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PECULIARITIES OF TEMPLATE ASSISTED ELECTRODEPOSITION ONE-DIMENSIONAL NICKEL NANOSTRUCTURES FROM CHLORIDE ELECTROLYTE

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Abstract. This work is dedicated for the study of the effect of the adding of ethanol to chloride electrolytes during the electrochemical synthesis of nickel nanotubes in the pores of the polymer template. A detailed study of the dynamics of the main structural parameters of nickel precipitate with variation of the deposition potential, both without and with using ethanol, was carried out. The effect of the change of potential and the adding of surfactant on the morphology of one-dimensional nickel nanostructures grown in the pores of the polymer template was shown, and the effect of structural parameters on the electrical conductivity of nickel nanotubes was analyzed.

Keywords: *Magnetic nanotubes, template synthesis, electrodeposition, ion-track membranes.*

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1. Introduction

Synthesis of metallic magnetic nanomaterials with a controlled shape and size is one of the interesting tasks of modern material science. The unique properties of elongated nanostructures, including the anisotropy of magnetic and optical properties, as well as the ability to carry out controlled synthesis, make it possible to find applications for these nanostructures as sensitive elements of sensors: optical sensing, plasmonic resonance sensors (Sarkar *et al*., 2011), magnetic resonance sensors, trenches, and capacitors (Melzer *et al*., 2015), magnetic media for targeted delivery (Kozlovskiy *et al*., 2018), etc.

Among the methods for the synthesis of prolonged nanostructures, template synthesis is one of the reliable methods for obtaining the form of patterns given by a template. Advantages of template synthesis in high performance and cost-effectiveness, allow duplicating a complex topology in one step. In addition, using masks and patterned synthesis, it is possible to produce complex three-dimensional microstructures - elements of microcircuits.

For the template synthesis of nanostructures, both a rigid matrix (for example, SiO2 / Si, PI / Si, etc. (Hoppe *et al*., 2008; Kaniukov *et al*., 2016; Zhang & Zhao, 2009) and a flexible polymer film (Hulteen & Martin, 1997; Shumskaya *et al*., 2017) are used.

Among the methods of synthesis themselves are the simplest and repeat the method of electrochemical deposition into the pores of the templates (Martin, 1994; Kartopu *et al*., 2012). To this approach, electrolytes, based on chlorides, sulfides, and metal nitrides can be used (Kong *et al*., 2015; Kaniukov *et al*., 2017; Zhang *et al*., 2007). To control the physical properties and the crystal structure, various chemical components are used that increase or decrease the deposition rate, for example, NaOH, barium salts, alcohols or weak organic acids.

Presented our work is a part of a complex study devoted to the determination of the influence of synthesis conditions on the structural and physical properties of ferromagnetic nanotubes. The work considers the influence of the adding of surfactant to the electrolyte and the synthesis voltage on the deposition rate Ni in the pores of ion-track polymer templates, as well as determining the structure characteristics and electrical conductivity of arrays of elongated nanostructures.

2. Experimental part

Ion-track membranes (TM) based on polyethylene terephalate (PET) of Hostaphan® production of company «Mitsubishi Polyester Film» (Germany) with pore density $4.0*10^7$ cm^{-2}, thickness 12 microns and diameters 380±20 nm were used for fabrication of nanotubes by method of electrochemical deposition (Fig. 1a). The features of obtaining and characterizing PET templates are discussed, and the methodological aspects of obtaining in work (Shlimas *et al.*, 2018). The cathode was a thing gold film produced by magnetron spattering. Electrochemical deposition in pores of PET was carried out in the range from 1.5 V to 2 V with step of 0.25 in the potentiostatic mode. The electrodeposition cell is shown on the figure 1b.The electrolyte$NiCl_2 \times 6H_2O$ (100 g/l) was used for synthesis. Boric acid (H_3BO_3) (45 g/l) and ascorbic acid $C_6H_8O_6$ (1.5 g/l) were added in each electrolyte, H_3BO_3 was used for control of pH level of solution, ascorbic acid act as a buffer to maintain the pH. Temperature of solutions was 25°±2°C and acidity was pH=3.

Synthesis process was discussed in (Kozlovskiy *et al.*, 2019) and could be described by the following equation:

$$NiCl_2 \rightarrow Ni^{+2} + Cl_2^{-2}$$
$$Ni^{+2} + 2e \rightarrow Ni^0(s) \downarrow$$

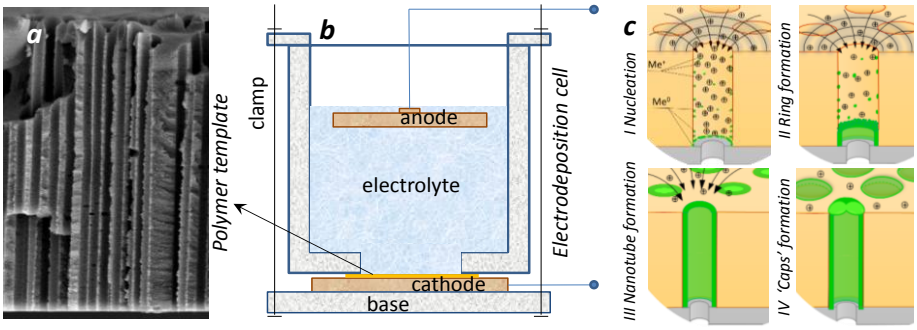

Figure 1. Ion-track template (a), principal scheme of electrodeposition cell (b), stages of electrodeposition (c)

The electrodeposition in the pores of the templates consists of several stages (Fig.1c): *I* - nucleation (most actively occurring on the cathode), *II*- growth of the nuclei with the formation of the primary ring - the base of the nanotube, *III*- layer-by-layer deposition of metal ions with the formation of dense walls of the nanotubes, *IV* - the deposition to the surface with the formation of "caps".

Ethyl alcohol was used for assessment of the effect of surfactant additives on the rate of synthesis and the structural properties of nanostructures. The use of surfactants is caused by decrease in the surface tension of the liquid due to adsorption at the interface, which makes it easier to distribute and reduce the interfacial tension during synthesis. This can significantly change the growth mechanism of nanostructures.

Investigation of structure and dimensionality of obtained nanotubes was carried out by using scanning electron microscope (SEM) Hitachi TM3030 equipped with system of microanalysis Bruker XFlash MIN SVE at accelerating voltage of 15 kV.

X-ray phase analysis (XRD) was performed on a D8 ADVANCE ECO diffractometer (Bruker, Germany) using CuKα radiation in angles 2θ = 40-90°with steps 0.03°. The software BrukerAXSDIFFRAC.EVAv.4.2 and the international ICDD PDF-2 database were used for identification of the phases and study the crystal structure.

Volt-ampere characteristics (IVC) were made from an array of nanostructures, an area of 1.0 cm^2. Sample with deposited nanostructures was placed between the two metal plates, which cover only the part where there are nanostructures in the film. The plates were connected tocurrent source with a serial connection of a multimeter.

3. Results and discussion

The study of the electrodeposition of nickel nanostructures is necessary to establish the basic dependencies for obtaining structures with predetermined structural and physical parameters (Fig. 2).

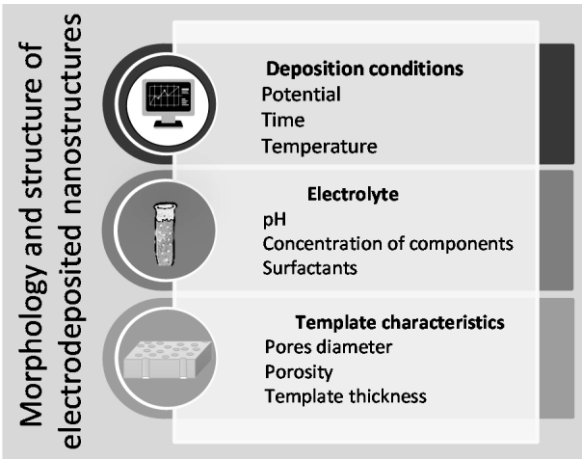

Figure 2. Factors, influencing on structure and morphology of nanostructures during electrodeposition in porous template

Variation of the deposition parameters, as well as the parameters of the template, leads to a change in the deposition rate (Kozlovskiy *et al*., 2017). By varying the deposition rate, the composition, morphology, and structural parameters of the resulted nanostructures can be controlled. The growth of the deposition rate can be caused by an

increase in the temperature and the potential difference of deposition, as well as a decrease in the pores diameter of the template. In addition, the deposition rate will depend on the concentration of metal ions in the electrolyte, and the acidity of the electrolyte will allow stabilizing metal ions in the solution and, corresponded deposition rate. Traditionally, aqueous sulfate and chloride electrolytes are used (Sofiah *et al*., 2017; Tishkevich *et al*., 2019) to precipitate nickel nanostructures, as well as water-alcohol compositions. Alcohols allow one to change the physical properties of the electrolyte, such as dielectric constant, viscosity, adsorption, etc. Thus, the addition of surfactant changes the rate of nucleation and electrodeposition on the surface of the electrode, which leads to a change in nucleation process and the properties of the resulting precipitate.

Previously in work (Tishkevich *et al*., 2019) we shown morphology, structural and magnetic changes on prolonged nanostructures synthesized under different conditions were formed from sulfate electrolyte. Images of nanostructures deposited from chloride electrolyte are shown in Figure 3. Length and diameter of prolonged nanostructures are corresponded to the thickness of the membrane, and amounted to 11±0.5 μm and 380±20 nm.

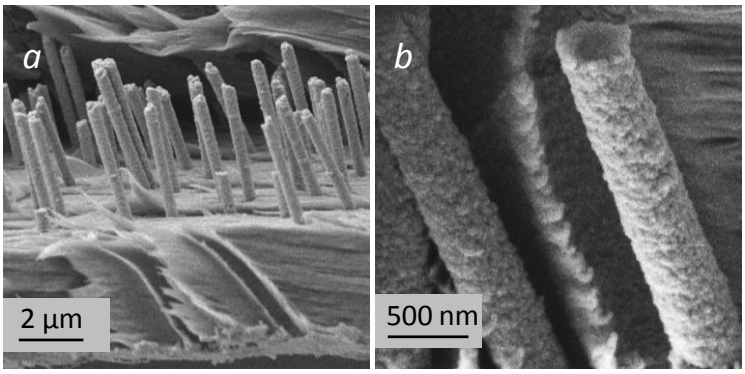

Figure 3. Nickel nanotubes in partially dissolved template: Typical SEM image of array (a), enlarged fragment (b)

An important part of the study is the use in the electrolyte of a surfactant – ethanol. X-ray diffraction analysis method was used to indicate structural changes depending of electrolyte composition and deposition voltage. All reflections in the diffractograms (Fig.4) have low intensities, which are characteristic for diffraction at nanoscale objects.

Analysis of X-ray diffractograms observed polycrystalline structures of samples with *fcc* phase, cubic syngony of the spatial group Fm-3m (225). There is no impurity of oxide phases in the nanotube structure. At the same time, changes in the shape of the peaks for different samples are obvious. To assess the influence of the synthesis conditions on the texture of nanotubes, as well as the structure parameters the value of the texture coefficients *TC (hkl)*, the lattice parameters *a*, the crystallite size *L*, the degree of crystallinity, the coefficient of deformation ε, the dislocation density *δ*, microstrains were calculated.

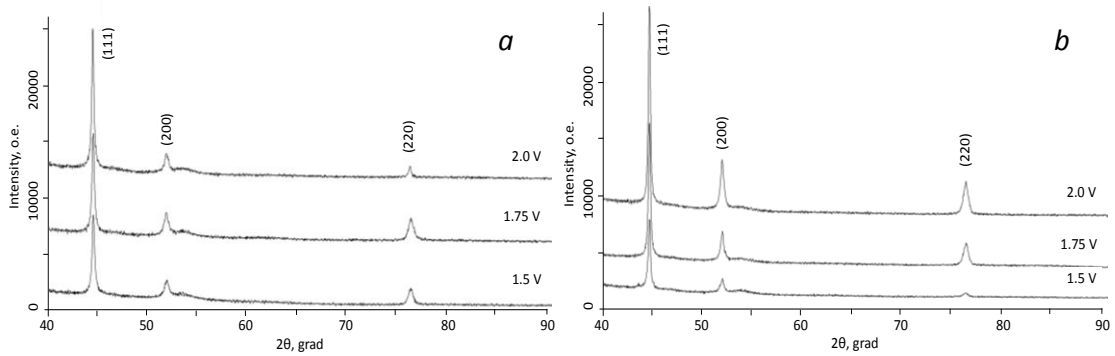

Figure 4. X-ray diffraction patterns of samples deposited from solutions without (a) and with ethanol (b)

The change in the potential difference and electrolyte solutions leads to a change in the degree of texturization of the obtained samples. The results of calculation of texture coefficient are in the Table 1.

Table 1. Texture coefficients of Ni nanotubes

U, V	TC (hkl)			TC (hkl) (with ethanol)		
	111	200	220	111	200	220
1.5	2.234	0.424	0.221	2.435	0.342	0.213
1.75	2.452	0.342	0.213	2.134	0.314	0.763
2.0	2.532	0.231	0.345	2.325	0.432	0.212

An increase in the potential difference leads to change in the texture coefficients, and an increase in the degree of polycrystallinity of nanostructures. There is also a slight change in texture when ethanol is added to the electrolyte. The intensity of types (200) and (220) increases, that indicates an increase in the degree of polycrystallinity.

Analyzing the width and area of the line of diffraction maxima, it is possible to estimate the contribution of various defects to the change in the properties of the material. In this case, the broadening of the widths of diffraction lines can be due to microstrains in the structure, which are associated with the accumulation of dislocations, as well as the crushing of crystallites associated with crystallization processes. An analysis of the angular dependence of physical broadening makes it possible to estimate the influence of both factors. The Williamson-Hall method was applied for assessment of the effect. The change in the synthesis conditions and electrolyte solution leads to a change in the main crystallographic characteristics (Table 2 and 3).

Table 2. Data of crystallographic characteristics

U, V	*a*, Å		*L*, nm	
	Without ethanol	With ethanol	Without ethanol	With ethanol
1.5	3.5122	3.5156	24.79±2.13	28.17±1.76
1.75	3.5143	3.5171	24.51±2.11	29.43±2.11
2.0	3.5171	3.5157	33.95±2.65	27.91±1.52

Table 3. Structure parameters

U, V	Microstrains		ε		δ, $m^2 \cdot 10^{15}$		Crystallinity degree, %	
	Without ethanol	With ethanol	Without ethanol	With ethanol	Without ethanol	With ethanol	Without ethanol	With ethanol
1.5	0.046	0.034	0.177	0.134	0.126	0.1627	80,6	71
1.75	0.067	0.042	0.235	0.213	0.1155	0.1665	76,7	76,8
2.0	0.089	0.052	0.315	0.275	0.1284	0.1868	75,5	84,6

Changes in the lattice parameters with increasing of deposition potential indicate the occurrence of inclusions in the crystal lattice. This effect is most obvious at a voltage of 2 V. An increase in crystallite size confirms this assumption. As was shown earlier (Kozlovskiy *et al*., 2017; Kaniukov *et al*., 2018), with an increase in the deposition voltage, the rate of the formation of nanostructures significantly increases, which leads to an increase of non-uniformity of the process and the appearance of defects in the structure and inclusions. The formation of additional stresses in the structure was observed resulting from the formation of inclusions and regions with a high degree of defectiveness. As a result, the structure shows an increase in the distortion of the crystal lattice and a change in the interplanar distances that lead to an increase in the microstresses in the crystal structure. When ethanol is added, this effect is not observed. Almost all parameters indicate the perfection of the crystal structure.

The addition of additive surfactants leads to a decrease in the degree of microstresses and deformations in the structure, providing the increase in the degree of crystallinity and a decrease in deformation and distortion in the crystal structure. This fact can have a significant effect on the performance characteristics of nanostructures, such as conductive or magnetic properties. While using standard electrolyte, at large deposition potential, a rapid evolution of hydrogen was observed, which passivates the anode and leads to an uneven growth of nanostructures. Addition of surfactant additives to electrolytes leads to a decrease in the growth rate, while at high potential differences there was no evolution of hydrogen. Figure 5 shows SEM images of synthesized nanostructures with the addition of surfactants and without surfactants.

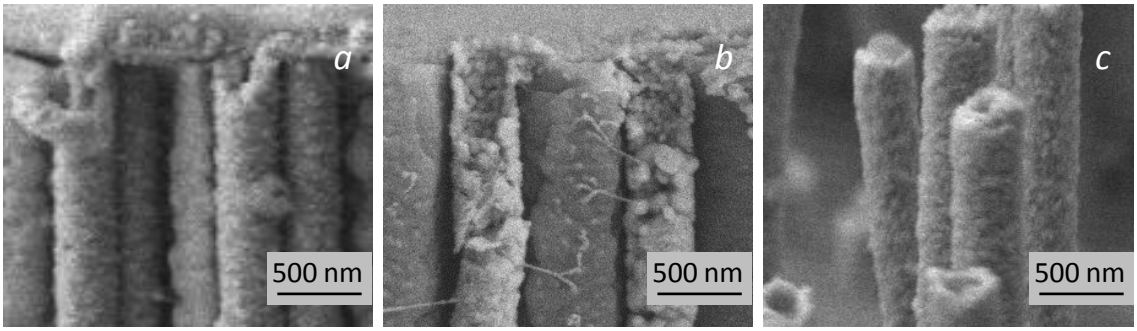

Figure 5. SEM – images of synthesized nanotubes: U=1.5 V (a); U=2.0 V (b); U=2.0 V with ethanol(c)

It can be seen from the presented images, that nanostructures are obtained in the form of tubes at potential difference of 1.5 V. However, at difference in the applied potentials of 2.0 V, porous inclusions are observed in the walls of nanotubes, which can be due to the influence of the impurity on the formation of the nanotube structure. In

turn, the addition of additive surfactants leads to the absence of inclusions in nanostructures even at a potential difference of 2.0 V.

One of the important characteristics is the conductive properties for potential practical applications of nanostructures. Such parameters as chemical composition, crystal structure, geometric characteristics and morphology of the surface affect the transport characteristics of nanostructures. The results of the change in conductivity are shown in Table 4.

Table 4. Conductivity of the nanotubes arrays depending on the electrolyte solution

U, V	Conductivity, Sm	
	Without ethanol	With ethanol
1.5	0.79	0.81
1.75	0.69	0.85
2	0.65	0.96

It can be seen from the presented data, that an increase in the potential difference up to 2.0 V for electrolyte without ethanol leading to large distortions and deformations of the crystal structure, as well as the formation of amorphous inclusions in the structure, leads to a decrease in the conductivity. Addition of surfactant additives leads to an increase in conductivity, which is due to the high degree of crystallinity of nanostructures and the more perfect structure of nanotubes.

4. Conclusion

Nickel nanotubes were synthesized in the pores of the ion-track membranes. Electrochemical deposition into the porous templates was carried out in the voltage range from 1.5 to 2 V with a step of 0.25 in the potentiostatic mode from chlorine electrolyte and water-alcohol chlorine electrolyte. The influence of deposition conditions on the texture, the degree of crystallinity, the dislocation density and microstrains were calculated, as well as on the change in the main parameters characterizing the crystal structure, is shown. An increase in the synthesis voltage leads to an increase in the deposition rate and, as a consequence, a thinning of the walls of the nanotubes, up to the formation of a granulated structure, and an increase in its defectiveness. Adding alcohol to the electrolyte reduces the deposition rate and promotes the formation of nanostructures with a less efficient crystalline structure. This is due to the increase in conductivity for the synthesized samples with the addition of ethanol, reducing the amount of amorphous inclusions, creating additional defects in the structure that prevent the movement of electrons.

Information is important not only for determining the fundamental principles of obtaining nickel nanotubes with predetermined morphology, structural parameters and electrophysical characteristics, but it can also be useful in practice when selecting modes for industrial production of one-dimensional nanostructures using the template synthesis method. The established effects will allow for controlled production of nickel-based metal nanotubes in a given morphology and structure in flexible porous templates for microelectronics tasks.

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