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> APPLIED ELECTROCHEMISTRY AND CORROSION PROTECTION OF METALS

Study of Properties of Lustrous Nickel Coatings Deposited from a Low-Concentration Chloride Electrolyte

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Abstract—Effect of electrolysis modes on the physicomechanical properties of lustrous nickel coatings deposited from a low-concentration chloride electrolyte was examined. Results obtained in an experimental study of the industrial use of the given electrolyte are presented.

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Use of dilute electrolytes meets requirements of environment protection because this can diminish the content of heavy metal ions in wastewater and atmosphere and even enable development of low-waste and waste-free technologies. A considerable economical effect can be achieved owing to a decrease in the reagent consumption for preparation and adjustment of the electrolyte and lower expenses and energy expenditure for wastewater purification. In some cases, coatings with new functional properties can be obtained.

Chloride nickel-plating electrolytes are advantageous over sulfate and sulfate-chloride electrolytes in having a higher electrical conductivity, causing no anode passivation, and exhibiting a weaker tendency toward coagulation of sols [1, 2].

It was shown in [3] that, in the course of electrolysis in a chloride nickel-plating electrolyte, the near-cathode layer is alkalized and colloidal and finely dispersed compounds of the metal being electrodeposited are formed. It follows from [4] that particles of the hydroxide being precipitated upon alkalization of the solution bear a positive charge if a metal chloride is the starting salt, and a negative charge if this is the metal sulfate.

The stability of colloidal and finely dispersed compounds and basic salts of nickel in the near-cathode layer in the presence of nickel chloride may result in that unreduced molecules of nickel compounds, contained in a dispersed particle, are incorporated into a coating and thereby lead to changes in coating properties [luster, internal stress (IS), microhardness, adhesion, corrosion resistance, uniformity of the deposit distribution over article surfaces, and porosity].

The goal of our study was to examine properties of nickel coatings deposited from a low-concentration chloride electrolyte and the possibility of their use for deposition of protective-decorative coatings.

EXPERIMENTAL

We used an electrolyte of composition (electrolyte 1) (g l^{-1}): NiCl₂·6H₂O 100, NiSO₄·7H₂O 5, H₃BO₃ 35, chloramine B 1.5; still bottoms of 1,4-butynediol (SBB) 5 ml l^{-1} . The electrolysis mode was the following: temperature 20–60°C, pH 1.0–5.0, cathode current density 0.5–12 A dm⁻² [5]. Nickel was deposited onto articles made of St.3 steel, M1 copper, and L63 brass in a 250-ml cell. The sample surface was pretreated by the known methods [6]. NPA-1 nickel served as anodes.

The microhardness of coatings with thicknesses of no less than 25 μ m on a copper plate was determined with PMT-3 microhardness meter at an indenter load of 50 g in conformity with GOST (State Standard) 2999–75. The

internal stresses were found by the method described in [7], with a flexible horizontally arranged cathode. A $35 \times 10 \times 0.05$ mm copper cathode being tested was preliminarily annealed at a temperature of 700°C for 30 min [8] and then was cooled in a closed furnace to room temperature. The substrates were insulated on one side with a poly(vinyl chloride) lacquer. Deviations of the cathode from the original position were recorded using a MIR-2 microscope. The IS was calculated by the formula

$$IS = \frac{Ed^2z}{3\delta l^2}$$

where *E* is the elastic modulus of the substrate material; *d*, cathode thickness (m); *z*, cathode end deflection (m); δ , coating thickness (m); and *l*, length of the coated part of the cathode (m).

Changes in the luster of the nickel coatings were studied on $50 \times 60 \times 0.5$ mm steel plates with an FB-1A luster meter. As the reference whose luster was taken to be 100% served a polished copper plate coated with a 20-µm-thick layer of lustrous nickel from the electrolyte of composition (g l⁻¹): NiSO₄·7H₂O 260–300, NiCl₂ 6H₂O 40–60, H₃BO₃ 30–40, 1,4-butynediol (100%) 0.12–0.2, saccharine 1.5–2.0, and phthalimide 0.08–0.12. The electrolysis was performed at pH 4.0–5.0, temperature of 55–65°C, and current density of 3–8 A dm⁻².

The strength of coating adherence to the base was determined by multiple 90° bending of a coated sample until its complete fracture in conformity with GOST 9.302–88. The sample size was $25 \times 5 \times 1$ mm, and the coating thickness, 20 µm. We examined the outward appearance of the coatings with an MIM-7 microscope at ×487.5 magnification. The porosity was determined by application of filter paper in conformity with GOST 9.302–88.

The phase composition of the nickel coatings was examined with a DRON-1.5 X-ray diffractometer with $Cu_{K\alpha}$ radiation and a nickel filter. The X-ray diffraction patterns we obtained were indexed by the Frevel–Rinn method [9]. The angular correction of the diffractometer was determined using a reference (quartz). The scanning rate was 1 deg min⁻¹. The throwing power of the electrolyte was studied with a dismountable angled cathode with an angle of 60° between its sides [10]. The current efficiency (CE) by nickel and hydrogen was

determined by the method described in [3].

One of the most important tasks in the field of electrodeposition of metals is to develop an electrolyte and conditions in which coatings with prescribed properties can be deposited. The physicomechanical properties of electrolytic deposits, important quality characteristics of coatings, predetermine their application areas.

One of properties characterizing the quality and corrosion resistance of electroplated coatings is their porosity. It is known that this property depends on whether IS appears in deposits and on the quality of the preliminary treatment of the substrate surface, substrate material, current efficiency, and electrolysis modes. Finding reasons for pore formation in deposits is one of the most important issues in electrolytic deposition of metals and alloys.

It can be seen in Fig. 1a that the porosity of coatings deposited at a temperature of 20°C, pH 1.0, and coating thickness of 6 μ m at current densities of 1–5 A dm⁻² increases from 13 to 15 pores cm⁻² and then decreases to 12 pores cm⁻² as the current density is raised to 9 A dm⁻². It was found that the porosity of 6- μ m-thick coatings deposited at a cathode current density of 5 A dm⁻² and pH 1.0 decreases from 15 to 9 pores cm⁻² as the electrolyte temperature is raised from 20 to 60°C (Fig. 1b). For coatings deposited at a current density of 5 A dm⁻² and a temperature of 20°C, the porosity decreases from 15 to 9 pores cm⁻² as the electrolyte prize pH is raised from 1.0 to 4.0. As the pH value is raised further (to 5.0), the porosity increases to 11 pores cm⁻² (Fig. 1c).

As the thickness of a coating deposited at a cathode current density of 5 A dm⁻² and pH 1.0 increases from 1 to 12 μ m, the porosity first sharply decreases and then, in the range 9–12 μ m, varies only slightly. For example, as the thickness of nickel coatings is raised from 1 to 9 μ m, the porosity decreases from 36 to 10 pores cm⁻², and when the thickness is raised further to 12 μ m, the porosity decreases to 8 pores cm⁻².

We studied how the IS in nickel coatings depends on electrolysis modes (Fig. 2). Measurements were made at the completion instant of electrolysis. Tensile stresses were observed. It can be seen in Fig. 2a that, as the cathode current density is raised from 1 to 5 A dm⁻², the IS increases from 235 to 245 MPa, and upon further increase in the current density from 5 to 9 A dm⁻², decrease from 245 to 225 MPa at an electrolyte pH 1.0 and temperature of 20°C. As the electrolyte



Fig. 1. Porosity *N* of nickel coatings vs. (a) cathode current density j_c , (b) electrolyte temperature *T*, and (c) electrolyte pH. Coating thickness 6 µm. (a, b) pH: (*I*) 1.0, (*2*) 5.0, and (*3*) 3.0. (a) Temperature 20°C, SBB concentration 5.0 ml l⁻¹. (b) Current density 5 A dm⁻², pH 3.0, SBB concentration 5.0 ml l⁻¹. (c) Temperature 20°C, SBB concentration 5.0 ml l⁻¹. SBB concentration (ml l⁻¹): (*I*) 1.0, (*2*) 5.0, and (*3*) 8.0.

temperature is raised from 20 to 60° C (Fig. 2b), the IS of 6-µm-thick coatings deposited at a cathode current density of 5 A dm⁻² and pH 1.0 decreases from 245 to 165 MPa. As pH is raised from 1.0 to 4.0, the IS in nickel coatings deposited under the same conditions as



Fig. 2. Internal stress IS of nickel coatings vs. (a) current density j_c , (b) electrolyte temperature *T*, and (c) electrolyte pH. Conditions of a and b are similar to those in Fig. 1. (c) Temperature 20°C, current density 5 A dm⁻², SBB concentration 5.0 ml l⁻¹.

those for the preceding series, somewhat increases, from 245 to 255 MPa, and then, upon an increase in pH to 5.0, sharply grow to 280 MPa (Fig. 2c).

At an electrolyte temperature of 20° C and pH 1.0 the microhardness of nickel coatings first increases from 2500 to 2650 MPa as the cathode current density is raised from 1 to 5 A dm⁻², and then, on raising the cathode



Fig. 3. Microhardness *H* of nickel deposits vs. (a) current density j_c and (b) temperature *T*. (a, b) Coating thickness 20 µm. pH: (1) 1.0, (2) 3.0, and (3) 5.0. (a) Temperature 20°C; (b) current density 5 A dm⁻².

current density to 9 A dm⁻², decreases to 2400 MPa (Fig. 3a). As the electrolyte temperature is raised from 20 to 60° C, the microhardness of nickel coatings deposited at a cathode current density of 5 A dm⁻² and pH 1.0 decreases from 2650 to 2350 MPa (Fig. 3b).

For electrolytes in which metals discharge only from ions, such a dependence is unusual. However, for an electrolyte in which finely dispersed compounds of the metal being electrodeposited are reduced at the cathode together with ions, the observed dependence of the coating microhardness on the current density, presumably, indirectly confirms the specificity of the cathodic process. If the reduction potential of finely dispersed particles is not reached yet, or if it is already reached, but reduction is incomplete because of the polydispersity of the particles, then the amount of unreduced particles in a coating grows. This changes the structure-sensitive properties of the coatings. After the full reduction potential of finely dispersed nickel compounds is reached and these compounds are monodisperse, the amount of inclusions of this kind in a coating decreases and, therefore, the microhardness decreases. The possibility of formation of finely dispersed nickel compounds in the near-cathode layer in a chloride electrolyte was demonstrated in [3].

The strongest luster of nickel coatings is observed at those cathode current densities at which the highest microhardness of deposits is reached. The dependence of the IS and porosity on the cathode current density is also confirmed by the dependence of variation of the coating microhardness in electrolytes containing finely dispersed compounds of the metal being electrodeposited.

According to X-ray diffraction data for coatings deposited from a low-concentration chloride electrolyte at pH 1.0, temperature of 20°C, and current densities of 1 and 9 A dm⁻², the γ -NiOOH phase is present in the coatings, but the number of its reflections is substantially smaller at 9 A dm⁻². This is also confirmed by the fact that, as the reduction potential of nickel hydroxide (-0.720 V) is reached at the cathode, dispersed nickel compounds start to be incorporated into a coating.

A study of how the electrolyte pH affects the surface microprofile of nickel coatings deposited from the chloride electrolyte under study at a cathode current density of 5 A dm⁻² and temperature of 20°C demonstrated that the surface of nickel coatings obtained at pH 1.0 is smoother than that at pH 5.0. The reason is that the dispersed nickel compounds obtained in the electrolyte at pH 1.0 are more finely dispersed than those at pH 5.0. In addition, more finely dispersed compounds have time to be fully reduced at the cathode in a larger amount, compared with coarsely dispersed compounds. Images of nickel coatings deposited from a low-concentration chloride electrolyte at a temperature of 20°C and pH 1.0 and 5.0 were obtained with a Quanta 200 scanning electron microscope. Histograms of the nickel coatings demonstrated that their surface has a deeper profile at pH 5.0, compared with pH 1.0. The microprofile of nickel coatings deposited at pH 1.0, temperature of 20°C, and current density of 5 A dm⁻² shows that finer hydroxide inclusions are formed on the surface, compared with those obtained at a current density of 1 A dm⁻². Presumably, this occurs because the reduction potential of nickel hydroxides is reached at a higher current density, i.e., the hydroxides are partly reduced, with the hydroxide inclusions formed on the surface being finer than those obtained at a low current density. Because the hydroxides formed at a lower current density have not enough time to be reduced, the inclusions produced in this case are coarser.

The corrosion resistance was determined using the Corrodcote technique. Coatings deposited from a lowconcentration chloride electrolyte compare well in corrosion resistance with coatings deposited from the widely industrially used sulfate-chloride electrolyte (electrolyte no. 2, GOST 9.305-84) containing 1,4-butynediol as a luster-forming additive. The electrolyte had the following composition (g l^{-1}): nickel sulfate heptahydrate 250-300, boric acid 25-40, sodium chloride 10-15, 1,4-butynediol 0.2-0.5, formalin 0.5-1.2, and chloramine B 2.0-2.5. The deposition was carried out at pH 4.5-5.5, electrolyte temperature of 40-50°C, and cathode current density of 2.5-3.5 A dm⁻². The adhesion of nickel coatings deposited from the chloride electrolyte to the base of steel, copper, and copper alloys satisfies GOST 9.302-88.

The chloride lustrous-nickel-plating electrolyte compares well in throwing power with sulfatechloride lustrous-nickel-plating electrolytes containing 1,4-butynediol as a luster-forming additive. As the cathode current density is raised from 0.5 to 9 A dm⁻², the throwing power of the low-concentration chloride electrolyte decreases from 26 to 16% at pH 1.0, and from 22 to 13% at pH 5.0.

The properties of nickel coatings deposited from the chloride electrolyte under study were compared with those of nickel coatings deposited from a sulfate-chloride electrolyte containing 1,4-butynediol (GOST 9.305–84) (see the table). It can be seen in the table that the nickel coatings deposited from the low-concentration chloride electrolyte (electrolyte no. 1) surpass those deposited from the sulfate-chloride electrolyte (electrolyte no. 2) in microhardness and luster, are about the same in porosity, adhesion, and current efficiency; and are inferior to the latter only in the IS. The throwing power of the chloride electrolyte is somewhat higher than that of the sulfate-chloride electrolyte.

Use of a chloride nickel-plating electrolyte diluted in its main component will make it possible to diminish the content of nickel ions in wastewater and to develop low-waste and waste-free technologies. Industrial electrodeposition of lustrous nickel coatings mostly employs electrolytes operating at elevated temperatures (40–60°C). This leads to an increased energy expenditure and faster evaporation of water from baths and requires permanent electrolyte adjustment, additional time Properties of nickel coatings deposited from the chloride electrolyte under study and sulfate-chloride electrolyte (GOST 9.305–84)

Parameter	Values of parameters for a coating deposited from indicated electrolyte	
	chloride no. 1	sulfate-chloride no. 2
Microhardness, MPa	2350-2650	1900–2100
Internal stress, MPa	165–280	125–190
Porosity at a thickness of 6 μm, pores cm ⁻²	9–15	13–18
Adhesion to a base made of steel, copper, and copper alloys	Satisfies GOST 9.302–88	
Current efficiency by nickel, %	92–96	93–98
Luster, %	96–99	90–92
Throwing power, %	13–26	8–14

for heating a bath to the necessary temperature, and permanent control over the electrolyte temperature. The electrolyte developed in the study operates at both elevated and room temperatures.

It is desirable to maintain the current density within the range 0.5-5 A dm⁻² at a temperature of 20°C and 1-12 A dm⁻² at 60°C.

The chloride lustrous-nickel-plating electrolyte was used in a 500-1 bath. The electrolyte was adjusted on taking into account the passed amount of electricity (A h l⁻¹). Upon a prolonged operation of the electrolyte with 80 A h l⁻¹, 1.5 ml l⁻¹ of SBB and 0.4 g l⁻¹ of chloramine B was added. The main components of the electrolyte were adjusted once in a month on the basis of the results of a chemical analysis. For an electrolyte operating at 60°C, the solution volume was brought to the initial level not rarer than once in 1–2 shifts, with the pH value simultaneously adjusted. Water used for this purpose was taken from the first uncirculated washing bath (catching bath), which saves salts carried

(1) It was shown that the dependence of the microhardness, internal stress, and porosity on the cathode current density (1-9 A dm⁻²) has an extremal nature. The maximum values of microhardness, internal stress, and porosity are 2650 MPa, 245 MPa, and 15 pores cm⁻², respectively. The manner in which these physicomechanical properties of nickel coatings depend on the pH value and temperature of the electrolyte was determined and quantitative results were presented.

away by articles from the nickel-plating bath. To obtain

high-quality deposits, the electrolyte was subjected to chemical and selective purification not rarer than once

in 1.5–2 months.

(2) It was found that nickel coatings deposited from a low-concentration chloride electrolyte (electrolyte no. 1) compare well in corrosion resistance with coatings deposited from the sulfate-chloride electrolyte widely used in the industry [electrolyte no. 2, GOST (State Standard) 9.305-84].

(3) It was demonstrated that the throwing power of the low-concentration chloride electrolyte is within the range 13-26%.

(4) Technological recommendations for industrial use of the suggested chloride electrolyte for lustrous nickel plating were substantiated and confirmed in practice.

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