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**Al₂O₃-Co AND Al₂O₃-Fe COMPOSITES OBTAINED BY THE ELECTROCHEMICAL METHOD.
PART II. MAGNETIC PROPERTIES OF Co AND Fe NANOWIRES**

**ELEKTROCHEMICZNA METODA OTRZYMYWANIA KOMPOZYTÓW Al₂O₃-Co I Al₂O₃-Fe.
CZ. II. WŁASNOŚCI MAGNETYCZNE NANODRUTÓW KOBALTU I ŻELAZA**

Anodic alumina membrane (AAM) was used as a template to prepare highly ordered Co and Fe nanowire arrays. The effect of a uniform magnetic field with a flux density of 0.7 T parallel to the membrane surface, on the electrodeposition of Co and Fe nanowires has been investigated. The morphology of the deposits did not change regardless of magnetic field was applied or not. The homogeneous deposits in pores were obtained in both cases. The magnetization measurements demonstrated that the external magnetic field influenced on magnetic properties of the nanowires.

Keywords: anodic alumina membrane, nanowire arrays, cobalt, iron

W celu otrzymania nanodrutów Co i Fe zastosowano membranę tlenku glinu o porowatej uporządkowanej strukturze. W procesie elektroosadzania kobaltu i żelaza badano wpływ jednorodnego pola magnetycznego o gęstości strumienia 0,7 T i kierunku równoległym do powierzchni membrany, na morfologię osadu katodowego. Stwierdzono, że nie zależy ona od tego, czy process prowadzono w polu magnetycznym, czy bez. W obu przypadkach metale zostały osadzone jednocześnie w porach membrany. Pomiary własności magnetycznych wskazują, że zewnętrzne pole magnetyczne zastosowane w procesie elektroosadzania nanodrutów wpływa na ich własności magnetyczne.

1. Introduction

Nanostructured porous materials are recently of increasing interest because of their unique properties [1]. The considerable attention has been focused on nanotubes [2], nanowires [3] and nanoporous materials due to their specific electronic, magnetic, optoelectronic, biomedical or mechanical features. An important template material for fabrication of nanostructured materials is anodic alumina membrane (AAM) formed by anodization of pure aluminium [1]. Various methods are used for the preparation of nanowires in AAM, but electrodeposition has been proved to be a simple and low cost technique for producing large arrays of the nanowires. It has been found that such materials can be successfully used in singleelectron devices, nanoelectrodes or microfluidic [3,4].

Magnetic nanowires electrodeposited into AAM templates have been investigated by numerous research groups [5]. The effects of AAM pore diameter, current density, pH, nanowires annealing, appli-

cation of external magnetic fields and pulse current methods on the structure and magnetic properties of the nanowires have been studied [6-8]. Recently, Co and CoFe based alloys have received particular attention as the nanowire materials, because of their high saturation magnetization and elevated Curie temperature [9]. This research work describes electrolytic incorporation of Co and Fe into AAM under external magnetic field as well as structural and magnetic properties of the nanowire arrays.

2. Experimental

Co and Fe nanowires arrays were prepared by DC electrodeposition into the nanometer-sized pores of anodic aluminum membranes. The nanoporous anodic alumina membranes were prepared in a two-step anodizing process described by Masuda [10]. Prior to anodizing, a commercial aluminum sheet (99.999% purity) was degreased in acetone, annealed in an inert atmosphere (Ar) for 3 h at

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500°C to remove any residual stress, and then electropolished at a constant-voltage condition of 48 V for 20 s at 16°C in a HClO₄ and C₂H₅OH mixture. The polished foil was anodized in 3 wt% oxalic acid solution at 40 V for 24 h at 2°C. After first anodization, aluminium foil were etched in a solution of phosphoric acid (5 wt%) and chromic acid (1.8 wt%) to remove the irregular oxide layer. The subsequent anodization was conducted for 5 h at the same condition as the first one. After the second anodizing step the aluminum substrate was chemically removed from the backside by immersion in a diluted CuCl₂/HCl solution. The barrier layer at the bottom of the samples was chemically removed in 5 wt% H₃PO₄ solution (15 min at 30°C). Dissolution of the nanopores walls by H₃PO₄ resulted also in the widening of the nanopores diameter [11]. The electrical contact to membrane was ensured by vapour deposited gold layer covered with electrodeposited copper outer layer. The electrolytic cell used in the present study and procedure of the membrane preparation were described in details in a previous paper [12].

The Co and Fe nanowire arrays were electrodeposited into the AAM pores from sulfate electrolytes with the compositions listed in Table 1. An appropriate pH of the baths was adjusted with H₂SO₄. All deposition experiments were carried out at room temperature.

TABLE
Electrolyte compositions

Electrodeposition of metals	Concentration of components [mol/dm ³]			pH
	CoSO ₄ ·7H ₂ O	FeSO ₄ ·7H ₂ O	H ₃ BO ₃	
Co	0.5	0	0.3	3.0
Fe	0	0.5	0.3	2.8

Each electrolysis was carried out in a three-electrode cell with a saturated calomel electrode (SCE) as a reference. A platinum foil and a pure iron foil (to prevent Fe²⁺ to Fe³⁺ oxidation) were used as counter electrodes for cobalt and iron deposition, respectively. Experiments were performed in the potentiostatic mode (IPS AJ potentiostat) at a potential of -1.2 V (vs SCE) for 2.5 min. 0.7 T homogeneous magnetic field (HV7, Walker Scientific) parallel to the electrode surface was superimposed simultaneously.

The morphology of the Co and Fe nanowire arrays was examined by means of a Scanning Electron Microscope (FE Gemini LEO 1530). The structural analysis of the electrodeposited nanowire arrays was performed using an X-ray diffractometer (Bruker Discover D8) with a monochromatized CuK_α radi-

ation. The magnetic characteristics were determined by using of a vibrating sample magnetometer (Quantum Design PPMS). The measurements were performed at room temperature, with the maximum magnetic fields ($H_{\max} \leq 10^4$ Oe) parallel (i.e. perpendicular to the wire axis) or perpendicular (i.e. parallel to the wire axis) to the membrane plane.

3. Results and discussion

Surface and cross-section of as-prepared nanoporous anodic alumina membrane were observed by means of a scanning microscope. It was found that the membrane has a perfect hexagonal nanopore arrangement with uniform pore diameter. The pore diameter was in the range of 60-80 nm, while the interpore distance was approx. 110 nm.

Cobalt and iron were deposited under and without external magnetic field. No changes in the morphology of the deposits were observed. In both cases homogeneous deposits in pores were obtained. Distinct parallel arrangement of the metallic nanowires was revealed. It is well known that the length of the nanowires is dependent on the electrolysis time, while the diameter of a single nanowire is determined by the pore dimension. It was found that the cobalt and iron nanowires grew uniformly and after 2.5 min. of deposition their lengths achieved 1 μm and 2 μm, respectively.

In the presented research work a homogeneous external magnetic field of 0.7 T parallel to the template surface was applied during electrodeposition. It was reported that superimposition of the parallel magnetic field during Co [14] and Fe [15,16] deposition resulted in a better quality of thin layers. Kahn and Petrikowski [13] found better filling of the pores of anodic alumina with cobalt, if an external magnetic field was applied during electrodeposition. Generally, the application of the external magnetic field enhances deposition of the metals in comparison to the process carried out without magnetic field. It is known [13, 14] that parallel external magnetic field induces the magnetohydrodynamic (MHD) effects, since generated Lorentz force ($\vec{F}_L = \vec{J} \times \vec{B}$ where \vec{J} is the current density and \vec{B} is the magnetic flux density) leads to a disturbance of the electrolyte flow at the electrode surface. The MHD effect affects the reduction of hydrogen ions at negative potentials in acidic electrolytes. Krause and coworkers [14] described mechanism of the hydrogen evolution on gold electrode. It takes place by several stages, namely discharging of the hydrogen ions, adsorption of the atomic hydrogen, recombination and separation of the bubbles from the electrode surface.

Hydrogen bubbles adsorbed on the oxide surface block the pores for metal deposition. Under magnetic field fast desorption of the hydrogen bubbles due to forced convection is observed and homogeneous deposits in the pores of membrane are produced.

The XRD patterns for the Co and Fe nanowire arrays are shown in Fig. 1. The diffraction peaks correspond to the (111), (200) and (220) face centered cubic (fcc) polycrystalline Co reflections, while the

base center cubic (bcc) reflections were found in the polycrystalline Fe sample. The patterns of Al_2O_3 and Au/Cu substrate were also detected.

Magnetic properties of Co and Fe nanowires were investigated. Fig. 2 shows the hysteresis loops of the Co nanowire electrodeposited without application of the external magnetic field (Fig. 2a) and under superimposed external magnetic field (Fig. 2b).

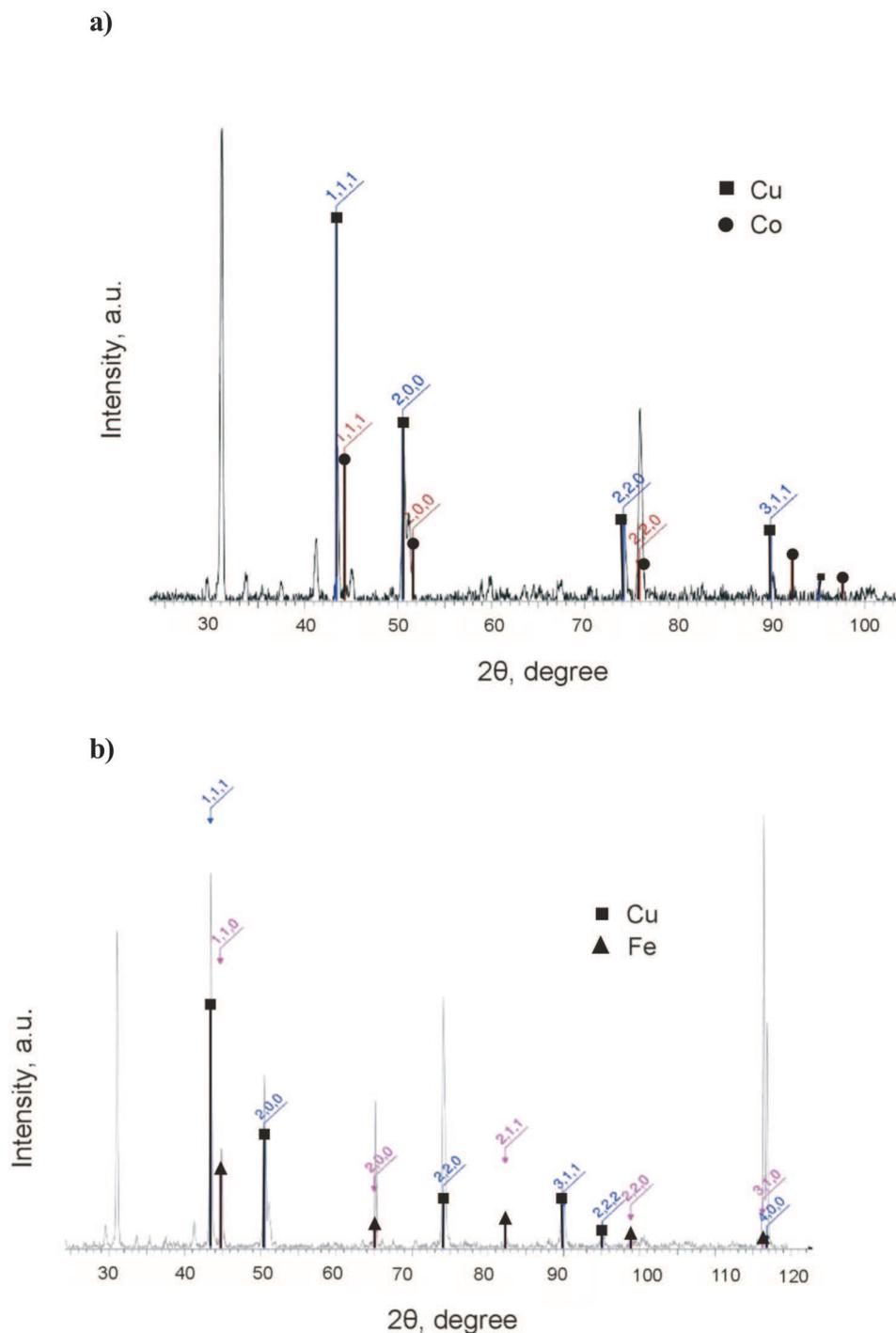


Fig. 1. XRD pattern of (a) Co and (b) Fe nanowire arrays

In both cases hard magnetic materials were obtained. The hysteresis loop determined for the cobalt nanowires deposited with no superimposed magnetic field characterized with high coercivity.

The measurements of magnetic nanowires were carried out with application of the magnetic field in perpendicular and parallel direction to wire axis. Coercivity values 750 Oe (magnetic field parallel to wire axis) and 150 Oe (magnetic field perpendicular to wire axis) were obtained for cobalt samples deposited without magnetic field. It shows that an easy magnetization axis is parallel to the wire axis.

Coercivities of 460 Oe (magnetic field parallel to wire axis) and 190 Oe (magnetic field perpendicular to the wire axis) for cobalt sample electrodeposited under magnetic field were determined. Higher value saturation magnetization (M_s) was observed in perpendicular direction. It suggests that easy axis

of magnetization is perpendicular to the wire axis in this case.

Fig. 3 shows the hysteresis loops of the Fe nanowire arrays obtained in electrodeposition process without external magnetic field (Fig. 3a) and under superimposed external magnetic field (Fig. 3b). In both cases hard magnetic materials were produced. Coercivities of the iron samples deposited without magnetic field application were 370 Oe (magnetic field parallel to wire axis) and 240 (magnetic field perpendicular to the wire axis) were determined.

Higher values of corecivity of the iron nanowires deposited under magnetic field were found and they were 567 Oe (magnetic field parallel to wire axis) and 190 Oe (magnetic field perpendicular to the wire axis).

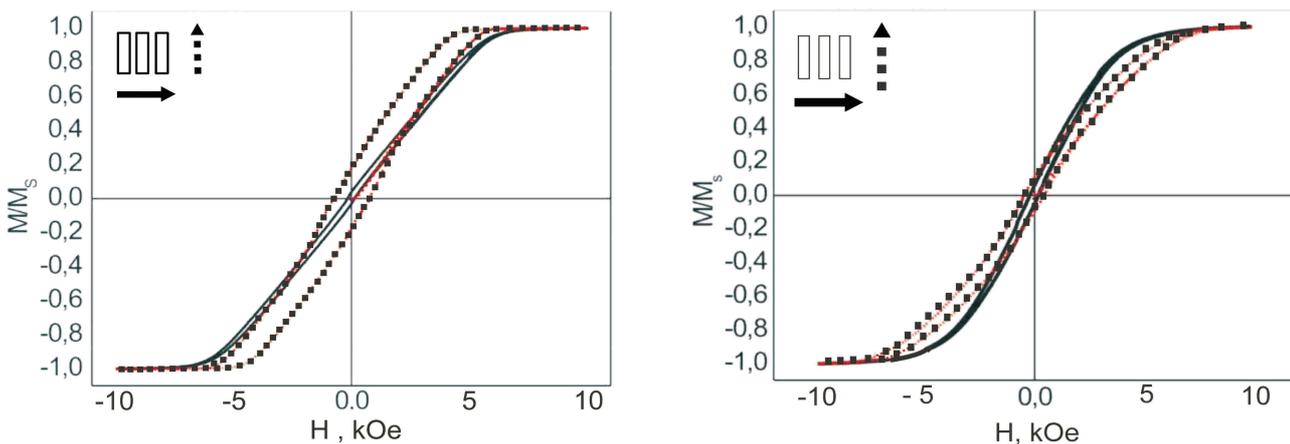


Fig. 2. Hysteresis loops for Co nanowire arrays for the magnetic fields applied parallel (dotted line) and perpendicular (solid line) to the nanowire axis electrodeposited without (a) and under (b) external magnetic field

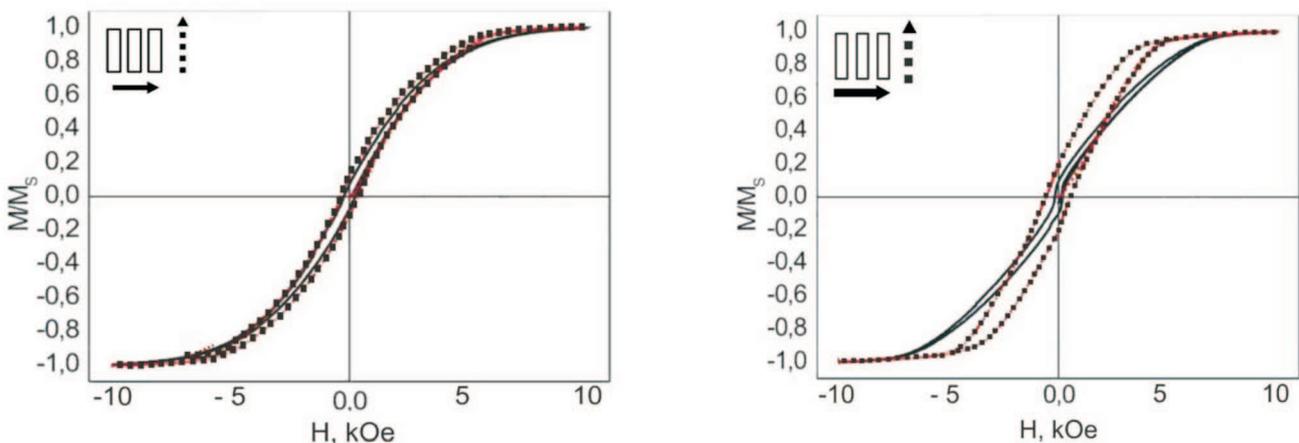


Fig. 3. The samples were electrodeposited a) without (a) and b) under (b) external magnetic field. Hysteresis loops for Fe nanowire arrays, with the magnetic fields applied parallel (dotted line) and perpendicular (solid line) to the nanowire axis

The hysteresis loops for Fe nanowire arrays obtained during electrodeposition without external magnetic field confirmed the lack of anisotropy (comparable values of saturation magnetization in both directions), while the magnetization easy axis of the Fe nanowire arrays produced with superimposed external magnetic field is parallel to the wire axis. It seems that such difference may be due to MHD effects.

The hydrogen coevolution can change pH of the solution at the electrode surface. Alkalization in the vicinity of the cathode leads to spontaneous precipitation of iron hydroxides, which are then incorporated into deposit changing magnetic properties of the iron nanowire arrays. Parallel external field applied during electrolysis causes MHD effect, which is favorable for removal of the hydroxide precipitates from the electrode surface. Specific edges in hysteresis loops are visible for the nanowires electrodeposited with superimposed external magnetic field. The edges in hysteresis loop can arise from strong dipolar interactions and magnetic flux existed between the nanowires. However, further detailed studies are required to confirm this process.

Comparison of the hysteresis loops registered at the same conditions showed that the application of the external magnetic field during electrodeposition can change the easy axis of the magnetization. The magnetic field applied parallel to the easy axis induces uniaxial anisotropy of the cobalt nanowires in the direction of the field. This observation can be understood, since the magnetic fields can change the chemical potential of ions and growth habit of nanocrystals. Koza *et.al* [16] observed the influence of the magnetic field on the nucleation process, however, further studies on the detailed mechanism are needed.

4. Conclusions

The effect of the external magnetic field on the electrodeposition of polycrystalline Co and Fe nanowire arrays was studied. It was found that the deposition under external magnetic field strongly influences the magnetic properties of the nanowire arrays. The electrodeposition with superimposed external magnetic field changes easy axis of the Co nanowire arrays. The edges effect in the hysteresis loops for Fe nanowires electrodeposited with superimposed external magnetic field was observed. This is probably due to magnetostatic interactions

between of wires. The magnetization easy axis parallel to the wire axis for Fe samples was found.

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