was dissolved in 1% H_3PO_4 at 60 °C for 20 minutes. The solution could completely dissolve the oxide film, but did not react with the Al substrate. The partial oxide dissolution in acid is described in accordance with Equation 3:

$$Al_2O_3\,(s) + 6\,H^+ \rightarrow 2\,Al^{3+}\,(aq) + 3\,H_2O \quad (3)$$

The Al sheet was then reanodized for 12 hours to create the desired long-range ordering. The oxide film was removed in 1% H_3PO_4 for 6 minutes and the Al sheet anodized again for 30 minutes.

After anodization, the Al sheet was cleaned in water. The pores were opened in 1% H_3PO_4 for 6 minutes and the anodic alumina membrane (AAM) was obtained.

A two-electrode electrochemical cell was used for cobalt deposition within the pores of the template membrane. Cobalt nanowires were grown at room temperature from a 400 g/L of $CoSO_4.7H_2O$ and 40 g/L of H_3BO_3 electrolyte (pH = 3.0 at 25 °C) at a constant potential of 1.20 V[7].

A portion of a partially dissolved AAM sample (dissolved for only 10 minutes) was mounted on aluminum supports, coated with a film of gold and submitted to EDX analysis.

Then, the alumite film was completely dissolved in 50 mL of 1.25 M NaOH solution, in order to free the cobalt particles from the AAM and obtain a very soluble aluminate, $Al(OH)_6^{3-}$, in accordance with Equation 4.

$$\alpha\text{-}Al_2O_3\,(s) + 3\,H_2O\,(l) + 6\,OH^-\,(aq) \rightarrow 2\,Al(OH)_6^{3-}\,(aq) \quad (4)$$

After complete dissolution, a drop was put on a silicon substrate and the morphologic measurements of the Co nanowire was performed using a Topometrix II® Atomic Force Microscopy, and Jeol 2000 FX transmission electron microscope.

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The crystallographic structure of electrodeposited nanowires was investigated by X ray diffraction analysis (XRD) using a Miniflex diffractometer with a dwell time of 1°/min, in the θ-2θ Bragg-Brentano geometry.

Fourier transform infrared Spectroscopy (FTIR) spectroscopy was carried out using a Nicolet Magna-IR 760 spectrometer. The analyses were performed in the IV reflectance mode in the 4000-400 cm^{-1} range, with a resolution of 4 cm^{-1} and accumulation of 32 scans.

3. Results and Discussion

The XRD pattern for the Co nanowires obtained in the pores of AAM is shown in Figure 2. The diffraction peaks of the XRD pattern correspond to the (111), (101) and (110) polycrystalline cobalt reflections and to the alumina reflections, respectively.

The nanostructure of cobalt nanowires is complicated and consist either of mostly hcp grains or fcc grains or a mixture of both[8].

After dissolving the AAM template in 1.25 M NaOH, the cobalt nanowire array was put on a silicon substrate and observed using AFM (Figure 3) and TEM (Figure 4). The diameter of the nanowire is about 200 nm, which is dependent on the pores of the anodic alumina template. The diameter of a nanowire is determined by the pore diameter and the length by the quantity of the electrodeposited material.

The aspect ratio of a shape is defined as the length of the major axis divided by the width of the minor axis. Thus, nanowires have aspect ratios greater than 20. According to Figure 3 and Figure 4, in this studied system the aspect ratio is about 100.

It is seen from the EDX spectrum, Figure 5, that the nanowires contain only cobalt and oxygen. The Al peaks are due to the support and the Au peaks to the gold film sputtered on the surface of the sample.

The alumina films were characterized using FTIR analysis. It was observed a band near 900-1000 cm^{-1} due to Al-O-Al stretching. The Co bands are marked in Figure 6 and can confirm the formation

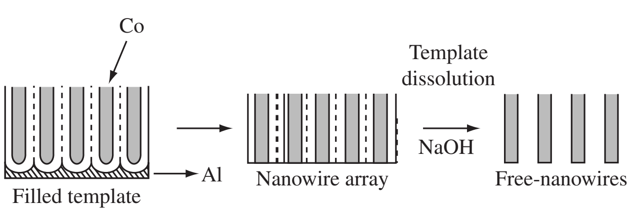

Figure 1. Template-method to obtain nanowires.

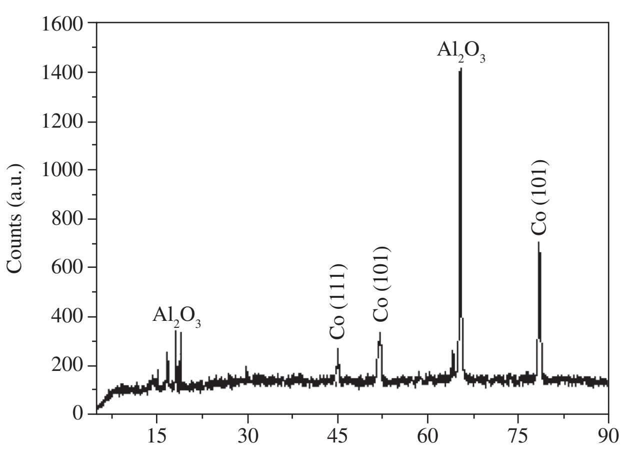

Figure 2. X ray diffraction profile of Co nanowire/AAM.

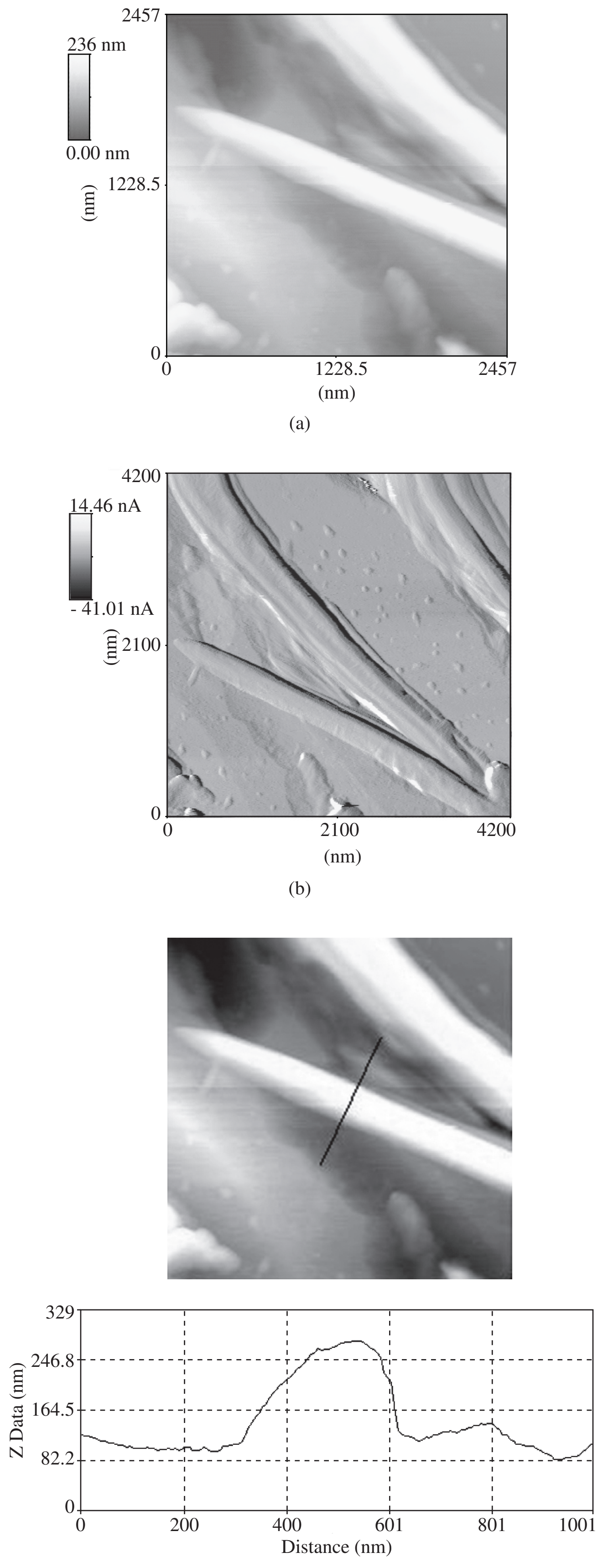

Figure 3. AFM micrographs of Co nanowires: a) Topographic; b) Phase Image; and c) profile along the indicate line.

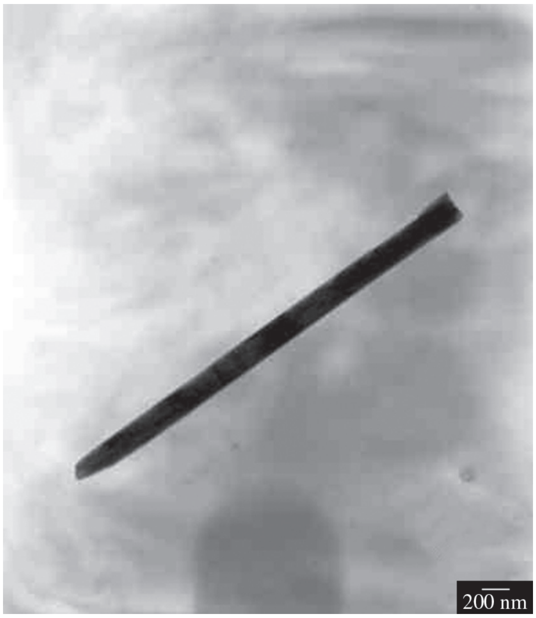

Figure 4. TEM micrograph of Co nanowires freed from the alumite film.

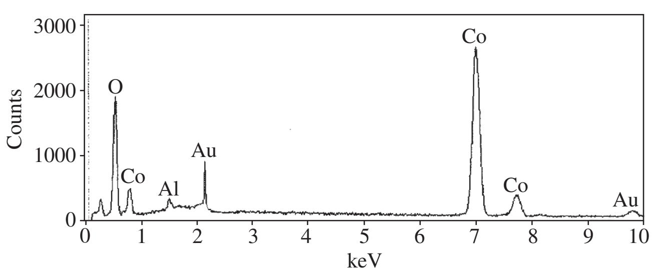

Figure 5. EDX spectra of Co nanowire.

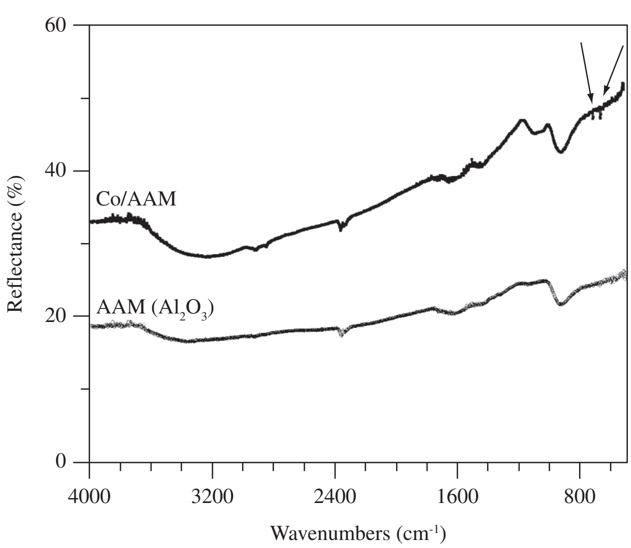

Figure 6. FTIR spectra of AAM and Co/AAM.

of cobalt nanowires into pores of the anodic alumina. FTIR spectra showed two peaks at 665 and 703 cm^{-1}, which are attributed to the presence of cobalt oxide in the sample.

Dorsey[9] has characterized anodic alumina films by FTIR and observed a similar behavior. The porous structure developed in the films was accompanied by a shift in Al-O-Al absorption band to 900-1000 cm^{-1} and an OH absorption (1300-1600 cm^{-1}).

4. Conclusions

Cobalt nanowires with diameter of about 200 nm were prepared by the electrodeposition method. Morphologic observations by AFM and TEM indicate that the nanowires are uniform in size and shape, which confirms that electrodeposition is a good procedure to make these 1-D nanostructures.

As a continuation of the present work, we intend to obtain AAMs with low diameters (< 200 nm) with controlled aspect ratio, and determine the magnetic properties of the electrodeposited nanowires (magnetic anisotropy, hysteresis behavior, coercivity, saturation magnetization, ferromagnetic resonance). The intention is obtain small diameters nanowires, which high aspect ratios, and consequently a rich variety of novel properties, including perpendicular magnetic anisotropy, enhanced coercivity, and giant magnetoresistance GMR.

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