MATRIX SYNTHESIS, STRUCTURE AND PROPERTIES OF MAGNETIC NANOWIRES

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Abstract. Magnetic nanowires (NWs) of pure Fe, Co, Ni, alloys FeCo, FeNi and layered Ni/Cu were obtained by galvanic deposition into the pores of track membranes. The process of deposition was investigated and non-linear character was found. The obtained ensembles of NWs were tested by SEM, TEM, X-ray, Magnetometry and Mössbauer spectroscopy. Element concentration in NWs is differ from concentration of electrolyte and change slightly along the NW length (for alloys). For layer NWs the layers thickness and composition was determined. Different phases in alloys were found. Magnetometry measurements confirmed the magneto-hard properties of FeCo NWs and soft magnetic properties of FeNi NWs. It was also shown that increase of grooving voltage leads to increase of magneto-hard properties due to formation of microcrystalline structure.

1. Introduction

Obtaining of nanoscale materials and investigation of their properties (often unique) is a very important task. Among these materials are one-dimensional - nanorods, nanowires (NWs). In the present work, arrays (ensembles) of magnetic metals of the iron group (Fe, Co, Ni) were obtained by matrix synthesis based on porous matrices. The essence of the process of matrix synthesis is to obtain the required material in the pores of a pre-fabricated matrix of another material [1]. The matrix, the required material and the way of its "insertion" into the pores - can be completely different. So, very often porous alumina [2] or polymeric track membranes are used as matrices. It is known that track membranes are made by "radiation technologies" [3] by irradiating the polymer film with high-energy particles (accelerated heavy ions or fission fragments) and subsequent etching of the formed latent tracks until the formation of through pores. Application in matrix synthesis and fine filtration are the main areas of use of such membranes.

2. Samples preparation
**Matrixes.** In the present work, metal NWs were synthesized in the pores of track membranes (TM, manufactured by JINR, Dubna) by electrochemical method (galvanic deposition) [4-6]. Parameters of TM - thickness (8-15 microns), pore density (106 - 10 8 pores per square centimeter) and their diameter (0.03-0.5 microns) - determine the geometric characteristics of the resulting "casts", "replicas". The change in the electrodeposition regimes made it possible to change the structure of the NPs obtained. It should be noted that the wide possibilities of changing the parameters of the electrochemical method makes it possible to obtain NWs of various types - both homogeneous from one metal [7] and from several metals (so-called alloys) [8], and heterogeneous-from two (or more) metals alternating along the length of NW. Each of the above types of NWs has its own characteristics and potential applications.

**Galvanic process.** In this paper, NWs were obtained both from pure iron, cobalt and nickel, and from their alloys (FeCo, FeNi). The production of NWs from alternating layers of Cu / Ni, Fe / Ni and others were started. Solutions of salts (as a rule, sulfates) of the corresponding metals were used. In all cases, the process of electrodeposition was studied and its nonlinearity (determined by the slowing down of diffusion in narrow pore channels) and features both at the first seconds of growth (determined by the change in the surface charge) and in the last stages of pore filling were shown. An example of the electrodeposition curve (current versus time) for precipitation of the iron is shown in figure 1.

For alloys, it is shown that their composition is significantly different from the composition of the growth electrolyte and this difference also depends on the growth voltage. In addition, the composition may vary slightly along the length of the TM. For layer NWs, grown in the so-called "pulse mode" the optimal conditions for obtaining compositions, additives and growth voltage are chosen. It is shown that the thicknesses of layers from different metals, as well as their ratio to the thicknesses of layers from another metal, can change during growth. In all the cases described above, growth was carried out in one electrolyte, in one growth cell ("one-bath method"). However, it is shown that with a small number of alternating layers, the so-called "two-bath" method (with the transfer of a growing sample from one electrolyte to another) is often more convenient.

**Electron microscopy.** After growing, structural studies of the obtained NWs ensembles were carried out: it was shown that for NWs of small size (less than 100 nm) the diameter is often higher than the pore diameter. It is shown that dispersion of the lengths of NWs can be reduced by conducting growth at lower voltage and with stirring of the solution. In a number of cases (growth at high speed, with the application of a magnetic field), it was possible to obtain NWs hollow inside. Examples of SEM images obtained are shown in Fig. 2. For multilayer NWs it was possible to clearly identify the alternation of layers of different composition, which often differed in diameter. The obtained TEM images are shown in figure 2.
**Figure 2.** a – SEM image of Cu/Ni NWs with cavities on their tops, b – TEM image of Cu/Ni NWs with elemental analysis.

**X-ray diffraction** analysis made it possible to determine the type of lattice: bcc for iron NWs, fcc for nickel NWs and hcp for cobalt; for alloys the bcc structure was retained. The plots, illustrated dependence of X-ray spectra on grooving voltage (figure 3).

X-ray spectra for Fe, Ni and Co are given in figure 3. For Fe and Ni the dependences of spectra on grooving voltage are also presented.

**Figure 3.** X-ray spectra for Fe and Ni (different grooving voltage is indicated in Fig) and for Co samples

A crystallite size of 20-50 nm was also determined by a rough estimation by the line half-width. For Cu/Ni this is in accordance with the TEM data obtained. The calculated cell parameters turned out to be somewhat less than the parameters for the bulk material. This small - in the third sign - difference ("compression") may be due to the peculiarities of metal growth in small volumes.

**Magnetic properties.** Investigation of magnetic properties was carried out by obtaining hysteresis loops. These results, obtained on a vibration magnetometer for NWs ensembles of FeCo and FeNi alloys, are shown in figure 4.
Figure 4. Hysteresis loops for non-oriented samples of NWs ensembles from FeCo and FeNi alloys synthesized at different growth voltages.

It is seen that for the first alloy of the loop, the remanent magnetization is much wider and the coercive force is higher. In addition, it can be seen that an increase in the growth rate leads in both cases to a broadening of the loop (i.e., to an increase in the magneto-hard properties), apparently due to a reduction in the size of the crystallites (as confirmed by x-ray data). FeNi alloy, grown in pores of small diameter by properties approached magnetically-hardened. The study of "oriented" samples also showed that the widest hysteresis loop in all cases is observed in the case of a parallel direction of the IR and the external field (the geometry of the "out-of-plane"), when the field is directed along the surface, the loop becomes very narrow, and in the intermediate case (angle 45° - intermediate value).

Mössbauer spectroscopy of iron-containing samples showed that for pure iron obtained at a low growth rate the spectrum is close to the classical sextet (i.e., to a bulk α-iron that does not have a distinguished direction of magnetization). Mossbauer spectra obtained for samples grown at different voltages are presented in figure 5.

Figure 5. Mössbauer spectra of samples of NP massifs of iron synthesized at various growth voltages of 600, 750 and 900 mV.

Analysis of the spectra shows that at the same time, the acceleration of growth leads to the appearance of the selected direction of magnetization, which can be estimated by the ratio of the intensities of the lines 2 and 5 of the sextet. Complex investigation of Cobalt and Nickel alloys suggest the existence of different phases in these samples (which is also confirmed by x-ray data). In addition, in these alloys, an increase in the growth voltage also leads to a change in the ratio of line intensities, indicating the appearance of magnetization directed at an angle to the NWs axis. The estimation of the
crystal field indicates that the higher field is in FeCo alloy. So, some correlation exist between magnetometry data (hysteresis loops - measurements at the "macro-level") and the data of Mössbauer spectroscopy (fields on nuclei- "micro-level").

The study of layer structures has also shown that their growth can be influenced by the magnetic field. The first data indicate the possibility of using such structures, including contact of metals with different magnetic properties, in devices of spintronics. Thus, the first successful experiments on the generation of THz (terahertz) radiation were carried out when a high-density current was passed through the ensemble of NWs, each of these NWs included one transition between two various metals [9]. For "multi-layer" NWs, the effect of a giant magnetoresistance (GMR) has been studied.

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3. References

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