

Nanowires of iron group metals: fabrication by matrix synthesis technique and investigation of structure and magnetic properties

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Abstract. Nanowires (NW) of iron group metal alloys (Fe-Ni, Fe-Co) were obtained using matrix synthesis technique based on polymer track matrixes. The galvanic process was investigated and it was found that it consists of different stages. Deposition of metal inside the pores has non-linear character due to diffusion limitation. The specific features of the next part (formation and growing of the “caps”) was also studied. Electron microscopy, X-rays analysis, Mössbauer spectroscopy and magnetic hysteresis were applied to investigate the dependence of structure and magnetic properties of the NW on electrodeposition conditions. It was found that the composition of two-component NWs differs from the composition of electrolyte and different at different parts of NW. Mössbauer spectroscopy gave possibility to estimate hyperfine parameters for Fe-Co NWs. For Fe-Ni NWs it was supposed that the spectra could be presented as superposition of at least three magnetic sextets with hyperfine parameters B_{hf} 27-33 T. It was shown that Fe-Co samples have “hard magnetic” properties, while Fe-Ni samples have “soft magnetic” parameters. The dependence of these parameters on the synthesis was demonstrated.

1. Introduction

Matrix synthesis. The obtaining and application of different types of nanomaterials are the main trends at the last time. The method of matrix synthesis are one of the most perspective among other techniques of nanomaterial fabrication [1]. The main idea of method is to fill the pores of specially prepared matrix by any desired material. The obtained structures are replicas of the pores [2]. Different mediums could be used as the matrixes-porous alumina, different zeolites, porous silica and polymer track membranes. Different materials could be used as a “filler”- polymers, dielectrics, some sorts of crystals and metals.

In this work polymer matrixes were used as the templates and their pores were loaded (electrodeposited) by metals in order to obtain so-called nanowires (NWs).

Track membranes. The process of fabrication of track membranes (TM) is well known- irradiation of thin polymer film with swift heavy ions followed by chemical etching of obtained latent tracks. The main parameters of TM are porous density (per sq. cm of the surface) and the diameter of the pores. These parameters could be specified at the stages of irradiation and etching. The main application of



such membranes is fine filtration in medicine, biology, food production and so on [3]. Another application is matrix synthesis, mentioned above.

Filling of the pores. In this work electrochemical (galvanic) deposition of metal into the pores of TMs were used. For this electrolytes- the salt(s) of corresponding metal(s) with some additives – were used. By varying of the deposition parameters different types of the NWs could be obtained.

Additional possibility of changing the properties could be obtained by using multicomponent NWs- due to variation of composition. In this case the correlation between composition of electrolyte and deposition regimes with the properties of obtained materials should be investigated. Such processes and relationships were investigated for bulk materials and for thin films- for these cases some approaches for compositions of electrolytes and galvanic regimes were developed [4]. At the same time, the features of electrodeposition into the narrow pores were not studied for multicomponent compositions [5,6].

So, this work is devoted to features of obtaining of two-component NWs and to investigation of some properties of obtained materials.

2. Experiment

Matrixes and obtaining of NWs. Commercial TM (made in JINR, Dubna: PET (Polyethyleneterephthalate) film with thickness 10-15 μm and pores with surface density 10^8 - 10^9) were used in first experiments. For other experiments PET matrixes (parallel pores and lower density- 10^6 - 10^8) were specially prepared using U-400 (JINR, Dubna).

For deposition of bi-component NWs the following electrolytes were used:

1) iron-nickel NWs: $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ - 16 g/l, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ - 40 g/l, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ - 16 g/l, ascorbic acid – 1-2 g/l, sodium lauryl sulfate – 1 g/l.

2) iron-cobalt NWs: $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ – 150 g/l, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ – 43 g/l, $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ – 40 g/l, ascorbic acid – 2 g/l, pH = 1.2.

Note, that the main problem was to found and maintain the optimal pH. Ascorbic acid was used mainly to prevent oxidation of Fe^{2+} to Fe^{3+} , while sodium lauryl sulfate stimulate penetration of electrolyte into narrow pores.

Electrodeposition was carried out in home-made galvanic cell. Potentiostat –galvanostat Elins P-30S was used as a current source for two-electrode connection. Electrodeposition was carried out using potentiostatic regime (constant voltage). The dependence of current of time was measured during the process, giving information about the stages of electrodeposition.

After formation of metal NWs they were removed from the host matrix by dissolving of polymer in concentrated alkali. If MWs remain in matrix so-called “metal-polymer composite” is formed.

Electron microscopy investigation of obtained NWs was carried out using standard techniques: SEM TESLA BS-340, FEI QUANTA 200 and FEI Scios working in secondary electron regimes were used. The elemental composition of some samples was estimated using EDAX analyzer (FEI QUANTA 200), while transmitted microscopy was done at TEM FEI Osiris.

Structure investigations. X-rays measurements of the samples were done at X'PERT PRO – diffractometer (PANalytical, $\text{CuK}\alpha$ ($\lambda = 1.5418 \text{ \AA}$, with Ni filter) using standard methods.

Mössbauer spectroscopy was done at MS-1104Em spectrometer (with ^{57}Co (Rh) source) at room temperature using standard technique. Isomer shifts were measured relative to metallic α -Fe foil.

Magnetic measurements were carried out for iron-nickel and iron-cobalt alloys at Vibrating Sample Magnetometr LakeShore 7407 at room temperature.

3. Results and discussions

Galvanic deposition of Fe-Co NWs was done at potentiostatic regime: the obtained dependences of current on time (potentiostatic curves) at different voltages are shown in Fig.1 for different pores (100 nm and 300 nm).

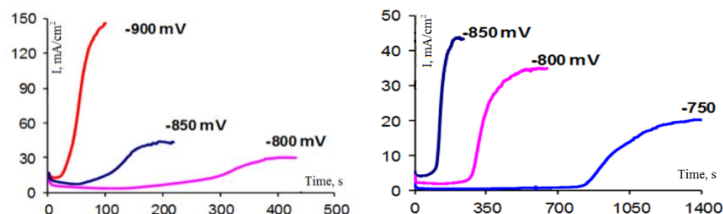


Figure 1. The dependence of current on time for deposition of Fe-Co alloy at different voltages. Temperature 200 C, pores diameter 100 nm (left) and 300 nm (right).

The grooving process could be estimated using these results: the speed of this process is rather fast and varied from 2 $\mu\text{m}/\text{min}$ to 25 $\mu\text{m}/\text{min}$.

Galvanic deposition of Fe-Ni NWs was also done at potentiostatic regime and obtained results are shown in Fig.2.

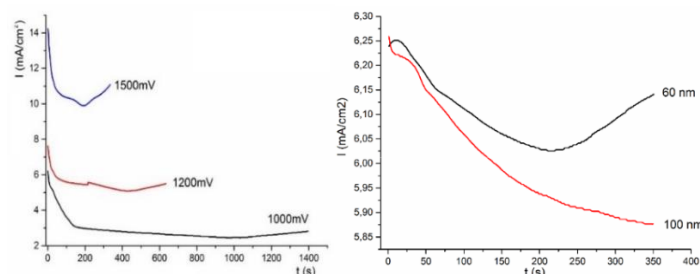


Figure 2. The dependence of current on time for deposition of Fe-Ni alloy at different conditions. Pores diameter 100 nm, voltage 1 V, 1.2 V, 1.5 V (left) ; pores diameter 60 nm and 100 nm, voltage 1.5V (right). (Temperature 200 C).

It is found that the pores of small diameter are filled faster and increase of the voltage accelerate all the processes. It is easy to see that in all cases the process consists of different parts.

First part – initial reduction of current is caused by changing the concentration of electrolyte inside the pores. Second part (main part) – gradual growth of metal wires inside the pores. This process has non-linear character, with a minimum: the decreasing of current is found to be turned to increase; this effect is most pronounced for nano-size pores. It could be explained by changing of concentration due to diffusion limitation inside the narrow pore channels. Another explanation is inconstancy of the pores diameter: it was found that the channels are narrower in the middle part, and this is most apparent for thin pores. The third part of the curves – fast rise of current is related with the formation of metal deposit on the external surface outside the pores (formation of so-called “caps”). An evaluation of cathode current density has shown that in spite of a steep rise in the current in the third part of the chronoamperogram, the magnitude of the cathode current density is several times lower than that in the first and second of parts of the curves. The reduction of current density is caused by a sharp increase in the voltage drop across the cathode layer (≈ 1 mm thick).

We found that current increase (at the last stage) is not proportional to the increasing cathode surface area: while the surface area becomes about 20 times larger after the filling of pores with metal, the current value increases only by 3-5 times. This effect depends on electrode potential and doesn't depend on pores diameter. Possible explanation is the shift of the cathode potential in the positive direction due to increased value of ohmic voltage drop in the solution in the vicinity of the cathode. Electrical resistance of the solution should be taken into consideration to explain this phenomenon. So, metal deposition inside the pores proceeds at more negative potentials and, therefore, at higher rates rather than one on a plane surface which takes place at more positive potentials, i.e., at lower rates.

It is easy to see that growing of “the caps” outside the pores then leads to coalescence of these caps with formation of continuous surface.

It could be concluded that grooving of two-component NWs have the same character as grooving of pure metals. At the same time, the composition of NWs in alloy is different from the composition in

electrolyte. It could be supposed that changing of growing condition during the deposition could lead to different composition of metals in different parts of NWs.

Electron microscopy study of the ensemble of free-standing Fe-Ni NWs is presented in Fig.3.

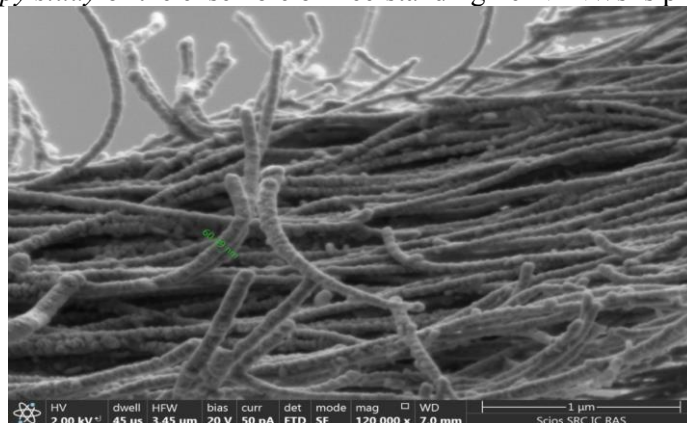


Figure 3. SEM images of Fe-Ni nanowires (diameter 60 nm).

Diameter (60 nm) and parallel orientation of NWs could be estimated. Using TEM it was found that NWs have crystal structure with small grains. Elemental analysis demonstrated that the main elements (Fe –approximately 55% and Ni- approximately 43%) distributed inside the bulk of NW, while oxygen was found at the surfaces of NWs (obviously due to formation of oxides). It was also found that metals concentration slightly changed along the NW's length. Fig 4. demonstrated SEM images of Fe-Co alloys NWs together with the results of elemental analysis.

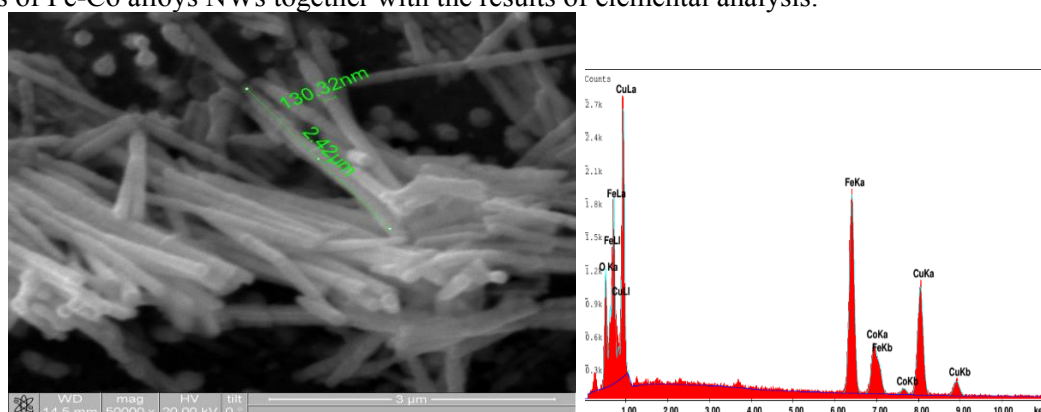


Figure 4. SEM image of Fe-Co nanowires (left), corresponding results of elemental analysis (right).

The obtained results (for both types of samples) demonstrated that NW's diameters is higher than the diameter of matrix pores – it could be explained by compression of polymer during the electrical deposition of metal. It was also found that the composition of two-component NWs differs from the composition of electrolyte and different at different parts of NW. This effect is more pronounced for higher grooving voltage and for pores with small diameter. It could be explained by difference in deposition potentials of two metals and by diffusion limitation.

Structure investigations. X-rays measurements were done for Fe-Co samples. It was found that NWs have polycrystalline structure and cell parameters close to the parameters of pure Iron. The lines of Cobalt were not found. It could be explained by formation of solid solution on the base of Iron, where cobalt is interstitial impurity and slightly effects on the cell parameter. In a first approximation the dependence on growing voltage was not found. It was also found that the cell parameter slightly depends on pore diameter, but its average value ($d = 2,854$) is lower than the parameter of pure bcc Iron ($d = 2,8664$). It could be explained both by formation of solid solution and by compression during the alloy growth inside the pores of matrix.

Mössbauer spectra. Our first results obtained for NWs from pure Fe were published in [7]. In this work two groups of Fe-Co NWs samples were investigated: - the first one- three samples grown at pH=1.2 (constant pores diameter -100 nm and different deposition potentials -0.7 V, -0.75 V and -0.8 V); the second - four samples on Fe-Co NWs (constant deposition potential -0.75 V and different pores diameter 30 nm, 50 nm, 100 nm and 200 nm). Mössbauer spectra of all the samples have typical 6-peaks shape with different intensity ratio- the last one was used for estimation of hyperfine parameters B_{hf} at Fe^{57} nuclei.

For the first group samples the dependence of spectral parameters on deposition voltage was studied. It was shown that hyperfine parameters actually doesn't change up to potential -0.75 V, but for higher potential (-0.8 V) parameters B_{hf} for all lines drop down at 0.5 T.

It should be noted that relative intensity of second and fifth lines are different for different samples, indicating the spontaneous magnetization of Fe. It is known that this relative intensity determined by equation $I_{2,5} = 4\sin^2\vartheta/(1 + \cos^2\vartheta)$, where ϑ is the angle between the magnetic moment M and the direction of gamma-quantum [8]. So, this ratio gave us possibility to determine the space orientation of M in NWs – the highest angle was found to be approx. 40°.

For second group of samples the dependence of spectral parameters of pores diameter was investigated –it was shown in Fig.5 (left).

For NWs with diameters 30 and 50 nm hyperfine parameters B_{hf} slightly differs from the same for other samples. Calculation shows that the angle ϑ (and, therefore, the sample magnetization) increased with the increase of NWs diameter. Fig.5 (right) demonstrated the Mössbauer absorption spectra for Fe-Ni samples with diameter 30 nm.

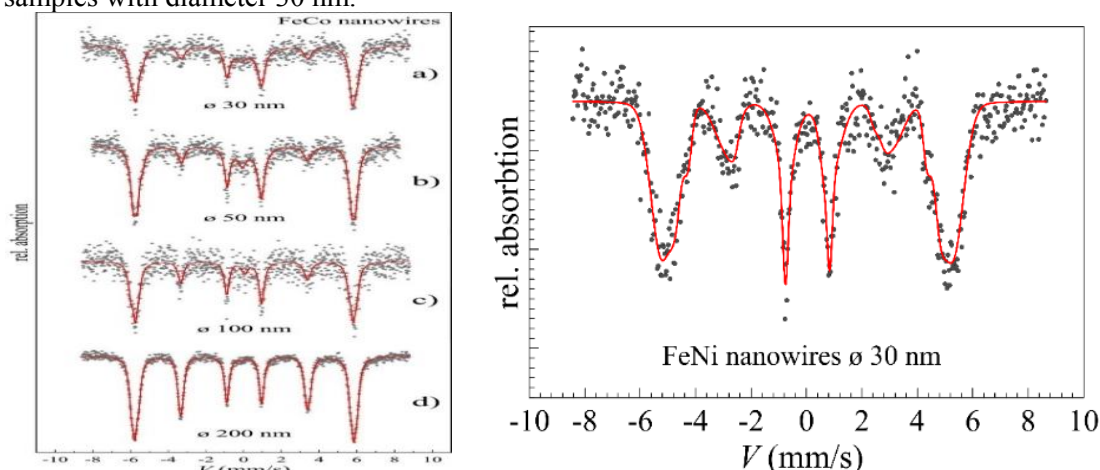


Figure 5. Mössbauer spectra of Fe-Co NWs, deposited into the pores with diameter 30 nm, 50 nm, 100 nm and 200 nm (a,b,c and d, resp.) at the deposition voltage -0.75 V (at the left side). Mössbauer spectra of Fe-Ni NWs (at the right side).

The typical magnetic splitting and changing of relative intensity of the lines, which indicated spontaneous magnetization of iron in Fe-Ni samples. It was found that the spectra could be presented as superposition of at least three magnetic sextets with hyperfine parameters B_{hf} 27-33 T. Supposedly they correspond to bcc and f_{cc} phases of alloy Fe-Ni with different local positions of Ni near Fe.

Finally, it should be mentioned that Mössbauer experiments results are in good agreement with the X-rays diffraction data and results of microanalysis.

Magnetic measurements were carried out for both Fe-Co and Fe-Ni NWs using vibrating magnetometer at room temperature. The obtained data are presented in Fig.6.

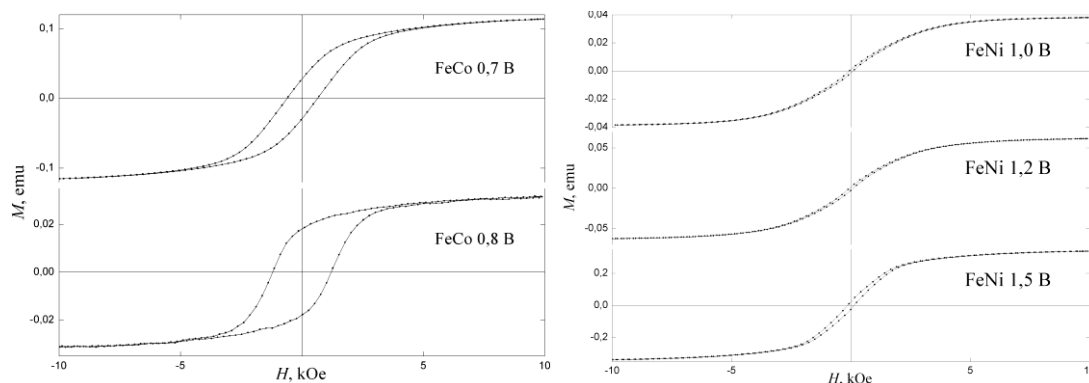


Figure 6. The hysteresis loops. At the left side - Fe-Co (growing voltage 0,7V and 0,8V); At the right side - Fe-Ni- (growing voltage 1, 1,2 and 1,5 V).

It could be concluded that all samples are ferromagnetic. Fe-Co samples have “hard magnetic” properties: coercive force 630 Oe (and r. magnetization 27 memu) and 1100 Oe (r. magnetization 18 memu) - for growing voltages 0.7 and 0.8 V (respectively). (For sample with growing voltage 0.85V (not shown) the coercive force is even higher -1200 Oe (r. magn. - 12 memu)).

At the same time Fe-Ni samples have “soft magnetic” parameters. Coercive force was found to be 75 Oe (r.magn. 1 memu), 80 Oe (r.magn. 1.3 memu), and 140 Oe (r.magn. 2.2 memu), for growing voltage 1, 1.2 and 1.5V (respectively).

In all cases these parameters depend on growing conditions- it could be explained that increasing of voltage leads to acceleration of the process and therefore – to structure with small-grains.

4. Conclusions

It was found that the process of electrodeposition of two-component NWs has the same character as deposition of pure metals. For example, it has non-linear character, due to diffusion limitation inside the narrow pores. The composition of two-component NWs differs from the composition of electrolyte and different at different parts of NW.

Mössbauer spectroscopy demonstrated that hyperfine parameters (for Fe-Co NWs) actually doesn't change up to growing potential -0.75 V, but for higher potential (-0.8 V) parameters B_{hf} for all lines drop down at 0.5 T. For Fe-Ni NWs the spectra could be presented as superposition of at least three magnetic sextets with hyperfine parameters B_{hf} 27-33 T.

It was shown that Fe-Co samples have “hard magnetic” properties, while Fe-Ni samples have “soft magnetic” parameters. Moreover, for all samples magnetic parameters depend on growing voltage because of increasing of voltage leads to acceleration of the process and to the formation of small-grains structure.

Acknowledgments

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