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Phase Composition of Galvanic Iron-Nickel Alloys Obtained Using Pulsed Current

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The paper presents the results of studying the phase composition of iron-nickel alloys obtained by unsteady electrolysis. It was found that the use of a unipolar pulse current leads to a significant increase in the crystallization overvoltage at the crystallization front at the moment of the pulse action, which affects the component composition of the coatings. The phase composition of the alloys formed at the cathode differs from that shown in the iron-nickel equilibrium diagram.

Keywords: pulse current, cathode overvoltage, phase, alloy, equilibrium diagram, lattice spacing, microdistortion, vacant site.

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Introduction

The widespread use of galvanic coatings in mechanical engineering leads to the need to improve the existing methods and develop the new ones for their electroplating, in order to implement the necessary physical and chemical properties in them. One of the simplest and most promising methods for obtaining metal coatings is the use of pulsed current in the electrodeposition process. By setting the parameters of the pulsed current in the process of electrocrystallization of coatings on the cathode, it is possible to change their structure and phase composition in a wide range [1], which in turn determine their physicochemical properties.

The purpose of this work is to study the effect of the pulsed unipolar current on the fine structure and phase composition of iron-nickel electrolytic alloys.

I. Materials and method

To obtain the iron-nickel alloys, we used an aqueous electrolyte solution, g/l: $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ – 180,

$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ – 60, H_3BO_3 – 8, NaCl – 8 (pH = 2 - 2.5). The coatings were obtained on a previously degreased copper substrate. The deposition was carried out with the pulsed current, whose average density remained unchanged - $j_{av} = 1.5 \text{ A/dm}^2$. In all the experiments, the electrolyte temperature was maintained within the range of 292 - 297 K. The current pulse repetition rate (f) varied from 30 to 1000 Hz, and the pulse ratio (Q is the ratio of the period to the pulse duration) varied from 2 to 32.

We used DRON-2.0 diffractometer to study the fine structure and phase composition of the iron-nickel films. The survey was carried out in monochromatic $\text{Co K}\alpha$ - radiation. The crystalline lattice spacing a was determined from the visible maximum of the diffraction line (220) for the α -phase based on iron with a BCC lattice and along the line (311) in the γ -phase based on nickel with a FCC lattice, taking into account their width and survey geometry correction. As a standard we used annealed iron and nickel samples. The average value of the mosaic blocks (D) and the value of microdistortions ($\Delta a/a$) were determined by the approximation method [2]. The dislocation density ρ was estimated from the true intrinsic broadening of the diffraction line.

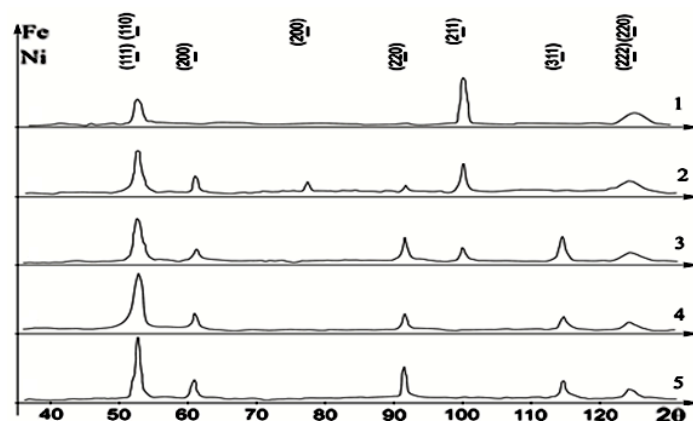


Fig. 1. Diffraction patterns of Fe-Ni alloys: 1 – $f = 30$ Hz, $Q = 32$; 2 – $f = 200$ Hz, $Q = 8$; 3 – $f = 100$ Hz, $Q = 4$; 4 – $f = 200$ Hz, $Q = 4$; 5 – $f = 1000$ Hz $Q = 4$.

The elemental composition of the alloys was carried out on X-ray spectrometers VRA-20, VRA-30 and an electron microscope "REMMA 102-2".

II. Results and discussion

One of the conditions for the appearance of a solid phase is the creation of non-equilibrium conditions at the crystalline phase - liquid (gas) interface. The measure of non-equilibrium of such conditions during the electrocrystallization of metals and alloys from aqueous solutions of electrolytes is the cathodic overvoltage - η , which is numerically equal to the difference in the values of the current and equilibrium cathode potentials. The magnitude and rate of its change in time affect the size and rate of nucleation of a new phase and, accordingly, the structure of the resulting films [3, 4].

In terms of its effect on the structure and phase composition of metals and alloys, cathodic overvoltage is similar to the melt undercooling rate during metallurgical processes ($10^5 - 10^6$ K/s), which makes it possible to obtain metastable states in electrolytic coatings at room temperatures.

The use of a pulsed current, in contrast to a direct one, allows to effectively influence the process of electrocrystallization. By changing the parameters of the pulsed current, and, consequently, influencing the rate of rise and fall of the cathode potential, we can control the ratio of iron and nickel atoms in electrolytic alloys [5].

The deposition of alloys at low frequencies (30 Hz) and high duty cycle (16 - 32) leads to the fact that the overvoltage at the cathode reaches its maximum value (0.4 - 0.5 V). The potential shifts to the electronegative region and the fraction of the discharge of the more electrochemically negative element iron increases on the cathode surface ($E_{st,Fe} = -0.44$ V, $E_{st,Ni} = -0.25$ V), at the same time the discharge current of nickel ions reaches the limiting value. The iron content in the alloys is 67.2 - 70.3 at. %. Deposition at high frequencies > 500 Hz and duty cycle equal to 2-4 leads to the fact that the overvoltage at the cathode decreases to 0.12 - 0.16 V and, as a consequence, the fraction of

discharging nickel ions (of the more electropositive component) increases, while that of iron decreases up to 43.7 - 46.1 at. %.

A change in the concentration of elements in the alloy leads to a change in its phase composition. The study of the phase composition of the coatings was carried out using X-ray structural analysis (Fig. 1). We found that the sequence of phase changes with increasing nickel content in the coating corresponds to the equilibrium diagram for the iron-nickel system (Fig. 2) [6]. It should be noted that the regions of existence of individual phases do not coincide with the data for iron-nickel equilibrium diagrams, as well as for the systems that have passed through long-term low-temperature annealing.

This feature was observed in [7], in which the Fe-Ni alloy was obtained using direct current. The region of

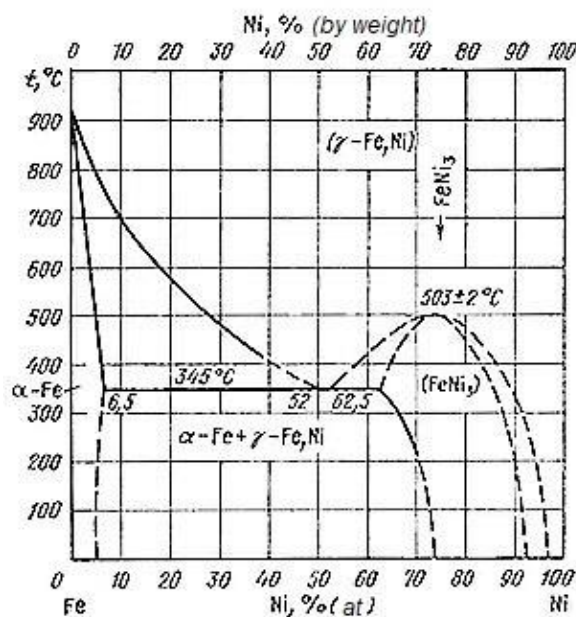


Fig. 2. Equilibrium diagram of an alloy of the Fe-Ni system subjected to prolonged annealing.

Table 1

No.	Phase composition of Fe-Ni alloys obtained by pulsed current					
	Deposition modes and phase composition					
	f , Hz	Q	η , B	Fe_xNi_y	BCC	FCC
1	1000	4	0.19	$\text{Fe}_{46.1}\text{Ni}_{53.9}$	–	+
2	1000	16	0.24	$\text{Fe}_{50.4}\text{Ni}_{49.6}$	–	+
3	500	2	0.18	$\text{Fe}_{45.4}\text{Ni}_{54.6}$	–	+
4	500	16	0.28	$\text{Fe}_{57.6}\text{Ni}_{42.4}$	+	+
5	200	4	0.25	$\text{Fe}_{51.8}\text{Ni}_{48.2}$	–	+
6	200	8	0.31	$\text{Fe}_{55.9}\text{Ni}_{44.1}$	+	+
7	100	4	0.28	$\text{Fe}_{53.9}\text{Ni}_{46.1}$	+	+
8	100	16	0.39	$\text{Fe}_{64.9}\text{Ni}_{35.1}$	+	+
9	30	32	0.55	$\text{Fe}_{70.3}\text{Ni}_{29.7}$	+	–

existence of single-phase alloys (α -solid solution) with an iron-based BCC lattice increased to 20 at.% of nickel.

When comparing the data given in Table 1 with the data of the equilibrium diagram of alloys obtained by the metallurgical method, there is a significant increase in the region of existence of the α -phase with iron-based BCC lattice. In metallurgical iron-nickel alloys, the formation of the γ -phase based on nickel with FCC lattice began when the nickel content in the alloy exceeded 5 - 7 at. %, while during the pulsed current deposition, this occurred when the nickel content reached ≈ 30 at. %. We also observed a significant decrease in the region of existence of two-phase solutions - α and γ (from 29.7 at.% to 48.2 at.% of nickel) in comparison with metallurgical alloys.

With the nickel content above 48 at. % the alloys were formed single-phase with nickel-based FCC structure.

Preliminary results of X-ray diffraction studies indicate that the diffraction lines obtained from metal films are broadened, and the observed maxima are shifted towards larger glancing angles compared to the standards. The line broadening could be influenced by both the refinement of mosaic blocks and the formation of microstresses in the coating as the result of crystal lattice distortion due to a large number of point and linear defects. It is also worth considering the possibility of including hydrogen in the structure of the resulting phase.

To determine the distortions of the crystal lattice, which caused the broadening of the diffraction maxima, from the planes with large indices, we carried out the measurements of its spacings. In the initial state and annealed at the temperature above that of recrystallization.

An initial study of the dependence of the lattice parameter on the conditions for obtaining metal films from iron-plating and nickel-plating electrolytes showed that in films obtained with direct current, the lattice spacing increases $a_{\text{Fe}} = 0.2873$ nm, $a_{\text{Ni}} = 0.3526$ nm in comparison with the reference values $a_{\text{Fe}} = 0.2866$ nm, $a_{\text{Ni}} = 0.3524$ nm. This is explained by the simultaneous release of hydrogen with metal ions on the cathode surface, which, penetrating into the structure of the deposit, leads to the formation of supersaturated solid solutions. Comparing the degree of distortion of the

crystal lattices of iron and nickel films, we found that the iron film lattice is more distorted ($\Delta a/a = 2.4 \cdot 10^{-3}$) than the nickel one ($\Delta a/a = 0.6 \cdot 10^{-3}$). This is due to the high affinity of iron for hydrogen; iron absorbs hydrogen approximately 7 times more than nickel [8]. The second reason causing an increase in the spacing is that iron has BCC lattice, in which the largest pores, where a hydrogen atom can penetrate, are tetrahedral ones [8]. Their radius is 0.291 r , where r is the radius of atoms at lattice sites ($d_{\text{tetFe}} = 0.074$ nm), while for nickel, which has FCC lattice, these are octahedral - 0.41 r ($d_{\text{octNi}} = 0.1016$ nm). Considering that the radius of the hydrogen atom is ($d_{\text{H}} = 0.092$ nm), this leads to the fact that the introduction of hydrogen into the crystal lattice of iron distorts it to a greater extent than the crystal lattice of nickel.

A distinctive feature of the structure of electrolytic coatings obtained with a pulsed current at high cathodic overvoltages is a high concentration of point and linear defects in the crystal lattice. This corresponds to the excess energy of discharging particles up to 10 kT, which exceeds the energy of atoms at premelting temperatures [10]. The excess energy of atoms is quickly dissipated, but such a significant deviation from equilibrium cannot but affect the nature of the crystal lattice construction.

To assess the degree of distortion of the structure of the alloys, they were annealed. We chose two temperatures as annealing temperatures, 523 K, at which the process of decomposition of a supersaturated solid solution of hydrogen begins, and 693 K, at which the decomposition is completed and the process of recrystallization in the alloy begins.

The analysis of the lattice spacing of the alloys showed that the deposited metal ions at high cathode overvoltages do not have time to diffuse to their equilibrium sites, this leads to the metal becoming oversaturated with vacant sites, as a result of which the lattice spacings become smaller than the reference values (Table 2). Internal compressive stresses arise in the alloys (–). As the cathodic supersaturation decreases, the dominant factor contributing to the crystal lattice distortion is hydrogen introduced into the vacant sites and into the interstices of atoms of the deposited metals. This thereby leads to a change in the sign of internal stresses in the coatings – from compression (–) to tension (+).

Table 2

Influence of pulsed current parameters on the lattice parameter in iron-nickel films

No.	Microdistortions in electrolytic films					
	f , Hz	Q	Fe_xNi_y	A_{init} , nm	A_{annl} , nm	$\Delta a/a_{\text{annl}}, 10^{-3}$
1	1000	4	$\text{Fe}_{46.1}\text{Ni}_{53.9}$	0.3583	0.3581	+0.6
2	1000	16	$\text{Fe}_{50.4}\text{Ni}_{49.6}$	0.3575	0.3574	+0.4
3	500	2	$\text{Fe}_{45.4}\text{Ni}_{54.6}$	0.3577	0.3578	-0.3
4	500	16	$\text{Fe}_{57.6}\text{Ni}_{42.4}$	0.3584	0.3586	-0.4
5	200	4	$\text{Fe}_{51.8}\text{Ni}_{48.2}$	0.3586	0.3588	-0.4
6	200	8	$\text{Fe}_{55.9}\text{Ni}_{44.1}$	0.3584	0.3586	-0.6
7	100	4	$\text{Fe}_{53.9}\text{Ni}_{46.1}$	0.3557	0.3582	-0.7
8	100	16	$\text{Fe}_{64.9}\text{Ni}_{35.1}$	0.2876	0.2879	-1.0
9	30	32	$\text{Fe}_{70.3}\text{Ni}_{29.7}$	0.2868	0.2871	-1.1

In the coatings deposited at a frequency of 1000 Hz, we observed less distortion of the crystal lattice in comparison with the coatings obtained at high cathodic overvoltages and the coatings obtained at direct current. This is associated with a decrease in the cathode polarization amplitude at higher vibration frequency, which leads to the formation of thermodynamically stable nuclei of large sizes. In addition, the shortening of the pause leads to a decrease in the pulsations of the electrode potential. During the pause, the potential does not have time to fall below the metal precipitation potential, therefore, its deposition during the period of the high-frequency pulsed current proceeds continuously, as with direct current. High-frequency potential fluctuations change the angle of wetting of the cathode surface with hydrogen bubbles, thereby accelerating their separation from it [5]. This leads to a decrease in the concentration of embedded hydrogen in the metal. The above factors lead to the formation of a low-defect, coarse-crystalline structure.

Experiments have shown that isothermal annealing of coatings at 693 K brought the deposits to a state close to equilibrium. The size of the mosaic blocks increased from 40 - 70 to 420 - 510 nm, the dislocation density decreased from 10^{11} cm^{-2} to 10^9 cm^{-2} . In Fe-Ni alloys, in the initial state having a body-centered cubic lattice, during annealing, we observed precipitation from the α -phase based on iron and an increase in the amount of the γ -phase based on nickel, due to the occurrence of collective crystallization processes. The performed X-ray structural analysis of the samples after annealing showed that the observed phase structure of the alloys corresponds to the equilibrium diagram.

One of the causes of the more intensive increase in size of the mosaic blocks at 693 K can be explained by the fact that hydrogen, which is in the crystal lattice in a partially ionized state [11] in the form of Cottrell clouds, lowers the diffusion mobility of dislocations and prevents the rearrangement of dislocations from "horizontal" groups into "vertical" ones. As the temperature rises, Cottrell clouds decay, hydrogen diffuses from the

coating, the mobility of dislocations increases, and the mosaic block boundaries become more mobile.

Analyzing the results obtained for the change in the fine structure of iron-nickel alloys depending on the annealing temperature, it can be assumed that the cause of the crystal lattice spacing decrease at high supersaturations on the cathode is the formation of a defect structure. It is possible that the introduction of hydrogen into the deposit structure has an effect as well; however, the factor of non-equilibrium crystallization predominates, as evidenced by the high concentration of vacant sites and dislocations, and a decrease in the lattice spacings in the initial samples as compared to the annealed ones.

Conclusions

1. Studies have shown that the use of pulse current allows, without changing the composition of the electrolyte solution, to change the cathodic overvoltage, and, consequently, to control the structure and phase composition of the coatings being formed.

2. Pulse current allows to expand the region of existence of α -solid solution up to 29.7 at.% of nickel and γ -solid solution - up to 48.2 at.% of nickel.

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Фазовий склад гальванічних залізо-нікелевих сплавів, отриманих за допомогою імпульсного струму

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У роботі наведені результати дослідження фазового складу сплавів залізо-нікель, отриманих при нестационарному електролізі. Встановлено, що використання уніполярного імпульсного струму призводить до значного збільшення кристалізаційної перенапруги на фронті кристалізації в момент дії імпульсу, що впливає на компонентний склад покриттів. Фазовий склад сплавів, що утворюється на катоді, відрізняється від представленого на рівноважній діаграмі стану залізо-нікель.

Ключові слова: імпульсний струм, катодна перенапруга, фаза, сплав, діаграма стану, період решітки, мікрОВикривлення, вакансія.