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APPLIED ELECTROCHEMISTRY AND CORROSION PROTECTION OF METALS

Electrodeposition of Nickel from Sulfate Solutions in the Presence of Aminoacetic Acid

O. A. Taranina, N. V. Evreinova, I. A. Shoshina, V. N. Naraev, and K. I. Tikhonov

St. Petersburg State Technological Institute, St. Petersburg, Russia

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Abstract—Kinetics of nickel electrodeposition from sulfate electrolytes in the presence of aminoacetic acid at pH of 2.0 and 5.5 in the temperature range 20–50°C is considered.

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It is known [1] that various To obtain high-quality coatings composed of iron-group metals, it is recommended to introduce aminoacetic acid into the electrolyte [1, 2], mostly as a buffer additive [3]. It is known, however, that glycine forms complexes of various compositions with many metals [4]. Published data on the influence of glycine on the kinetics of electrode reactions in electrolyses of nickel salt solutions are scarce.

The goal of this study was to examine the kinetics of electrode processes and coating deposition conditions in an electrolysis of a nickel sulfate electrolyte containing aminoacetic acid.

EXPERIMENTAL

The study was performed under the following conditions: solution composition (M): $NiSO_4$ 0.36, NaCl 0.20, aminoacetic acid concentrations in the range 0.13–0.30; pH 2.0 and 5.5; temperature range 20–50°C. The solutions were prepared from $NiSO_4 \cdot 7H_2O$ and NaCl of chemically pure grade and NH_2CH_2COOH of analytically pure grade. The necessary pH value was set using concentrated sulfuric acid or sodium hydroxide (both of analytically pure grade). The concentration of nickel ions in solution was determined by complexonometric titration [5], and the current efficiency (CE) by nickel, by the gravimetric method. Deposits were obtained in the galvanostatic mode, using a B5-47 stabilized power source. Polarization curves were measured potentiostatically in a thermostated three-electrode glass cell. A 1-cm^2 plate of electrolytic nickel served as the working electrode; nickel of N0 brand, as auxiliary electrodes; and saturated silver chloride, as reference. The potentials were recalculated to the standard hydrogen electrode scale. The buffer capacity was determined by potentiometric titration, following the procedure described in [6]. Electronic absorption spectra of solutions were recorded with an SF-56 spectrophotometer in the range 190–1100 nm in quartz cuvettes with a layer thickness $l = 1$ cm.

The current efficiencies by nickel at various glycine concentrations at 40°C are listed in Table 1 in relation to the current density and solution pH. It can be seen that the manner in which the CE varies with the aminoacetic acid concentration depends on the pH value. For example, at pH 5.5, introduction of 0.13 M of glycine somewhat raises the CE, whereas further increase in the glycine concentration hardly has any effect because the CE fluctuates within 1–2%. However, the presence of glycine results in that the outward appearance of the coatings is improved, with the coatings becoming light gray and lustrous, and the range of current densities at which high-quality coatings are obtained is extended (to 10 A dm^{-2}).

Another behavior is observed at pH 2.0: the CE sharply decreases as the glycine concentration is raised. Probably, presence of aminoacetic acid in the electrolyte makes lower the hydrogen evolution overvoltage. It should be noted, however, that, under the conditions studied, the increase in the CE with the current density is preserved. Similar dependences were observed at temperatures of 20 and 50°C. Metal deposits obtained from a solution with pH 2.0 are light gray, matte, and show no cracking.

Table 1. Current efficiency by nickel at various glycine concentrations and pH values of the electrolyte

Glycine concentration, M	pH	CE, %, at indicated current density, A dm^{-2}						
		0,5	1	1,5	2	3	6	10
0	2.0	–	93.6	–	–	81.5	–	–
	5.5	81.2	92.9	93.8	99.1	–	–	
0.13	2.0	–	33.6	–	42.5	48.3	67.3	76.4
	5.5	94.7	96.8	98.8	98.6	–	–	–
0.18	2.0	–	25.3	–	36.4	44.6	61.1	71.5
	5.5	96.8	97.3	97.3	96.5	–	–	
0.30	2.0	–	16.4	–	29.8	35.7	46.0	53.8
	5.5	95.8	97.5	99.1	99.5	–	–	

The whole set of cathodic polarization curves and values of the CE by nickel were used to calculate partial curves of discharge of nickel ions. These results are presented in Figs. 1a and 1b, whence follows that an increase in the glycine concentration makes lower the discharge rate of nickel ions. Plotted in the semilog coordinates, the partial polarization curves (Fig. 2) have, in a certain range of current densities, almost the same slope ratio of 0.18 V for all of the electrolytes studied. This fact indicates that the discharge rate of nickel ions is limited by the same stage, presumably by the transfer of a first electron. As the glycine concentration in the solution increases, the potential is shifted in the negative direction by the same value, irrespective of the solution acidity (Table 2).

Table 2. Potential shift ΔE at various glycine concentrations and current densities

Glycine concentration, M	ΔE, mV, at indicated value of log I (I, A dm^{-2})			
	pH 2,0		pH 5,5	
	0,1	–0,1	0,1	–0,1
0	0	0	0	0
0,13	80	80	75	80
0,18	90	95	105	85
0,3	130	140	125	110

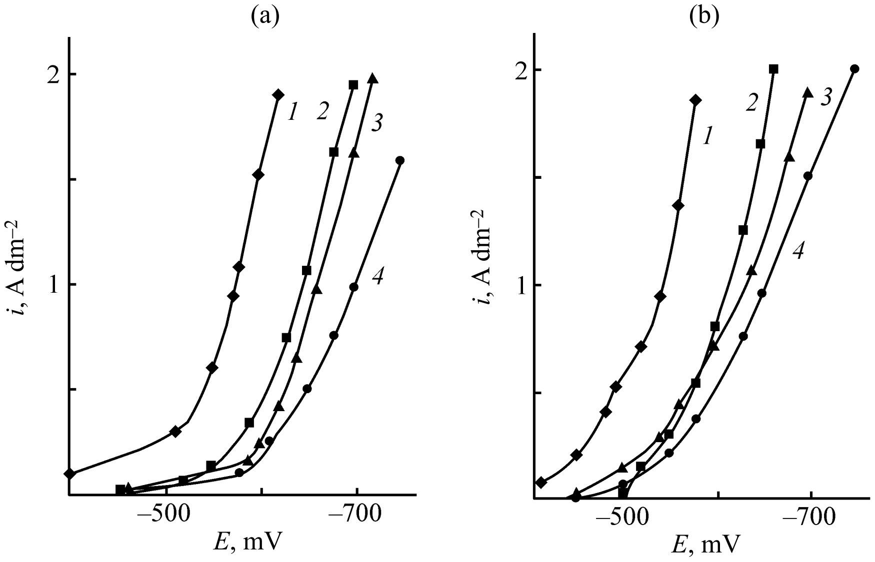

Fig. 1. Partial polarization curves of discharge of nickel ions at pH (a) 2.0 and (b) 5.5. (i) Current density and (E) potential; the same for Figs. 2 and 4. Aminoacetic acid concentration (M): (*1*) 0, (*2*) 0.13, (*3*) 0.18, and (*4*) 0.3; the same for Fig. 4.

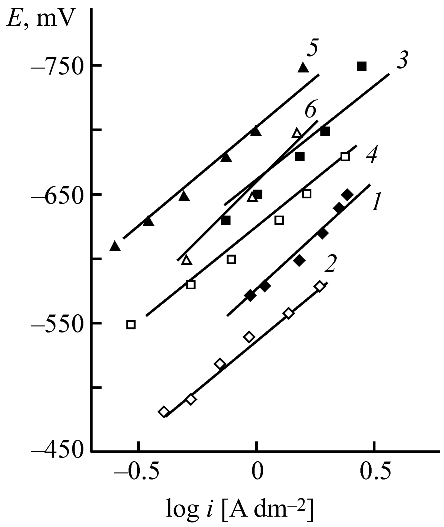

Fig. 2. Partial polarization curves of nickel deposition, plotted in the Tafel coordinates, at pH (*1, 3, 5*) 2.0 and (*2, 4, 6*) 5.5. Aminoacetic acid concentration (M): (*1, 2*) 0, (*3, 4*) 0.13, and (*5, 6*) 0.3.

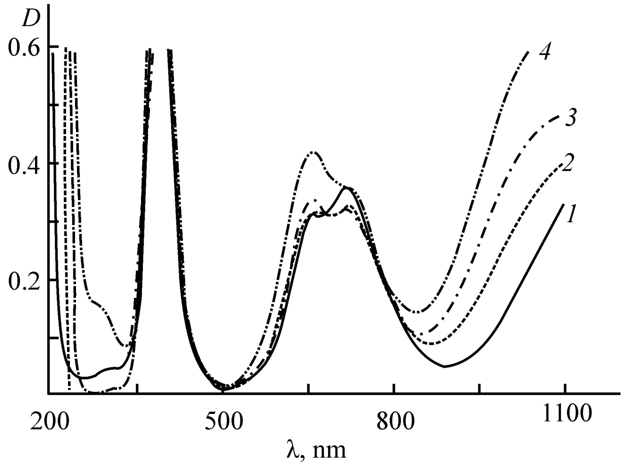

Fig. 3. Electronic absorption spectra of $NiSO_4$ solutions at pH (*1, 2*) 2.0 and (*3, 4*) 5.5. (*D*) Optical density and (λ) wavelength. Aminoacetic acid concentration (M): (*1*) 0, (*2, 4*) 0.3, and (*3*) 0.13.

It can be suggested that the discharge of nickel ions is hindered by nickel complexes of various compositions, appearing in the solution. With the fact that, depending on the glycine concentration, $NiGly^+$ and $NiGly_2$ species ($\log \beta_1 = 5.65$, $\log \beta_2 = 10.51$ [7]) can be formed taken into account, the shift of the potential from the equilibrium value will be proportional to $2.3RT\log \beta_i /nF$ [8] and equal to –0.164 and –0.405 V, respectively. Therefore, it seems reasonable to suggest that complexes of the type $NiGly^+$ can appear. However, electronic spectroscopy data confirm the formation of complex species in the solution bulk only for weakly acidic electrolytes (Fig. 3). At pH 2, glycine is present in solution as a cation $H_3N^+CH_2COOH$, which can only be coordinated to nickel ions via oxygen. However, with the low affinity of nickel for oxygen-containing ligands taken into account, formation of $NiGly^+$ or $NiCly_2$ is unlikely, which is indicated by the complete coincidence of the electronic absorption spectra (Fig. 3, curves *1* and *2*). As the solution acidity decreases (pH 5.5) and the amount of unprotonated glycine increases, the intensity of the bands at 300 and 650 nm grows (Fig. 3, curves *3* and *4*), which confirms the formation of a complex compound [9]. Thus, the too large values of $\Delta E/\Delta \log i$ for the polarization curves, irrespective of the solution acidity and glycine concentration, and the rise in the overvoltage are possibly due to a simultaneous adsorption of glycine on the electrode surface.

The apparent activation energies of discharge of nickel ions were calculated from the temperature dependence

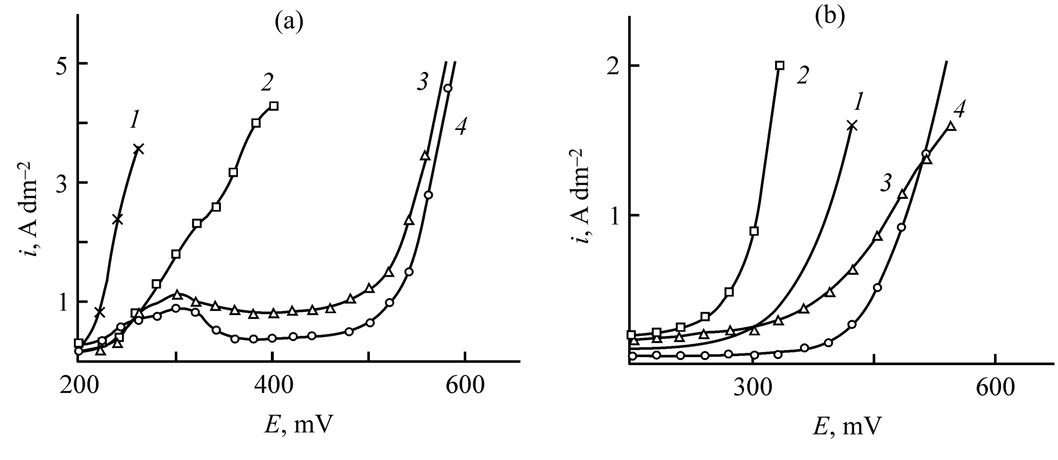

Fig. 4. Anodic polarization curves of nickel at pH (a) 2.0 and (b) 5.5.

of the cathodic process in the solutions under study. It was found that, at pH 2.0 and aminoacetic acid concentrations of 0.13 and 0.3 M, these energies are, respectively, 45.5 and 53.2 kJ mol^{-1}, and for solutions with pH 5.5 at the same concentrations of glycine, 31.4 and 34.0 kJ mol^{-1}. These values also confirm the slow course of the electrochemical event complicated by the adsorption of glycine.

The presence of aminoacetic acid in the electrolyte also affects the rate of the anodic process, with the nature of this influence determined by the solution acidity. In electrolytes with pH 2.0 (Fig. 4a), the dissolution rate decreases with increasing glycine concentration and a passivity plateau is observed at concentrations exceeding 0.18 M. According to [10], the ionization of nickel at pH 2 occurs via formation of a catalytic complex with sulfate ions. Probably being adsorbed on the electrode surface, aminoacetic acid displaces SO_4^{2-} ions and thereby has an inhibiting effect. In solutions with pH > 2, no passivity is observed (Fig. 4b); the process of nickel ionization is also retarded as the glycine concentration in the electrolyte increases.

The buffer capacity of the electrolyte in the presence of glycine exceeds that with boric acid. In addition, the electrolytes studied can be used to obtain lustrous coatings at current densities of up to 10 A dm^{-2} without introduction of brightening additives.

CONCLUSIONS

(1) It was found that presence of glycine in a nickel sulfate electrolyte makes lower the discharge rate of nickel ions under any of the conditions studied.

(2) Electronic spectroscopy data confirmed the formation of nickel complexes with glycine in the solution bulk only at pH 5.5 in the concentration range studied.

(3) An analysis of partial polarization curves demonstrated that the discharge rate of nickel ions in a glycine-containing sulfate electrolyte is limited by the electrochemical stage of transfer of a first electron, complicated by the adsorption of glycine.

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