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THE MORPHOLOGY OF THE ALUMINA FILMS FORMED IN THE ANODIZATION PROCESS OF ALUMINIUM IN THE ORTHOPHOSPHORIC ACID SOLUTION. THE Co-Fe ALLOYS ELECTRODEPOSITION INTO OBTAINED ALUMINA PORES

MORFOLOGIA WARSTEWEK TLENKU GLINU OTRZYMANYCH W PROCESIE ANODOWEGO UTLENIANIA ALUMINIUM W ROZTWORZE KWASU ORTOFOSFOROWEGO. ELEKTROOSADZANIE STOPÓW CoFe W PORACH OTRZYMANEGO TLENKU

The optimal parameters of the anodic oxidation of aluminium in orthophosphoric acid solution was determined. In the pores of the obtained Al_2O_3 membranes with the ordered nanometric structure Co-Fe alloys were electrodeposited. The Al_2O_3 membranes were obtained in the two-stage anodic oxidation of aluminium in the 0.17 M H_3PO_4 solution in the temperature 1^0C and at the electrolysis voltage 180 V. The influence of the anodizing process parameters on the thickness of oxide films and the diameter of pores and the distance between them in the alumina membranes were determined.

The electrodeposition of Co-Fe alloys was carried out from sulphate baths containing sulphates (VI) of copper (II) and cobalt (II) of different composition, in potentiostatic conditions. The optimal electrolysis conditions were determined, where the cathodic deposits of the best quality were obtained. The conditions are: the electrolyte composition: 0.3 M Fe; 0.5 M Co; pH = 3, the potential: -0.760 V (vs. SHE[1)]).

Keywords: anodic oxidation of aluminium, nanowires, Co-Fe alloy

Określono optymalne parametry anodowego utleniania aluminium w roztworze kwasu ortofosforowego W porach uzyskanych membran Al_2O_3, o uporządkowanej strukturze nanometrycznej, osadzano elektrolitycznie stopy Co-Fe. Membrany Al_2O_3 otrzymywano w procesie dwuetapowego utleniania aluminium w roztworze 0,17 M H_3PO_4, w temperaturze 1°C, przy napięciu elektrolizy 180 V. Zbadano wpływ parametrów anodowania na grubość warstewek tlenkowych, średnicę porów i odległości między nimi w membranach tlenku glinu.

Elektroosadzanie stopów Co-Fe prowadzono z roztworów siarczanowych (VI) zawierających jony miedzi (II) i kobaltu (II) o różnym składzie, w warunkach potencjostatycznych. Określono optymalne warunki elektrolizy, w których otrzymano osady katodowe najlepszej jakości. A mianowicie: skład elektrolitu : 0,3 M Fe; 0,5 M Co; pH = 3, potential: −0,760 V (wzgl. SEW).

1. Introduction

The possibility of coating aluminium and its alloys with oxide films has considerably increased the range of the use of this metal in various industry domains.

The Al_2O_3 oxide films on aluminium are obtained in the process of the electrolysis, where the sample being oxidized is the anode, and the cathode is lead or aluminium. Depending on the purpose of the anodized element, different electrolytes are used: most frequently the solutions of sulphuric, oxalic, orthophosphoric, chromic or boric acid [1-20].

The process is conducted in fixed electrical current conditions (voltage and current values) and at constant temperature.

During the anodic oxidation of aluminium the following electrode reactions take place:

$$\text{anodic} : Al \rightarrow Al^{3+} + 3e \quad (1)$$

$$\text{cathodic} : 2H^+ + 2e \rightarrow H_2 \quad (2)$$

The oxide film is formed as the result of the reaction between the Al^{3+} and O^{2-} ions:

$$2Al^{3+} + 3O^{2-} \rightarrow Al_2O_3 \quad (3)$$

O^{2-} ions are formed in the reaction:

$$6OH^- \rightarrow 3H_2O + 3O^{2-} \quad (4)$$

The oxide films with the ordered structure are obtained in a two-stage anodizing process in the result of which an Al_2O_3 membrane of a hexagonal cell structure and the regular distribution of pores are obtained. The diameter, the height of pores and the distance between them depend on the parameters used in the anodizing process [17-21].

Also some changes in the Al_2O_3 morphology in the individual stages of this process occur [3-4, 9, 12]. In the first stage of the anodizing an alumina film of disordered structure (the pores are not ideally perpendicular to the surface of aluminium) of pores is obtained. The aluminium oxide formed

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1) *SHE – Standard Hydrogen Electrode*

during the first anodizing is removed chemically: characteristic cavities remain on the surface. In the second stage of the anodizing a new oxide film is formed in the cavities; the said film is characterized by an ordered structure.

Thin oxide films on the aluminium with the porous and ordered structure, i.e. membranes, have found common use as the template for fabrication of nanowires.

One of the methods of obtaining the materials of this type is the cathodic deposition of metals or alloys in the pores of an Al_2O_3 film.

The careful preparation of an aluminium oxide matrix guarantees that the materials of an even and closely packed structure are obtained. This way the metal and metal alloy nanowires or Al_2O_3 – metal (alloy) multi-layer composite systems are obtained.

The process of the cathodic deposition of a "foreign" metal can be conducted with the use of DC, AC, pulsating or reversing current.

The cathodic reaction of the reduction of metal ions (5) is accompanied by the codeposition of hydrogen (6):

$$Me^{n+} + ne \rightarrow Me \tag{5}$$

$$2H^{+} + 2e \rightarrow H_2 \tag{6}$$

The codeposition of hydrogen is an unfavourable process since it reduces the cathodic current efficiency of the metal deposition, clogs up the pores in the film with the gaseous hydrogen, and increases the pH value near the reactive surface. The increase of the pH value may be the reason of the precipitation of the metal hydroxide on the Al_2O_3/ electrolyte phase interface, and even the damages of the porous ordered structure of the aluminium oxide film.

Along with the development of the information technologies, the methods of obtaining films used for the production of the magnetic data carriers of the high magnetic flux density attract particular interest. The magnetic materials used for the production of data carriers are based on the obtaining of the films of the high magnetic anisotropy oriented perpendicularly to the film surface. To obtain magnetic data carriers, most frequently the electrodeposition of the nanowires of cobalt or its alloys is used (e.g. CoFe, CoNi, CoNiFe, etc.) in aluminium oxide pores [20, 21-31].

In the presented study the nanowires of Co-Fe alloy (about 66,5 wt % of Co and 33,5 wt % of Fe) were obtained.

2. Experimental procedure

2.1. Materials

The samples made of aluminium of the purity 99.999% (Goodfellow) the composition of which is presented in Table 1 were used.

Before the investigation the samples were annealed in the temperature 500°C in argon atmosphere for three hours. Then, the annealed samples were subjected to degreasing by immersing them into the 5% NaOH solution for one minute in the temperature of 70°C, and then for 30 seconds into 1:1 HNO_3 solution in room temperature. After that the samples were rinsed and dried. After degreasing the samples were polished (Struers electropolishing machine, LectroPol-5).

TABLE 1

Composition of aluminium

Al	Cu	Fe	Mg	Si
%	ppm			
99,999	0,3	0,3	1,2	0,8

2.2. Anodic oxidation of aluminium

The process of the anodic oxidation of aluminium was conducted in two stages. As an electrolyte the 0.17 M H_3PO_4 solution was used. The area of the sample surface was 1.94 cm^2.

In the first stage of anodizing the voltage was 180 V, electrolysis time 2 hours, and temperature 1°C. The temperature was kept stable by a cryostat and cooling blocks. An electrolyser made of Teflon® was used. Aluminium sheets were used as the cathode and the anode. Mixing was performed with RW 11 basic "Lab Egg" mechanical mixers. The diagram of the measuring system was presented in the previous paper [20].

The oxide film obtained during the first stage was removed be immersing the sample in the solution containing 0.4 M H_3PO_4 and 0.2 M CrO_3 in the temperature 80°C for two hours. After the removal of the oxide film the second stage of anodizing was conducted. The duration of this stage was 20 hours, voltage 180 V, and temperature 1°C. Then the samples were subjected to the process of widening pores. This process consisted in the heating of the electrolyte up to 30°C and leaving it in contact with the sample for one hour (without current flow). The second stage of anodizing was conducted in the measuring set as in the first anodizing.

The next stage was the chemical removal of the substrate aluminium. The mixture of 0.2 M HCl and 0.1 M $CuCl_2$ solution was used. The process was conducted in room temperature for two hours. Then the barrier film on the sample surface having no contact with the electrolyte (the external surface) was removed. To this end the sample was etched in the 10% H_3PO_4 solution in the temperature 45°C for 50 minutes. After this stage the membrane pores become open.

After the processes of the removal of the substrate aluminium, the barrier film, and after the opening of pores a thin film of gold was sputtered (Emitech K575X) on the sample (at the side where the substrate aluminium was removed) , and then copper from a sulphate bath was electrodeposited under a potentiostatic conditions. This way the porous Al_2O_3 membranes on the Cu base were obtained.

2.3. Cathodic deposition of Co-Fe alloy

The Co-Fe alloy was incorporation into membrane pores in the process of the electrochemical deposition of metals. The process was conducted from the sulphate baths containing Co^{2+} and Fe^{2+} ions and with the use of direct current (Atlas potentiostat) in room temperature. The investigated sample (membrane) was installed in a Teflon® electrolyser in the horizontal position. As the counter electrode a platinum sheet, and as reference electrode a saturated calomel electrode (SCE) were used [21].

In order to choose appropriate conditions of electrolysis (potential, pH, electrolyte composition) cooper or gold sheets

were used as the cathode which were installed in the electrolyzer instead of membranes. In these measurements the cyclic voltammetry was applied.

3. Results and discussion

3.1. The preparation of alumina membranes

The preparation of a membrane is a very important stage in the process of obtaining of nanowires. Appropriate choice of parameters during anodizing is fundamental for the thickness of the oxide film and the pore sizes: their diameters and the distance between them.

The relationship between the thickness of the oxide films and time, temperature, and electrolysis voltage during the anodic aluminium oxidation as well as the chemical treatment time was determined.

3.2. Influence of anodizing time and temperature on the thickness of the oxide film

These measurements were carried out in the time range from 1 up to 48 hours at three temperature levels: 1, 4 and 7°C. The results of these investigations are presented in Table 2 and Fig. 1.

TABLE 2

Average thickness of oxide films

Anodizing time, h	Thickness of oxide film, μm		
	1°C	4°C	7°C
1	0,66	1,52	1,99
2	2,53	3,22	3,77
5	4,68	6,27	8,19
24	14,98	21,59	27,84
48	28,73	29,18	29,59

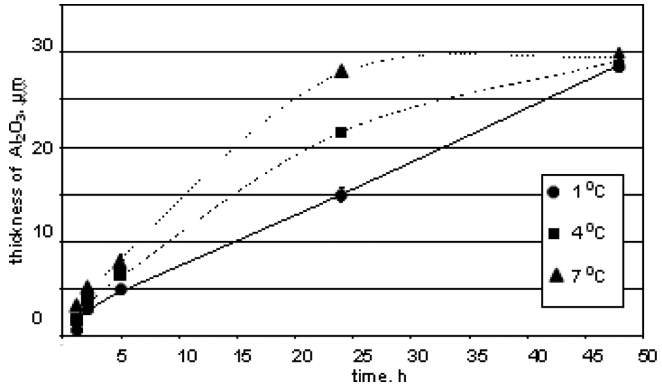

Fig. 1. The relationship between the thickness of the oxide film and anodizing time and temperature

These relationships show that in the initial stage the formation rate of oxide is height, and it decreases over the course of time. Since the maximum process time was 48 hours, the maximum on diagram (as on fig.2) has not been achieved yet.

Such a course of this relationship is in agreement with the expectation, since in the oxide film there are two areas:

- Al – Al_2O_3 interface – formation of the oxide
- oxide – electrolyte interface – the dissolution of oxide.

Since both stages take place with a determined rate the summary rate is the effective rate of these processes. This is illustrated in Fig. 2.

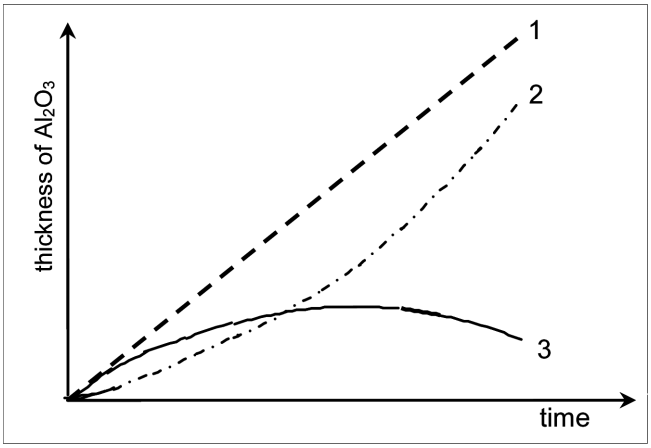

Fig. 2. The relationship between the Al_2O_3 film thickness and the anodic oxidation time [32]:
1 – the Al_2O_3 film thickness resulting from the Faraday's law
2 – the thickness of the oxide film dissolved by the electrolyte
3 – the effective thickness of the obtained oxide film

3.3. The influence of the electrolysis voltage on the distance between pores in an oxide film

The processes of the anodic oxidation of aluminium are usually conducted at a constant electrolysis voltage. The electrolysis voltage has to be appropriately selected for two reasons: too low voltage causes irregular distribution of the pores in an oxide film, whereas too high voltage leads to the excessive heat generation and in turn to the breaking of the oxide.

The measurements of the anodic oxidation of aluminium were carried out as the function of the electrolysis voltage within the range of 120 - 200 V, and the influence of the voltage on the distance between pores in the Al_2O_3 membranes was determined. The anodizing time was 24 hours, temperature 1°C, and the 0.17 M H_3PO_4 electrolyte was used. The distance between pores was determined from SEM microphotos. The results of these measurements are presented in Table 3 and Fig. 3.

TABLE 3

The influence of the electrolysis voltage on the distance between pores

Voltage	Distance between pores*
[V]	[nm]
129	270 ±29
140	303±25
160	373 ±38
180	443±20
200	460±37

* measurement error – standard deviation

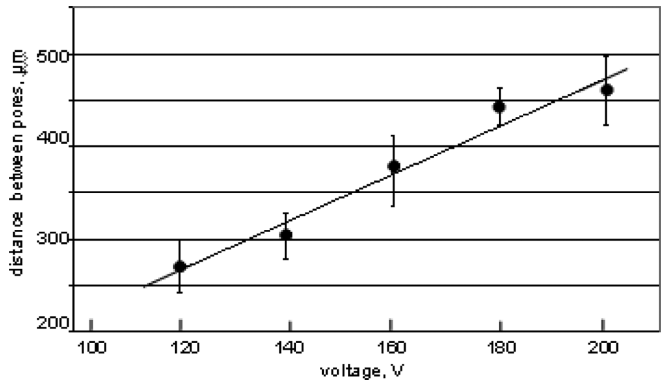

Fig. 3. The relationship between the distance between pores and the electrolysis voltage; anodizing conditions: 0.17 M H_3PO_4 solution, time 24 h, temperature 1°C

The course of the relationship presented in Fig. 3 indicates that the distance between Al_3O_3 membrane pores is directly proportional to the electrolysis voltage.

Additionally, the microscopic observations (SEM) showed that the most uniformly distribution of the pores in oxide films was obtained for the electrolysis voltage 180 V.

3.4. The influence of the chemical treatment time on the diameter of the pores in Al_3O_3 films

The chemical treatment, applied after second anodizing, is a very important stage in the process for obtaining membranes used as a template to produce of nanowires. The Al_3O_3 membranes obtained in the anodizing process (electrolysis voltage 180 V) were etched in the 0.17 M H_3PO_4 solution in the temperature 30°C. In this process, pores become widened, and the etching time is a factor affecting the diameter of the pores in an oxide film. The effect of the chemical treatment time within the range of 0 up to 180 minutes was investigated.

On the basis of the SEM images, the diameters of the pores in the membranes were determined. The results of those measurements are given in Table 4 and presented in Fig. 4. They indicate that with the increase of the etching time the diameter of pores also increases. Thanks to the appropriate selection of the pore widening time, it is possible to control their diameter, and by this also the diameter of the nanowires obtained by the building metals into the pores of the used membrane.

TABLE 4

The relationship between the diameter of pores and the chemical treatment time of the Al_2O_3 membranes

Time	Diameters of pores*
[min]	[nm]
0	105±29
30	152±32
60	164±17
90	201±24
120	204±17
150	218±23
180	232±25

* measurement error – standard deviation

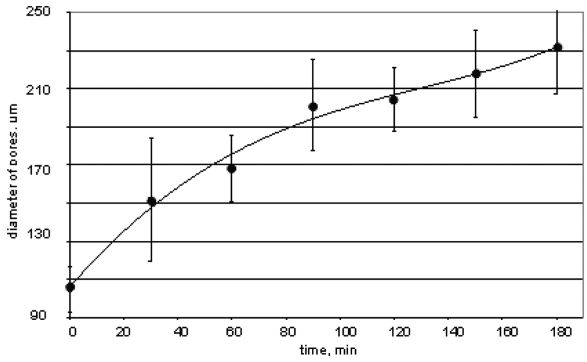

Fig. 4. The influence of the chemical treatment time on the diameters of pores in Al_2O_3 membranes; anodizing conditions: 0.17 M H_3PO_4 solution, temperature 1°C, the voltage 180 V

Summarizing, on the basis of the investigations carried out as the optimum conditions of the process of the anodic oxidation of aluminium the following parameters were applied [33]:

- 1^{st} stage of anodizing: voltage = 180 V, time = 2 hours, temperature = 1°C
- time of removal of Al_2O_3: 2 hours
- 2^{nd} stage of anodizing: voltage = 180 V, time = 20 hours, temperature = 1°C
- widening of pores: time = 1 hour, temperature = 30°C
- removal of barrier film: time = 50-55 minutes, temperature = 40°C.

The microscopic observations (SEM) of the oxide films obtained in these conditions are shown in Fig. 5f. In Fig. 5, also the morphology of the Al_2O_3 films obtained after each of the process stage is shown

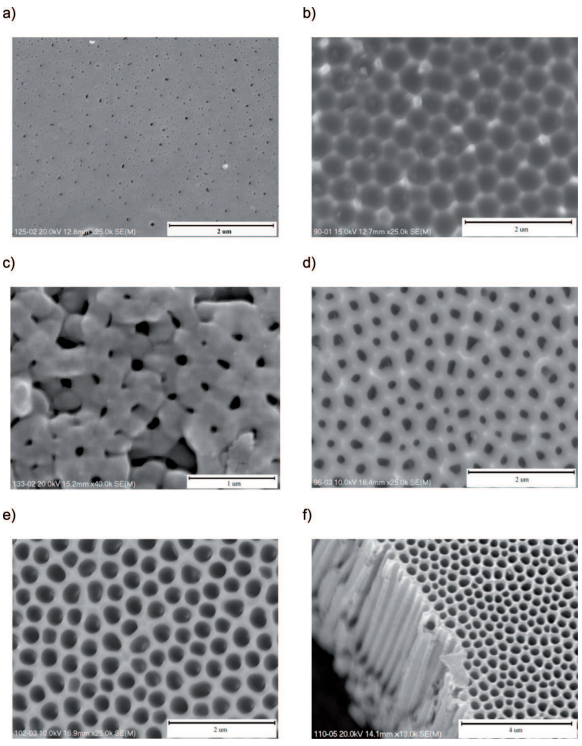

Fig. 5. SEM images of the membrane after each of the process stage: a – after the first stage of anodizing, b – after the removal of Al_2O_3, c – after the second stage of anodizing, d – after the widening of pores e – after the removal of the barrier film f – the membrane prepared for cathodic deposition of Co-Fe nanowires

3.5. Electrodeposition of Co-Fe nanowires

The Co-Fe alloy was cathodic deposited from the sulphate baths in potentiostatic conditions. To choise the optimum electrodeposition conditions a cyclic voltammetry was conducted. The process of the cathodic deposition of Co-Fe alloys was carried out on a copper cathode from the solutions of different composition and different pH value, which are given in Table 5.

TABLE 5

The composition of the electrolytes used for the alloy deposition

composition of the electrolytes		pH
Chemical type of compounds	Contens of Co and Fe, mol/dm^3	
140,55 g/dm^3 $CoSO_4 \cdot 7H_2O$ 27,80 g/dm^3 $FeSO_4 \cdot 7H_2O$ 44,03 g/dm^3 $C_6H_8O_6$ 25 g/dm^3 H_3BO_3	0,5M Co 0,1M Fe	3,0
140,55 g/dm^3 $CoSO_4 \cdot 7H_2O$ 111,20 g/dm^3 $FeSO_4 \cdot 7H_2O$ 44,03 g/dm^3 $C_6H_8O_6$ 25 g/dm^3 H_3BO_3	0,5M Co 0,4M Fe	3,0
140,55 g/dm^3 $CoSO_4 \cdot 7H_2O$ 139,01 g/dm^3 $FeSO_4 \cdot 7H_2O$ 44,03 g/dm^3 $C_6H_8O_6$ 25 g/dm^3 H_3BO_3	0,5M Co 0,5M Fe	3,0
140,55 g/dm^3 $CoSO_4 \cdot 7H_2O$ 166,81 g/dm^3 $FeSO_4 \cdot 7H_2O$ 44,03 g/dm^3 $C_6H_8O_6$ 25 g/dm^3 H_3BO_3	0,5M Co 0,6M Fe	3,0
140,55 g/dm^3 $CoSO_4 \cdot 7H_2O$ 83,34 g/dm^3 $FeSO_4 \cdot 7H_2O$ 44,03 g/dm^3 $C_6H_8O_6$ 25 g/dm^3 H_3BO_3	0,5M Co 0,3M Fe	2,0 3,0 4,0 5,0

On the basis of the obtained results it was found that the Co-Fe alloy deposits within the potential range from -1.2 V to -0.4 V (vs. SHE).

These alloys were subjected to microscopic observations (SEM). The most uniformly deposit was obtained at the potential -0.760 V (vs. SHE) from the solution of the 0.3 M Fe; 0.5 M Co composition and pH= 3. These parameters were applied in the process of the cathodic deposition of the Co-Fe alloy in the pores of Al_2O_3 membranes. The membranes with the pores of the diameter 0.232 μm, the distance between pores 0.443 μm , and the height 20 μm were used.

The obtained nanocomposites were observed with the use of a scanning microscope. In Fig. 6 an example of a microphoto of the Al_2O_3 – Co-Fe film is shown in two magnifications.

On the basis of the microphotos the height and the diameter of the obtained nanowires were determined which amounted to 2.53 μm and 0.2 μm, respectively. The height of alumina membranes was approx. 20 μm, therefore the height of the nanowires constitutes approx. 13% of the membrane thickness. The Co-Fe alloy was built uniformly into every pore.

The composition of the obtained Co-Fe nanowires was determined, depending on the ratio of the concentration of Co^{2+} and Fe^{2+} ions in the electrolyte.

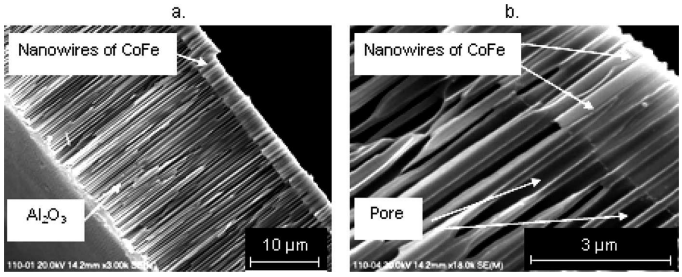

Fig. 6. SEM images of Co-Fe nanowires obtained at the cathodic deposition at direct current in potentiostatic conditions (-0.760 V) from the electrolyte of the 0.3 M Fe; 0.5 M Co composition and pH = 3: a – magnification 3,000 x, b – magnification 18,000 x

For this purpose a series of investigations of the electrodeposition of the CoFe alloy with the use of the electrolytes of a different composition (pH = const. = 3) in potentiostatic conditions (E = -0.760 V, vs. SHE) were carried out.

The obtained deposits were dissolved in 2.5 M HCl and the concentration of Fe^{2+} and Co^{2+} ions was determined by the inductive coupled plasma mass spectrometry (ICP-MS) method.

The results of the analysis were presented in Table 6 and in Fig. 7.

The relationship presented in the graph indicates that the ratio of the concentration of Fe^{2+} and Co^{2+} ions in the electrolyte is directly proportional to ratio of the number moles of metals deposited in the alloy. This relationship can be described by the following equation:

$$(n_{Fe}/n_{Co})_{deposit} = 0.0847 + 0.739(C_{Fe2+}/C_{Co2+})_{electrolyte} \quad (7)$$

The correlation coefficient is high and it amounts to r = 0.9975.

Additionally, an analysis of the alloy composition was performed with the use of the energy dispersive X-ray spectroscopy (EDXS). The results of this analysis are presented in Table 7 and Fig. 8.

TABLE 6

The results of the chemical analysis of the Co-Fe alloy composition

Electrolyte			Cathodic deposit						
Concentration		$\frac{c_{Fe^{2+}}}{c_{Co^{2+}}}$	Masses of metals In cathodic deposit m· 10^4		Composition of alloy				$\frac{n_{Fe}}{n_{Co}}$
mol/dm^3			g		at. %		wt %		
Fe^{2+}	Co^{2+}		Fe	Co	Fe	Co	Fe	Co	
0,1	0,5	0,2	1,847	8,982	17,84	82,16	17,1	82,9	0,22
0,3	0,5	0,6	1,995	3,962	34,69	65,31	33,5	66,5	0,53
0,4	0,5	0,8	2,456	3,673	41,39	58,61	40,1	59,9	0,71
0,5	0,5	1,0	2,531	3,293	44,81	55,19	43,5	56,5	0,81
0,6	0,5	1,2	2,785	3,080	48,87	51,13	47,5	52,5	0,96

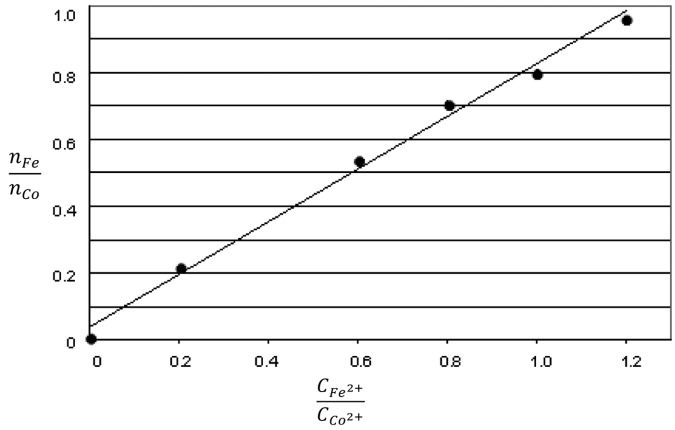

Fig. 7. The relationship between the ratio of the number of moles (n_{Fe} / n_{Co}) of both metals in the cathodic deposit (Co-Fe alloy) and the ratio of the concentrations of ions (C_{Fe2+} / C_{Co2+}) in the electrolyte

TABLE 7

The chemical composition of the membrane containing Co-Fe nanowires (**EDXS** method)

Element	Composition of the analysed sample	
	[weight %]	[at. %]
Co	38,99	30,35
Fe	23,38	19,2
Al	28,41	48,3
Au	9,23	2,15

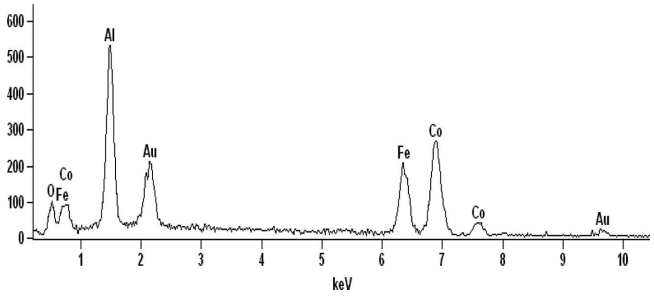

Fig. 8. The EDXS analysis of the chemical composition of the membrane containing Co-Fe nanowires

In Fig. 8 the Al peaks come from the Al_2O_3 "matrix", and the Au and Cu peaks from the substrate. Therefore, the composition of the obtained Co-Fe nanowires in weight percentage is 62.5% of Co, and 37.5% of Fe.

These values are nearly to those determined by the inductive coupled plasma mass spectrometry (ICP-MS) method (Tab. 6, the solution of the 0.3 M Fe and 0.5 M Co) by which the composition 66.5% Co and 33.5% Fe (weight percentage) of the Co-Fe alloy was obtained. The composition of the CoFe alloy, obtained by ICP-MS method was considered as more reliable, since this analysis relates to the entirety of a sample, whereas the EDXS analysis concerns only the composition of a fragment of the sample surface.

4. Conclusions

In the process of the two-stage anodizing of aluminium in the 0.17 M H_3PO_4 solution the Al_2O_3 aluminium oxide membranes of the ordered structure were obtained.

The thickness of the oxide film during the anodizing at the constant electrolysis voltage 180 V, depends on the time of anodic oxidation and the temperature, and it changes from a few μm (after 1 hour) up to approx. 30 μm (after 48 hours).

The distance between pores is directly proportional to the electrolysis voltage. Within the range of 120 - 200 V, this distance increases from 270 nm (0.27 μm) up to 460 nm (0.46 μm) (temperature 1°C, anodizing time – 24 h).

The diameter of pores depends on the time of the chemical treatment and it increases with the increase of the time. The diameter of the pores of the membrane without chemical treatment was 100 nm (0.1 μm), whereas the etching treatment for 180 minutes increases it up to 230 nm (0.23 μm).

The optimal conditions of the obtaining of the Al_2O_3 membranes of the ordered structure were determined: the electrolysis voltage 180 V, the temperature 1°C. The aluminium oxide membranes of the thickness of approx. 20 μm, the pore diameters of 0.23 μm, and the distance between pores 0.43 μm obtained in these conditions were used as the template for building in Co-Fe alloy in their pores.

The optimal conditions for the cathodic deposition of Co-Fe alloy in alumina membranes were determined. The conditions are as follows: the potential: -0.760 V (vs. SHE), the electrolyte composition: 0.3 M Fe; 0.5 M Co; pH = 3. The Co-Fe nanowires were obtained, the height of which was 2.53 μm, and the diameter 0.23 μm. The Co-Fe nanowires were deposited uniformly in each pore. On the basis of the analysis it was found that the composition of the Co-Fe alloy (in weight percentage) is as follows:

- 62.5 % Co and 37.5 % Fe (EDXS),
- 66.5 % Co and 33.5% Fe (ICP-MS).

The detailed investigations carried out allow to design a process which would lead to the obtaining of the Co-Fe alloy nanowires of the required composition in the process of the cathodic deposition of metals in alumina membrane pores.

The investigations of the magnetic properties of the obtained nanowires are presented in a separate paper [32].

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