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# 中俄双边新材料新工艺研讨会



# 中国有色金属学会 编

By the Nonferrous Metals Society of China





## 内 容 提 要

本书收录了第十四届中俄双边新材料新工艺研讨会提交的全部论文,内容涵盖了 纳米材料、稀有金属和合金、新能源和储能材料、电子信息材料、生物医用材料、航 空航天材料、表面工程技术、陶瓷复合材料、新型冶金工艺和材料加工技术等领域。 本书可供材料及其加工领域的科研、技术和管理人员阅读,也可供大专院校有

本书可供材料及具加上领域的科研、技术和官理人页阅读,也可供大专院校有 关师生参考。

#### **Brief Introduction**

The book contains all the papers submitted to the 14<sup>th</sup> Sino-Russia symposium on advanced materials and technologies. The topic to be discussed covers from nanomaterials, rare metals and alloys, new energy and energy-saving materials, electronic information materials, biological and polymer materials, aerospace materials and surface engineering technology, ceramic and composite materials, new metallurgical processes to materials processing technology.

This book can be used for researchers, technicists and managers in materials and processing fields and teachers and students in universities.

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## Metal Nanowires- New Type of Nanomaterial: Fabrication by Matrix Synthesis Technique and Investigation of Structure and Properties

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**ABSTRACT:** Ensembles of Nanowires (NW) of iron group metals-pure metals (Fe, Ni and Co) and their alloys (Fe-Ni, Fe-Co) were obtained using matrix synthesis technique based on polymer track matrixes. Compositions of electrolytes were chosen – the salt of one corresponding metal (in the first case) and two salts (for second case). 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 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

*Nanowires*. The obtaining and application of different types of nanomaterials are the main trends in our time. One of the types of nanomaterial is Nanowires (NWs)- (another names are "1D structures", nanorods, nanotubes etc). There are different ways of obtaining of such materials. In most cases the separate single 1D-structures could be obtained. But in our case we obtain massives (ensembles) of identical parallel wires, fixed of the common base. These structures are wery perspective for practical applications. One way of application determined by very high surface of these materials- so, they could be used as surfaces for cooling and for chemical catalysis. Another way of application determined by very small radius of curvature of each individual wire-this lead to great increase of electrical field at the ends of the wires. It could be used for emission of electrons ("cold cathodes") or for emission of ions (in mass-spectroscopy). It can also be used for modulation of signal in non-linear optics units. There are different types of NWs- homogeneous one-metal NWs, homogeneous multi-component NWs ("alloys") and heterogeneous multicomponent structures, consists of alternating layers of different composition ("layered structures"). All variety of structures could be obtained by electrochemical methods – so, in order to obtain such ensembles of NWs the method of "Matrix synthesis" is used.

*Martix synthesis*. This method is 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 (Polyetheleneterephthalate) film with thickness 10-15  $\mu$ m 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 mono-component NWs the electrolytes of corresponding salts (mostly- sulphates) were used. For deposition of bi-component NWs the following electrolytes were used:

(1) iron-nickel NWs: NiSO<sub>4</sub>·7H<sub>2</sub>O - 16 g/L, NiCl<sub>2</sub>·6H<sub>2</sub>O - 40 g/L, FeSO<sub>4</sub>·7H<sub>2</sub>O - 16 g/L, ascorbic acid- 1-2 g/L, sodium lauryl sulfate- 1 g/L.

(2) iron-cobalt NWs: FeSO<sub>4</sub>·7H<sub>2</sub>O – 150 g/L, CoCl<sub>2</sub>·6H<sub>2</sub>O – 43 g/L, AlCl<sub>3</sub>·6H<sub>2</sub>O – 40 g/L, ascorbic acid – 2 g/L, pH = 1.2.

Electrodeposition was carried out in home-made galvanic cell. Potentiostat –galvanostatElins 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, CuK $\alpha$  ( $\lambda$  = 1.5418 Å, with Ni filter)) using standard methods.

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

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

#### **3** Results and discussions

Results obtained for pure metals presented in our previous works.

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).



Fig.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  $\mu$ m/min to 25  $\mu$ m/min.

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



Fig.2 The dependence of current on time for deposition of Fe-Ni alloy at different conditiones. 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.

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.

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.

Fig.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.



Fig.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 NW's 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 NW's have polycrystalline structure and cell parameters close to the parameters of pure Iron. The lines of Co 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<sup>57</sup> 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  $I_{2.5} = 4\sin^2\theta/(1 + \cos^2\theta)$ , where  $\theta$  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  $\vartheta$  (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.



Fig.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.

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



Fig.6 The hysteresis loops. At the left side - Fe-Co (growing voltage 0.7 V and 0.8 V); At the right side - Fe-Ni-(growing voltage 1 V, 1.2 V and 1.5 V)

At the same time Fe-Ni samples have "soft magnetic" parameters. Coercetive 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 V, 1.2 V and 1.5 V (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.

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