Contemporary level of technical development makes it possible to create the nano-dimensional objects, which possess special physical-chemical and mechanical properties. This opens up new possibilities in such high-technological spheres of production as electronics and aerospace industries, in instrument manufacturing and power engineering. One of the techniques, which make it possible to synthesize the nano-structured and nano-dimensional films, is the electrodeposition of metals. The variation of technological parameters and composition of the electrolyte ensures controlled influence on the process of electrosynthesis of coatings and obtaining precipitation with the assigned properties.

It is possible to considerably extend the range of functional characteristics of metallic coatings during electrodeposition of alloys with different component and quantitative composition [1, 2]. The alloying of base metal with one or several components leads to a cardinal change in the specific properties of the obtained alloy [3, 4]. Thus it is possible to obtain magnetically hard and magnetically soft materials,
wear-resistant and corrosion-resistant coatings, galvanic precipitations with high electrocatalytic activity and anti-friction coatings.

The alloy of nickel with iron is a multifunctional electrolytic alloy. Depending on the specified requirements, the Ni–Fe films can serve as a magnetic material, the electro-catalyst, protective-decorative or wear-resistant coating. Properties of the Ni–Fe precipitations are determined by the composition and crystalline structure. The modification of the structure of precipitations at the nano-dimensional level leads to a substantial change in the structurally dependent properties of coatings. This aspect underlies the electrochemical synthesis of alloys with the assigned properties.

Thus, the targeted formation of the Ni–Fe alloys with the predicted functional characteristics requires the establishment of the influence of electrodeposition conditions on the structure and properties of the obtained coatings.

2. Literature review and problem statement

The process of the electrodeposition of Ni–Fe alloy has been intensively investigated for a long period. The undiminsing interest in these coatings is caused by the combination of such useful properties as low thermal-expansion coefficient, high corrosion resistance, properties of a magnetically soft material. Magnetic properties of the Ni–Fe alloy are widely needed in the microelectronic industry. Permalloy, which contains 20% of iron, plays the key role in contemporary electronic nano-devices [5, 6] and in the so-called magnonics [7]. The influence of the conditions of electrolysis on the composition and magnetic saturation of the Ni–Fe thin films is examined in [8]. It was established in [9] that the identical magnetic susceptibility of thin skins and nano-wires of the Ni–Fe alloy corresponds to different composition of the alloys whose structure differs. A change in pH of the electrolyte of the alloy deposition affects magnetic characteristics of the obtained coatings [10]. It is shown that an increase in pH from 2.1 to 4.3 leads to a decrease in the magnitude of magnetic saturation, while the values of coercive force pass the minimum at pH 2.9. [11] examined a possibility of the modification of magnetic and mechanical properties of the Ni–Fe alloys by changing the composition of alloy [21].

As the analysis of scientific literature data reveals, the most common deposition electrolytes of the Ni–Fe alloys are the sulfate electrolytes. At the same time, the composition, structure and properties of galvanic precipitations depend on the character of the utilized electrolyte. It is shown in [22, 23] that the methanesulfonate electrolytes possess valuable features. The coatings, precipitated from such electrolytes, are characterized by high mechanical and magnetic properties [24, 25]. Methanesulfonate electrolytes are the new and insufficiently studied ones. Interesting results, obtained when studying the electrodeposition of metals and alloys from such electrolytes, predetermined the choice of subject of the present research. It appears expedient to establish the influence of sodium saccharinate on the composition, structure and properties of the Ni–Fe precipitations obtained from the methanesulfonate electrolyte.

3. Research goal and objectives

The goal of present study is to establish the character of influence of sodium saccharinate on the composition and properties of the Ni–Fe alloy, obtained from the methanesulfonate electrolyte. This will make it possible to develop new technologies for the application of unstressed, solid and magnetic coatings with the Ni–Fe alloy, ensuring improved functional characteristics of articles.

To accomplish the set goal, the following tasks have been set:

– to establish the influence of the composition of electrolyte and parameters of electrolysis on the composition of the electrodeposited Ni–Fe alloy, and to reveal a degree of action of sodium saccharinate on the content of iron in the alloy;
– to determine the effect of sodium saccharinate on the properties of the electrolytic Ni–Fe precipitations and to establish the dependence of coating properties on the structural changes, caused by organic additive.
4. Materials and methods for examining the composition, structure and properties of the coatings with the Ni–Fe alloy

4.1. Composition of electrolytes and methods for determining the content of components in the electrolyte and the Ni–Fe alloy

Composition of the deposition electrolyte of the Ni–Fe alloy: 1.00 M Ni(CH₃SO₄)₂·4H₂O; 0.30 M NaCl; 0.70 M H₂BO₃; +0.02 M C₆H₅O₂H·X M Fe(CH₃SO₄)₂, where X=0.03; 0.05; 0.08; 0.09; 0.11. We used sodium saccharinate as a special organic additive. Temperature of the electrolysis is T=333 K, current density is i=0.1–7.0 A/dm², pH 3. Nevertheless, the use of sodium saccharinate is not a complicating factor when applying the alloys with assigned composition. The greatest practical interest is demonstrated in the composition of iron(II) ions in the electrolytes and the content of iron in the Ni–Fe alloys using a photocolorimetric method applying the photocolorimeter KFK-2-UKhL 4.2 (Russia). The solutions of salts of nickel(II) and thiocyanate complex of iron(III) have different coloring; therefore, it is possible to isolate a region of the spectrum in which the light absorption by the solution of thiocyanate of iron(III) is large while the light absorption, by the solution of nickel(II) salt is insignificant. At such a wavelength, optical density of the solution will be determined almost entirely by the iron concentration. For this reason, we measured optical density of the solutions of nickel(II) sulfate and thiocyanate of iron(III) with different light filters. The light filter, which corresponds to a wavelength of 490 nm, is optimal.

We measured concentration of nickel(II) ions in the electrolyte. The titration was conducted in the presence of tartaric acid. Hydrogen pH index was measured using a glass electrode of the brand ESK-10601/7 (Belarus) in a set with the universal ionomer EV-74 (Belarus).

4.2. Methods for examining the structure and properties of coatings with the Ni–Fe alloy

The internal stresses of nickel-iron coatings were determined by the method of the flexible cathode [25]. Equation for calculating the internal stresses \( \sigma \) (MPa) takes the form:

\[
\sigma = \frac{E_d (d_1 + d_2)}{3l_d},
\]

where \( E_d \) is the modulus of elasticity of cathode plate, MPa; \( d_1 \) is the thickness of cathode, m; \( d_2 \) is the thickness of precipitation, m; \( l \) is the length of the working part of cathode, m; \( z \) is the deflection of the end of cathode from initial position, m.

The structure of electroplatings was studied using the X-ray diffractometer DRON-3 in the monochromatized Cu-Kα-emission. Calculation of the crystallite dimensions was conducted by the Scherrer formula:

\[
L = \frac{bk}{\beta \cos \theta}
\]

where \( \lambda \) is the wavelength of X-ray radiation; \( \beta \) is the half-width of the diffraction line of the sample; \( k \) is the shape factor (\( k=0.940 \)); \( \theta \) is the diffraction angle.

Microhardness by Vickers was measured using the instrument PMT-3 (Russia) at load \( P=100 \) g and thickness of the coating 25 µm. The value of microhardness was determined by formula [25]:

\[
H = \frac{1854 P}{l^2},
\]

where \( l \) is the length of diagonal of the diamond pyramid indentation, µm.

We measured magnetic parameters of the Ni–Fe electroplating using a magnetometer with a vibrating sample and stationary measuring coils.

Microphotographs of the surface of coatings were obtained using the electron raster microscope-microanalyzer REMMA-102-02 (Ukraine).

5. Results of examining the influence of sodium saccharinate on the composition and properties of coatings with the Ni–Fe alloy

Composition of the Ni–Fe alloy depends on the content of salts of the alloy-forming components in the electrolyte and conditions of electrodeposition. An increase in the concentration of iron(II) ions in the solution at a constant concentration of nickel(II) ions naturally leads to an increase in the content of iron in the alloy (Fig. 1). Deposition current density affects the composition of alloy in a complex way. An increase in the current density to 1 A/dm² leads to an increase in the content of iron in the alloy. Further change in the current density towards larger values contributes to reducing the share of iron in the obtained precipitations. Probably, diffusion limitations for the ions of iron(II) become essential in the region of high current densities. This can lead to a certain reduction in the relative contribution of the current of electric reduction of iron(II) ions to the total current of the alloy deposition.

The greatest practical interest is demonstrated in the Ni–Fe alloys that contain about 20 % of iron. Such alloys are used as the magnetically soft films, protective-decorative and wear-resistant coatings. Given this, we obtained precipitations of similar composition in the further studies. The content of iron(II) ions in the electrolyte in this case equaled 0.08 mol/l.

The influence of sodium saccharinate on the composition of the Ni–Fe alloy, deposited from such electrolyte at different current densities, is shown in Fig. 2. As experimental data reveal, in the presence of sodium saccharinate in the electrolyte at current density 1 A/dm², a coating with the smaller content of iron is precipitated. However, at a current density of 2 A/dm² and larger, the influence of additive on the composition of alloy is insignificant. Apparently, in this case, the examined additive influences the kinetics of electrodeposition of nickel and iron to alloy in equal degree.

Thus, the use of sodium saccharinate is not a complicating factor when applying the alloys with assigned composition. It is obvious that the ratio of metals in the alloy under the conditions of experiment is mainly determined by the concentration of ions in the alloy-forming metals in the electrolyte.
Fig. 1. Influence of the concentration of iron(II) ions in electrolyte and current density on the content of iron in the Ni–Fe alloys.

Fig. 2. Dependence of composition of the Ni–Fe alloy, obtained at \(X=0.08\) in the presence of 6 mmol/l of sodium saccharinate and without the additive, on current density, A/dm\(^2\): 1 – 0.25; 2 – 1; 3 – 2; 4 – 4; 5 – 6; 6 – 7.

The use of sodium saccharinate during electrodeposition of the Ni–Fe alloy from the methanesulfonate electrolyte is predetermined by the need for improving the mechanical properties of coatings. Precipitations obtained without organic additives are characterized by high internal stresses. This leads to the splitting of coatings and flaking from the base. Introduction of sodium saccharinate into the electrolyte contributes to a decrease in the internal tensile stresses. Fig. 3 shows that with an increase in the concentration of additive in the electrolyte, internal stresses of the obtained precipitations change symbatically. In the presence of 6 mmol/l of sodium saccharinate it is possible to precipitate practically unstressed coatings.

The effect of current density on the internal stresses manifests itself only at small concentrations of the additive. In this case, at high values of current density, a reduction in the internal stresses is observed. This effect cannot be linked to the action of sodium saccharinate. Since the examined substance is an anionic additive, shift of potential towards a more negative region must lead to a reduction in the adsorption of the additive. Consequently, the effectiveness of the action of sodium saccharinate on the internal stresses of precipitation should decrease. Apparently, reduction in the internal stresses with an increase in current density is caused by a change in the composition of alloy.

Introduction of sodium saccharinate into the electrolyte leads to an increase in the microhardness of coatings with the Ni–Fe alloy (Fig. 4). With an increase in the current density the microhardness is somewhat reduced. This can be linked to two factors. With an increase in the current density, the composition of alloy changes towards a decrease in the content of iron. Furthermore, because of reduction in the adsorption at the cathodic surface, the effect of additive on the structure of precipitations decreases.

In order to investigate magnetic parameters of the Ni–Fe precipitations, we received magnetic hysteresis loops (Fig. 5). The coating, precipitated from the electrolyte that does not contain organic additive, is characterized by a quite high value of the coercive force, equal to 14 E. Introduction of sodium saccharinate into the electrolyte leads to considerable reduction in the coercive force whose magnitude reached 4 E. Remanent magnetization of the samples in this case does not change.

Reduction of the magnitude of coercive force of the Ni–Fe precipitation in the presence of sodium saccharinate is a positive effect. This is caused by the fact that such films are mainly used as the low-coercive magnetically soft materials.
6. Discussion of results of examining the influence of sodium saccharinate on the composition, structure and properties of coatings with the Ni-Fe alloy

The experimental data obtained testify to the fact that sodium saccharinate weakly influences a composition of the Ni-Fe alloy, precipitated from the methanesulfonate electrolyte. At the same time, effect of this organic additive on the properties of coatings is rather significant. Since all the investigated properties are structurally sensitive, then the action of additive on the properties of coatings should be identified with a change in the structure of precipitations.

The increased microhardness of coatings with the Ni-Fe alloy when compared to nickel is predetermined by a considerable grain refining. Fig. 6 shows that the morphology of the Ni-Fe precipitation differs from that for nickel. Surface of the alloy is characterized by the clearly expressed micro-crystallinity. The size of crystallites of the Ni-Fe precipitations, obtained in the presence of sodium saccharinate, decreases with an increase in the concentration of additive (Fig. 7). This should obviously lead to an increase in the microhardness of coatings, which is actually observed in the experiment.

The influence of sodium saccharinate on the structure of the Ni-Fe precipitations is linked to the fact that, when adsorbed at the surface of cathode, the additive changes conditions for the electrocrystallization. In addition, sodium saccharinate is partially decomposed on the cathode. Decomposition products in this case fall into the precipitation. A decrease in the size of grains of the Ni-Fe precipitations and the presence of impurities in the crystal lattice of coatings results in the elevated microhardness of samples.

Fig. 5. Magnetic hysteresis loops of the Ni-Fe precipitations, obtained at $X=0.08 \text{ M}, I=2 \text{ A/dm}^2$ in the presence of sodium saccharinate, mmol/l: 1 — 0, 2 — 6

![Diagram](image)

Fig. 7. Dependence of the size of crystallites of the Ni-Fe alloy on the concentration of sodium saccharinate in the electrolyte. The content of iron ions in the electrolyte is 0.08 mol/l, precipitation current density is 2A/dm²

The presence of defects and changes in the structure of nickel, alloyed by iron, is predetermined by the fact that nickel and iron coprecipitate in the form of a solid solution, the parameters of crystal lattice of components of which are different. The parameter of crystal lattice of the obtained Ni-Fe alloy comprises 0.35513 nm, which differs somewhat from the value that corresponds to the face-centered cubic structure of nickel (0.35170 nm). Distortions in the structure lead to the occurrence of high internal stresses in the Ni-Fe alloy.

Introduction of sodium saccharinate into the electrolyte contributes to a reduction in the internal tensile stresses. This is mainly connected with the introduction of decomposition products of the additive to precipitation. Reduction in the internal stresses affects magnetic properties of precipitations. The lower the internal stresses, the less the coercive force of the alloy. This creates a possibility of employing such alloys as the shields of electromagnetic radiation. Furthermore, the obtained films are required for the creation of filters, phase inverters and gates in SHF equipment, magnetic circuits, pole pieces.

7. Conclusions

1. We investigated dependence of the composition of the Ni-Fe alloy on the concentration of iron(II) ions in the methanesulfonate electrolyte and on the precipitation current density. It is established that the content of iron in the alloy grows with an increase in the concentration of iron(II) ions in the electrolyte. The dependence of the composition of alloy on the current density passes the maximum at current density $1 \text{ A/dm}^2$. Introduction of sodium saccharinate into the electrolyte leads to a reduction in the share of iron in the alloy at precipitation current density to $2 \text{ A/dm}^2$. We did not observe any essential influence of the additive on the composition of alloy in the region of large values of current density.

2. It is established that the introduction of sodium saccha-
rinate into the methanesulfonate electrolyte of the Ni–Fe alloy deposition contributes to an increase in the micro-hardness of precipitations. An increase in the concentration of additive in the electrolyte leads to the growth of the values of microhardness and reduction in the internal stresses of coatings. The Ni–Fe alloy, obtained in the presence of sodium saccharinate, is characterized by the lowered properties of coatings. It is shown that the investigated properties of the Ni–Fe precipitations are determined by the structure of coatings. Organic additive is adsorbed at the cathodic surface and changes conditions for the electrocrystallization of alloy. A decrease in the size of precipitation grains and inclusion of decomposition products of the additive in coating predetermine an increase in the microhardness of coatings. Reduction in the internal stresses as a result of sodium saccharinate decomposition products entering the precipitation enables a decrease in the coercive force of the Ni–Fe films.

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1. Introduction

Corrosion causes significant economic losses as it leads to the failure of pipelines, parts of machines, boilers and other metal products. In addition, as a result of this process, equipment breaks down, damaged equipment can lead to an accident, or even a disaster that could affect people and environment. One of the major problems caused by corrosion is the loss of world metal reserves, which in turn leads to significant environmental damage inflicted by steel production.