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The structure, composition and magnetic properties of direct-plated fcc Co–Pt-based tubular nanostructures

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ABSTRACT

Co–Pt-based tubular nanostructures were prepared by direct plating into track-etched polycarbonate templates from a single electrolyte containing a Pt-p-salt and Co-sulphamate. These tubular nanostructures, with a diameter of 200 nm and lengths up to 5 μm, were obtained with potentiostatic depositions at potentials of −1.9 V to −2.5 V, measured against a Ag/AgCl electrode for 60 min. A detailed TEM/EDS analysis showed that the tubes consisted of randomly orientated nanocrystals of an FCC Co–Pt phase and that the composition of an individual nanotube varies along its length. The formation mechanism of the Co–Pt-based tubular nanostructures can therefore be explained via partial Au-coverage of the template and the appropriate relative rates of the deposition and diffusion of the Pt and Co electro-active species, most probably assisted by hydrogen evolution. The as-deposited Co–Pt-based nanotubes, with an aspect ratio of 10, are magnetically isotropic and have a coercivity of 10 kA m^{-1}. The easy axis of the magnetization was found to be perpendicular to the axis of the tube.

1. Introduction

The focus in recent years on the research and development of metal and magnetic nanostructures with a tubular geometry has been inspired by their technological importance in advanced electronic and magnetic devices. Furthermore, their large surface-to-volume ratio makes them interesting for chemical and biological separations or for catalytically driven processes [1–6].

Since the search for novel geometries continues to be an important aspect of magnetic nanotechnology a lot of effort has been dedicated to ferromagnetic tubular nanostructures, the synthesis of which has presented a major challenge. Cobalt and nickel nanotubes have been grown on biomolecular microtubules by the adsorption of a Pd or Pt catalyst, followed by electroless deposition [7]. By using consecutive electroless deposition coaxial Ni/CoNiFe nanotubes were successfully synthesized in track-etched polycarbonate templates [8]. Pulsed electro-deposition in track-etched membranes was used in order to synthesize Co and Fe nanotubes [9]. Commercially available porous alumina membranes have been used as templates for Ni and Co nanotube synthesis by electro-deposition [10,11], and the template-mediate method, where the metal salts were infiltrated in porous alumina, followed by chemical deposition and hydrogen reduction, was used in order to synthesize Fe–Pt- and Fe_3O_4-based nanotubes [12]. Recently, it was reported that ferromagnetic nanotubes can be obtained directly by electro-deposition into alumina templates. Nickel-based tubular nanostructures of different diameters were directly synthesized using electro-deposition [13,14]; furthermore, Co–Pt-alloy-based nanotubes were also successfully electro-deposited into alumna-based templates [15]. Fu et al. [15] proposed a mechanism where the Co–Pt nanotube formation is based on the amount of conductive layer (Au) sputtered on the bottom of the Al_2O_3 template and Cheng at al. [16] presented the hypothesis that metallic nanotube arrays can be obtained in fully covered alumina templates, due to the hydrogen evolution, which influences the nanotube length. At more negative potentials the tube morphology could be preserved for longer lengths, whereas at higher potentials the tubes close more rapidly due to there being less hydrogen evolution.

In this contribution we report on the direct plating of Co–Pt-based nanotubes into track-etched polycarbonate template membranes. A detailed TEM/EDS analysis was used in order to determine the Co–Pt nanotube stoichiometry, which was used as an explanation for the Co–Pt nanotube formation mechanism. The influence of the nanotubes' dimensions, their morphology and their crystal structure on the magnetic properties is also discussed.

2. Experimental

The electrochemical deposition of the Co–Pt-based nanostructures was preformed in a standard three-electrode cell containing 100 ml of electrolyte. The electrolyte consisted of 2 mmol l^{-1} of Pt-p-salt ($Pt(NH_3)_2(NO_2)_2$), 4 mmol l^{-1} of

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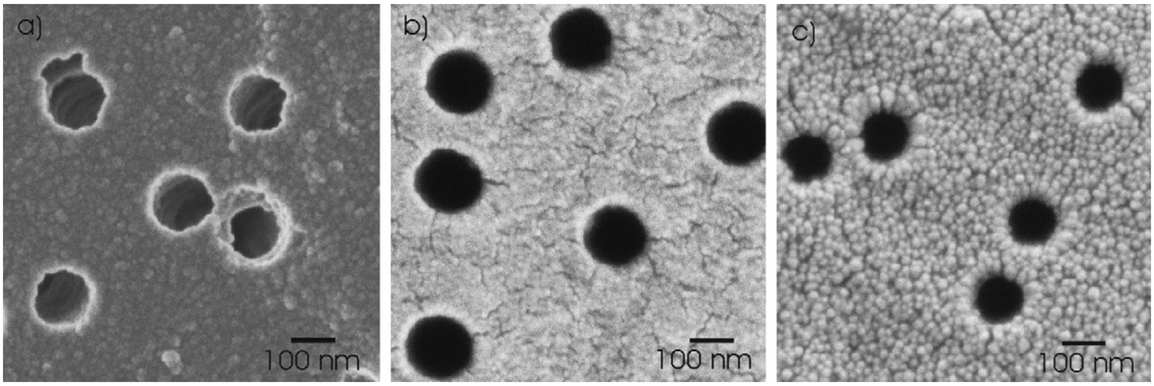

Fig. 1. FEG-SEM image of the back side of the polycarbonate template before the Au sputtering (a) and SEM image of the back side of the polycarbonate template sputtered with Au for 40 s (b) and sputtered with Au for 300 s (c).

Co-sulphamate ($Co(SO_3NH_2)_2$), 20 mmol l^{-1} of ammonium citrate ($(NH_4)_2C_6H_6O_7$) and 0.2 mmol l^{-1} of glycin (NH_2CH_2COOH) [17]. A Pt sheet was used as the counter electrode. The bottom of the track-etched polycarbonate template, with an average pore diameter of 200 nm and a thickness of 10 μm, was sputtered with Au for times of 40–300 s and used as a cathode. This template was glued from all sides on the SiO_2/Au substrate in order to promote electro-deposition only from the top side of the template. The potentiostatic depositions were preformed from 60 to 180 min using potentials between −1.9 V and −2.5 V. The potential was referenced against the Ag/AgCl electrode. The pH was adjusted to 8 using NaOH, and a temperature of 60 °C was maintained during the electro-deposition experiments, while the solution was constantly stirred using a magnetic stirrer. After the deposition the Co–Pt-based nanostructures were released from the template by dissolving it in an organic solvent (CH_2Cl_2). The as-deposited Co–Pt-based nanostructures were characterized using the FEG-SEM Zeiss Supra 35 VP and a Jeol 840 SEM microscope equipped with energy-dispersive X-ray spectroscopy (EDXS). The specimens for cross-sectional TEM were prepared by the following procedure. The residual material, which was obtained after the removal of the polycarbonate template, was mixed with two-component epoxy glue and gently applied between two Si wafers. These stacks were then further cut so that they could easily be introduced into aluminum disk holders. After mechanical polishing to ∼100 μm and thinning in the center of the disc to 20 μm by using a dimple-grinder, the final, thin electron-transparent specimen foil was obtained by ion milling in a Baltec RES010. The samples were examined by a JEM-2100 LaB_6 transmission electron microscope (TEM) equipped with a JEOL EDS system. For the quantitative EDS analyses Co–Pt internal standards were used. The magnetic response was measured using a vibrating-sample magnetometer.

3. Results

The polycarbonate template was sputtered with Au in order to increase the cathode efficiency. Fig. 1 shows FEG-SEM images of the back side of the polycarbonate template before (Fig. 1a) and after the Au sputtering for 40 s (Fig. 1b) and 300 s (Fig. 1c). The un-treated polycarbonate template shows an irregularly arranged pore structure with an average diameter of around 200 nm. After the 40 s of Au sputtering the template still shows an open pore structure. The surface of the template is covered with gold particles (the composition of which was determined by EDS) in a size range between 10 and 30 nm. After the Au was sputtered for 300 s the template pores are covered with Au particles to a greater extent, resulting in a pore diameter (at the bottom of the pore) of around 130 nm.

Fig. 2a is a FEG-SEM micrograph of the Co–Pt-based nanostructures deposited at −1.9 V for 60 min in the PC template sputtered with Au for 40 s taken after the removal of the template. The obtained Co–Pt nanostructures with a composition close to $Co_{35\pm2}Pt_{65\pm2}$ (determined by EDS) have a tubular morphology and are fairly uniform in terms of length (2 μm) and diameter (200 nm), the latter of which is determined by the template; however, there are also some irregularities observed in the nanotube array, such as *x* and *y* crossings, which can be ascribed to the template's geometry. Fig. 2b shows an array of the Co–Pt-based nanotubes deposited at −1.9 V for 60 min in the PC template sputtered with Au for 300 s. In comparison with the tubes deposited in the PC template sputtered with Au for 40 s, the obtained nanotubes show a much denser structure with thicker tube walls and consequently smaller tube diameters, which in some cases resulted in closed tubes.

The SEM/EDS investigation made on samples deposited into PC template sputtered with Au for 40 s, at more negative potentials, i.e., −2.1 V (Fig. 3a) and −2.5 V (Fig. 3b), for 60 min showed that the length of the nanotubes increases with a decreasing applied potential, reaching a length of ∼5 μm when deposited at −2.5 V. The tubular morphology was preserved at all applied potentials. However, when the deposition was preformed at −1.9 V for 180 min closed tubes with lengths of ∼6 μm were observed to form (Fig. 4). The lengths of the nanotubes deposited at different applied potentials and the approximate composition of the Co–Pt nanotubes determined with the EDS analyses are summarized in Table 1. The

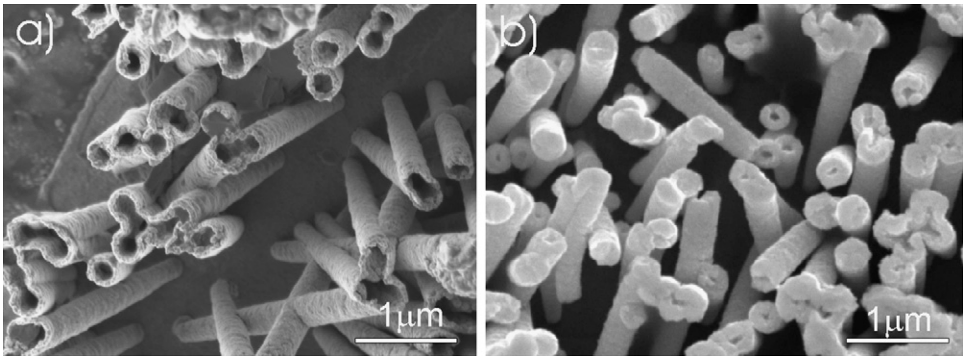

Fig. 2. FEG-SEM micrograph of the Co–Pt nanotube array deposited into the PC template sputtered with Au for 40 s at −1.9 V vs. Ag/AgCl for 60 min after the removal of the PC template (a), SEM micrograph of the Co–Pt nanotube array deposited into the PC template sputtered with Au for 300 s at −1.9 V vs. Ag/AgCl for 60 min after the removal of the PC template (b).