APPLIED ELECTROCHEMISTRY AND CORROSION PROTECTION OF METALS

Electrodeposition of Lustrous Nickel Coatings from a Sulfate Electrolyte in the Presence of Organic Substances

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Abstract—Electrodeposition of nickel from a sulfate electrolyte containing 2,5-dimethyl-3-hexine-2,5-diol, formaldehyde, and benzaldehyde was studied.

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Nickel coatings find use as protective-decorative coatings and serve for improving the mechanical wear resistance and for special purposes. These coatings have a high corrosion resistance in the atmosphere, in alkali solutions, and some organic acids, which is largely due to the strongly pronounced ability of nickel to be passivated [1, 2]. Of particular industrial interest are lustrous nickel coatings deposited from electrolytes in the presence of various organic substances.

The main advantages of lustrous coatings over matt layers are the following: saving of nonferrous metals; elimination of the labor-consuming, expensive, and harmful polishing procedure and the associated excess expenditure for materials and working power; and the possibility of performing a continuous process in deposition of nickel layers onto various metals. Therefore, a study of the electrochemical nickel plating with organic substances is topical for development of modern technologies.

Lustrous coatings are commonly obtained using a rather large number of various organic substances: sulfo compounds of the aromatic series, unsaturated alcohols and glycols with a double or triple bond (2-butine-1,4-diol, propargyl alcohol, and their derivatives), lactones (coumarin and its derivatives), nitrogen-containing compounds (quinoline etc.), amine-substituted thiocarbamide, alkyl-substituted nitriles, aldehydes, ketones, dyes, and condensation products [1-3]. However, only some of these organic substances are successfully used in practice. The reason is that many of the suggested additives rapidly decompose in the course of electrolysis and formation of decomposition products markedly deteriorates the quality of lustrous deposits [1, 2].

To obtain lustrous nickel coatings, GOST (State Standard) 9.305–84 "Metallic and nonmetallic inorganic coatings" recommends to introduce into sulfate electrolytes 2-butine-1,4-diol together with other organic additives. The working current densities in these electrolytes do not exceed 8 A dm⁻². In various companies engaged in development of sulfate nickel-plating electrolytes for deposition of lustrous coatings, the composition of luster-forming additive is classified commercial information. However, the working current densities in these electrolytes do not exceed 6 A dm⁻². Therefore, the main problem in nickel plating is in development of high-performance electrolytes that would enable deposition of lustrous coatings at high current densities.

In this communication, we report results of a study of how a homolog of 2-butine-1,4-diol (diatomic unsaturated alcohol 2,5-dimethyl-3-hexine-2,5-diol (DHD), formaldehyde (in the form of formalin, a 37% aqueous solution), and benzaldehyde affects the process of nickel electrodeposition from a sulfate electrolyte. We could not find any evidence about use of DHD as a luster-forming additive in nickel-plating electrolytes. Formaldehyde and benzaldehyde are used together with other organic additives in nickel- and tin-plating electrolytes to obtain lustrous coatings [1–4].

EXPERIMENTAL

The study was carried out in electrolytes of composition (g l⁻¹): NiSO₄·7H₂O 150–300, NaCl 10⁻¹⁵, H₃BO₃ 30–40, Na₂SO₄·10 H₂O 50–80, at pH 2–5 and temperatures of 20–50°C. The electrodeposition was performed in electrolytes without agitation and with mechanical agitation. Nickel was deposited onto steel samples to a thickness of 6–15 μ m, with nickel anodes used. Polarization curves were measured with a P-5828 potentiostat. The luster of the coatings was measured by the photoelectric method with a FB-2 device. The leveling power of the electrolytes, *P*, was determined by the direct method of profilographic measurements of the sample surface on a sinusoidal microprofiler. *P* was calculated by the formula [5]:

$$P = 2.3a/2\pi h_{\rm av} \log (H_0/H_{\rm fin}),$$

where *a* is the amplitude of the sinusoidal microprofile; h_{av} , average coating thickness (10 µm); and H_0 and H_{fin} , initial and final amplitudes of the sinusoidal microprofile, respectively.

The pH of the near-electrode layer was measured by the procedure described in [6].

The results obtained in a study of how the DHD concentration and current density affect the outward appearance of the coatings are presented in Table 1. It can be seen that matt and silvery coatings are obtained at additive concentrations of 0.5–1 and 4.5–5.0 g l⁻¹. At the same time, at DHD concentrations of 1.5–4.0 g l⁻¹ matt, silvery, and lustrous coatings are produced at $i_c = 2-5$ A dm⁻².

It was found that the quality of nickel coatings deposited from electrolytes with DHD additive depends on electrolyte agitation, temperature, and pH value. For example, silvery coatings are obtained without electrolyte agitation at working current densities in the whole range under study, and semilustrous coatings are deposited at $T = 20-30^{\circ}$ C. The highest quality coatings

DHD concentration, g l-1	Current density, A dm ⁻²	Coating	Luster, %
0.5-1.0	1	Matte	10
	2–4	Silvery	20-25
	5	Matte with burn-on	-
1.5-2.0	1	Matte	10
	2–4	Lustrous	40-45
	5	Silvery	20–25
	6	Silvery with burn-on	_
2.5-3.0	1	Silvery	20
	2–5	Lustrous	40–45
	6	Silvery with burn-on	
3.5-4.0	1	Silvery	20
4.5-5.0	2–4	Lustrous	40-45
	5	Silvery	20
	6	Matte with burn-on	_
	1	Matte	10
	2–4	Silvery	20–25
	5	Matte with burn-on	_

Table 1. Effect of the DHD concentration and current density on the outward appearance of coatings. Electrolyte composition, $g l^{-1}$: NiSO₄·7H₂O 200, NaCl 20, H₃BO₃ 30, and Na₂SO₄·10H₂O 50; pH 4.5, $T = 40^{\circ}$ C, mechanical agitation



Fig. 1. Current efficiency by nickel, CE, vs. the cathode current density i_c . Electrolyte composition (g l⁻¹): NiSO₄·7H₂O 200, H₃BO₃ 30, NaCl 15, Na₂SO₄·10H₂O 50; pH 4.5, $T = 50^{\circ}$ C, mechanical agitation; the same for Fig. 2. (1) Electrolyte and (2–4) electrolyte + DHD (g l⁻¹): (2) 2, (3), and (4) 5.

are obtained at pH 4-5.

In electrolytes without organic additives and in those with DHD, the current efficiency by nickel increases with the cathode current density in the conditions under study (Fig. 1). Presence of the DHD additive in a nickel-plating electrolyte makes lower the current efficiency by nickel. The strongest decrease in the current efficiency is observed at a concentration of 5 g l^{-1} (Fig. 1, curves l-4).

Lustrous nickel coatings deposited from an electrolyte with DHD have an insignificant luster (40–50%). To raise the luster of the coatings, we studied the effect of an additional introduction of formaldehyde and benzaldehyde into the electrolyte. Data on how the formaldehyde concentration affects the outward

appearance of the coatings are listed in Table 2.

It can be seen that lustrous coatings are obtained at formaldehyde concentrations of 0.5 to 10 ml l^{-1} and current densities in the range 1-8 A dm⁻². At the same time, the widest range in which lustrous coatings are obtained is observed at formaldehyde concentrations of 8–10 ml l^{-1} . It should also be noted that the luster of the coatings substantially increases in this case. The current efficiency by nickel in the presence of DHD and formaldehyde is 65–78%.

Additional introduction of benzaldehyde into an electrolyte containing DHD and formaldehyde makes substantially wide the range of current densities in which lustrous coatings are obtained. Data on the influence exerted by the benzaldehyde concentration in the electrolyte and by the current density on the outward appearance of nickel coatings are listed in Table 3. At a benzaldehyde concentration of 0.5-1 g l⁻¹ in the electrolyte, we observed two ranges of current densities at which lustrous coatings are deposited. The first and second ranges are at 2-5 and 10-16 A dm⁻². At a higher benzaldehyde concentration $(1.5-2 \text{ g } \text{ l}^{-1})$, lustrous coatings are obtained in the range 2-7 A dm⁻². The current efficiency by nickel in these nickel-plating electrolytes varies within the range 65–95% at $i_{\rm c}$ = 2-16 A dm⁻².

In the electrolyte under study with organic additives, we examined the influence exerted by the nickel sulfate concentration, agitation, temperature, and pH value on the outward appearance of the coatings and on the current efficiency by nickel. It was found that variation of

Formaldehyde concentration, g l ⁻¹	Current density, A dm ⁻²	Coating	Luster, %
0.5-4.0	1 2–4 5	Silvery Lustrous Silvery	20 60–65 25
5–7	6 1–6 7–8	Matte with burn-on Lustrous Silvery	60-65 20-25
8–10	9 1-8 9	Matte with burn-on Lustrous Silvery with burn-on	6570

Table 2. Effect of the formaldehyde concentration and current density on the outward appearance of coatings. Electrolyte composition, g l^{-1} : NiSO₄·7H₂O 200, NaCl 20, H₃BO₃ 30, and Na₂SO₄·10H₂O 50; pH 4.5, $T = 40^{\circ}$ C, mechanical agitation

Table 3. Effect of the benzaldehyde concentration and current density on the outward appearance of coatings. Electrolyte composition, g l^{-1} : NiSO₄·7H₂O 200, NaCl 15, H₃BO₃ 30, and Na₂SO₄·10H₂O 50; DHD 8; formaldehyde 10 ml l^{-1} ; pH 4.5, $T = 40^{\circ}$ C, mechanical agitation

Benzaldehyde concentration, g l ⁻¹	Current density, A dm-2	Coating	Luster, %
0.5-1	1	Silvery	20
	2–5	Lustrous	65-70
	6–9	Silvery	20–25
	10–16	Lustrous with burn-on	70–80
	17		-
1.5-2	1	Silvery	20
	2–7	Lustrous	65–75
	8–10	Lustrous with burn-on	_

the nickel sulfate concentration from 150 to 250 g l⁻¹ does not change the working range of current densities. However, the quality of the coatings is sharply deteriorated at a nickel sulfate concentration of 300 g l⁻¹ (matt coatings are produced. The current efficiency by nickel grows with increasing nickel salt concentration. High-quality coatings with high luster are obtained when the electrolyte is agitated at a temperature of 40–50°C. Lack of agitation and a temperature lowered to 20–30°C impair the quality of the coatings.

We measured cathodic polarization curves in nickel-plating electrolytes (Fig. 2). It was shown that introduction of organic substances into the electrolyte leads to enhancement of the cathodic polarization, with the strongest polarization observed in the electrolyte



Fig. 2. Current density i_c vs. the electrode potential $-E_c$ in the nickel-plating electrolyte. (1) Electrolyte; (2) 1 + DHD, 3 g l⁻¹; (3) 2 + formaldehyde, 8 ml l⁻¹; and (4) 3 + benzaldehyde, 1 g l⁻¹.

in which DHD, formaldehyde, and benzaldehyde are simultaneously present (Fig. 2, curves 1-4).

Electrolytes used to obtain lustrous nickel coatings have a leveling power. It can be seen in Fig. 3 that the maximum degree of leveling (P = 0.6) is observed at $i_c =$ 4 A dm⁻². At higher current densities ($i_c = 5-8$ A dm⁻²), it sharply falls to P = 0.15. Further increase in i_c leads to a rise in the degree of leveling.

The leveling effect is related to the luster of electrolytic coatings because luster formation is also a process in which the surface is leveled and coarse microscopic irregularities with heights of 0.2 to 100 μ m and more are eliminated. In luster formation, very small submicrometer irregularities (~1.5 μ m and less) are smoothed [7].

Thus, it was shown that introduction into a sulfate nickel-plating electrolyte of a homolog of 2-butine-



Fig. 3. Leveling power *P* of the nickel-plating electrolyte vs. the current density i_c . Electrolyte composition (g l⁻¹): NiSO₄·7H₂O 200, H₃BO₃ 30, NaCl 15, Na₂SO₄·10H₂O 50, DHD 3; formaldehyde 8 ml l⁻¹ and benzaldehyde 1 g l⁻¹; the same for Fig. 4.

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Fig. 4. pH value of the near-cathode layer vs. the current density i_c in the nickel-plating electrolyte.

1,4-diol (unsaturated diatomic alcohol 2,5-dimethyl-3-hexine-2,5-diol), together with formaldehyde and benzaldehyde, makes it possible to obtain lustrous uniform coatings at current densities in the ranges 2-7and 10-16 A dm⁻².

It is known that, for matte coatings to be formed, it suffices that the additive is adsorbed on the cathode surface and the electrocrystallization overvoltage increases, whereas deposition of lustrous coatings requires that an adsorption layer of certain composition should be present on the cathode surface. Layers of this kind can be formed from organic substances and products of secondary reactions in the near-cathode layer. In the case of simultaneous deposition of a metal and evolution of hydrogen, the adsorption layer may be composed of hydroxides and other basic compounds [1].

The assumption that nickel hydroxides are formed in the near-cathode space was confirmed by measurements of the pH of the near-cathode layer (pHs). It can be seen in Fig. 4 that pHs markedly increases at $i_c = 1-4$ A dm⁻²; at higher current densities, the pH of nickel salt hydrate formation (7.2) is reached. The results we obtained suggest the lustrous nickel coatings are deposited if an adsorption layer composed of organic substances and hydrolysis products of the nickel salt is formed on the electrode surface.

Thus, we developed a sulfate nickel-plating electrolyte with new organic additives, which can be used to obtain lustrous uniform coatings at low and high current densities. The electrolyte has the following composition (g l⁻¹): NiSO₄·7H₂O 150–250, NaCl 10–15, H₃BO₃ 30– 40, Na₂SO₄·10H₂O 50–80, DHD 2–3; formalin (37% solution) 8–10 ml l⁻¹ and benzaldehyde 0.5–1 ml l⁻¹. Deposition conditions: temperature 40–50°C, cathode current densities $i_c = 2-5$ and 10–16 A dm⁻², anode current density 1–2 A dm⁻², pH 4.5, NPAN nickel anodes, agitation of the electrolyte mechanical or with compressed air.

CONCLUSIONS

(1) A study of the process of nickel electrodeposition from a sulfate electrolyte with addition of a diatomic alcohol, 2,5-dimethyl-3-hexine-2,5-diol, formaldehyde, and benzaldehyde demonstrated that, in the simultaneous presence of these substances, lustrous nickel coatings with leveled surface are obtained at current densities in the ranges 2-7 and 10-16 A dm⁻².

(2) A sulfate electrolyte from which lustrous uniform coatings can be deposited at low and high current densities was developed.

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