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Mossbauer research of Fe/Co nanotubes based on track membranes

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ABSTRACT

Fe/Co nanostructures obtained by template synthesis have been researched in this study. It was shown that the obtained nanostructures are single-phase Fe/Co nanotubes with a high degree of polycrystallinity and body-centered cubic structure with a length of 12 μm, possessing diameter of 110 ± 5 nm, and wall thickness of 18–20 nm. The direction of easy magnetization axis lies along the nanotubes axis due to the anisotropy shape of the nanotubes. Mossbauer spectroscopy showed that the hyperfine magnetic field (H_n) values on ^{57}Fe nuclei increase with increasing number of Co atoms near Fe atoms. Substitution of one Fe atom on Co atom leads to an increase of (H_n) to approximately 9.0 ± 0.4 KOe, herewith shift of the Mossbauer line decreasing to about 0.004 ± 0.002 mm/s. The local magnetic texture along the nanotubes axis was found with the average angle between magnetic moment and the nanotubes axis $\bar{\vartheta} = 25 - 29^{\circ}$.

1. Introduction

At present, the development of modern science and technology has reached a level such that new materials composed of particles with very small sizes and specific properties are needed. Rapidly developing nanotechnology is a solution for this problem. Synthesis of nanostructures is one of the existing issues of this field. Nanostructures should exhibit unique physicochemical properties due to structural and size effects. Changes of properties are not only due to decreasing sizes but also because at this level, quantum–mechanical effects and wave nature of processes begin to play a significant role. Nanotechnology can make progress in many areas of science and technology by providing fundamentally new qualities to nanomaterials and nanosystems.[1,2]

Artificially ordered magnetic nanostructures cause particular interest not only by understanding the fundamental properties, but also by the variety of possible applications.[3] Nanoscale magnetic arrays can be used for storage of information with ultrahigh density of recording.[4–6] Sensors based on nanostructures have better resolution and sensitivity, high efficiency of catching, and fast response because of their large surface area for adsorption and short time of diffusion.

Biomagnetism is another field of prospective application of nanostructures. Several investigations could be conducted by manipulating magnetic nanowires using magnetic interactions. Biomagnetism finds applications in cell separation, biosensing, and therapeutics. The ability to control physical properties of nanostructures by varying shape, size, and chemical composition [7–9] provides broad prospects for their use in biocatalysis [10], biodetection [11,12], bioseparation [13], drug delivery [10,14,15], genes [16,17], and study of microrheological processes [18] as well as contrast liquids [10,18].

The template synthesis method is one of the most popular and perspective methods to obtain nanostructures. This method is based on the use of porous materials; in our case, on the use of track membranes (TMs) made from polyethylene terephthalate (PET). Simplicity and practicality of this method make it suitable for mass production of nanomaterials and manufacture of samples with small sizes. This method is based on full or partial filling of porous template by electrochemical deposition of metals from electrolyte solution containing salts of those metals and additional additives for improving quality of coating [19]. Nanoreplicas obtained by electrochemical methods have higher density and crystallinity than the structures obtained by other methods such

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as electron beam lithography [20], chemical deposition from gas phase [21], pulsed laser deposition [22], and some other methods discussed in Refs. [23–25]. Another advantage of this method is that it allows obtaining composite ordered nanostructure arrays with controlled stoichiometry.

The Fe/Co nanostructures obtained by template synthesis using TMs based on PET have been researched in this study by the methods of energy-dispersive X-ray spectroscopy (EDX), scanning electron microscopy (SEM), X-ray diffraction (XRD), magnetic measurements, and Mossbauer spectroscopy.

2. Experimental methods

The TMs based on PET for the production of Hostaphan® by Mitsubishi Polyester Film (Germany) with pore density of 1.0×10^9 cm^{-2} and diameter 110 ± 5 nm were used as template matrices for template synthesis of Fe/Co nanotubes. The method used to obtain nanotubes is described in Ref. [26]. An electrolyte was used for electrochemical deposition with the following composition: $CoSO_4 \times 7H_2O$ (110 g/l), $FeSO_4 \times 7H_2O$ (110 g/l), H_3BO_3 (25 g/l), $C_6H_8O_6$ (3 g/l). The process of deposition was carried out at voltages of 1.5 and 2 V in the potentiometric mode. The growth process of nanostructures was monitored by Agilent 34410A multimeter using the chronoamperometry method. As conductivity of a solution depends on pH, a constant level of pH = 3 was maintained by adding ascorbic acid.

The structure and dimension of nanotubes were investigated using SEM Hitachi TM3030 with EDX spectroscopy system Bruker XFlash MIN SVE at an accelerating voltage of 15 kV. The inner diameter of Fe/Co was measured by the water flow measurement method for determining gas permeability [27]. The range of measured pressures was 0.008–0.020 MPa. XRD studies were conducted on D8 ADVANCE diffractometer using Cu (Kα)-radiation (λ = 1.5405 Å) of X-ray tube and graphite monochromator on diffracted beam. The following parameters determine the mode of operation of the tube: U = 40 kV and I = 40 mA. Diffraction patterns were recorded at 2θ ranging from 10° to 90° with a step size if 0.02°, and the time of measurement at each point was 9 s.

Magnetic characteristics of Fe/Co nanotubes have been studied on the universal measuring system (automated vibrating magnetometer), Liquid Helium Free High Field Measurement System of Cryogenic Ltd (London, UK). Measurements were made by measuring induced electromotive force of induction in signal coils oscillating at a certain frequency by magnetized sample in the range of magnetic field ±2 T at room temperature and T = 9 K.

Mossbauer studies were conducted using spectrometer MS1104Em operating in constant acceleration mode with a triangle-shaped change of Doppler velocity of source relatively to the absorber. Cores ^{57}Co in matrix Rh were used as source. The Mossbauer spectrometer was calibrated at room temperature using standard absorber α-Fe. The methods for reconstructing distributions of hyperfine parameters of Mossbauer spectra and model fitting using a priori information about object implemented in the program SpectrRelax were used for processing of the Mossbauer spectra [28].

3. Results and discussion

Fig. 1 shows experimental I/t curves describing dependences of amperage on the time of electrochemical deposition. There are two main stages of deposition. The first stage (1) corresponds to start of filling of template and directly to the growth of nanotubes inside tracks. The second stage (2) is the end of filling of the membrane holes and output of metal on the membrane surface. Subsequent

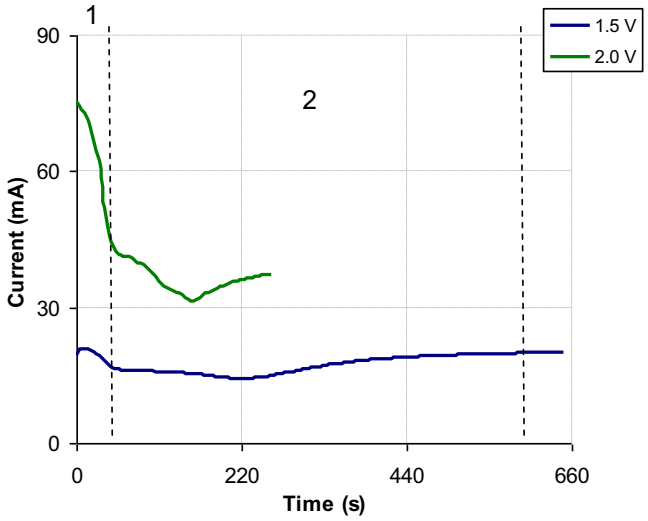

Fig. 1. I/t curve of Fe/Co nanotube deposition process.

amperage growth is caused by growth of the conductive layer on the surface, and hence further deposition did not seem appropriate.

The time of deposition was determined by using I/t curves; this time corresponds to the maximum length of nanotubes (NT) (complete filling pores of template) – 650 s for U = 1.5 V and 260 s for U = 2 V. Incomplete filling of metal pores was performed to avoid blockage or formation of "caps" on the surface of the nanotubes. The time of deposition was decreased to 600 s at U = 1.5 V and 240 s at U = 2 V.

The formation of Fe/Co nanotube arrays at selected modes was controlled by using a scanning electron microscope. Before testing, the samples were released from template matrix by dissolving them in 9.0 M sodium hydroxide solution for 60 min. Then, the samples were treated in ultrasonic bath at 85% acetic acid solution for 10 s to remove polymer residues. Fig. 2 shows SEM images of nanotubes without polymer template.

Analysis of SEM images of obtained nanotubes (Fig. 2b) shows that the height of nanotubes is equal to the thickness of template (12 μm) and their diameters are equal to the diameters of the pores of template matrices. Because of the insufficient resolution of SEM analysis of inner diameters, d Fe/Co nanotubes were not produced, and hence the pore diameters of PET template and inner diameters of nanotubes located in PET templates were determined using the method of gas permeability determination based on measuring the change of gas pressure in a closed chamber at pressures ranging from 0.008 to 0.020 MPa with a step size of 0.004 MPa. The following formula is used to calculate inner diameters:

$$r^3 = \frac{Q \cdot 3l}{\sqrt{\frac{2\pi}{R \cdot T \cdot M}} \Delta\rho \cdot 4n} \quad (1)$$

where Q is the gas volume passed through the nanotubes [m^3/h], r is the pore radius [m], M is the molar mass [kg/mol], R is the universal gas constant [J/mol × K], T is the temperature [K], n is the pore density [1/m^2], l is the membrane thickness [m], and Δp is the applied air pressure [Pa].

The calculated pore diameters are 111 ± 3 nm, which are in good agreement with data obtained by SEM measurements. The inner diameters of Fe/Co nanotubes determined by the method of gas permeability were 69 ± 1 and 75 ± 1 nm for U = 1.5 and 2 V, respectively. The parameter d was used to calculate appropriate wall thicknesses of NT – 21 and 18 nm. Wall thickness was determined as half of the difference between outer and inner diameters.