# METALLIC NICKEL NANOTUBES: INFLUENCE OF DEPOSITION PARAMETERS ON THEIRS STRUCTURE AND MAGNETIC PROPERTIES

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Arrays of Ni nanotubes have been synthesized in pores of polyethylene terephthalate membranes by electrochemical method. Morphological and structural characteristics were studied by scanning electron microscopy, gas permeability, energy-dispersive X-ray spectroscopy and X-ray diffraction analysis. It was shown that Ni nanotubes have lateral dimensions corresponding to the parameters of the membrane pores (length ~12 μm and pore diameters 400 nm) with the thickness of tube-walls in the range from 60 nm to 160 nm, depending on the deposition conditions. Ni nanotubes have the face-centered cubic lattice phase. The dependence of crystal structure parameters on temperature and voltage of synthesis has been established. Dependences of main magnetic parameters (coercivity value and magnetization of saturation and squatness) on deposition parameters have been studied. Significant magnetic anisotropy was found, but no evidence of influence of deposition parameters on magnetic properties was found.

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## Introduction

Nowadays a great attention is given to the nanostructures (NSs) due to their unique properties and application prospects as devices for chemical and biological practice[1,2] and catalysis,[3] objects for the biomedicine,[4,5] as well as sensitive elements of the magnetic field actuators.[6-9] There are many methods of NSs design like the spontaneous coalescence, hydrothermal synthesis, electrochemical deposition etc.[10-13]

In present work the electrochemical deposition method was used for a synthesis of magnetic NSs, which made it possible to control the structure, element and phase composition by means by varying the deposition parameters. The deposition process was carried out in the pores of polyethylene terephthalate (PET) membranes. The use of the pores with pre-determined geometry lead to synthesis of NSs with a desired form.

In this work the structural and magnetic properties of Ni nanotubes (NTs) and analysis of dependences of their properties on the deposition parameters i.e., temperature and potential were investigated.

## Experimental

Ni NSs synthesis has been realized in the pores of the ion track polymer films on the base of the PET of the Hostaphan® type from the «Mitsubishi Polyester Film» (Germany) with thickness 12 μm, pores diameters 400 nm and density 4 $\times 10^7$ $cm^{-2}$. Before the synthesis a gold layer with thickness 10 nm was deposited by the magnetron sputtering in vacuum served as a cathode for the electrodeposition process. Electrochemical synthesis was carried out in the potentiostatic mode at cathode voltages in the range 1.25 to 2.0 V using the electrolyte $NiSO_4.6H_2O$ (100 g $L^{-1}$), $H_3BO_3$ (45 g $L^{-1}$), $C_6H_8O_6$ (1.5 g $L^{-1}$) at temperatures 25, 35 and 50 $^0$C. The process was controlled chronoamperometrically by the multimeter Agilent 34410A.

Investigation of the structure and morphology of the synthesized NTs was carried out by the scanning electron microscopy (SEM) on the Hitachi TM3030 set up equipped with the Bruker XFlash MIN SVE the energy-dispersive

X-ray analysis (EDX) with the accelerating voltage 15 kV. X-ray diffraction (XRD) analysis was made on the D8 ADVANCE diffractometer with the use of X-ray tube with Cu anode and graphitic monochromator on the diffracted beam. The XRD patterns were recorded in the angles range $2\theta$ ~ 30–70˚, with the step $2\theta$ ~ 0.02˚.

Macromagnetic properties were investigated using the vibrational magnetometer (the Liquid Helium Free High Field Measurement System (Cryogenic Ltd.)). The measurements were implemented by the induction method, through a determination of the induced electromotive force of the induction in signal coils by a magnetized sample oscillating with a definite frequency at magnetic field B ± 3 T at temperature 300 K.

## Results and Discussion

### Synthesis

Synthesis of Ni NSs was carried out inside pores of the dielectric ion track membranes due to a gold cathode layer on the bottom part of membranes and the high degree of surface hydrophilicity (contact angle ~45°-47°). That allowed the electrolyte get inside pores. The gold cathode layer was thin (about 10 nm) and pores stood opened. This fact determined the hole structure of deposited NSs.[14] To investigate influence of electrodepositing parameters i.e., temperature and voltage, three sets of samples were made at different temperatures (25, 35 and 50 °C). In every set voltage was changed in a range from 1.25 to 2 V by step of 0.25 V. The upper level of temperatures was determined by temperature of dissolved gases releasing. The range of voltage was limited by deposition potential of Ni (the lower level) and by potential of water dissociation that led to the rapid evolution of hydrogen in the electrolyte (the upper level). The huge role of hydrogen evolution in forming nanotubes has been shown earlier.[15]

Aanalyzing of typical time dependence of current during deposition (figure 1) we found that process had four stages, which were determined by the size of cathode area at a moment, and amount of ions near it. The first stage, nucleation, was carried out on the interface insulator-cathode inside of pores and the nuclease of metal were formed on pores walls and on the cathode. This process led to exhaustion of electrolyte in pores and current dramatically decreased and stood almost constant during the next stage of the deposition, 1d structure growing. This second stage ended when the pores were completely filled with metal and the deposition proceeded on the upper part of membrane and, at first, the cups on the top of NSs grew (the third stage) and then the thin metallic layer was formed (the fourth stage).[16] During the two final stages, the cathode area became larger and the concentration of metal ions increased to the level of concentration above the membrane surface. The details of synthesis process and or the stages of growth process have already been reported.[17]

### Structure characterization

By analysis of SEM images, it was determined that the obtained NSs had external dimensions corresponding to the original template parameters i.e., length of 12 mm and external diameters of 400 nm with a minor size deviation (within 5-8%). By permeability method, it was established that the NSs are hollow and have internal diameters, which increase with an increase in the voltage and/ or decrease in the deposition temperature. Thus, the wall thickness changes from 60 to 160 nm (figure 2a). This fact could be explained by the presence of two competing factors. A circular form of electrode induced the tubular growth due to the "tip effect" and could been seen mostly at higher voltage and/or temperature of a process. On the other side, due to a low voltage, the ions diffusion rate could overcome the "tip effect". This leads to a formation of NTs with thick walls and even rigid NSs in the form of wires. Influence of these two factors on the wall thicknesses (*h*) is shown on figure 2a. Dependences of a morphology of the deposited structure on the electrode form, temperature and voltage of a deposition process on was discussed in detail in an earlier report.[17]

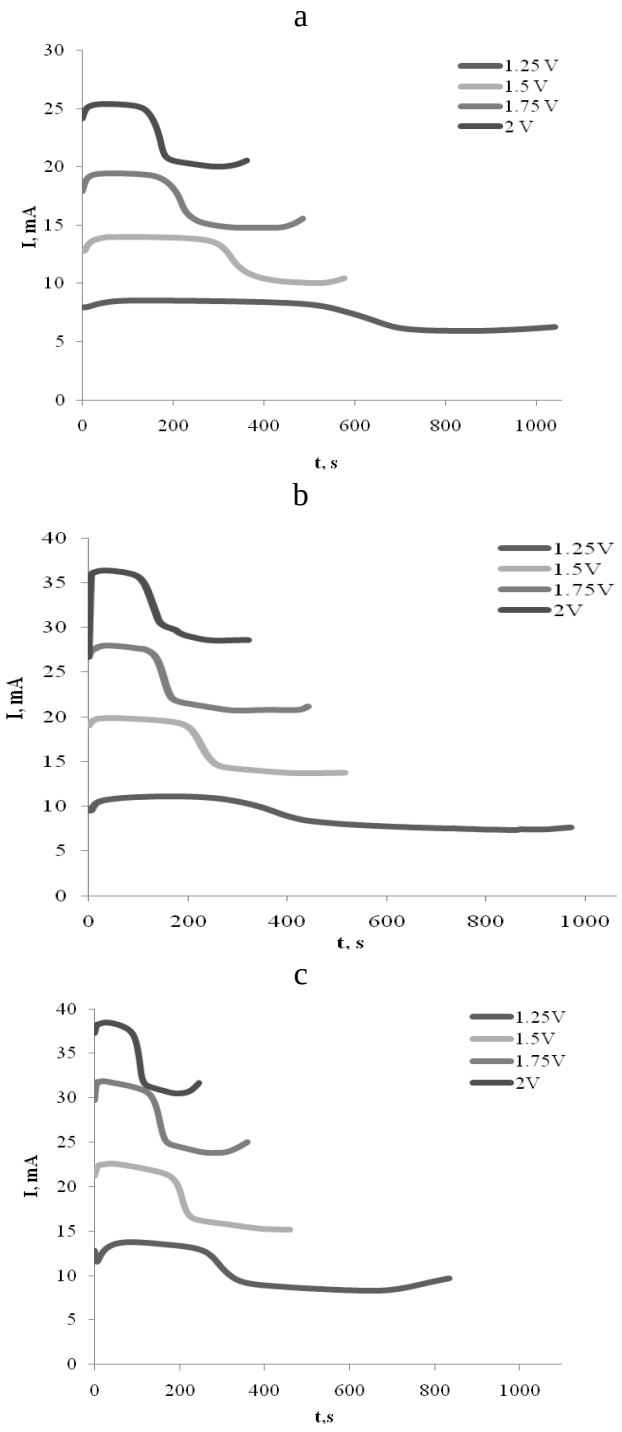


**Figure 1.** Time dependence of current of electrochemical deposition process: (a) t=25 °C, (b) t=35 °C, (c) t=50 °C.

XRD investigations of the samples prepared at different synthesis conditions were carried out to determine their influence on the crystal structure. A wide peak at the angle ranges 2θ = 20-35º and a small peak at the 2θ = 53-55º observed on the XRD spectra. These peaks are belonged to the PET membrane, where the studied NTs were during the analysis. All the XRD spectra have specific peaks for the diffraction on nanosized objects.

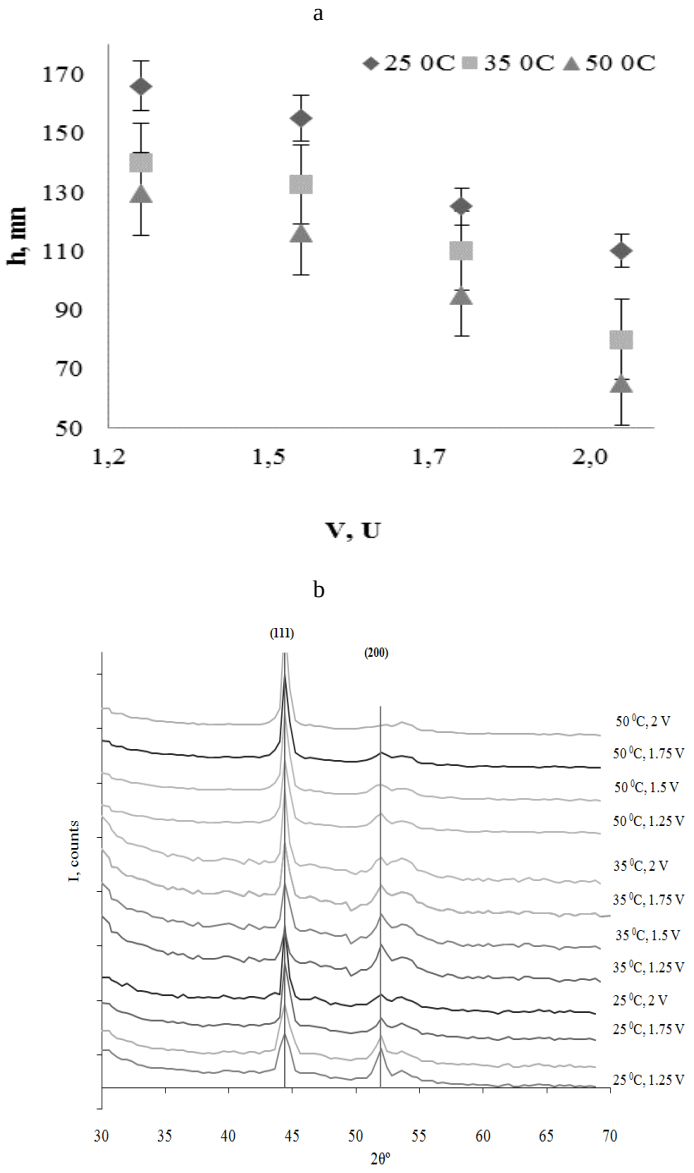


**Figure 2.** (a) Influence of deposition parameters on the wall thicknesses; (b) X-ray diffraction spectra of Ni NTs arrays.

Analysis of the XRD spectra shows that the Ni NTs possess the face-centered cubic (*fcc*) lattice phase with the crystal structure parameters being different from the reference values. On the XRD spectra one could observe ϕτ increase of the intensity of the peak with the Miller indexes (*hkl*) (111) with the increasing of voltage during the synthesis process and decrease of the intensity of the (200) peaks. This makes it evident the dominance of the [111] texture direction in the NTs crystal structure. The texture coefficients (TC(*hkl*)) have been calculated according to the Harris equation. Results of calculations are shown in table 1. The tendency of definition of priority texture direction along the NTs axis is explained by the intensification of the impact of hydrogen evolution in electrodeposition process.[15]

Lattice parameter (*a*) and crystals size (*L*) are shown in table 2. The parameters of crystalline structure change with deposition conditions. The most evident reason of these changes is inclusion of contaminants in the crystals structure such as hydrogen and salts, leading to the increase of lattice parameter and crystals size.

## Magnetic properties

The investigation of macromagnetic properties has been carried out by the vibration magnetometry at temperature 300 K at magnetic field $B$ = ±3 T for parallel and perpendicular directions of the field with respect to orientation of the NTs axis. The typical hysteresis loops obtained for the studied samples are presented in figure 3. Insets of images show enlarged detail of the hysteresis loops at fields up to 0.4 T. Using them, the main magnetic characteristics were determined ($H_c$ = coercivity and $M_r$ / $M_s$ = squareness ratio of hysteresis loop). These characteristics are presented in table 3.

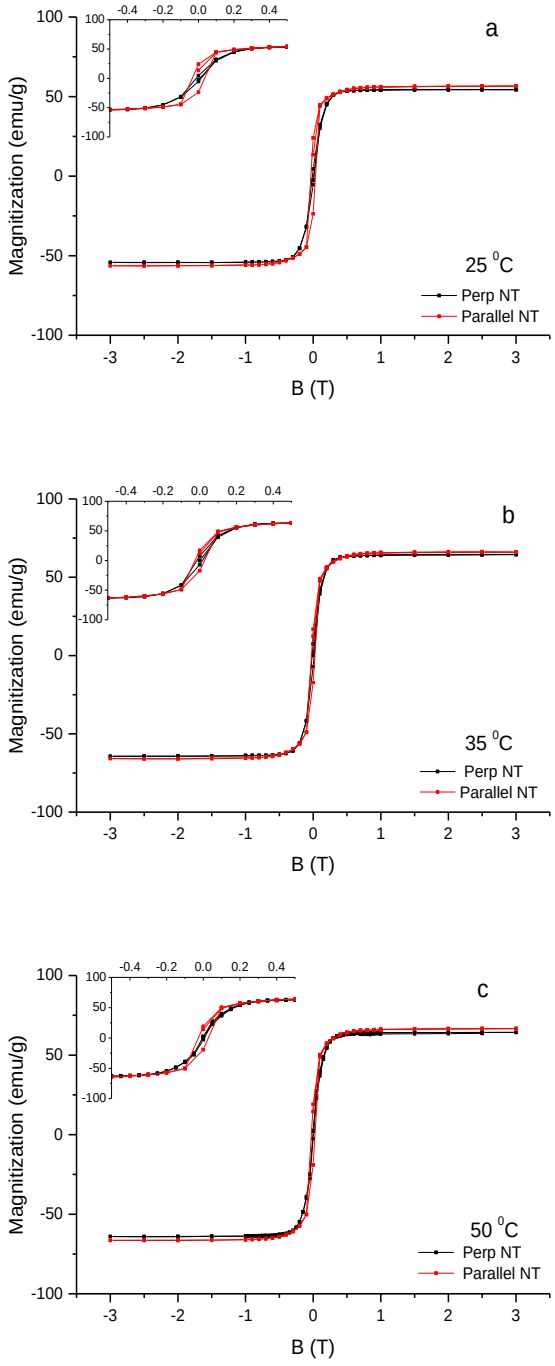


**Figure 3.** Hysteresis loops of Ni NTs synthesized at 1,75 V and temperatures: a) 25 °C, b) 35 °C, c) 50 °C.

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**Table 1.** Crystalline parameters of nanotubes.

| Temperature of synthesis, °C | 2θ° | (hkl) | TC(hkl) | | | |
|---|---|---|---|---|---|---|
| | | | 1.25 V | 1.5 V | 1.75 V | 2.0 V |
| 25 | 44.559 | 111 | 1.3415 | 1.4762 | 1.5741 | 1.7831 |
| | 51.930 | 200 | 0.9714 | 0.8224 | 0.6741 | 0.5421 |
| 35 | 44.559 | 111 | 1.3541 | 1.5413 | 1.6107 | 1.8741 |
| | 51.930 | 200 | 0.8702 | 0.7055 | 0.5467 | 0.4531 |
| 50 | 44.559 | 111 | 1.4531 | 1.5731 | 1.7762 | 1.9102 |
| | 51.930 | 200 | 0.5431 | 0.4211 | 0.3513 | 0.2365 |

**Table 2.** Crystalline parameters of Ni NTs.

| Synthesis temp., °C | Para-meters | Voltage of synthesis, V | | | |
|---|---|---|---|---|---|
| | | 1.25 | 1.5 | 1.75 | 2.0 |
| 25 | *a*, Å | 3.517 | 3.5179 | 3.5192 | 3.5211 |
| | *L*, nm | 24.77 | 25.73 | 26.91 | 28.11 |
| 35 | *a*, Å | 3.5181 | 3.5194 | 3.5201 | 3.5232 |
| | *L*, nm | 25.15 | 26.11 | 27.21 | 29.34 |
| 50 | *a*, Å | 3.5195 | 3.5201 | 3.5216 | 3.5266 |
| | *L*, nm | 26.65 | 28.17 | 29.76 | 31.23 |

The experimental data show strong magnetic anisotropy of Ni NTs arrays in the entire range of the synthesis parameters coercivity and squatness value for parallel (∥) orientation of the field relative to the NTs axis is several times higher than the values for the perpendicular (PD) field direction. The anisotropy of the magnetic properties is caused by crystalline anisotropy, detected in the X-ray analysis, and shape anisotropy, caused by the fact that in an external magnetic field NTs with high aspect ratio (~100) need higher energy of demagnetization along their axis than in the perpendicular direction of the field.[18]

**Table 3.** Magnetic parameters of Ni NTs.

| $T_{synthesis}$, °C | Voltage, V | $H_C$, Oe | | $M_r/M_s$ | |
|---|---|---|---|---|---|
| | | PD | ∥ | PD | ∥ |
| 25 | 1.25 | 160 | 240 | 0.14 | 0.25 |
| | 1.5 | 140 | 260 | 0.10 | 0.31 |
| | 1.75 | 130 | 330 | 0.09 | 0.39 |
| | 2 | 150 | 280 | 0.09 | 0.28 |
| 35 | 1.25 | 160 | 210 | 0.12 | 0.22 |
| | 1.5 | 150 | 280 | 0.12 | 0.25 |
| | 1.75 | 170 | 280 | 0.12 | 0.26 |
| | 2 | 130 | 250 | 0.11 | 0.24 |
| 50 | 1.25 | 50 | 330 | 0.07 | 0.30 |
| | 1.5 | 80 | 250 | 0.08 | 0.25 |
| | 1.75 | 70 | 270 | 0.04 | 0.29 |
| | 2 | 250 | 320 | 0.13 | 0.29 |

The values of the main magnetic characteristics of the Ni NTs are closely linked with their crystal structure. Considering the study of the structural features of NTs a strong correlation of the parameters of crystal structure of the samples with the temperature and the voltage of synthesis is established. An expected correlation of the main magnetic parameters with the synthesis conditions has not been proved, because, despite the variation of structural parameters, a dependence of the magnetic properties was not observed (see the data in table 3) in the considered range of deposition parameters.

## Conclusions

Ni NTs have been obtained using ion-track PET membranes, by means of the electrochemical synthesis at various potentials and temperatures. Investigations of the morphological and structural characteristics of the NTs using SEM, EDX and XRD make it possible to determine that Ni NTs have lateral dimensions corresponding to the pores parameters (length ~12 μm and pores external diameters 400 nm) with the tubes walls thickness in the range from 60 nm to 160 nm, depending on the deposition conditions. The XRD analysis shows that the Ni NTs possess the *fcc* lattice phase with the crystal structure parameters being different from the reference values.

There is no evidence of the dependence of the changes of the magnetic parameters values on the experimental range of the voltage and temperature during the synthesis. Investigation of magnetic properties shows a significant magnetic anisotropy.

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