

## THE FEATURES OF Ni-Fe NANOWIRES ELECTROCHEMICAL DEPOSITION INTO POROUS ALUMINA TEMPLATE

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### I. INTRODUCTION

The arrays of numerous metallic nanowires (NWs) with straight-ordered configuration have attracted a lot of attention due to their shape anisotropy and extremely large surface area. The combination of this unique structure with uncommon magnetic, optical and transport properties can be used to develop novel functional nanomaterials for magnetic, electronic, biomedical and optical nano-scale devices [1, 2].

There are different methods to fabricate NWs including electrochemical deposition into porous alumina (PA) template. Such advantages of this method as low cost, simplicity and efficient testability do it very attractive from the practical point of view [3, 4]. The features of electrochemical deposition of various metals (and their composition) into the PA template are still the needed research issue.

In this work, the technique of Ni and Ni-Fe NWs formation by dc electrochemical deposition into PA template with various heights is presented. The structural and chemical properties of PA/Ni and PA/Ni-Fe NWs were investigated and discussed.

### II. RESULTS AND DISCUSSION

In our work, the home-made PAs were prepared using dc anodization of Al foil. First, the samples of commercial aluminium foil (99.995%) with 60×48 mm size and ~100 μm thickness were annealed at 350 °C for 1 h. Then, the samples were electropolished in a mixture of chloric and acetic acids 1:4 (volumetric ratio) at T ~ 8° C and voltage of 25±2 V for ~ 1 to 2 min to reduce the surface roughness. Next, the samples were washed in distilled water and dried under dry air stream. Before anodization, the technological frame has been formed along the perimeter and in the center of the substrate. It is necessary to strengthen the mechanical stability of a free-standing membrane and to restrict certain zones with identical surface area. The frame destination and its formation procedure are described in details elsewhere in [5]. Thick porous alumina films with ordered structure of pores have been prepared by two-step anodization in aqueous solution of oxalic acid (H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>) (0.3 M) at 15° C. The first stage of anodization was performed under the constant voltage 50±5 V for 25 min. After the first anodization, the preformed oxide film was removed by wet chemical etching in a mixture of phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) (0.5 M) and chromic acid (H<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>) (0.2 M) at 80±5° C for 5 min. The second stage of anodization was performed under the same conditions for 1 to 4 h.

Then, electrochemical etching of the barrier layer at the bottom of pores was carried out using gradual reduction of forming voltage down to 15±2 V. Further, the detachment of alumina from the substrate was performed by Al dissolution in a saturated solution of cupric chloride and hydrochloric acid (HCl+CuCl<sub>2</sub>). Chemical dissolution of the rest of a barrier layer at the pore bottom and chemical pore widening was performed in 4 wt. % H<sub>3</sub>PO<sub>4</sub> (30° C) for 15 min. Finally, an electric contact metal (Ta 300 nm + Ni 300 nm or Ta 300 nm + Cu 300 nm) layer was sputtered onto the back side of PA, and protective coverage of chemically resistant varnish HSL (perchlorovinyl lacquer) coated the metal layer. As a result, the alumina template with ordered structure (Figure 1) of 30-90 μm thick with pore diameter of 50 ± 5 nm has been fabricated.

We used the galvanostatic dc deposition mode to synthesize Ni and Ni-Fe NWs arrays in PA template fabricated by aluminum foil anodizing in oxalic acid aqueous solution. It has been found experimentally that, by applying a low current density 3.0 mA·cm<sup>-2</sup> during galvanostatic dc deposition through a porous template, the highly ordered, densely packed NWs with uniform geometrical parameters of about 25 μm long are formed. The solution for Ni-Fe NWs electrodeposition was prepared using NiSO<sub>4</sub> heptahydrate and FeSO<sub>4</sub> hexahydrate as sources of Ni and Fe ions, and H<sub>3</sub>BO<sub>3</sub> as a stabilizer. To fabricate Ni NWs, we used solution containing NiSO<sub>4</sub> hexahydrate and NiCl<sub>2</sub> hexahydrate as a nickel source, and boric acid as a stabilizer. NaOH was used to adjust the solution pH by the pH meter HI83141 (HANNA instruments). Preventers (Na<sub>2</sub>SO<sub>4</sub>, CuSO<sub>4</sub>) were added to decrease corrosion activity of the electrolyte.

All experiments were performed at room temperature (22 ± 2° C) using 3 cm<sup>2</sup> area samples at the constant current density of 3 mA·cm<sup>-2</sup> and various deposition duration from 10 to 150 min. The alumina thickness was varied in the range of 30-90 μm. All the electrochemical processes (anodizing and deposition) were carried out in the two-electrode cell. The graphite plate was used as the auxiliary electrode. In Figure 1, the SEM cross-section views of PA/Ni-Fe (a, b, c) and PA/Ni (d) composites prepared at the same current

density ( $3 \text{ mA}\cdot\text{cm}^{-2}$ ) for 10, 90, 150 min (a, b, c) and 10 min (d) and for various thickness (HPA) of alumina template: a, b, d  $\sim 30 \mu\text{m}$ , c  $\sim 90 \mu\text{m}$ , correspondingly, are presented.

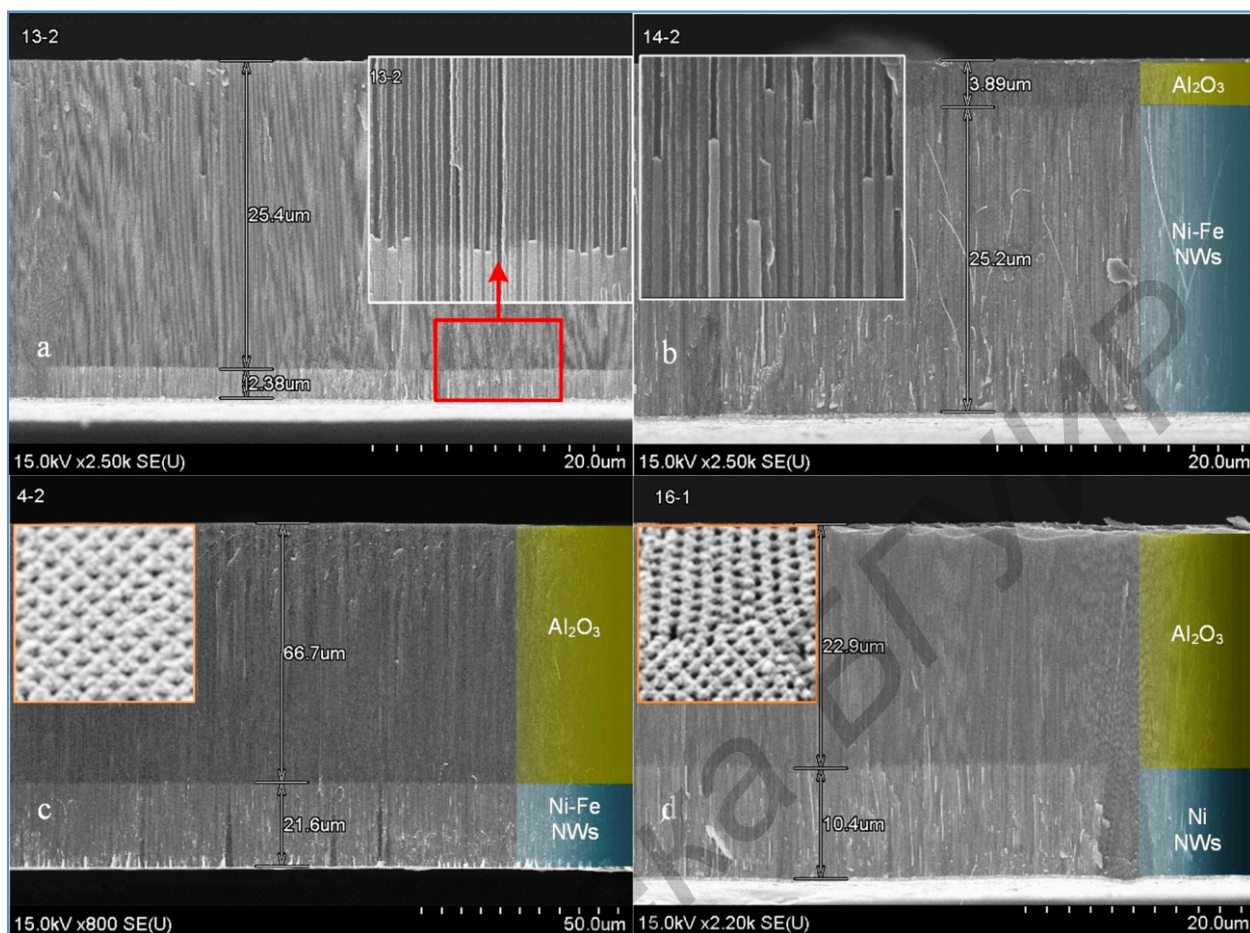


Figure 1. SEM cross-sectional views of the alumina template after galvanostatic dc deposition of Ni-Fe (a, b, c) and Ni (d) NW arrays under the following conditions: current density  $3 \text{ mA}\cdot\text{cm}^{-2}$ , deposition duration 10 min (a, d), 90 min (b) and 150 min (c). In the insets: the top-view SEM images of the template (red frame) and the enlarged image of the deposition front depending on deposition duration

From Figure 1 it is evident that NWs fill each of pores. Both pores and NWs have smooth and straight edges; diameter of a NW is equal to diameter of the pore. It should be noted that the cross-sectional SEM images were obtained by cleaving the PA, thereby the detachment of some NWs from their pores occurred.

Under increase of deposition duration (with other parameters being equal) the NWs length increases almost linearly to  $25 \mu\text{m}$  that corresponds to the aspect ratio (a. r.) 500.

The growth rate for Ni-Fe NWs  $v_m$  is twice less than for Ni NWs with other parameters being equal. The growth rate dependence on the oxide thickness for Ni NWs is more obviously expressed. In the case of Ni-Fe NWs, the growth rate almost does not depend on HPA in the range of 30 to  $65 \mu\text{m}$  and decreases only achieving HPA  $\sim 90 \mu\text{m}$ . The obtained results and the scanning electron microscopy data show that NWs quality (smoothness, thickness homogeneity, continuity) depends on evenness of deposition process as well as on perfection of a template. The evenness of deposition process, in turn, depends on the pore filling rate and, partly, on the template thickness, especially in the case of Ni.

Further, the results of crystal structure investigations are discussed. The XRD patterns of PA/Ni and PA/Ni-Fe composites are shown in Figure 2 and summarized in Table 1.

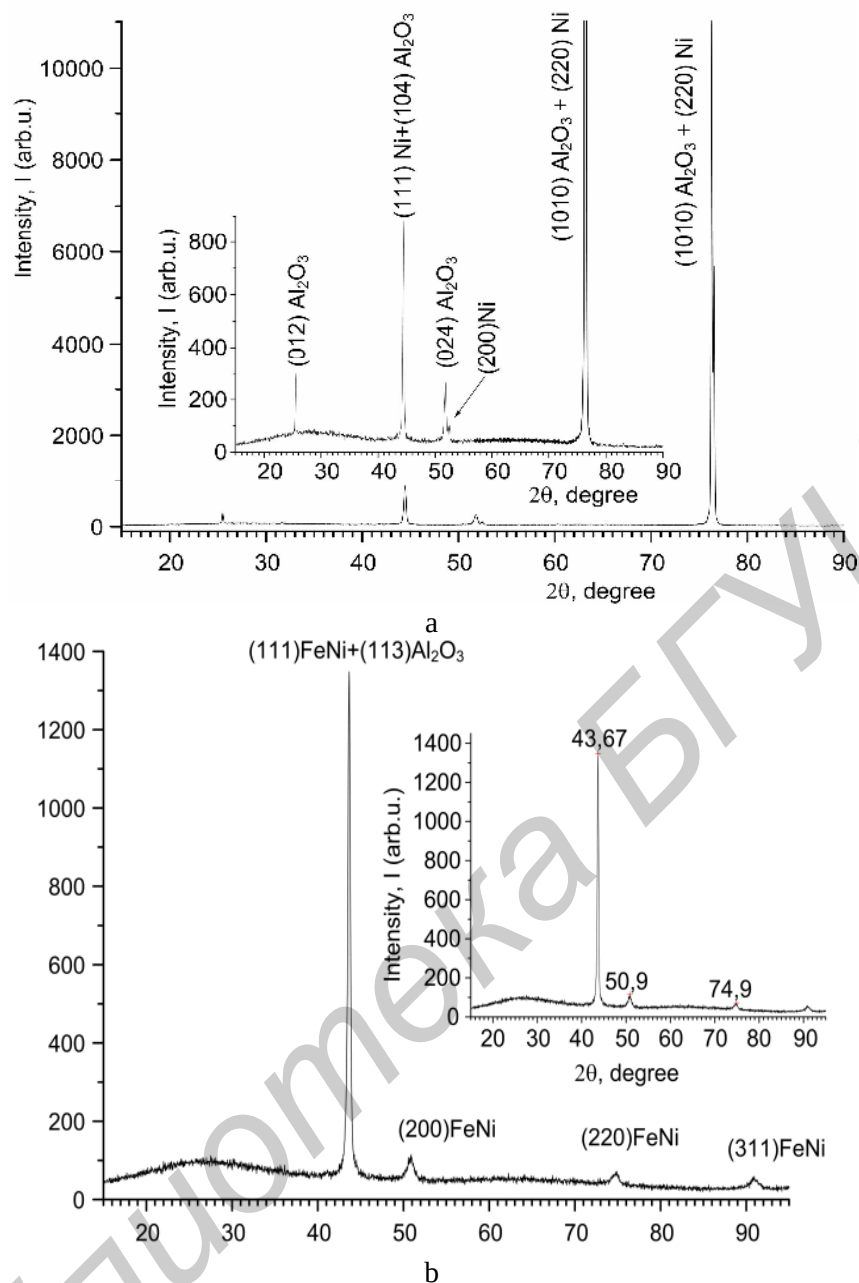


Figure 2 – XRD patterns of PA/Ni and PA/Ni-Fe composites: a – XRD pattern for Ni NWs in alumina template with  $H_{ox}$  of 65  $\mu\text{m}$ ; current density 3  $\text{mA}\cdot\text{cm}^{-2}$ , deposition duration 120 min. b – XRD pattern for Ni-Fe NWs inside the alumina template with  $H_{ox}$  of 50  $\mu\text{m}$ ; current density 3  $\text{mA}\cdot\text{cm}^{-2}$ , deposition duration 90 min

Table 1 – The crystallite sizes for Ni and Ni-Fe NWs in alumina template

Sample	Ni, NWs				Ni-Fe, NWs			
	111	200	220	311	111	200	220	311
Orientation	111	200	220	311	111	200	220	311
I, %	11	1.3	100	-	100	29	9	7
D, nm	17.9	18.3	35.3	-	17.9	9.1	6.9	7.8

The arrays of vertically ordered, straight and smooth polycrystalline Ni NWs with the preferred growth orientation of (220) and Ni-Fe NWs with preferred (111) orientation have shown ferromagnetic properties [5].

Chemical microanalysis was performed by dint of hardware-assisted scanning electron microscope Bruker QUANTAX 200 (Zeiss A.G.). Chemical composition and components content in NWs correspond to Ni – 15 % Fe if take into consideration these main elements quantity only, without oxide and impurities. The scans are shown in Figure 3 as energy dispersive analysis data.



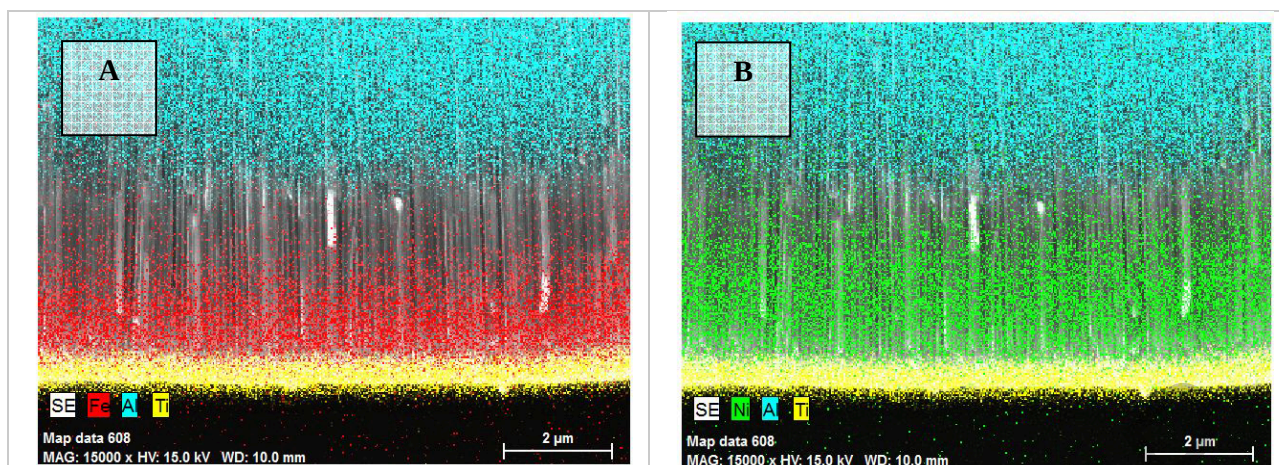


Figure 3 – Contrasting color coded images (distribution maps) for Fe (A) and Ni (B) in  $10 \times 8 \mu\text{m}$  region showing phase contrast fluctuations (oxide pores filling) along the scanning area

The abnormal character of electrochemical deposition of Ni-Fe films and the reason for such behavior are considered. Standard potential for  $\text{Ni}^{2+}$  ions deposition ( $\varphi^0\text{Ni}^{2+}/\text{Ni} = -0.250 \text{ V}$ ) is higher than for  $\text{Fe}^{2+}$  ( $\varphi^0\text{Fe}^{2+}/\text{Fe} = -0.441 \text{ V}$ ). That is, theoretically, Ni should be deposited on the cathode firstly. However, experimental results have shown that Fe is precipitated foremost. A reason for this abnormal effect under Ni-Fe films co-deposition may be the hydrogen evolution reaction at the cathode resulting in the solution' pH increase near the electrode surface.

### III. CONCLUSIONS

The arrays of compact Ni-15%Fe NWs with high aspect ratio ( $\sim 500$ ) and diameters of 50 nm have been fabricated using porous alumina template by electrochemical dc deposition at low current density of  $3 \text{ mA} \cdot \text{cm}^{-2}$ . The influence of thickness and structural order of a template on the growth rate and uniformity of deposition process of NWs have been discussed, as these features define the quality of NWs. The comparative analysis of morphological and structural properties of Ni-Fe NWs vs. Ni NWs and bulk Ni was performed. The arrays of vertically ordered, straight and smooth polycrystalline Ni NWs with the preferred growth orientation of (220) and Ni-Fe NWs with preferred (111) orientation have shown ferromagnetic properties.

### ACKNOWLEDGMENTS

This study was supported by the Ministry of Education, Republic of Belarus and the State Scientific and Research Program "Nanotechnologies and nanomaterials".

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