

Voltammetric Analysis of Phase Composition of Zn-Ni Alloy Thin Films Electrodeposited from Weak Alkaline Polyligand Electrolyte

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The phase composition of Zn-Ni alloy films electrodeposited from a slightly alkaline polyligand electrolyte was analyzed by anodic voltammetry method. The mechanism of films anodic dissolution in alkaline ammonia-glycinate solution not containing metal ions is proposed. The main peaks correspond to the zinc dissolution from η -phase and from γ -phase of the initial film and the nickel-enriched phase formed during the film dissolution. The nickel content in the nickel-enriched phase is determined, as well as nickel and γ -phase content in the original film, depending on the ratio of metal ion concentrations in the electrolyte at various ratios of glycine and ammonia concentration. It is shown that films in a wide range of these ratios ($[\text{Ni}^{2+}]:[\text{Zn}^{2+}] = (2-5):1$ and $[\text{Gly}]:[\text{NH}_3(\text{NH}_4^+)] = (2-9):5$) contain mainly γ -phase with nickel content in the range of 15.8-18.2%.

Keywords: Alloy, Zn-Ni, Phase composition, Anodic linear stripping voltammetry.

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1. INTRODUCTION

The Zn-Ni alloys may provide either sacrificial protection or barrier film protection for steel [1]. The zinc-nickel alloys containing of 10-15 wt. % nickel possess higher corrosion resistance and better mechanical properties against zinc [2]. Such coatings provide a sacrificial protection to steel and are recommended to replace environmentally hazardous cadmium coatings [3-4]. Other authors prefer the range of 15-18 wt. % Ni [5-6]. The commonly employed Zn-Ni alloy in the aeronautical industry has 15-22 wt. % [7].

Multilayer coatings consisting of thin layers of metals, alloys and oxides have the best anticorrosive, mechanical and catalytic properties [8-10] compared to classical single-layer coatings. Anticorrosive and mechanical properties of coatings depend on their phase composition. There are 5 known phases for zinc-nickel alloys (a solid solution of Ni in Zn with hexagonal structure, containing up to 1 wt% Ni), δ -phase ($\text{Ni}_3\text{Zn}_{22}$), γ -phase (an intermetallic compound $\text{Ni}_5\text{Zn}_{21}$ with a bcc structure), β -phase (NiZn) and α -phase (a solid solution of Zn in Ni) [11].

In electrodeposited coatings, the XRD method finds mainly η -phase of the nickel solid solution in zinc, the intermetallic γ -phase and the α -phase of the zinc solid solution in nickel [12]. However, during the formation of thin films, other phases may appear, for example, γ_1 -phase (Zn_3Ni) [17]. Moreover, during the anodic dissolution of the films the additional phases can also appear.

In the case of thin films, the stripping voltammetry method [18] is a convenient method for analyzing their phase composition. However, the correctness of its use depends both on the solution used and on the accuracy of electrolysis parameter selection. The films are dissolved both in electrolytes for alloy deposition [13-14, 18-21] and in solutions that do not contain metal ions [15, 16], both in acidic [19] and in alkaline solutions.

From 2 to 5 peaks can be observed on anodic linear stripping voltammetric (ALSV) depending on the composition of the alloy and the conditions for its dissolution. Most authors argue that the first anodic peaks correspond to the dissolution of zinc from its η -phase, δ -phase, γ -phase and α -phase. The last peak at more noble potential corresponds to the dissolution of nickel from its phases. However, other authors believe that in the potential range of last peak, not only Ni dissolves, but the dissolution of Zn-Ni alloy also takes place. Depending on the composition of the alloy, the last peak associated with γ -phase or α -phase dissolution.

The deposits from the alkaline bath are characterized by a homogeneous phase composition. In the case of two phases the corrosion cell tends to form in corrosive environments. The coatings by single phase alloys obtained from the alkaline bath may exhibit generally higher corrosion protection. Alkaline electrodeposition gives a more uniform deposit, which offers better corrosion protection to the underlying metal. However, in alkaline baths, the zinc and nickel species must be stabilized with a complexing agent to prevent precipitation as metal hydroxides.

In this paper, the effect of nickel and zinc ions content in weakly alkaline polyligand ammonia-glycinate electrolyte on the chemical and phase composition of electrodeposited films were examined using anodic linear stripping voltammetry.

2. EXPERIMENTAL

Zinc-nickel alloy films were deposited in a weakly alkaline ammonia-glycinate polyligand electrolyte. Both nickel and zinc ions in this electrolyte forms complex compounds with both ammonia and glycine in this electrolyte. The influence of films phase composition was investigated in series of electrolytes (Table 1) with constant total nickel and zinc ion concentration and constant total lig-

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and (ammonia and glycine) concentration; pH was 9.0.

Table 1 – Solution composition

Solution number	Components concentration in electrolyte, mol/l			
	Ni ²⁺	Zn ²⁺	Gly ⁻	NH ₄ ⁺ (NH ₃)
1	0,01	0,05	0,12	0,30
2	0,04	0,02	0,12	0,30
3	0,05	0,01	0,12	0,30
4	0,01	0,05	0,18	0,24
5	0,04	0,02	0,01	0,12
6	0,05	0,01	0,12	0,30
7	0,01	0,05	0,27	0,15
8	0,04	0,02	0,27	0,15
9	0,05	0,01	0,27	0,15

The ratio of metal ion concentrations $M = [\text{Ni}^{2+}]:[\text{Zn}^{2+}]$ was varied from 5:1 to 1:5 at the ratio of ligand concentrations $L = [\text{Gly}]:[\text{NH}_3(\text{NH}_4^+)] = 2:5$ (solutions 1-3 in Table 1), 3:4 (solutions №4 - №6) and 9:5 (solutions №7-№9).

Zinc-nickel alloy films of 50-230 nm thickness were deposited for 3.5 minutes on a platinum electrode in a galvanostatic mode. For comparison, we used the same current density of 3 mA/cm², which is lower than the value of the limiting current density for all solutions.

Electrochemical studies were carried out using potentiostat PI-50.1. The results were transferred from analogue form to digital by means of the two-channel voltmeter and Telex program for PC (5-100 signals per second). The silver chloride reference electrode was used.

3. RESULTS AND DISCUSSION

The Zn-Ni alloy films were anodically dissolved in ammonia electrolyte containing Cl⁻ ions to avoid passivation of Ni and not containing more noble metal to avoid the reaction of replacement of Zn by Ni²⁺. Furthermore, in order to increase the separation of the peaks of dissolution of zinc and nickel, the pH of the solution was higher than that of the electrolyte for alloy deposition. Dissolution of zinc begins at electrode potential of -1.32 V. Nickel dissolves at potential values of above 0.4 V in this solution.

The calculation of chemical and phase composition of zinc-nickel films was carried out taking into account the following preliminary results:

1) X-ray phase analysis of coatings of 10-20 μm thickness obtained under the test conditions showed that coating containing only γ -phase deposits when the nickel to zinc ion concentration ratio in electrolyte is 2:1 and 5:1. The coating containing η - and γ -phases deposits when the mentioned ratio is 1:5;

2) chemical analysis of the coating composition obtained at a current density of 3 mA/cm², showed the nickel content to within 20 %;

3) chemical analysis of the solution after dissolution of about 20 alloy films in the potentiostatic regime at potential values below -0.8 V showed the presence of nickel traces, and analysis of the deposit accumulated on the platinum electrode revealed the presence of nickel and zinc in approximately equal amounts.

Figures 1, 3 and 5 present ALSV of the films obtained in the studied electrolytes with deconvoluted

peaks. The curves have 2-3 well-defined main peaks and 2 more peaks that overlap main peaks.

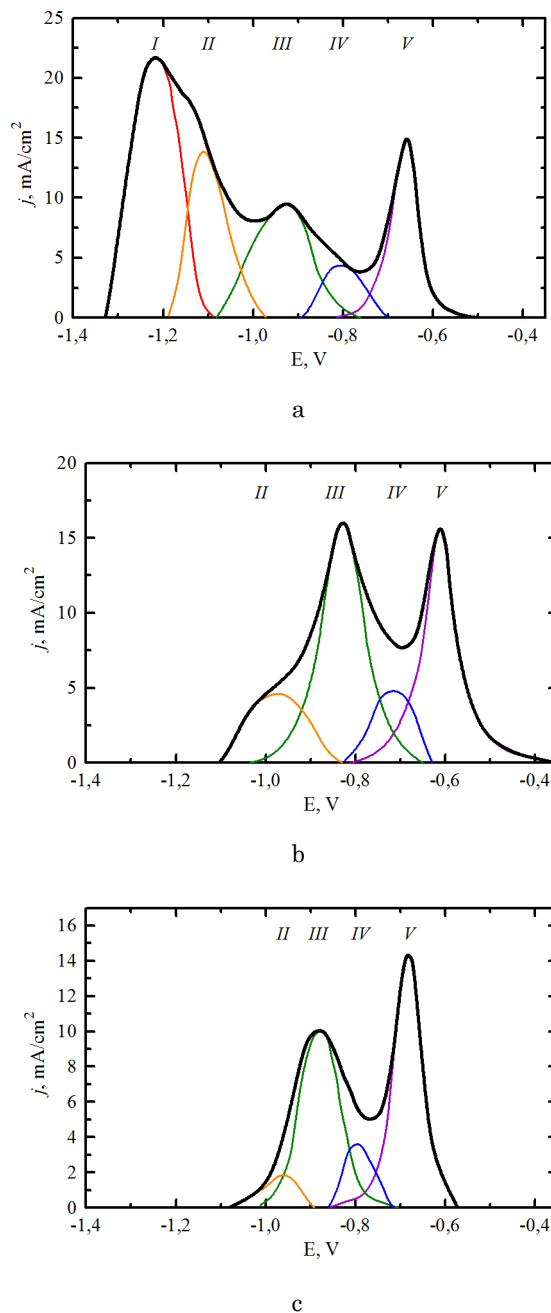


Fig. 1 – ALSV on Pt in solutions, containing 0.12 mol/l Gly, 0.30 mol/l NH₃(NH₄⁺) and 0.06 mol of metal ions. The [Ni²⁺]:[Zn²⁺] concentration ratio: a – 1:5; b – 2:1; c – 5:1. Potential scan rate is 5 mV/s

Taking into account preliminary experiments, we consider that the first four peaks are related to the zinc dissolution from different phases (Fig. 1a). In the P_I peak, zinc dissolves from the η -phase of the initial alloy film. The nickel content in the coating surface increases and it is possible that surface is passivated with intermediate products of zinc dissolution. It is likely that in the P_{II} peak (which is the shoulder of P_I peak) zinc also dissolves from the η -phase, but under conditions of the changed surface. It is also possible that a transient δ phase forms in this case.

In the peak of P_{III} , zinc dissolves from the γ -phase of the initial alloy. In the P_{IV} peak (shoulder of P_{III} peak),

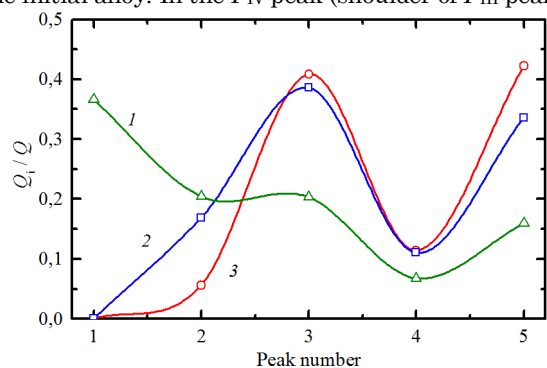


Fig. 2 – Distribution of fraction of amount of electricity under the ALSV peaks from Fig. 1: 1 – from Fig. 1a; 2 – from Fig. 1b; 3 – from Fig. 1c

zinc also dissolves from the γ -phase, but under conditions of the surface been changed as a result of nickel accumulation and, possibly, the presence of surface intermediate zinc compounds, for example η -phase.

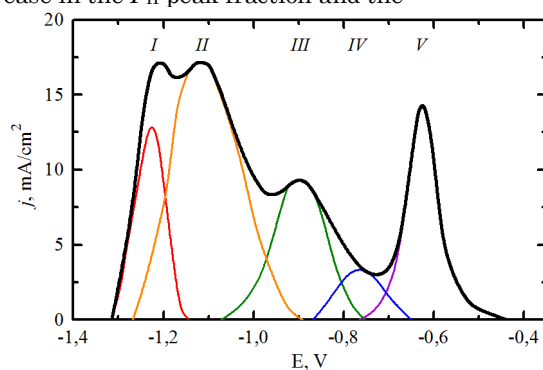
In the P_V peak, the phase that was not present in the original alloy dissolves. This phase forms as a result of the enrichment of the surface with nickel. This is not a pure nickel, as the potential of this peak is more than 1 V less than the potential of nickel dissolution beginning in this solution. In this peak, α -phase or β -phase of the zinc-nickel alloy enriched with nickel due to dezincification of the surface dissolves, depending on the initial alloy composition and, possibly, the potential sweep rate. After this peak, the current drops to 0. It further increases at the much higher potential values (in the region of oxygen evolution).

When the ratio of the metal ion concentrations M increases, the number of peaks decreases (for each value of the ratio of the ligand concentrations L) and the alloy becomes homogeneous. Moreover, the area under ALSV curves decreases, which indicates a decrease in the current efficiency during alloy deposition (compare a, b, c of Fig. 1, 3, 5).

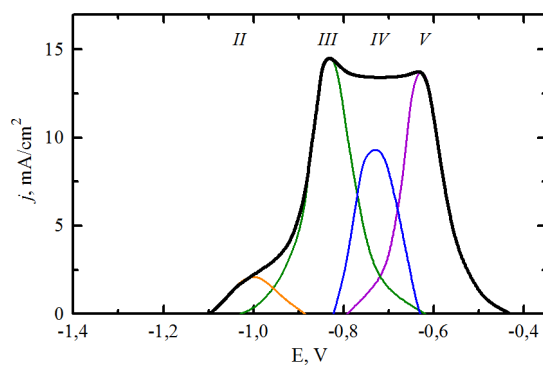
In contrast to the alloy deposited in electrolyte having $M = 1:5$ (Fig. 1a), the ALSV dissolution of the alloy obtained at $M = 2:1$ (Fig. 1b) the P_I peak disappears, the P_{II} peak decreases and the P_{III} peak increases. I.e., the alloy contains mainly γ -phase at such electrolyte composition. With further increase in M (Fig. 1c), the P_{II} peak decreases even more. Moreover, the height of P_{III} peak also decreases, but the height of the P_V peak increases in comparison with the P_{III} peak. I.e., the alloy is enriched with the γ -phase, but electrolysis efficiency decreases.

Fig. 2 shows the amount of electricity distribution consumed for alloy dissolution in the peaks. The amount of electricity was calculated according to the area under peaks of the ALSV curves the area under the entire ALSV. Only in the case of alloy deposition from the solution with $M = 1:5$, the amount of electricity consumed to dissolve zinc decreases with the increase in the peak number, i.e., with an increase in the nickel content in the phase (curve 1). The distribution of peaks contribution in the cases of $M = 2:1$ (curve 2) and $M = 5:1$ (curve 3) has the same form. Though the

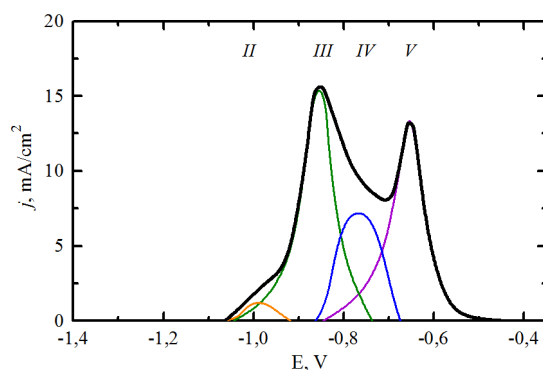
contribution of the peak P_V increases due to the decrease in the P_{II} peak fraction and the



a



b



c

Fig. 3 – ALSV on Pt in electrolytes, containing 0.18 mol/l Gly-, 0.24 mol/l $\text{NH}_3(\text{NH}_4^+)$ and 0.06 mol of metal ions. The $[\text{Ni}^{2+}]:[\text{Zn}^{2+}]$ concentration ratio: a – 1:5; b – 2:1; c – 5:1. Potential scan rate is 5 mV/s

increase in the P_{III} peak fraction.

As L increases (glycine fraction increasing), the height of the P_I peak decreases, and its shoulder turns into a P_{II} peak (Fig. 3a), which may indicate increase in the degree of surface passivation by intermediate compounds of zinc dissolution from η -phase with decreasing of its content in the alloy. With increase of M (Fig. 3b) the P_{IV} peak also increases, which is apparently associated with an increase in the degree of surface passivation by intermediate products of zinc dissolution as the η -phase content in the alloy decreases (the height of P_{II} peak decreases). At $M = 5:1$ (Fig. 3c), the

P_V peak height decreases, compared to the P_{IV} peak.
The distribution of the amount of electricity under

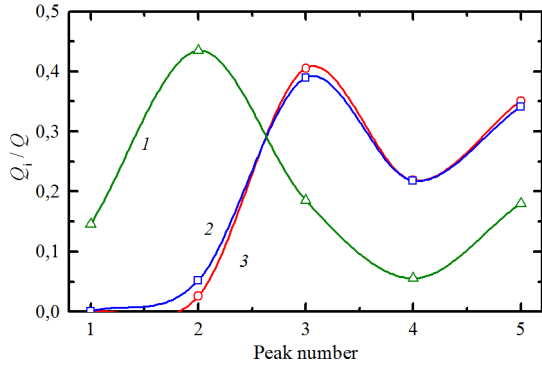
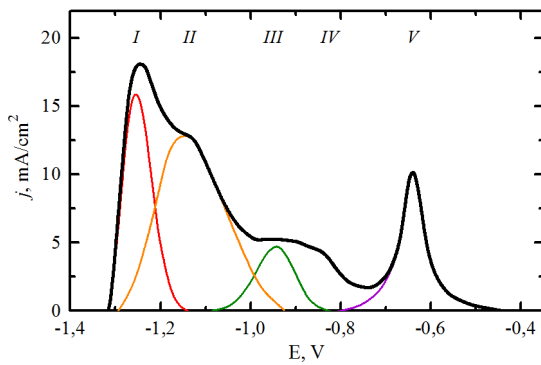
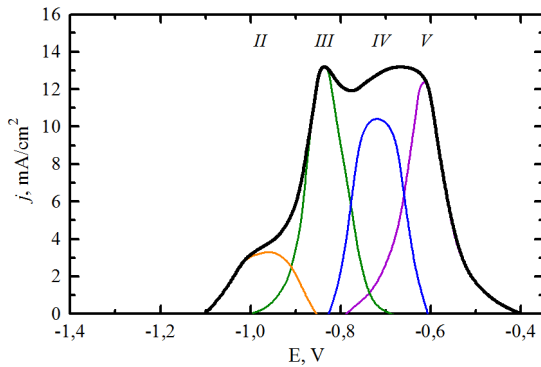


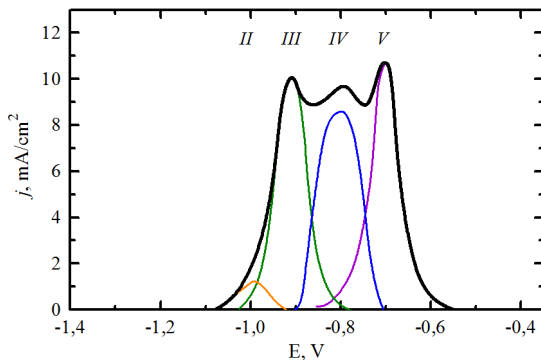
Fig. 4 – Distribution of the amount of electricity under peaks of ALSV curve Fig. 3: 1 – from Fig. 3a; – from Fig. 3b; 3 – from Fig. 3c



a



b



c

Fig. 5 – ALSV on Pt in solutions, containing 0.27 mol/l Gly,

0.15 mol/l $\text{NH}_3(\text{NH}_4^+)$ and 0.06 mol of metal ions. The $[\text{Ni}^{2+}]:[\text{Zn}^{2+}]$ concentration ratio: a – 1:5; b – 2:1; c – 5:1. Potential scan rate is 5 mV/s

peaks of ALSV curve obtained in the case of $L = 3:4$, is virtually unchanged when M is changed from 2:1 (Fig. 4, curve 2) to 5:1 (Fig. 4, curve 3). With the increase in the zinc ions content in electrolyte (curve 1), the distribution of the amount of electricity has the same form, but with a shift toward peaks corresponding to phases with a lower nickel content.

Under conditions of glycine prevalence above ammonia (Fig. 5), the height P_V peaks continues to increase, compared to Fig. 3. For $M = 1:5$ (Fig. 5a), the P_{III} peak height is significantly reduced. I.e., it confirms the nature of the influence of glycine on the alloy composition, which is reflected by mechanism of dissolution of the resulting films.

The curves of the distribution of the amount of electricity (Fig. 6), due to increase in the peak P_{IV} fraction, become less relief, and in the cases of nickel ions excess in the solution (curves 2 and 3) cease to be S-shaped.

According to the proposed scheme of coating dissolution, we will write the balance equations for the amount of electricity for the anode dependences with 5 peaks.

The balance equation for the first two peaks, corresponding to the dissolution of zinc from the η -phase, resulting in the dezincification of additional amount of gamma phase:

$$q_I + q_{II} = q(\text{Zn}_\eta) - q(\text{Zn}_{\eta\gamma}), \quad (1)$$

where q_1 and q_2 are the fractions of the amount of electricity Q under the peaks P_I and P_{II} , respectively; $q(\text{Zn}_\eta)$ is the fraction of the amount of electricity corresponding to the amount of electricity needed for zinc dissolution from the η -phase; $q(\text{Zn}_{\eta\gamma})$ is the fraction of the amount of electricity corresponding to the amount of electricity needed for zinc dissolution from γ -phase formed during dissolution.

At potentials of the peak P_{III} , zinc dissolves from the γ -phase of the initial coating, and from the γ -phase formed during zinc dissolution from the η -phase. In the peak P_{IV} , zinc dissolves from the γ -phase under conditions of further increase of nickel content in the surface.

Balance equation for the P_{III} and P_{IV} peaks:

$$q_{III} + q_{IV} = q(\text{Zn}_\gamma) + q(\text{Zn}_{\eta\gamma}) - q(\text{Zn}_{\gamma\alpha}), \quad (2)$$

where q_{III} and q_{IV} are the fractions of the amount of electricity Q under the P_{III} and P_{IV} peaks, respectively; $q(\text{Zn}_\gamma)$ is the fraction of the amount of electricity corresponding to the amount of electricity needed for zinc dissolution from the γ -phase of the original coating; $q(\text{Zn}_{\gamma\alpha})$ is the fraction of the amount of electricity corresponding to the amount of electricity needed for zinc dissolution from the α -phase formed during dissolution.

At the potentials of the P_V peak, deposit containing all the zinc spent on binding this nickel to the transient α -phase (or β -phase) is dissolved.

The balance equation for the P_V peak:

$$q_V = q(\text{Ni}) + q(\text{Zn}_{\gamma\alpha}), \quad (3)$$

where q_v is the fraction of the amount of electricity Q under the P_v peak; $q(\text{Ni})$ is the fraction of the amount of electricity needed for dissolve of all nickel.

$$q(\text{Ni}) = w(\text{Ni}_\alpha) - q_v, \quad (4)$$

where $w(\text{Ni}_\alpha)$ is the mass fraction of nickel in the α phase.

From (3) and (4):

$$q(\text{Zn}_{\gamma\alpha}) = (1 - w(\text{Ni}_\alpha)) = q_v. \quad (5)$$

Taking into account the ratio of the mole fractions in the γ -phase intermetallide:

$$q(\text{Zn}_\gamma) = 4.2 q(\text{Ni}_\gamma) \quad (6)$$

and

$$q(\text{Zn}_\eta) = 4.2 q(\text{Ni}_\eta) \quad (7)$$

from (2), (6) and (7):

$$q_{\text{III}} + q_{\text{IV}} = 4.2 q(\text{Ni}) - q(\text{Zn}_{\gamma\alpha}). \quad (8)$$

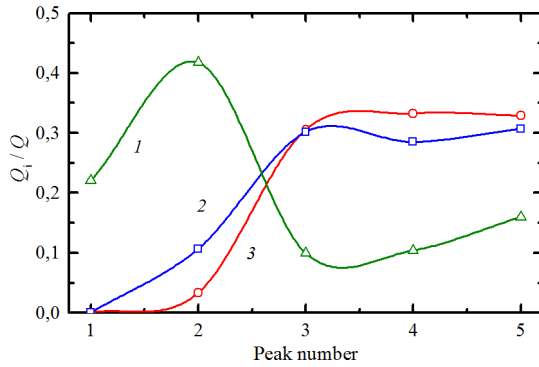


Fig. 6 – Distribution of the amount of electricity under peaks of ALSV curve of Fig. 5: 1 – from Fig. 5a; 2 – from Fig. 5b; 3 – from Fig. 5c

From (8), (4) and (5):

$$w(\text{Ni}_\alpha) = 0.192 (1 - (q_{\text{III}} - q_{\text{IV}})/q_v). \quad (9)$$

The dependence of the nickel content in the phase enriched with nickel on the ratio of the metal ion concentration in the electrolyte is presented in Fig. 7a.

From (4) we find the nickel fraction in coating $q(\text{Ni})$ and zinc fraction $q(\text{Zn})$. The dependences of nickel content in the coating on the ratio of metal ion concentrations in the electrolyte are shown in Fig. 7b.

Then, according to equation (5), the fraction in the nickel-enriched zinc phase is $q(\text{Zn}_{\gamma\alpha})$.

To determine the proportion of nickel contained in the γ -phase of the coating, we equate the expressions (10) and (11):

$$q(\text{Zn}_\eta) = q(\text{Zn}) - q(\text{Zn}_\gamma) = q(\text{Zn}) - 4.2 q(\text{Ni}_\gamma), \quad (10)$$

and

$$\begin{aligned} q(\text{Zn}_\eta) &= q(\text{Ni}_\eta) - (1 - w(\text{Ni}_\eta))/w(\text{Ni}_\eta) = \\ &= (q(\text{Ni}) - q(\text{Ni}_\gamma)) - (1 - w(\text{Ni}_\eta))/w(\text{Ni}_\eta), \end{aligned} \quad (11)$$

where $w(\text{Ni}_\eta)$ is the nickel fraction in the η -phase.

From the obtained equation we find $q(\text{Ni}_\gamma)$:

$$q(\text{Ni}_\gamma) = (q(\text{Zn}) - (1 - w(\text{Ni}_\eta))/w(\text{Ni}_\eta) - q(\text{Ni}))/$$

$$/(4.2 - (1 - w(\text{Ni}_\eta))/w(\text{Ni}_\eta)), \quad (12)$$

From (6) we define $q(\text{Zn}_\gamma)$.

The γ -phase fraction in the coating is determined by the equation:

$$q_\gamma = 5.2 \cdot q(\text{Ni}_\gamma), \quad (13)$$

Dependences of the γ -phase content in the coating on the ratio of metal ion concentrations in the electrolyte are shown in Fig. 7c.

The calculated nickel content in the phase, which dissolves at potentials of P_v peak (Fig. 7a), is close to the composition of the β -phase (NiZn). In solutions containing an excess of ammonia with respect to glycine, the $w(\text{Ni}_v)$ dependences of on M have same form. The values of $w(\text{Ni}_v)$ increase sharply with an increase in M from 1:5 to 2:1. At $L = 9:5$, this dependence has a different character: the values of $w(\text{Ni}_v)$ decrease with an increase in the nickel ions content in the solution.

The nickel content in the alloy (Fig. 7b) increases with the increase of its ions concentration in the solution. This growth slows down after M increase up to 2:1. The nickel content in alloy corresponds to the γ -phase at $M = 2:1$ and 5:1 and the coexistence of η and γ phases for $M = 1:5$.

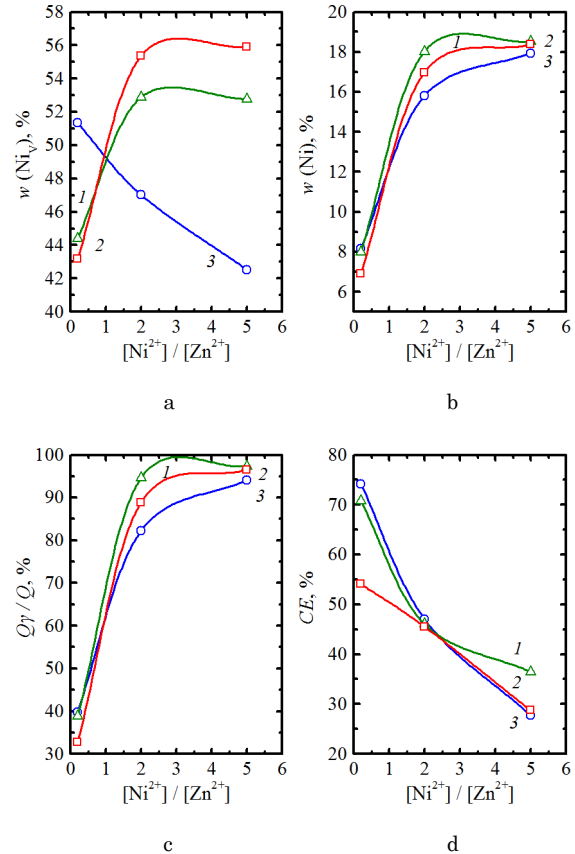


Fig. 7 – Dependences of nickel content $w(\text{Ni}_v)$ in the phase of P_v (a), nickel content $w(\text{Ni})$ film (b), γ -phases Q_γ/Q in films (c) and cathodic current efficiency CE (d) on $[\text{Ni}^{2+}]:[\text{Zn}^{2+}]$ concentration ratio in electrolytes. The $[\text{Gly}]:[\text{NH}_3(\text{NH}_4^+)]$ concentration ratio: 1 – 2:5; 2 – 3:4; 3 – 9:5

The calculated fraction of the γ -phase in the coating (Fig. 7c) increases by 2-3 times with M change from 1:5

to 2:1, with further increase in M varies insignificantly, approaching 100%.

With an increase in the of nickel ions content in solution, the current efficiency decreases (Fig. 7d) in all electrolytes. Moreover, the decrease in the current efficiency is enhanced in a solution with an increased nickel content ($M=5:1$) already at an almost equal content of glycine and ammonia in the solution ($L=3:4$), and with an increase of zinc ions content at $L=9:5$.

4. CONCLUSIONS

A mechanism of Zn-Ni alloy films dissolution in alkaline ammonia-glycinate solution under ALSV conditions is proposed. Anode voltammograms have generally 5 peaks: 3 main peaks (P_I , P_{II} and P_V) and 2 additional peaks (P_{II} and P_{IV}). At the main peaks zinc dissolves from the η -phase (peak P_I) and γ -phase (peak P_{II}) of the initial coating, and the nickel-enriched phase (P_V peak), which was formed on the surface of the electrode in the process of alloy dezincification. At additional peaks, zinc dissolves from the η -phase (peak P_{II}) and γ -phase (peak

P_{IV}) under the conditions of the changed surface layer.

According to this scheme of film dissolution, the calculation of nickel content in the alloy and the residue remaining on the electrode after dezincification of the films, as well as the γ -phase content in the alloy using deconvoluted of ALSV data, is given. It is shown that with an increase in the nickel ion content in solution, the alloy current efficiency decreases, the nickel content in the alloy and deposit after dezincification increases. The content of the γ -phase in the alloy, which is preferred for the protection of zinc-nickel alloy steel parts against corrosion, also increases. An increase in the ligands ratio in solution (glycine content increase) leads to a decrease in the cathodic current efficiency and a decrease in the content of the γ -phase coating.

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Вольтамперометрический анализ фазового состава тонких пленок Zn-Ni, электроосажденных из слабощелочного полилигандного электролита

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Фазовый состав пленок сплава Zn-Ni, электроосажденных из слабощелочного полилигандного электролита, проанализирован методом анодной вольтамперометрии. Предложен механизм анодного растворения пленок в щелочном аммиачно-глицинатном растворе, не содержащем ионов металлов. Основные пики соответствуют последовательному растворению цинка из η -фазы и из γ -фазы, исходно содержащихся в пленке, и фазы, обогащенной никелем, образовавшейся в процессе растворения пленки. Определено содержание никеля в обогащенной никелем фазе, а также содержание никеля и γ -фазы в исходной пленке в зависимости от отношения концентраций ионов металлов в электролите при различных соотношениях концентраций глицина и аммиака. Показано, что пленки в широком диапазоне этих соотношений, $[Ni^{2+}]:[Zn^{2+}] = (2-5):1$ и $[Gly]:[NH_3(NH_4^+)] = (2-9):5$, содержат преимущественно γ -фазу при содержании никеля в диапазоне 15.8-18.2 %.

Ключевые слова: Сплав, Цинк-никель, Фазовый состав, Анодная линейная вольтамперометрия.

Вольтамперометричний аналіз фазового складу тонких плівок Zn-Ni, електроосаджених зі слабколужного полілігандного електроліту

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Фазовий склад плівок сплаву Zn-Ni, електроосаджених зі слабо лужного полілігандного електроліту, проаналізовано методом анодної вольтамперометрії. Запропоновано механізм анодного розчинення плівок в лужному аміачно-гліцинатному розчині, що не містить іонів металів. Основні піки відповідають послідовному розчиненню цинку з η -фазы і γ -фазы, що початково містяться в плівці, і фазы, збагаченої нікелем, що утворилася в процесі розчинення плівки. Визначено вміст нікелю у збагаченій нікелем фазі, а також вміст нікелю і γ -фазы у вихідній плівці в залежності від відношення концентрацій іонів металів в електроліті при різних співвідношеннях концентрацій гліцину і аміаку. Показано, що плівки в широкому діапазоні цих співвідношень, $[Ni^{2+}]:[Zn^{2+}] = (2-5):1$ і $[Gly]:[NH_3(NH_4^+)] = (2-9):5$, містять переважно γ -фазу при вмісті нікелю в діапазоні 15.8-18.2 %.

Ключові слова: Сплав, Цинк-нікель, Фазовий склад, Анодна лінійна вольтамперометрія.

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