КИНЕТИКА ЭЛЕКТРООСАЖДЕНИЯ СПЛАВА ЦИНК-НИКЕЛЬ ИЗ СУЛЬФАТНО-ГЛИЦИНАТНОГО ЭЛЕКТРОЛИТА

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Проведено исследование кинетики электроосаждения сплава цинк-никель из кислого сульфатно-глицинатного электролита и свойств формирующегося покрытия в зависимости от состава электролита и режима осаждения. Хроноамперометрическое исследование электроосаждения сплава цинк-никель позволило установить, что при потенциалах поляризации –1,00 –1,05 В относительно ХСЭ процессы на электроде протекают с диффузионным контролем. Изменение потенциалов в область более отрицательных значений приводит к кинетическим затруднениям. На формирование сплава цинк-никель из сульфатно-глицинатного электролита оказывает влияние концентрация соли никеля. От ее содержания в растворе зависят поляризация процесса, перенапряжение кристаллизации, количество никеля в осадке. Максимальное перенапряжение кристаллизации формирования осадка соответствует содержанию NiSO₄ в электролите в количестве 0,12-0,14 моль/л. Этому же диапазону концентраций отвечают большие парциальные плотности тока электровосстановления никеля при электроосаждении сплава Zn-Ni. Установлено, что при содержании сульфата никеля более 0,16 моль/л количество никеля в осадке снижается. При электроосаждении сплава в результате выделения водорода отмечается повышение pHs приэлектродного слоя. Высказано предположение, что при катодной плотности тока более 10 мА/см² формирование сплава цинк-никель происходит при участии нейтральных и электроотрицательных комплексов. Определение защитной способности образцов в 3%-ном растворе NaCl методом хроновольтамперометрии и импедансной спектроскопии показало, что максимальной коррозионной стойкостью характеризуются образцы с содержанием никеля 14,4 %, полученные в растворе с концентрацией сульфата никеля 0,12-0,14 моль/л.

Ключевые слова: сплав цинк-никель, коррозионностойкое покрытие, сульфатно-глицинатный электролит, комплексообразование, концентрация компонентов

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KINETICS OF ELECTRODEPOSITION OF ZINC-NICKEL
ALLOY FROM SULFATE-GLYCINATE ELECTROLYTE

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Kinetics of electrodeposition of a zinc-nickel alloy from the acid sulfate-glycinate electrolyte and the properties of the formed coating have been studied depending on the composition of the electrolyte and the deposition mode. Chronoamperometric studies of the electrodeposition of the zinc-nickel alloy made it possible to establish that at polarization potentials of -1.00 -1.05 V relative to the CSE, processes on the electrode proceed with diffusion control. Changing the potentials to the region of more negative values leads to kinetic difficulties. The formation of the zinc-nickel alloy from the sulphate-glycinate electrolyte is affected by the concentration of the nickel salt. The process polarization, crystallization overvoltage, the amount of nickel in the alloy depends on its content in the solution. The maximum crystallization overvoltage corresponds to the $NiSO_4$ content in the electrolyte in the amount of 0.12-0.14 mol/l. Large partial densities of the electroreduction current of nickel during the formation of the Zn-Ni alloy correspond to the same range of concentrations. It was found that with the content of nickel sulphate more than 0.16 mol / l, the amount of nickel in the precipitate decreases. During electrodeposition of the alloy, the pH of the near-electrode layer increases as a result of hydrogen evolution. It is assumed that with the cathode current density of more than 10 mA/cm^2, the formation of the zinc-nickel alloy occurs with the participation of neutral and electronegative complexes. Determination of the protective ability of samples in a 3 % NaCl solution using both chronovoltamperometry and impedance spectroscopy showed that samples with a nickel content of 14.4 % obtained in the solution with a nickel sulfate concentration of 0.12-0.14 mol/l are characterized by maximum corrosion resistance.

Key words: zinc-nickel alloy, corrosion-resistant coating, sulfate-glycinate electrolyte, complexation, components concentration

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INTRODUCTION

A promising trend of increasing the protective ability of metallic coatings is the electrodeposition of alloys. Much attention is paid to zinc-based alloys, which are an alternative to cadmium coatings. A number of authors have shown that co-precipitation of zinc with iron group metals (zinc-nickel, zinc-cobalt, zinc-iron alloys [1-7]) promotes an increase in the protective ability of coatings and an improvement in their mechanical properties. Zinc-nickel alloys, as well as other zinc systems with metals of the iron group, are characterized by abnormal precipitation, in which zinc, a less noble metal, is predominantly deposited. Despite a great number of works on the electrodeposition of these alloys, some questions remain concerning the effect of the concentration of electrolyte components, the presence of a complexing additive in the solution and the electrolysis mode on the composition of the coating being formed, its physicochemical and mechanical properties.

For the deposition of alloys, electrolytes of different composition can be used, but preference should be given to low-concentration solutions [8-9], which have a lesser environmental hazard and provide coatings with a given complex of physical and mechanical properties. In this regard, electrolytes containing amino acids, in particular glycine (GLy), are of interest. It is known [10-12] that the presence of glycine in the solution of the electrodeposition of metals and alloys leads to the formation of complex compounds with metal ions. In addition to complexation, this component acts as a buffer additive.

Glycine has electron-donating, bridging properties, it belongs to bidentate ligands and is capable of forming heteronuclear complexes in the solution and on the electrode surface [13-17]. The complexation of electrorecovering metal ions (nickel (II), zinc (II)) with glycine has received considerable attention in the literature [10-23]. The authors analyze the ion equilibrium constants and the stability constants in nickel and zinc plating electrolytes [10, 21], the influence of the nature of the background anion on the buffer capacity of the nickel plating solution [22], and nickel electroplating kinetics [17, 23]. The formation of complexes of zinc and nickel ions with glycine ensures the convergence of the electrode potentials of the reducing ions and the production of uniform coatings of the zinc-nickel alloy.

The co-precipitation of Ni (II) and Zn (II) from a complex sulphate-glycinate electrolyte has not been studied enough [2, 12]. Therefore, the purpose of this work was to study the kinetics of electrodeposition of the zinc-nickel alloy from an acidic sulphate-glycinate

electrolyte and the properties of the coating being formed, depending on the composition of the electrolyte and the deposition mode.

EXPERIMENTAL

Electrodeposition of zinc, nickel and zinc-nickel alloy was carried out from sulphate-glycinate electrolyte. The content of the components in the electrolyte composition was selected on the basis of studying such physicochemical properties of solutions as viscosity and conductivity (χ). The kinematic viscosity (ν) was determined by the time of the fluid outflow (τ) through the capillary of the viscometer, $\nu = \tau \cdot k$, where k is the viscometer constant. To determine the flow time of the fluid, a VPG-2 viscometer with a capillary diameter of 0.56 mm (GOST 33-66) was used. The measurement error was 0.2-0.4%. The measurement of electrical conductivity was carried out with the help of conductometer EXPERT-002-2-6-H-C (TU 4215-004-52722949-2002, GOST 16851-71). The measurement error was ±0.25%. To increase the conductivity of the solution, sodium sulfate in the amount of 0.5 mol/l was introduced into the working electrolyte. In the earlier work [18], it was found out that in the concentration range of $ZnSO_4$ from 0.21 to 0.25 mol/l in the electrolyte of $ZnSO_4 + Na_2SO_4$ 0.5 mol/l + NH_2CH_2COOH 0.7 mol/l, the conductivity is stable and lies within 8.48-8.53 mS/m.

Electrochemical deposition of zinc, nickel and Zn-Ni alloy was carried out on steel of grade 45 from electrolytes containing $ZnSO_4$ 0.21 and 0.25 mol/l, $NiSO_4$ from 0.06 to 0.21 mol/l, Na_2SO_4 0.50 mol/l, glycine in the amount of 0.7 and 0.93 mol/l. Electrodeposition of the coating was carried out in the galvanostatic mode at cathode current densities of 5-20 mA/cm², temperature 22 ± 2 °C using a potentiostat P-8S. Pre-treatment of the working electrodes included mechanical cleaning of the steel surface with emery paper (P400-P1500), degreasing with an organic solvent, etching in 10% HCl and washing in distilled water.

The working surface of the electrode was 5 cm². The quantitative composition of the samples of the electrodeposited coating was determined by the X-ray fluorescence method using a Niton instrument with an accuracy of ±0.05%. The pH value of the near-electrode layer (pHs) was determined by measuring the potential of a micro-antimony electrode located at the surface of the working electrode, but not in contact with it (~ 0.1 mm) and applying a previously obtained E-pH calibration curve using standard buffer solutions.

Chronoamperometric study of the alloy formation was carried out at potentials of -1.00…-1.15 V relative to the silver chloride reference electrode

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(CSE). The current efficiency of the samples was determined by the gravimetric method. Determination of the protective ability of the studied coatings was carried out by the express method by registering potentiodynamic dependencies in a 3% NaCl solution at a potential sweep rate of 4 mV/s and using the method of impedance spectroscopy. The measurements were performed using an impedancemeter Z-500 on samples of the zinc-nickel alloy of cylindrical shape with an area of 0.5 cm^2 with an auxiliary graphite electrode in the frequency range of 500 kHz-1 Hz and amplitude of 5 mV.

The calculation of the partial current densities (i_j) during the electrodeposition of the alloy was carried out according to the formula:

$$i_j = i_{total} \cdot W \cdot \omega_j,$$

where i_{total} is the polarization current density, A/cm^2; W is the current efficiency in unit fractions; ω_j is the component fraction in the alloy in unit fractions. The experimental results are the average values of 3 parallel experiments.

RESULTS AND DISCUSSION

The study of physicochemical (ν, χ) and thermodynamic (activation enthalpy for the viscous flow) properties of zinc plating sulfate-glycinate electrolytes [18], as well as the analysis of literature data on the complexation of glycine with nickel ions [10, 16, 17, 19], zinc [2, 20, 21] allow us to consider the kinetics of the formation of a zinc-nickel alloy as a co-precipitation from complex metal ions with glycine and from hydrated ions.

Electrodeposition of Zn, Ni from the studied sulfate-glycinate electrolytes proceeds at high negative electrochemical potentials, with greater polarization observed in the initial period of the process during nickel plating. When nickel salt is introduced into the electrolyte ZnSO$_4$ 0.21 mol/l, Na$_2$SO$_4$ 0.50 mol/l, NH$_2$CH$_2$COOH X mol/l (where X is 0.7 and 0.93), the polarization of the alloying process decreases, which indicates the mutual influence of co-precipitating metals. A chronoamperometric study of the electrodeposition of the zinc-nickel alloy showed that at polarization potentials –1.00 and –1.05 V relative to the CSE i,1/√t-curves are extrapolated to the origin of the coordinates (Fig. 1). This may indicate that the processes on the electrode proceed with diffusion control [24].

At more negative potentials (–1.10 and –1.15 V), the rate of hydrogen evolution and, accordingly, the pHs of the near-electrode layer increase. According to [10, 19-21], the nature of the formed complexes depends on the pH of the solution, the ratio of the content of metal ions and glycine in the electrolyte and can vary from positively charged to neutral and negatively

charged particles. It can be assumed that at a potential of –1.15 V, neutral and electronegative complexes of metal ions take part in the electroplating process, whose reduction rate is lower than that of positively charged complex particles [10, 20]. As a result, additional kinetic difficulties arise and curves 3 and 4 are not extrapolated to the origin of the coordinates i-1/√t (Fig. 1).

Since the process of electrodeposition of the zinc-nickel alloy, depending on the polarization potential, is influenced by diffusion and kinetic limitations, the effect of nickel sulphate concentration on the process rate and the composition of the coating being formed was investigated. In the solutions of the deposition of zinc-nickel alloy with an increase in the concentration of NiSO$_4$ from 0.06 to 0.10 mol/l, an increase in ν and χ solutions is observed (Table 1). However, a further C_{NiSO4} increase leads to some decrease in both ν and χ, which may be a consequence of competing processes in the solution: on the one hand, the break of hydrogen bonds in the structure of water and, on the other hand, the formation of a large number of complexes with a lower degree of dissociation.
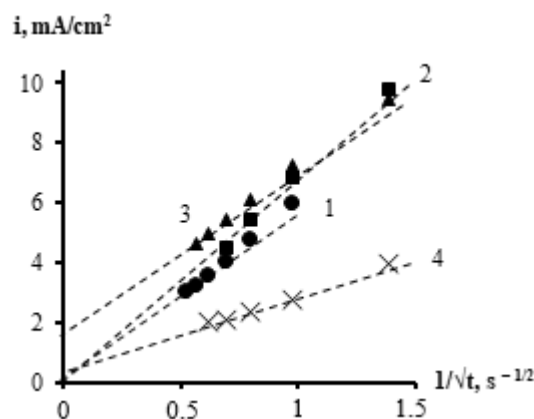

Fig. 1. i-1/√t electrodeposition curves of the zinc-nickel alloy in the solution containing, mol/l: ZnSO$_4$ 0.21, NiSO$_4$ 0.12, Na$_2$SO$_4$ 0.5, NH$_2$CH$_2$COOH 0.7, for polarization potentials, V: –1.0 (1); –1.05 (2); –1.10 (3); –1.15 (4)
Рис. 1. i-1/√t кривые электроосаждения сплава цинк-никель в растворе состава, моль/л: ZnSO$_4$ 0,21, NiSO$_4$ 0,12, Na$_2$SO$_4$ 0,5, NH$_2$CH$_2$COOH 0,7, при потенциалах поляризации, В: –1,0 (1); –1,05 (2); –1,10 (3); –1,15 (4)

The processes occurring in the volume of the solution are reflected in the kinetics of the electrodeposition of metals. It has been established that by varying the NiSO$_4$ content in the electrolyte, crystallization overvoltage (η_{cr}) changes during the alloy formation (Table 2). The maximum η_{cr} corresponds to the NiSO$_4$ content in the electrolyte 0.12-0.14 mol/l. The same concentration range corresponds to large partial current densities of Ni electroplating during the formation of the Zn-Ni alloy (Fig. 2a).

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Table 1

Influence of NiSO₄ concentration on the physicochemical properties of the deposition electrolyte of the zinc-nickel alloy containing, mol/l: ZnSO₄ 0.21, NiSO₄ X, Na₂SO₄ 0.5, NH₂CH₂COOH 0.7 at 25 °C

Таблица 1. Влияние концентрации NiSO₄ на физико-химические свойства электролита нанесения сплава цинк-никель состава, моль/л: ZnSO₄ 0,21, NiSO₄ X, Na₂SO₄ 0,5, NH₂CH₂COOH 0,7 при температуре 25 °C

X, mol/l	0.06	0.10	0.12	0.14	0.16	0.18	0.21
$\nu \cdot 10^6$, m²/s	2.17	2.40	2.43	2.12	2.32	2.18	2.79
χ, mS/m	8.37	8.46	8.50	8.43	8.67	8.60	8.47

Table 2

Crystallization overvoltage of electrodeposition of Zn-Ni alloys from the electrolyte containing, mol/l: ZnSO₄ 0.21, NiSO₄ X, Na₂SO₄ 0.50, NH₂CH₂COOH 0.7, at i_k = 5 mA/cm², t = 22 °C, pH of solution 5.5

Таблица 2. Перенапряжение кристаллизации электроосаждения сплавов Zn-Ni из электролита состава, моль/л: ZnSO₄ 0,21, NiSO₄ X, Na₂SO₄ 0,50, NH₂CH₂COOH 0,7, при i_k = 5 мА/см², t = 22 °C, pH раствора 5,5

X, mol/l	0.06	0.10	0.12	0.14	0.16	0.18	0.21
η_{cr}, mV	2	6	19	18	13	8	7

The composition of the alloy is influenced by the nature of the complex particles, determined by the ratio of the components in the solution. At a deposition current of 5 mA/cm², the nickel content in the sediment decreases with a nickel sulfate concentration in the solution of more than 0.18 mol/l, and at 20 mA/cm² – more than 0.16 mol/l. The study of the partial current densities of electroreduction of electroactive particles of nickel, zinc and hydrogen ions depending on the thickness of the forming coating (Fig. 2 b) showed that in the initial period of the formation of the Zn-Ni alloy, intense H₂ evolution is observed, leading to alkalization of the near-electrode layer. The pHs value of the near-electrode layer increases to 7.00-7.45 at the 10^{-th} second of polarization with a current of 5 mA/cm², depending on the concentration of NiSO₄. With a cathode current density of 20 mA/cm² it increases up to 7.70-10.40. Lower alkalization of the near-electrode layer corresponds to the content of NiSO₄ in the solution of 0.10-0.14 mol/l, pHs is 7.00-7.20 at 5 mA/cm² and 7.70-9.09 at 20 mA/cm².

The formation of neutral and negatively charged nickel complexes leads to the fact that the partial current of the nickel incorporation in the precipitate with increasing the sediment thickness at small cathode

current densities (5 mA/cm²) practically does not depend on the coating thickness, and at large i_k (20 mA/cm²) tends to decrease. Therefore, in order to increase the amount of nickel in the precipitate composition, it is advisable to carry out the process at current densities of less than 20 mA/cm².
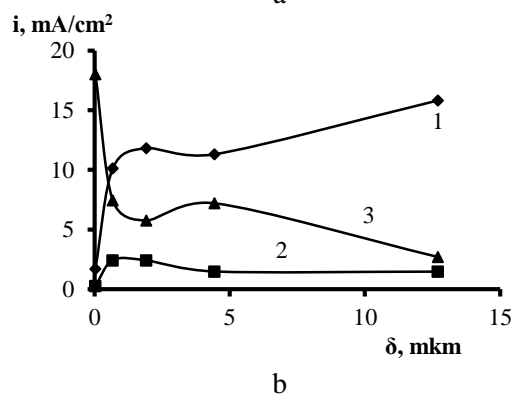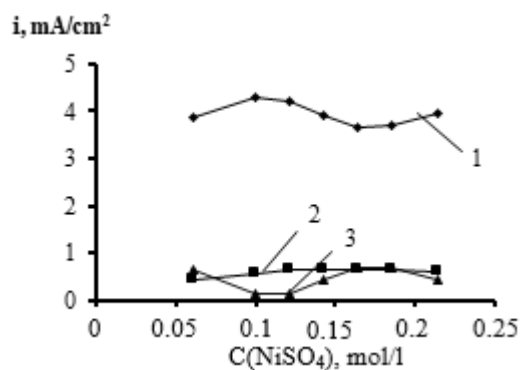

Fig. 2. Dependences of the partial deposition currents of the components of Zn-Ni alloy and H₂ evolution from the electrolyte containing, mol/l: ZnSO₄ 0.21, NiSO₄ X, Na₂SO₄ 0.50, NH₂CH₂COOH 0.7, on CNiSO₄ (a) and on the thickness of the coating at NiSO₄ content 0.12 mol/l (b): 1 – Zn, 2 – Ni, 3 – H₂
Рис. 2. Зависимости парциальных токов осаждения компонентов сплава Zn-Ni и выделения H₂ из электролита состава, моль/л: ZnSO₄ 0,21, NiSO₄ X, Na₂SO₄ 0,50, NH₂CH₂COOH 0,7, от C(NiSO₄) (a) и от толщины покрытия при содержании NiSO₄ 0,12 моль/л (b): 1 – Zn, 2 – Ni, 3 – H₂

With an increase in the concentration of NiSO₄ from 0.06 to 0.16 mol/l in the sulphate-glycinate electrolyte, the amount of Ni in the alloy increases from 10.6 to 14.7%. The protective ability (ΔE), determined by the width of the passive state range in the potentiodynamic study of the zinc-nickel alloy in 3% NaCl solution, is about 1.2 times more than ΔE of zinc coatings. Moreover, a large ΔE value corresponds to Ni content of 14.4%. The study of the protective ability of the samples by the method of impedance spectroscopy also showed that a sample obtained in the solution with a nickel sulphate content of 0.12-0.14 mol/l is charac-

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terized by the maximum resistance to the charge transfer in a corrosive environment.

CONCLUSIONS

Thus, it was found that the formation of a zinc-nickel alloy from a sulphate-glycinate electrolyte is influenced by the concentration of nickel salt. Its content in the solution affect the polarization of the process, crystallization overvoltage, the amount of nickel in the sediment. It was established that the increase in the alloy thickness results in the decrease in the nickel content in the alloy composition. It was assumed that with a cathode current density of more than 10 mA/cm^2, the formation of a zinc-nickel alloy occurs with the participation of neutral and electronegative complexes. On the basis of the conducted research, the range of nickel salt concentrations in the sulfate-glycinate electrolyte from 0.12 to 0.14 mol/l was selected.

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