Congruent Electrochemical Deposition of Co−Ni−Fe Films

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Abstract—Heating of chloride electrolyte up to 70°C ensures the normal codeposition of components of the Co−Ni−Fe alloy as a result of the discharge of iron, cobalt, and nickel ions at the high cathodic current density. The chloride electrolyte with filtration and pH correction by hydrochloric acid at the concentration $C_{Co} : C_{Ni} : C_{Fe} = 1 : 1 : 1$ provides the electrochemical deposition of Co−Ni−Fe films. The mechanism of anomalous deposition of Co, Fe, and Ni takes place due to the incomplete ionization of atoms and the different mobility of ions. The Co−Ni−Fe films lacking mechanical stresses with the uniform structure and the high magnetic properties are synthesized without using high annealing temperatures. The electrochemical deposition allows reproducible Co−Ni−Fe films to be obtained.

INTRODUCTION

The electrochemical deposition of Co−Ni−Fe coatings is used in many technological fields to decrease corrosion and deterioration, for magnetic and electric devises, and also for the synthesis of electrocatalytic materials. As compared with "dry" processes, the electrochemical deposition produces the more uniform coatings with the smaller number of defects and also makes it possible to increase, if necessary, the film thickness without inducing mechanical stresses.

In this study, we show the results on the electrodeposition of metal films based on the ternary system Co−Ni−Fe from the chloride electrolyte with the equal molar concentrations of components and the ratio Co : Ni : Fe = 1 : 1 : 1 at the temperature of 70°C with regard to the experience in the congruent deposition of the Ni−Fe permalloy [1] and the dependence of the deposition process on the ion charge [2].The goal of this study is to determine how the concentration of electrolyte components affects the composition, mechanical stresses, and magnetic properties of Co−Ni−Fe films.

THEORETICAL ANALYSIS

The alloy formation is determined by the peculiarities of the discharge of each electrolyte component, the specific features of the surface composition and structure of the cathode, the electric double layer structure, and the surface charge [3]. On the cathode, iron always evolves simultaneously with hydrogen.

The temperature has a strong effect on the coevolution of iron and hydrogen. At the low temperature (20−25°C), the discharge rate of iron ions exceeds the discharge rate of hydrogen ions only at the low current densities (up to 100 A/m^2−10 mA/cm^2). To obtain the high current efficiencies, the temperature and the current density should be high: 85−100°C (Fig. 1) and 50−100 mA/cm^2, respectively.

Furthermore, the current efficiency decreases with the decrease in the hydrochloric acid concentration. However, at the low concentration of hydrochloric acid, hydroxides are formed. To avoid their formation, pH 2−3 is maintained. The current efficiency also depends on the reaction of Fe^{3+} reduction to Fe^{2+}. These peculiarities of iron electrodeposition should be taken into account.

The book published relatively recently and devoted to the theory and practice of metal electrodeposition [4] shows the typical solution compositions used in the deposition of soft magnetic Ni−Fe alloys; however, it contains no information on the deposition of the ternary system Co−Ni−Fe.

As was shown in [5], for the 1 M solution concentration, the NiCl$_2$ solution has pH 5.8, the CoCl$_2$ solution has pH 4.7, and the FeCl$_2$ solution has pH 2.7, i.e., the hydrolysis of iron chloride increases more strongly the concentration of protons in the electrolyte.

The relative contents of metals in the electrolyte used in deposition of Co−Ni−Fe films and in the resulting deposits are the closest in a weak electrolyte containing no additives. The addition of ammonium

hydrate, boric acid, and saccharine to the electrolyte affects the film composition by changing the balance of ions.

Comparing the magnetization of the Co−Ni−Fe and Ni−Fe films as a function of the applied magnetic field showed that the slope of the magnetization line for the ternary system was higher by a factor of 1.7, which allowed considering the ternary system as the more promising for the use in magnetic field transducers. The possibility of optimization of magnetic parameters was demonstrated for the film composition $Co_{43.1}Ni_{35.3}Fe_{21.6}$.

In [6], the kinetics of electrodeposition of the Co−Ni−Fe alloy was considered. The experimentally found peculiarities of electrodeposition of the Co−Ni−Fe alloy were described by a sequence of chemical and electrochemical reactions proceeding in the electrolyte bulk, on the anode, and on the cathode.

In [7], the results are shown on the electrodeposition of films in the ternary system Co−Ni−Fe from the chloride electrolyte with equal molar concentrations of components and the molar ratio Co : Ni : Fe = 1 : 1 : 1 carried out at 70°C. A decrease in the electrolyte concentration led to the stronger potential drop in the interelectrode space on retention of the current value. The growth rate of the Co−Ni−Fe films increased with the increase in the current density but depended weakly on the concentrations of components at their 77-fold difference and was half the value calculated based on the Faraday law. The relative content of components Co, Ni, Fe in the films differed from their equal content in the electrolyte and depended strongly on the current density. At the high current density, cobalt and iron were deposited preferentially and the film composition was stabilized. The increase in the interelectrode space and the more active stirring of the electrolyte improved the uniformity and homogeneity of films. Moreover, the iron content in films decreased and the nickel content increased. The coercive force of Co−Ni−Fe films was low at the iron content in the interval of 15−30%, similar to permalloy, but the greater part of nickel was replaced by cobalt.

In [8], the dependence of the pH of chloride electrolytes with equal contents of components on the temperature and also the electrochemical deposition of Co−Ni−Fe films at 70°C were studied. The pH of the mixed electrolyte at all concentration of salts $CoCl_2$, $NiCl_2$, $FeCl_2$ was determined by the hydrolysis of iron chloride. The deposition from the electrolyte with 0.083 M concentration showed that the relative content of Co, Ni, and Fe in the film changed insignificantly at the high current densities, which was also true for the concentration of 0.48 M. The preferential deposition of cobalt was observed for all electrolyte concentrations.
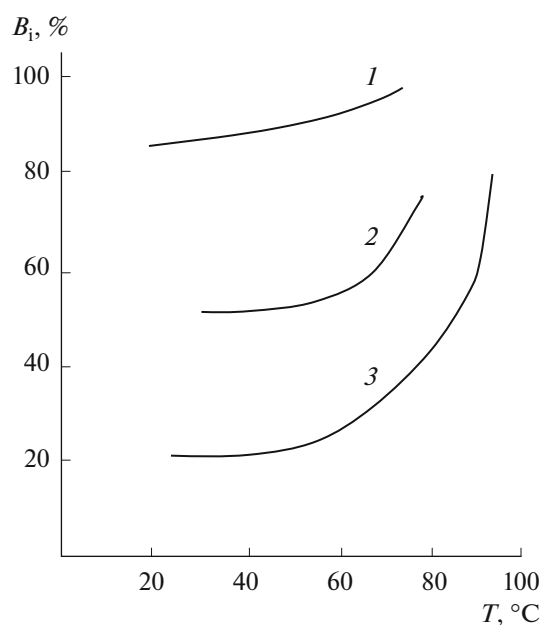

Fig. 1. Dependence of the current efficiency with respect to iron B_i on the temperature T of the electrolyte containing 1 M $FeCl_2$ and HCl, M: (*1*) 0.01, (*2*) 0.05, (*3*) 0.1.

EXPERIMENTAL

For the deposition of Co−Ni−Fe films, we used the chloride electrolyte with the equal molar content of salts $CoCl_2 \cdot 6H_2O$, $FeCl_2 \cdot 4H_2O$, and $NiCl_2 \cdot 6H_2O$ in deionized water. The following chemicals were added: boric acid H_3BO_3 20 g/L, sodium saccharinate $C_7H_4NaNO_3S \cdot 2H_2O$ 1.5 g/L, and hydrochloric acid 3 mL/L. The film was deposited from this electrolyte in an electrochemical setup with a galvanic bath of 2 L volume and a graphite anode [5]. The electrolyte had the temperature of 70°C maintained by a submersible heater and was stirred by a magnetic stirrer. The process was carried out in the galvanostatic mode. The following parameters of Co−Ni−Fe films were studied as a function of the electrodeposition conditions: composition, thickness, mechanical stresses, and magnetic properties.

The film parameters were measured with the use of instruments of the Center of Collective Use "Functional Control and Diagnostics of Micro and Nanosystem Equipment" at the Research and Industrial Center "Technological Center". The thickness of the films of magnetic field concentrators was measured by means of the MSA-500 analyzer of microsystems. The magnetic characteristics, namely, the coercive force and the magnetization were studied on the setup for controlling the magnetic parameters of films. The film composition was studied by means of the energy-dispersive X-ray microanalyzer PhilipsXL 40. The bending of plates was analyzed on the optical profilometer FRT MicroProb 100.

Table 1. The thickness H and the composition of Co−Ni−Fe films after their electrodeposition from the electrolyte containing 0.00625 M of each component and also saccharine or boric acid

No.	pH	U, V	I, mA	t, min	H, μm	V, nm/min	Co, %	Ni, %	Fe, %	Additives to electrolyte
1	2.62	6.8	500	30	4.34	145	42	13.5	44	
2	2.25	5.8	500	30	3.19	106	34	35	31	Saccharine, 3 g/L
3	2.8	8.1	570	30	4.36	177	51	20	30	
4	2.2	8.55	570	30	5.31	145	45.3	17.8	36.9	Boric acid, 20 g/L
5	2.35	7.75	534	30	4.5	150	44.5	24	31.5	Saccharine, 1.5 g/L
6	2.7	10.4	610	10	1.9	190	35.9	29.7	33.6	
7	2.55	8.3	610	10	2.8	88	50.6	13.7	35.7	Saccharine, 1.5 g/L Boric acid, 20 g/L

RESULTS AND DISCUSSION

1. Congruent Electrodeposition of Co−Ni−Fe Films

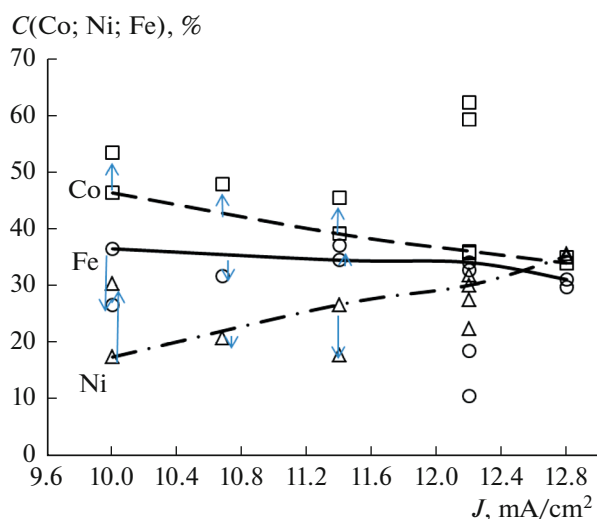For electrodeposition of Co−Ni−Fe films under galvanostatic conditions, we used the electrolyte with

Fig. 2. The percentage of components C(Co; Ni; Fe) in the films deposited from the electrolyte with the equal content (33 mol %) of salts $CoCl_2$, $NiCl_2$, $FeCl_2$ and the concentration of each salt of 0.00625 M as a function of the current density J in the interval of 10−12.8 mA/cm^2. The compositions of Co−Ni−Fe films without additives are shown by symbols which are connected by lines depending on the current density. The Co content is shown by squares and the dashed line. The Ni content is shown by triangles and the dash-and-dot line. The Fe content is shown by circles and the solid line. The composition of films obtained in electrolyte with additions of saccharine 3 g/L (at 10 mA/cm^2) and 1.5 g/L (at 10.7 mA/cm^2), boric acid 20 g/L (at 11.4 mA/cm^2) are shown by individual points. The arrows show how the film composition changes in the presence of the corresponding additive at the chosen current density.

the equal 0.00625 M concentrations of chlorides $CoCl_2$, $NiCl_2$, $FeCl_2$ in deionized water with the addition of 0.3 mL/L of 30% hydrochloric acid. Table 1 shows the results of deposition from the similar electrolytes but with addition of saccharine or boric acid.

Table 1 shows the parameters of the process: electrolyte pH, voltage between anode and cathode U, electric current I, deposition time t, film growth rate V, and also the additives to electrolyte, namely, boric acid H_3BO_3 and sodium saccharinate hydrate $C_7H_4NaNO_3S \cdot 2H_2O$.

Figure 2 shows the results of studying the film composition as a function of current density. As seen, the film composition depended on the current density and, at the current density of 12.1 mA/cm^2, the Co−Ni−Fe film composition was close to the electrolyte composition, namely, 33 mol % of each of salts $CoCl_2$, $NiCl_2$, and $FeCl_2$, i.e., the congruent electrodeposition of the ternary alloy Co−Ni−Fe was observed.

The additions to the electrolyte changed the film composition and disturbed the congruency of deposition in different ways. The addition of saccharine increased the content of Co and Ni and decreased the content of Fe. Boric acid (20 g/L) increased the Co and Fe content and decreased the Ni content. The simultaneous addition of 1.5 g/L saccharine and 20 g/L boric acid increased the Co content, slightly decreased the Ni content, and strongly decreased the content of Fe.

The electrolyte with the relatively low concentration (0.00625 M) of chlorides $CoCl_2$, $NiCl_2$, and $FeCl_2$ is promising for studying the congruency of the deposition of Co−Ni−Fe films with the thickness less than 1 μm but cannot be used in practice due to its exhaustion when thick films are deposited.

Table 2. The thickness of Co−Ni−Fe films and the bending of silicon plates 450 μm thick before and after the electrodeposition of films

Experiment no.	Plate no.	H, μm	$D0$, μm	$D1$, μm	I, mA	Additive to electrolyte
1	10	4.34	−3.6	170	500	
2	12	3.19	−8.9	106	500	Saccharine
3	15	4.36	−11.3	227	570	
4	16	5.31	−2.6	177	570	Boric acid
5	21	1.9	−6.2	83	610	
6	22	4.8	−5	14	610	Inhibitor
7	23	1.65	−10.9	102	640	
8	24	1.06	−11.1	55	640	Glycolic acid
9	25	1.4	−6.5	−6.5	610	Glycolic acid + inhibitor
10	28	1.15	−3.4	−3.6	610	Glycolic acid + inhibitor

2. The Effect of Additions to Electrolyte on the Bending of Silicon Plates with Electroplated Films of the Co−Ni−Fe Alloy

To obtain thick films, it is expedient to use the electrolyte composition with the equal concentrations (0.083 M) of each chloride $CoCl_2$, $NiCl_2$, and $FeCl_2$. Boric acid, saccharine, and hydrochloric acid were added to the electrolyte [8]. Boric acid is a complexing agent and decreases the mobility of metal ions. Hydrochloric acid stabilizes the electrolyte and rules out the formation of the precipitate of metal hydroxides. Saccharine is adsorbed on the cathode and thus limits the discharge of ions [9]. These additives improved the morphology of Co−Ni−Fe films, weakened the mechanical stresses, but decreased the deposition rate.

Table 2 shows the data on the thickness of Co−Ni−Fe films and the bending of silicon plates

Figure 3 shows the bending of silicon plates (solid bars, $D0$) before and (patterned bars, $D1$) after the electrodeposition of films of the ternary alloy Co−Ni−Fe from the electrolytes containing (1−2) saccharine, (3−4) boric acid, (5−6) inhibitor catapin, (7−8) glycolic acid, (9, 10) a mixture of glycolic acid and catapin.

The addition of boric acid and saccharine and also the individual additions of catapin and glycolic acid decreased the plate bending, whereas the mixture of catapin and glycolic acid totally ruled out bending of films with deposited Co−Ni−Fe films and strongly decreased the deposition rate.

Figure 4 shows how the composition of Co−Ni−Fe films and the deposition rate change with the concentration of boric acid and saccharine in the electrolyte. The film composition changed insignificantly, whereas the deposition rate decreased 1.5 fold when the additions of saccharine and boric acid were doubled. Saccharine deposited on the film surface and forming a white deposit.

3. Mechanical Stresses in Electroplated Co−Ni−Fe Films

The high mechanical stresses in thin magnetic films can cause the deformation and failure of devices due to exfoliation of films from silicon supports.

The thin $Fe_{70}Co_{29}Ni_1$ films with the high saturation of magnetic induction of 2.2 Torr at the coercive force of 60 Oe and the low mechanical stresses were prepared [12] by electrodeposition from chloride electrolyte. The mechanical stresses in the electroplated Co−Ni−Fe films decreased as the electrolyte temperature increased from 20 to 70°C at pH 0.3 and $J = 5$ mA/cm^2, increased as the nickel content in the deposit increased, and were inversely proportional to the grain size. The addition of ascorbic acid to the
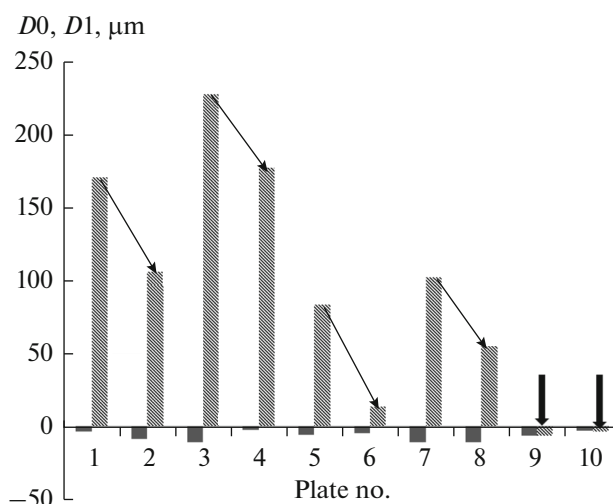

Fig. 3. Bending of silicon plates (solid bars) before $D0$ and (patterned bars) after $D1$ the electrochemical deposition of films of the ternary alloy Co−Ni−Fe from electrolytes with additions of (2) saccharine, (4) boric acid, (6) inhibitor catapin, (8) glycolic acid, and (9, 10) the mixture of catapin and glycolic acid.
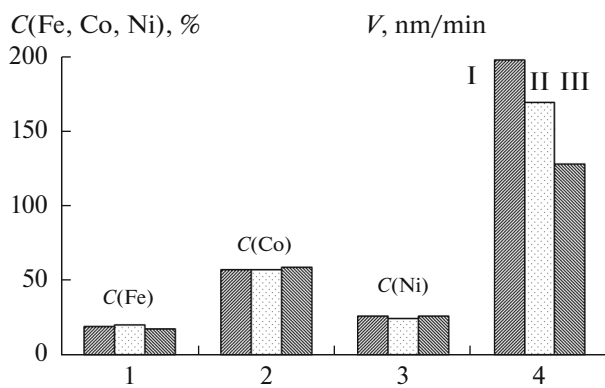
Fig. 4. Dependence of the composition C and the deposition rate V of the Co–Ni–Fe alloy films deposited at 70°C, the deposition time 150 min from the chloride electrolyte with the concentration of each component of 0.083 M in the presence of the following additives, at the current density of 12.1 mA/cm²:

I. 10 g/L H_3BO_3, 1.5 g/L saccharine, 2 mL/L HCl;
II. 10 g/L H_3BO_3, 3.0 g/L saccharine, 2 mL/L HCl;
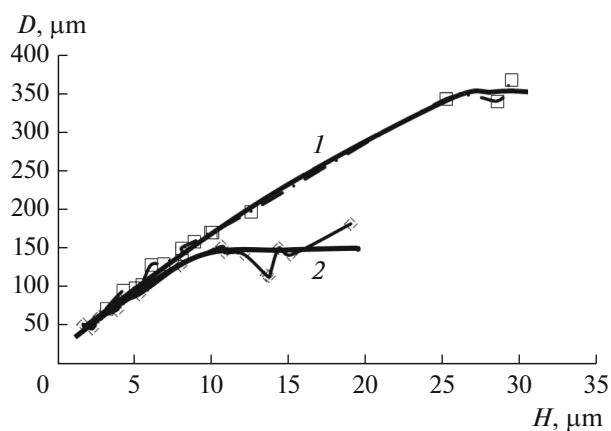III. 20 g/L H_3BO_3, 3.0 g/L saccharine, 2 mL/L HCl.

Fig. 5. Dependence of the bending D of silicon plates with the electroplated (*1*) Co–Ni–Fe and (*2*) Ni–Fe films on the film thickness H.

electrolyte stabilized the solution and allowed carrying out the deposition only at the high pH 2 which favored the low mechanical stresses.

The films of ternary alloy Co–Ni–Fe were deposited in [13] from a sulfate electrolyte with the varying content of saccharine. The lowest mechanical stresses of 61 MPa were observed at the saccharine concentration 0.004 M (0.9 g/L). As the electrolyte temperature increased from 25 to 50°C, the mechanical stresses decreased to 32 MPa.

To reveal the factors responsible for the appearance of mechanical stresses in Co–Ni–Fe films, we studied the bending of silicon plates with deposited films. The plate bending was analyzed on its back side. Figure 5 shows the measured geometrical parameters of plates.

According to Fig. 5, the bending was the maximum of 370 μm for the film 30 μm thick and the minimum for the film thickness of 2 μm. The support edges rose above plate's center on its front side, i.e., the film was contracted. The bending was determined only by the thickness of films of the ternary alloy Co–Ni–Fe. No exfoliation was observed.

According to the formula of Stoney [14], the bending of the support is proportional to the mechanical stresses in the film

$$\bar{\sigma} = D_{Si}, M_{Si} h_{Si}^2 / 3 h_f r_{Si}^2, \qquad (1)$$

where D_{Si} is the bending of the silicon plate; M_{Si} is the Young modulus of a silicon single crystal 1.09×10^{11} Pa [9]; h_{Si} is the thickness of the silicon support 450 μm; r_{Si} is the radius of silicon plate 50 mm; h_f is the magnetic film thickness.

For the film thickness of 15 μm and the bending of 180 μm, the mechanical stresses in the film of the ter-

nary Co–Ni–Fe alloy is 17.7 MPa. This value agrees by the order of magnitude with the mechanical stresses of 270–32 MPa found by means of an analyzer of mechanical stresses in [11].

The mechanical stresses in Co–Ni–Fe films appear due to the peculiarities of the electrochemical process of their deposition. Water dissociates to ions $H_2O \leftrightarrow H^+ + OH^-$. The dissolution of cobalt, nickel, and iron chlorides is accompanied by their hydrolysis. The salts $FeCl_2$, $NiCl_2$, and $CoCl_2$ are formed by the weak bases $Fe(OH)_2$, $Ni(OH)_2$, $Co(OH)_2$ and the strong acid—hydrochloric acid HCl. At the hydrolysis of salts formed by a weak base and a strong acid, the reaction proceeds via the cation and the solution becomes acidic [15].

$$MeCl_2 + H_2O \leftrightarrow MeClOH + H^+ + Cl^-. \qquad (2)$$

Hydrogen ions evolve on the cathode together with metal ions. Being adsorbed on the cathode, a part of protons lose their charge and form hydrogen molecules H_2. The molecules form gas bubbles observed at the metal electrodeposition.

It was found [16] that hydrogen dissolves in octo- and tetrapores of the metal lattice in its ionized state, accumulates in the pores and other defects in its molecular form, enters into chemical reactions with various elements and phases present in metals and alloys, and also adsorbs inside the metal on the surface of microvoids, pores, and microcracks, and segregates on lattice imperfections and grain boundaries.

In the end of electrochemical processes, hydrogen evolves from metal deposits giving rise to compressive stresses in the deposited film. For thin Co–Ni–Fe and Ni–Fe films, the relatively low mechanical stresses are almost the same, have the linear $D(H)$ dependence, but pass to saturation for Co–Ni–Fe films with the thickness larger as compared with Ni–Fe films. In the Co–Ni–Fe films, the mechanical

Table 3. Specific magnetization B/h, coercive force H_c, and the composition of the ternary Co−Ni−Fe films

Plate no.	1	2	3	4	5	6	7	8	9	10	11	12
B/h, nWb/μm	140	138	137	137	129	130	133	136	138	130	136	133
H_c, Oe	2.9	2.7	2.3	2	1.6	1.6	1.35	1.6	1.55	1.4	1.25	1.4
Co, at %	54.5	55.7	56.5	55.1	57	59.6	59.4	59	58.3	58.6	57.6	56.9
Ni, at %	23.2	22.4	22.7	24.1	22.5	24.9	24.9	26.3	26.6	27	28.4	30
Fe, at %	22.3	21.7	20.8	20.8	20.6	15.5	15.7	14.7	14.1	14.4	14	13.1

stresses reach the higher values as compared with the Ni−Fe films.

4. Magnetization and Coercive Force of the Permalloy and the Ternary Co−Ni−Fe Alloy

The magnetic properties, viz., the magnetization and the coercive force of films of the permalloy and the ternary Co−Ni−Fe alloy were studied based on the hysteresis loop of the magnetic field flux by means of an analyzer of magnetic properties of films. The composition of films on the plates was determined by the energy-dispersive X-ray microanalyzer.

Table 3 and Fig. 6 show the results of measurements of magnetic parameters: specific magnetization B/h, coercive force H_c, and the composition of the ternary Co−Ni−Fe films in at %.

The magnetization of Co−Ni−Fe films was 135 ± 5 nWb/μm for the Fe content from 13 to 23 at %. The coercive force H_c of Co−Ni−Fe films had the minimum of 1.25 Oe for the Fe content of 14 at %.

The X-ray diffraction analysis showed [17] that in the studied region of compositions, the Co−Ni−Fe films have the face-centered cubic lattice.

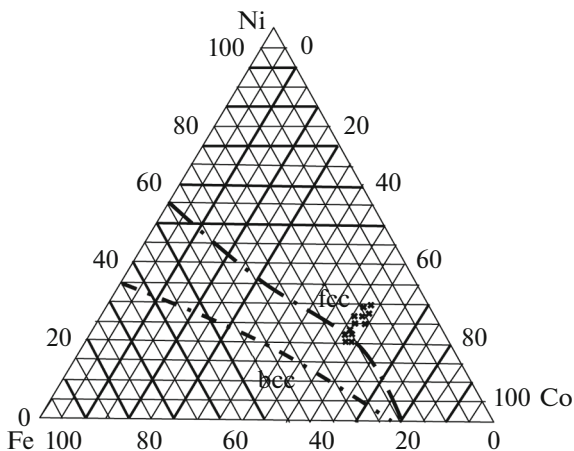Figure 7 shows the magnetization curve of the Co−Ni−Fe film.

By optimizing the deposition mode by choosing the current density of 12.1 mA/cm² and varying the electrolyte composition, the high values of magnetic induction of magnetization of 4000 nWb was obtained for the film thickness of 30 μm and the low values of coercive force of about 1 Oe.

5. Discussion

The following questions can be posed.

Why can the congruent electrodeposition of films based on metals of the ternary system Co−Ni−Fe be achieved by decreasing the electrolyte concentration?

Why does the composition of the Co−Ni−Fe film depend on the current density and stop to change at the high current density?

How do the additions to electrolyte change the film composition and disturb the congruency of deposition?

Assessing the deposition rate based on electrochemical potentials predicts the preferential deposition of nickel as normal; however, there are many factors that can affect the metal deposition.
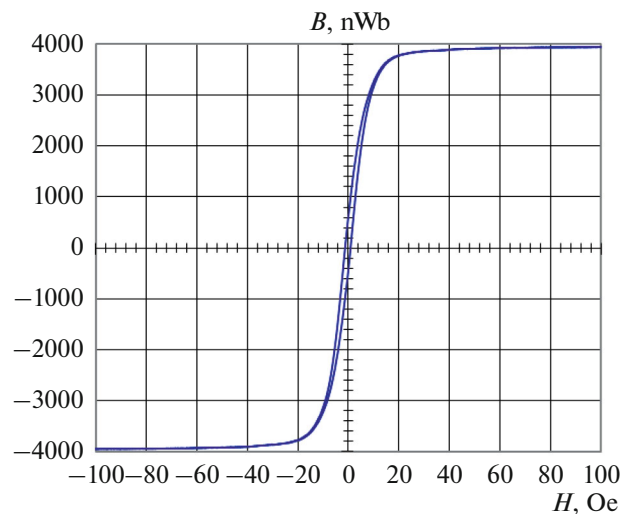

Fig. 6. The composition of the ternary alloy Co−Ni−Fe in the films deposited from chloride electrolytes.

Fig. 7. Dependence of magnetization B on the magnetic field strength H for the 30 μm thick Co−Ni−Fe film containing 16% Fe.

The flowing current disturbs the thermodynamic equilibrium giving rise to overvoltage, i.e., the shift of the electrode potential. The diffusion overvoltage is caused by the slow stage of substance transport through the stagnant layer adjacent to the cathode. The electrochemical overvoltage is associated with the slow stage of complex dissociation.

Iron, cobalt, and nickel are virtually undissolved in water. The existence of metal ions in water is associated with the presence of their salts. The deposition of a metal on the cathode is accompanied of the discharge of ions and decomposition of salt molecules. In the process, a layer of residues forms near the cathode, changing the electrolyte composition. The changes in the electrode potential as a result of changes in the reagent concentration in the space between the electrodes when current flows are called the concentration polarization associated with the slow supply of reagents and removal of products of electrochemical reaction [9].

The phenomena occurring in the electric double layer formed by charges near the cathode surface do not take into account the existence of ions with different charge and mobility in the electrolyte volume, the mass transfer, the stirring of electrolyte and its viscosity. The latter phenomena pertain to the electrolyte bulk properties.

The concentration polarization makes it possible to explain the dependence of the content of components in the Co–Ni–Fe film on the current density by the difference in the diffusion coefficients or mobilities of ions, the partial ionic currents that determine the mass transfer of electroactive ions to the electrode. The lower the electrolyte concentration, the smaller is the deviation of the film composition from the equilibrium state and the closer is the film composition to the electrolyte composition. This is why the congruent electrochemical deposition of the Co–Ni–Fe alloy proceeds at the low concentration of the main electrolyte components even without additions of boric acid and saccharine.

By the probe measurements of the pH it was shown [10] that near the cathode, the region of 0.6 mm with the enhanced pH 7 was formed at polarization with the current density of 5 mA/cm^2, as compared with the pH 2.7 observed at the current density of 1 mA/cm^2 in the solution of 0.2 M FeSO$_4$ and 0.8 M NiSO$_4$. The higher the current density, the wider is the deviation of the electrolyte composition near the electrodes from the uniform composition corresponding to the thermodynamic equilibrium. A sufficiently large region of concentration polarization is formed.

The peculiarities of the ionic current flowing in the electrolyte were clearly demonstrated at the working electrode potential from −1.3 to 0.6 V in a three-electrode electrochemical cell with the standard hydrogen electrode as the reference electrode by potentiodynamic measurements at a rate of 10 mV/s with moni-toring of the current through the electrode [11]. In the CoSO$_4$ solution, the anodic peak and a minimum were observed at the potential of 0.5 V. In the FeSO$_4$ the current peak was observed at −0.49 V. In the NiSO$_4$ solution where the conductivity was very low, the peak and the minimum were not observed. In the ternary electrolyte with concentrations the same as in individual solutions, namely, 0.2 M Ni, 0.005 M Fe, and 0.15 M Co, the anodic peak and the minimum were observed at the potential of 0.12 V, being determined by CoSO$_4$.

During the dynamic variation of the cathode potential, the transport of ions in the electrolyte leads to the heterogeneous distribution of the ion charge. The positive ions moving to the cathode form the electric double layer the internal field in which is directed oppositely to the external field between cathode and anode, thus compensating the latter. This results in a decrease in the current to the working electrode and gives rise to the current peak. A substantial difference between partial currents is observed, which is determined by the concentrations and mobilities of ions. The presence of the peak during dynamic measurements is associated with the kinetic properties of ions. The difference in the mobility of cobalt, iron and nickel ions determines the time and the difference in amplitudes of current peaks. The above results clearly demonstrate the difference in the dynamic characteristics of Co, Ni, and Fe ions and allows us to consider them as the factor determining the peculiarities of the electrochemical deposition of films based on the ternary system Co–Ni–Fe.

The increase in the current density extends the region of concentration polarization to the value where balance in observed between the reagent delivery and the removal of electrochemical reaction products. At the higher current densities, the composition stops to change.

The complexing agents and inhibitors added to electrolyte change the electrolyte composition in the region of concentration polarization, thus changing the mobility and the partial currents of ions. The film composition depends on the additions to electrolyte.

The electrolyte composition optimal for producing thick Co–Ni–Fe films with soft magnetic properties is 0.083 M for each chloride CoCl$_2$, NiCl$_2$, FeCl$_2$ at the appropriate choice of the current of 12.1 mA/cm^2. The electrolyte contains also boric acid, saccharine, and hydrochloric acid. These additions decrease the deposition rate, lower down the mechanical stresses, and improve the morphology of Co–Ni–Fe films.

CONCLUSIONS

The thick Co–Ni–Fe films with the high magnetic permeability and the low mechanical stresses were obtained by electrodeposition from the chloride electrolyte with the component ratio $C_{Co} : C_{Ni} : C_{Fe} = 1 : 1 : 1$

with filtration, at the deposition temperature of 70°C. Studying the electrochemical deposition of films based on metals of the ternary system Co−Ni−Fe when varying the electrolyte concentration made it possible to find that the congruent deposition occurred at the current density of 12.1 mA/cm^2 in the electrolyte containing 33 mol % of each salt CoCl$_2$, NiCl$_2$, FeCl$_2$ and the concentration of 0.00625 M and also with the addition of 0.3 mL/L 30% hydrochloric acid at the temperature of 70°C.

The mechanical stresses in the films were associated with hydrogen absorption. The optimization of the deposition mode and the electrolyte composition allowed the soft magnetic Co−Ni−Fe films with the high magnetization and the low coercive force to be synthesized. The results obtained are explained by the effect of the concentration polarization. The survey of the literature [17−54] showed the absence of analogous studies.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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