



Condensed Matter and Interphases (Kondensirovannye sredy i mezhfaznye granitsy)

Original articles

DOI: <https://doi.org/10.17308/kcmf.2020.22/2962>

Received 08 March 2020

Accepted 15 April 2020

Published online 30 September 2020

ISSN 1606-867X

eISSN 2687-0711

Cathodic Deposition of Zinc-Nickel Coatings from a Dilute Ammonium Chloride Electrolyte with a High Glycine Concentration

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Abstract

This study determined the kinetics of the synthesis, the chemical composition, and morphology of zinc-nickel coatings electrolytically obtained from low-concentration (0.04 M ZnCl₂, 0.08 M NiCl₂) ammoniacate and ammonia-glycinate chloride solutions. Transient electrochemical methods (cyclic voltammetry and linear sweep voltammetry) allowed us to determine that the cathodic deposition of Zn–Ni alloy coatings, regardless of the presence of glycine in the ammonium chloride electrolyte, is limited by the stage of diffusion mass-transfer of ions, whose electrochemical reduction (the charge transfer stage) is irreversible. The introduction of relatively high concentrations of glycine (0.3 M) in the electrolyte allows obtaining smoother coatings, which is demonstrated by the results of scanning electron microscopy. At the same time, energy dispersive X-ray spectroscopy demonstrated that the atomic fraction of nickel in the potentiostatically deposited coating increases on average by 9.7%. It is possible that the alteration of the chemical composition results in a significant decrease (on average by ~15 %) in the current efficiency in electrolytes with glycine, since it catalyses the side reaction of hydrogen evolution.

Keywords: electrodeposition, zinc-nickel coatings, ammine electrolyte, glycine, current efficiency, voltammetry.

For citation: Kozaderov O. A., Tinaeva K. E., Tinaeva A. E., Burliaev D. V. Cathodic deposition of zinc-nickel coatings from a dilute ammonium chloride electrolyte with a high glycine concentration. *Kondensirovannye sredy i mezhfaznye granitsy = Condensed Matter and Interphases*. 2020; 22(3): 320–326. DOI: <https://doi.org/10.17308/kcmf.2020.22/2962>

1. Introduction

Zinc coatings acting as anodes in a “zinc-iron” pair ensure the effective protection of steel from corrosion [1]. The protective effect remains even when the galvanized surface has scratches or even exposed areas. When exposed to a moist atmosphere, carbon dioxide, and chlorides, the protective effect is enhanced by the formation of a dense layer on the metal surface. This layer consists of ZnO, basic salts of complex composition (including simonkolleite, Zn₅(OH)₈Cl₂·H₂O, and hydrozincite, 2ZnCO₃·3Zn(OH)₂), and other products of atmospheric corrosion of zinc [2]. Electrolytic zinc-containing alloys have a certain advantage over monometallic coatings: they combine the properties of two and more

metals, obtained by cathodic deposition from the electrolyte solution. Consequently, such coatings are often characterized by higher corrosion resistance in aggressive environments. Of particular interest are zinc-nickel coatings, as they form a smaller number of corrosion products and comply with the high standards of anticorrosion protection of steel [3, 4]. Zinc-nickel coatings with the concentrations of nickel of 8–17 % demonstrate 3–10 times better corrosion resistance than zinc coatings. Furthermore, the degree of steel hydrogenation is lower [4]. The protective properties of Zn–Ni coatings do not deteriorate at higher temperatures or after interaction with aluminium alloys.

Electrolytic formation of Zn–Ni alloys is performed by means of anomalous codeposition

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[6], when the deposition rate of nickel, which is more electropositive, is lower, than the deposition rate of zinc. Therefore, the coatings obtained from an electrolyte solution with equimolar concentrations of nickel and zinc ions, are characterised by relatively smaller concentrations of nickel [7]. By further adjusting the concentrations of nickel and zinc salts in the electrolyte solution, it is possible to obtain an optimal concentration of metals in the alloy coating required for the effective protection of a steel substrate from corrosion.

Zn and Ni yield high current efficiency when deposited from sulphate, chloride, and sulphate-chloride electrolytes. The concentrations of the doping element, i.e. nickel, in such zinc-nickel coatings may vary greatly. Coatings with nickel concentrations of 10–15 %, which is optimal regarding both the anticorrosive properties and resistance to hydrogen embrittlement, are obtained from industrial ammoniacate electrolytes. These electrolytes have high scattering ability [8], but are characterised by the high concentrations of their components.

If we change the concentration of ions of the deposited metals and introduce organic additives to the electrolyte solution, we can optimise the codeposition of metals, by altering the conditions of the complexation process, and obtain coatings with better functional properties, such as increased corrosion resistance, low porosity, and luster. This paper considers the codeposition of zinc and nickel from an electrolyte with comparatively low concentrations of metal chlorides (0.04 M ZnCl_2 , 0.08 M NiCl_2). Besides ammonia, we also used a considerably large concentration (0.3 M) of aminoacetic acid (glycine) as an additional complexation additive. An advantage of glycine is the buffer effect occurring due to its protonation/deprotonation ability. Another advantage of glycine is that it can be adsorbed on both positively and negatively charged electrode surfaces, which happens because glycine ions are bipolar in aqueous solutions [9].

The aim of our study was to determine the kinetics of cathodic deposition, the chemical composition and morphology of zinc-nickel coatings, electrolytically deposited from low-concentration ammoniacate and ammonia-glycinatate chloride solutions.

2. Experimental

The zinc-nickel alloy was cathodically deposited on an Au or Cu substrate at room temperature from a slightly acidic ammonium chloride solution prepared on double distilled water. The solution had the following composition: zinc chloride – 0.04; nickel chloride – 0.08; ammonium chloride – 2, either without glycine (ammiacate deposition electrolyte, pH = 3.4), or with the concentration of glycine of 0.3 mol/l (ammonia-glycinatate deposition electrolyte, pH = 4.1).

The potential region of the cathodic deposition of the metals and their anodic dissolution in the deposition electrolytes was determined using cyclic voltammetry. Polarization curves were obtained in potentiodynamic mode at a potential scan rate $V = dE/dt = 10 \text{ mV/s}$ starting at the open-circuit potential $E(0) \approx 400 \text{ mV}$ and sweeping to the cathode region up to $E_c = -1200 \text{ mV}$. It was then swept back to $E_a = 200 \text{ mV}$ according to the standard hydrogen electrode (SHE) scale. The kinetics of the electrodeposition was determined using linear sweep voltammetry. The cathodic polarization curves were registered at various scan rates V within the potential range from $E(0)$ to E_c . For the potentiodynamic measurements the working electrode was a golden electrode, which was preliminary washed with double distilled water, polished using suede leather and an MgO aqueous suspension, degreased in ethanol, and dried in a flow of argon.

Zinc-nickel coatings of 4,5 μm thickness were obtained using potentiostatic cathodic polarization of a copper electrode at the deposition potential $E_{\text{dep}} = -1000, -900, -880, -860 \text{ mV}$ (according to the SHE scale). The working electrode, a copper plate with the geometric area of 1 cm^2 , was preliminary washed with double distilled water, degreased in ethanol, and dried in a flow of argon. The current efficiency was measured gravimetrically based on the difference between the mass of the copper plate before and after the electrodeposition and the corresponding transferred electric charge.

Potentiodynamic and potentiostatic measurements were performed using an IPC-PRO L computer-aided potentiostat. The reference electrode was a saturated silver chloride electrode, the auxiliary electrode was a platinum plate.

The measurements were performed at room temperature with natural aeration. The solution was not stirred.

The morphology of the surface of the obtained coatings was assessed and characterised using scanning electron microscopy (SEM) (JSM-6380LV microscope). The chemical composition of the coatings was determined by means of energy dispersive X-ray spectroscopy (EDX) (INCA 250 system). The results of the SEM and EDX studies were obtained using the equipment of the Centre for Collective Use of Scientific Equipment of Voronezh State University (<http://ckp.vsu.ru>).

3. Results and discussion

Fig.1 shows cyclic voltammograms obtained on the golden electrode in the ammoniacate and ammonia-glycinate solutions. We can see that when glycine is added, the cathodic peak potential (K) shifts in the positive direction by about 30–40 mV. The position of the peaks on the anodic branch of the cyclic voltammogram (A_1 , A_2 , A_3) is hardly influenced by the presence of glycine. According to [10], anodic peaks correspond to the dissolution of phases of various chemical composition. We can thus assume, that the presence of glycine in the electrolyte solution has practically no effect on the phase composition of the coating. According to [10], peak A_1 may

correspond to the oxidation of metallic Zn, peak A_2 to its dissolution from the zinc-nickel phase, and peak A_3 to the anodic oxidation of the nickel phase formed as a result of the selective dissolution of zinc at more negative potentials. It should be noted that the peaks registered for the solution with glycine are much lower than those registered for the solution without glycine. Taking into account the fact that the surface area below the anodic peaks is proportional to the number of the deposited metals, we can assume that the observed effect is caused by a decrease in the rate of electrodeposition. This may happen because the discharge from the metal glycinate complexes at the cathode is hindered, for instance, by electrostatic repulsion from the negatively charged surface [6].

At higher scan rates the peak current of the cathodic deposition (i_{\max}) increases, and the peak potential (E_{\max}) shifts towards the negative region regardless of the presence of glycine in the electrolyte (Fig. 2). The currents of the side cathodic process, hydrogen evolution reaction, also increase.

The dependency of i_{\max} on the potential scan rate is presented as a linear plot of i_{\max} vs. $V^{1/2}$, according to the Randles-Sevcik equation (Fig. 3). According to the theory of voltammetry of electrochemical processes [11], this indicates that the process of non-stationary diffusion

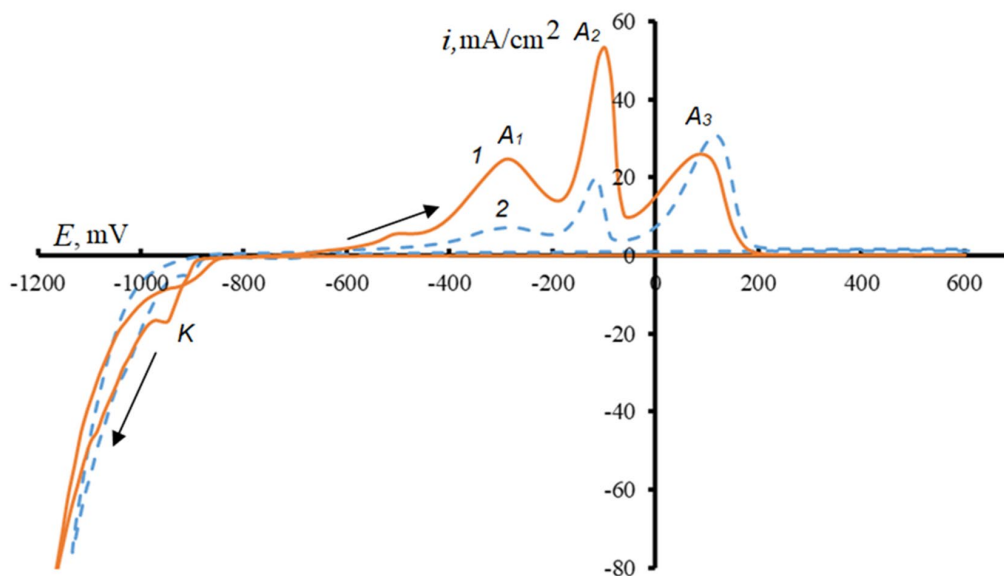


Fig. 1. Cyclic voltammograms, obtained on gold in a 0.04 M $ZnCl_2$ + 0.08 M $NiCl_2$ + 2 M NH_4Cl + x M NH_2CH_2COOH solution with $x = 0$ (1) and 0.3 (2)

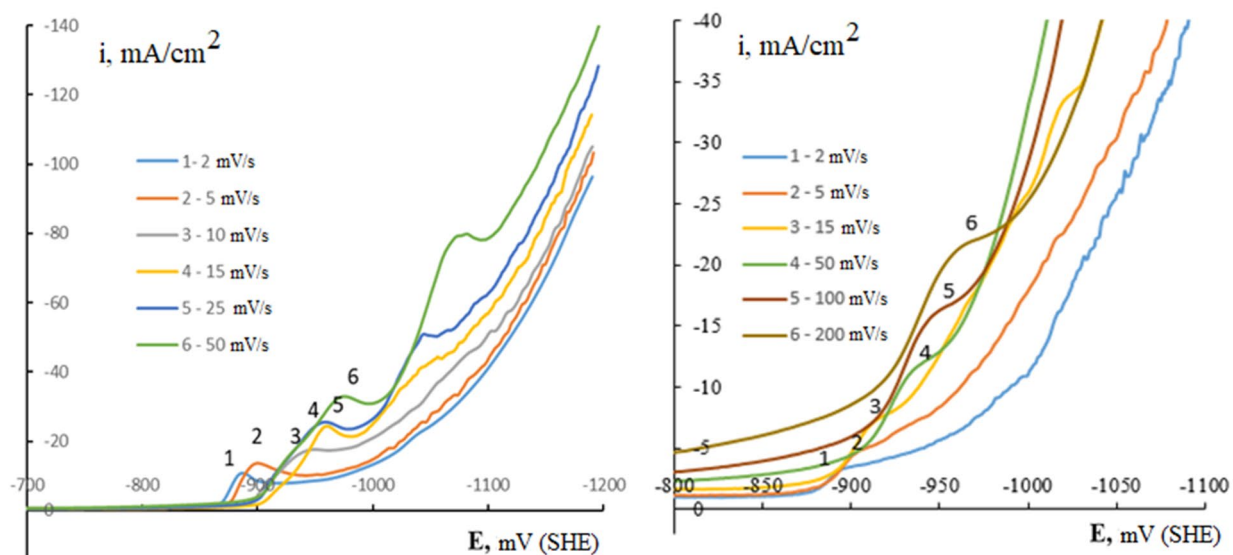


Fig. 2. Cathodic polarization curves of the Zn-Ni alloy deposition from a 0.04 M ZnCl_2 + 0.08 M NiCl_2 + 2 M NH_4Cl + x M $\text{NH}_2\text{CH}_2\text{COOH}$ solution with $x = 0$ (a) and 0.3 (b), obtained at different potential scan rates

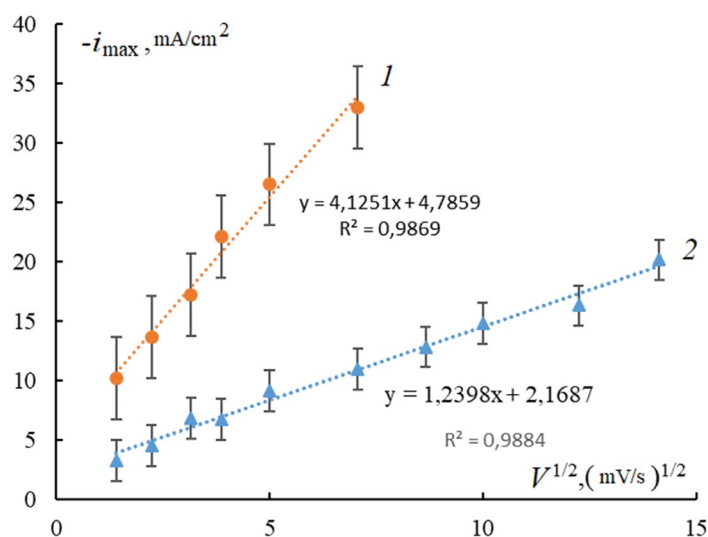


Fig. 3. The dependency of the density of the peak current of the Zn-Ni alloy cathodic deposition from a 0.04 M ZnCl_2 + 0.08 M NiCl_2 + 2 M NH_4Cl + x M $\text{NH}_2\text{CH}_2\text{COOH}$ solution with $x = 0$ (1) and 0.3 (2) on the potential scan rate, according to Randles–Sevcik equation

mass-transfer is inhibited. It should be noted that the curves are not extrapolated to the origin of the coordinates, which indicates the presence of side processes (namely, hydrogen evolution). The Y-interception corresponding to the rate of such processes is much lower, when glycine is added to the electrolyte solution.

In turn, the dependency of the peak potential on the cathodic voltammogram on the potential scan rate is linearized in the logarithmic coordinates

(Fig. 4). According to [11], this indicates that the charge transfer stage is irreversible.

The analysis of the morphology of the coatings deposited at a constant cathodic potential (Fig. 5) demonstrated that the zinc-nickel coatings deposited from the ammonium chloride solution without glycine are fine-grained. The size of the grains increases when the cathodic potential shifts towards the negative region. At the same time, adding aminoacetic acid to the electrolyte

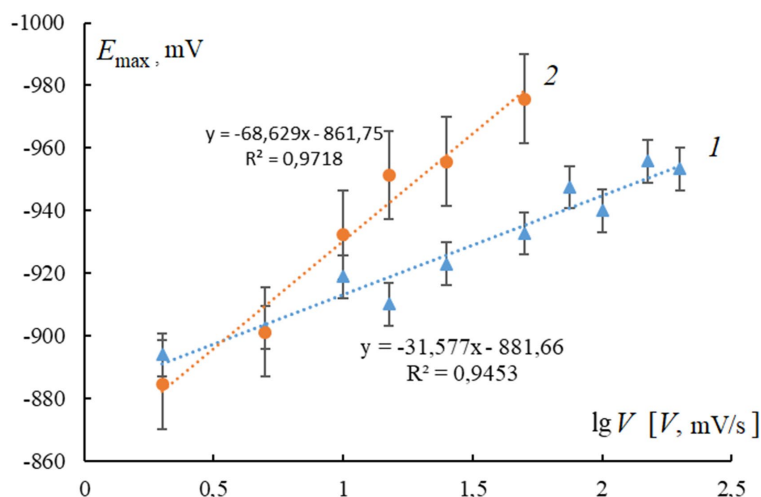


Fig. 4. The dependency of the peak potential of the Zn–Ni alloy cathodic deposition from a 0.04 M ZnCl_2 + 0.08 M NiCl_2 + 2 M NH_4Cl + x M $\text{NH}_2\text{CH}_2\text{COOH}$ solution with $x = 0$ (1) and 0.3 (2) on the potential scan rate

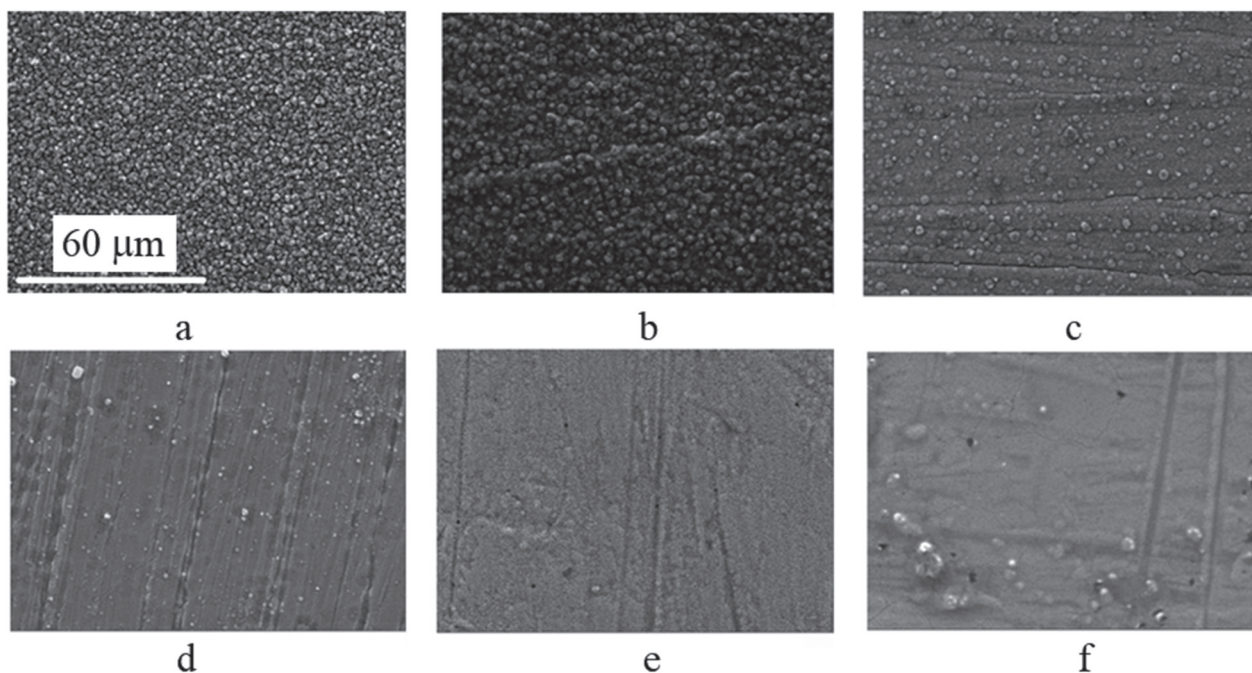


Fig. 5. SEM photographs of the surface of the zinc-nickel coatings deposited from the ammine (a, b, c) and ammonia-glycinate (d, e, f) electrolytes at different potentials: $E_{\text{dep}} = -860$ mV (a, d); -880 mV (b, e); -900 mV (c, f)

allowed us to obtain much smoother coatings regardless of the value of E_{dep} .

It is important to note that, according to the results of energy dispersive X-ray spectroscopy, the presence of glycine leads to the increase in the concentration of nickel in the coating on average by 9.7 at% (Table 1). At the same time, the coatings obtained from the ammoniacate electrolyte consist primarily of zinc, although its concentration in the electrolyte is low (0.04 M ZnCl_2).

The maximum current efficiency was obtained at the same electrode potential ($E_{\text{dep}} = -880$ mV) in ammonium chloride electrolytes both with and without glycine. The current efficiency of the zinc-nickel coatings deposited from the ammonia-glycinate deposition electrolyte is much lower (on average by ~15 %), than that of the coatings deposited from the ammonium chloride electrolyte without glycine. It is possible that the increase in the atomic fraction of nickel in the coating catalyses the side cathodic process,

Table 1. The current efficiency of the zinc-nickel coatings deposited from the ammoniacate (numerator) and ammonia-glycinate (denominator) electrolytes

E_{dep} , mV	Atomic fraction of Ni, %	Current efficiency, %
-1000	35.2 / -	57.4 / -
-900	10.1 / 17.3	73.3 / 70.9
-880	10.1 / 17.0	94.2 / 74.6
-860	6.3 / 21.3	88.6 / 66.0

hydrogen evolution, which results in a decrease in the current efficiency.

4. Conclusions

The kinetics of the electrodeposition of zinc-nickel coatings from dilute aqueous (0.04 M ZnCl_2 , 0.08 M NiCl_2) slightly acidic (pH 3–4) ammonium chloride solutions is not influenced by the presence of glycine: the limiting stage is the diffusion mass-transfer, and the charge transfer stage is irreversible. The addition of a relatively high amount of glycine (0.3 M) to the electrolyte resulted in a significant decrease in the rate of electrodeposition of the zinc-nickel alloy, an increase in the concentration of nickel in the coating on average by 9.7 at%, and better visual characteristics. The current efficiency in the solution with glycine is much lower. Presumably, this is the result of an increase in the rate of side processes, such as hydrogen evolution reaction, caused by a comparatively larger concentration of nickel as compared to zinc-nickel coatings deposited from the ammonium chloride electrolyte without glycine.

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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All authors have read and approved the final manuscript.

Translated by Yulia Dymant

Edited and proofread by Simon Cox