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Study of Ni/Fe nanotube properties

A. Kozlovskiy [a,b], A. Zhanbotin [a,b,*], M. Zdorovets [a,b], I. Manakova [b], A. Ozernoy [b], K. Kadyrzhanov [a], V. Rusakov [c]

[a] *L.N. Gumilyov Eurasian National University, 2, Satpayev Str., Astana 010008, Kazakhstan*
[b] *Institute of Nuclear Physics, 1, Ibragimov St., Almaty 050032, Kazakhstan*
[c] *Lomonosov Moscow State University, Leninskie Gory, Moscow 119991, Russian Federation*

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ABSTRACT

In this paper, we describe the synthesis, structure, and magnetic properties of Fe/Ni nanotubes fabricated in polyethylene-terephthalate (PET) ion-track membrane. Fe/Ni nanotubes were electrochemically deposited into PET membrane with cylindrical holes of diameter 111 ± 3 nm. Scanning electron microscopy, X-ray diffraction and Mössbauer analysis were used to determine the physical properties of the obtained nanostructures. It was found that the samples were single phase and had face-centered cubic structure with lattice parameter $a = 2.866 \pm 0.0008$ Å. It was assumed that the observed phase was a solid solution of iron substitution in nickel. According to Mössbauer data, the hyperfine field amounts to 337.75 ± 0.4 kOe. Energy-dispersive X-ray spectroscopy data show a metal ratio in the nanotubes of around Ni_{20}/Fe_{80}. The magnetic domains have sizes close to the thickness of nanotube wall with their magnetization vector oriented at an angle of 37.9 ± 1.1° to the axis of the nanotubes.

1. Introduction

In recent years, one-dimensional nanostructures have been studied intensively in the field of nanoscience and technology due to their unique properties, which are different from bulk material or crystalline powders. This concerns electrical, optical, magnetic, thermal, chemical and other characteristics [1–3]. They are used for example as nanoscale integrated devices, various sensors, and magnetic data storage devices. There are a lot of methods to obtain nanostructures [3]. The ion track technology provides membranes with nanopores to be used as template matrix, which are widely applied in various fields of science and industry [1,2,4]. The geometry of the track etched channels can be controlled at the stage of their preparation: the irradiation with heavy ions allows control of the pore density and chemical etching of latent tracks regulates the diameter of the pores. The method of electrochemical deposition is based on the number of deposited ions. Their deposition rate depends on the concentration of the electrolyte solution, current density between electrodes, and temperature. This method allows to obtain nanostructured composite objects made of different metals if different ions were used in the electrolyte. An important advantage of this method is the simplicity of preparation of metal nanostructures by controlling the amount of deposited charge and the deposition time. It is possible to obtain parallel oriented nanoscale structures. Varying the potential applied between electrodes leads to difference in ion deposition rate for two or three component solutions [5]. This work considers the process of Ni/Fe nanotube formation obtained by template synthesis method. Most of magnetic nanowires/nanotubes find applications in magnetic storage devices, magnetic sensors, etc. [6–10]. There are many applications of magnetic nanoparticles in medicine and biosensors technique [11–14]. But most of this techniques use powders with ball-like structure which is not applicable in some specific cases. Unlike this powders magnetic nanowires/nanotubes have 2D structure. This structure means that magnetic domains can have one direction orientation relatively to geometry of wire/tube. Such kind of nanowires/nanotubes can be arranged on bulk metal base which gives additional opportunity to use them for example as free-standing magnetic sensors. Thus, higher magnetic field of nanostructures means higher response to outer magnetic field. It is also expected higher coercivity due to size effect of thin wall nanotubes or small diameter nanowires. In this work nanostructures were studied by qualitative and quantitative analysis including to measure the magnetic properties by Mössbauer spectroscopy.

2. Experimental methods

Polyethylene terephthalate (PET) films Hostaphan® type produced by Mitsubishi Polyester Film (Germany) of 12 μm thickness were irradiated by ^{84}Kr ions with an energy of 1.75 MeV/n on

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* Corresponding author at: L.N. Gumilyov Eurasian National University, 2, Satpayev Str., Astana 010008, Kazakhstan.

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DC-60 cyclotron in Astana, Kazakhstan. This type and energy of ions allows us to keep energy loss – $\Delta E/\Delta l$ with the film almost constant. It gives very uniform latent tracks throughout the entire film thickness. Chemical etching of the irradiated membranes was done in 2.2 M NaOH solution at 85 ± 0.1 °C. 1.0% acetic acid solution and deionized water was used as a neutralizer as described in [4,15]. These chemical treatment conditions of radiation-modified polymeric material give isotropic holes of cylindrical shape. Scanning electron microscopy and gas permeation methods were used to check the diameter of the pores [16,17]. As a result the ion-track membranes (TM) with $10^9\,\text{cm}^{-2}$ pore density and 111 ± 3 nm diameter were used as a template for electrochemical Fe/Ni nanotube synthesis (fig. 1). The electrolyte was a aqueous solution of $NiSO_4 \times 7H_2O$ (110 g/l), $FeSO_4 \times 7H_2O$ (110 g/l), $NiCl_2 \times 6H_2O$ (5 g/l), H_3BO_3 (25 g/l) and $C_6H_8O_6$ (3 g/l). The method that used to obtain wires was also used to obtain nanotubes [18].

The nanotubes synthesis was carried out using a galvanic cell in potentiostatic mode at a voltage of 1.5 V at room temperature. Constant pH level was controlled by adding ascorbic acid to the electrolyte. The electrodeposition process was controlled by chronoamperometry using an Agilent 34410A multimeter. The gold cathode was formed on the surface of the etched polymer film using a JEOl JFC-1600 automatic coater with gold electrode. Sputtering mode of 30 nA, 30 s was used to form a 15 nm thick gold layer according to the coater settings. This layer thickness is not enough to close the pores completely. Analysis of SEM-images before sputtering Au and after allows to calculate changes of the diameter of the pores at the surface which are about ~10 nm. A gold plated copper electrode was used as anode placed in the solution.

Deposition of Fe^{2+} and Ni^{2+} ions happens when ions are located near the cathode surface. Concentration gradient generated at this case causes the flow of metal ions to the cathode. The contact of metal ions on the cathode surface leads to their entry into the growing nanostructures, which is normal deposition process according to Faraday law.

It is known, that usually the process of electrochemical deposition of metals in pores consists of 4 basic stages. The first stage corresponds to the start of filling pores and in our case happens at $t < 70$ s. This stage is characterized by a sharp drop of the current from 21 mA to 17 mA, which occurs as a result of the nucleation process at the cathode (Fig. 2b). During the second stage (Fig. 2a, 70–320 s) nanotubes grow within the pores (Fig. 2c). The process continues until the moment when the length of the nanotubes becomes equal to the thickness of the template (Fig. 2d). At the third stage, after the nanotubes reach the opposite side of the template, metal grows in three dimensions (volume growth) above the surface of the polymer film forming ‘‘caps” growing from the walls of the nanotubes (Fig. 2e). As a result of this process, the effective surface area of the deposition is increasing. At that stage, the registered current increases (Fig. 2a). The third stage continues until the metal islands overlap. The fourth stage corresponds to the formation of a continuous metal layer on the surface of the template (Fig. 2f), whereby the electric current saturates (not shown).

Incomplete pore filling of metal nanotubes was intentionally made avoid pore blockage and the formation of ‘‘caps”. The deposition time was thus decreased to 320 s. Under these conditions the length of the obtained Ni/Fe nanotubes was measured using SEM.

For SEM, Energy-dispersive X-ray spectroscopy, X-ray measurements the membranes were completely dissolved in 5 M NaOH at 80 °C. Subsequently the nanotubes were washed in a neutralization solution (1.0% acetic acid and deionized water).

The structure and dimensions of the nanotubes were studied using a JEOL 7500F and a Hitachi TM3030 scanning electron microscope with Bruker XFlash-MINSVE microanalysis system at an acceleration voltage of 15 kV, as well as a JEM-2100 transmission electron microscope with an acceleration voltage of 100 kV.

The X-ray measurements were performed with a D8 ADVANCE diffractometer using X-ray tube radiation with Cu – anode and a graphite diffracted beam monochromator. The operating mode of the tube was 40 kV and 40 mA. The diffraction patterns were recorded in the $2\theta = 30–75°$ angular range with steps of 0.03°. The accumulation time was 9 s per angle.

The Mössbauer studies were carried out using a MS1104Em spectrometer operating in constant acceleration mode with triangular mode of the source's Doppler speed referred to the absorber. The ^{57}Co nuclei in the Rh matrix were used as source. The Mössbauer spectrometer was calibrated at room temperature using a standard α-Fe absorber. The nanotubes were measured with the polymer matrix. The samples were placed so that the axis of the nanotubes was parallel to the γ-rays direction. The method of reconstructing the hyperfine parameter distributions implemented in the Spectr Relax program was used for processing the Mössbauer spectra [19].

3. Results and discussion

SEM imaging of the polymer matrices demonstrates that the chosen chemical etching method provided a uniform distribution of pore diameters [20–24], as well as a cylindrical shape along the entire length of the pores (see Fig. 1).

A standard I/t curve recorded during metal deposition from the electrolyte solution at a voltage of 1.5 V is shown in Fig. 2. By means of the obtained I/t curve, the volumetric growth rate of the nanotubes was calculated, amounting to $1.45 \times 10^{-13}\,\text{m}^3/\text{s}$ at a potential of 1.5 V. SEM pictures of Fe/Ni nanotubes are shown in Fig. 3.

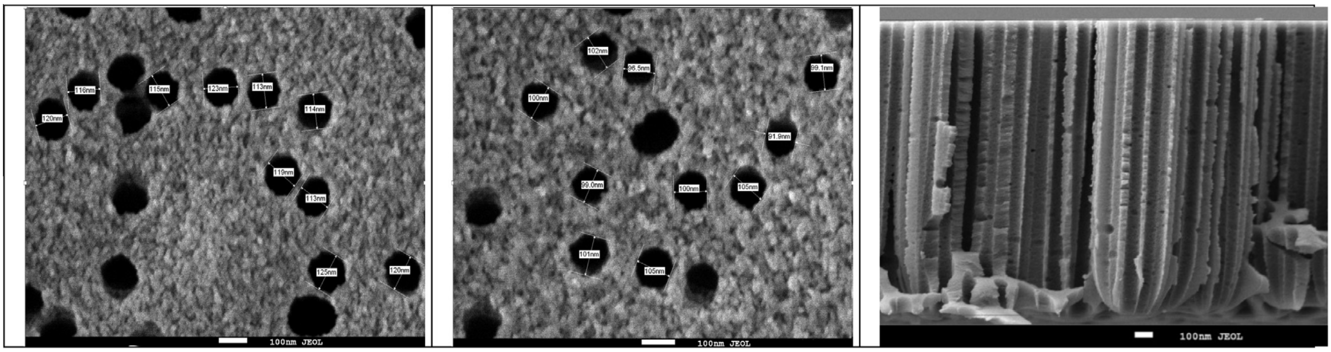

Fig. 1. SEM – images of the surface and the cross section of the track-etched PET film (scale bars: 100 nm).