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APPLIED ELECTROCHEMISTRY AND CORROSION PROTECTION OF METALS

Possibility of Raising the Deposition Rate of Nickel Coatings from a Chloride Electrolyte

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Abstract—Conditions under which nickel coatings can be deposited from a chloride electrolyte at a high rate were studied. The mechanism of this process was suggested and experimentally confirmed. The mass-transfer rate of nickel-containing particles was determined by chronopotentiometry, with temperature raised from 20 to 50°C. The dependence of pH_s on the current density was determined. Physicochemical parameters of the coatings (microhardness, internal stresses, porosity, luster, and adhesion) were measured.

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As known [1–3] that it is possible to accelerate electrodeposi-tion of metal coatings from electrolytes in which the discharge process involves, together with ions of electrodeposited metals, also finely dispersed particles of their compounds, capable of discharging to the metal in the same range of potentials as the ions themselves. In the course of nickel plating, a kinetically stable system of finely dispersed particles may appear in the near-cathode space and can intensify the electrodeposition process. In the optimal case, this system can be likened to a mobile system of pores, in which arise, in the course of electrolysis, electrosurface phenomena that cause stirring of the difficultly stirrable part of the diffusion layer. This system should not be necessarily thermally stable. It is sufficient that it should be kinetically stable during electrolysis and possess certain optimal parameters that enable the appearance of nonequilibrium electrosurface phenomena. The finely dispersed particles generated in the course of electrolysis may be composed of hydroxide and basic salt species.

To be discharged at the cathode, the finely dispersed particles should be positively charged. The charge can be imparted to them via adsorption of nickel cations, because it is known that inorganic ions contained in the particle core are primarily adsorbed on dispersed particles. As the cathode current density increases, the alkalization of the near-cathode space should become more pronounced because hydrogen evolution commonly occurs together with nickel deposition at the cathode. In high-performance electrolytes, it is necessary to lower the pH in the solution bulk or choose more effective buffering additives lest the pH value of the near-cathode layer, pH_s, be shifted too strongly toward the onset pH of hydrate formation for nickel, pH_h, thereby leading to rapid coagulation and formation of coarsely dispersed particles and their coagulation and, consequently, to their hindered discharge.

Nickel chloride was chosen as the main component for developing a high-performance electrolyte. Chloride electrolytes offer wide opportunities for acceleration of the nickel plating process, because the electrolyte should not contain large amounts of multiply charged ions, including sulfate ions, which exhibit coagulating capacity with respect to sols. In addition, according to [4], hydroxide species precipitated upon alkalization of the solution are positively charged if the starting salt is a chloride. If, however, the starting salt is a metal sulfate, negatively charged hydroxide species are formed, which is undesirable as regards the intensification of the nickel-plating process. The stability of finely dispersed hydroxide and basic salt particles in the near-cathode layer in the presence of nickel chloride and their positive charge can intensify the electrolysis process.

A promising way to make progress in electroplating is to devise and use high-performance electrolytes containing finely dispersed compounds of a metal being electrodeposited, which are reduced at the cathode [1, 2]. However, the mechanism by which the electrodeposition from these electrolytes can be intensified remains unclear.

To accumulate new facts useful for elucidating an implementable mechanism, fundamental aspects of nickel electrodeposition from a chloride nickel-plating electrolyte were studied.

EXPERIMENTAL

The study was carried out in a chloride nickel-plating electrolyte of composition (M): nickel chloride hexahydrate 1.0, boric acid 0.4, 1,4-buyinediol 5×10^{-3}; pH 1.0 at different temperatures. The electrolyte was prepared with distilled water from reagents of analytically pure grade. Polarization dependences were obtained with a PI-50-1-1 potentiostat by the potentiodynamic method at a potential sweep rate of 1 mV s^{-1}. Chronopotentiograms and potential-decay curves were measured with a PI-50-1-1 potentiostat with a PR-8 programming unit, synchronized with an S-8-12 storage oscilloscope. All measurements were made in a YaSE-2 electrochemical cell thermostated with a UTU-4 ultrathermostat. As electrodes under study served nickel plates with working areas of 3×3 (chronopotentiometric measurements) and 10×10 mm (polarization measurements and potential-decay curves). The inoperative sides of the electrodes were insulated with an epoxide compound. The potential of the electrodes under study was measured relative to a saturated silver chloride reference electrode and was recalculated to the hydrogen scale of potentials. The chronopotentiograms were obtained at current densities of 20–150 A dm^{-2} at different electrolyte temperatures. To exclude the influence of the natural convection, the current density was chosen so that the transient time should not exceed 1 min [5]. The pHs value was measured with a microscopic glass electrode.

The phase composition of the nickel coatings was studied with a DRON-1.5 X-ray diffractometer (Cu$_{K\alpha}$ radiation, nickel filter). The microhardness of the coatings was measured with a PMT-3 instrument at indenter loads of 5–50 g. The internal stresses (Is) were determined by the flexible-cathode method; adhesion to the base, by bending to an angle of 90° till fracture; porosity, by application of a filter paper; and luster, by FB-1A glossmeter.

Figure 1 shows how the product $j\tau^{1/2}$ depends on the current density for the chloride nickel-plating electrolyte at different temperatures. It can be seen that the product $j\tau^{1/2}$ is independent of the current density both at room temperature and under heating.

Figure 2 shows the temperature dependences of the product $j\tau^{1/2}$ in a chloride electrolyte and, for comparison, in a sulfate electrolyte, both containing the same amounts of nickel cations. For diffusion-controlled processes, the mass-transfer rate is proportional to the squared product $j\tau^{1/2}$. For the chloride nickel-plating electrolyte, the mass-transfer rate increases by a factor of 11.1 on raising the temperature from 20 to 50°C, and by a factor of 14.8, in the range 50–60°C. The total increase in the mass-transfer rate on raising the temperature from 20 to 60°C is by more than a factor of 163.3.

The sulfate nickel-plating electrolyte had the following composition (M): nickel sulfate heptahydrate 1.0, sodium chloride 0.3, boric acid 0.4, 1,4-butynediol 5×10^{-3}; pH 1.0. In this electrolyte, the mass-transfer rate increases by a factor of 6.5 on raising the temperature from 20 to 50°C, and by a factor of 10.7, in the range 50–60°C. The total increase in the mass-transfer rate on raising the

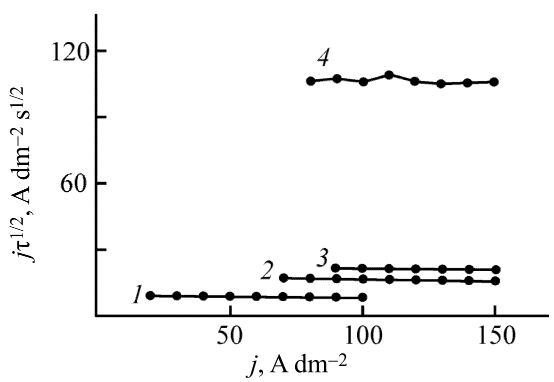

Fig. 1. Product $j\tau^{1/2}$ vs. the current density j at various temperatures of the chloride electrolyte. t (°C): (*1*) 20, (*2*) 40, (*3*) 50, and (*4*) 60.

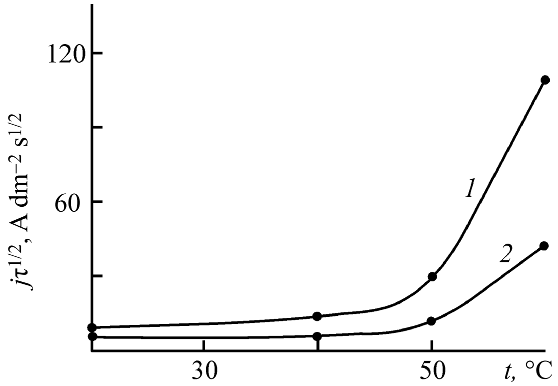

Fig. 2. Product $j\tau^{1/2}$ vs. the temperature t of (*1*) chloride and (*2*) sulfate electrolytes.

temperature from 20 to 60°C is by approximately a factor of 69.7. Sodium chloride was additionally introduced into the sulfate nickel-plating electrolyte for making the ionic strength of the solution the same as that of the chloride electrolyte and to improve the dissolution of nickel anodes. The increase in the mass-transfer rate on raising the temperature from 20 to 60°C in the chloride electrolyte is 2.3 times that in the sulfate electrolyte. Introduction of 1,4-butynediol into the chloride electrolyte in an amount of 5×10^{-3} M does not change the mass-transfer rate both at room temperature and upon heating, because the dependence of the product $j\tau^{1/2}$ on the current density is the same in both cases.

The experimental data obtained can make it possible to determine fundamental aspects of nickel electrodeposition under the conditions under consideration. For example, calculation of the diffusion coefficient of nickel ions at a temperature of 20°C by the Sand equation gives a value of 0.58×10^{-9} m^2 s^{-1}, which is in approximate agreement with reference data (for ultimately diluted solutions, D = 0.72×10^{-9} m^2 s^{-1}) [7].

Calculation for 60°C gives a value 77.58×10^{-9} m^2 s^{-1}, which is unlikely because the true diffusion coefficient has a more gradual temperature dependence in this temperature range. Consequently, discharging nickel compounds are not delivered to the cathode surface via diffusion, with the product $j\tau 1/2$ increasing more steeply at higher temperatures, especially above 50°C. Presumably, as temperature increases, hydrolysis becomes more pronounced and a more finely dispersed solid phase composed of basic nickel compounds is formed. A considerable increase in the amount of finely dispersed particles in the chloride nickel-plating electrolyte in the temperature range 20–60°C was also noted in [1].

The nondiffusion nature of the limiting cathode current densities is also indicated by the high temperature coefficients, whose values are as follows (% deg^{-1}): in the temperature range 20–60°C: 2.0 at pH 1.0, 2.1 at pH 3.0, 2.2 at pH 5.0; and in the temperature range 50–60°C: 4.8 at pH 1.0, 5.0 at pH 3.0, and 5.6 at pH 5.0 (Fig. 3). Commonly, the temperature coefficient $W = 100\Delta j_l / j_l \Delta t$ for the limiting diffusion current is 1.6–1.9 % deg^{-1} (for hydrogen ions, only 1.19 % deg^{-1}) [8]. Sure, the temperature coefficients can be judged from results of potentiometric measurements on solid electrodes only approximately. However, their values are anomalously high in the case in question.

The fact that the cathode current density is independent of the square root of the rotation rate of the disk electrode (in the range from 30 to 140 rps) and the limiting working cathode current density is independent of the potential sweep rate (at 30 to 80 mV s^{-1}) also points to the nondiffusion nature of the limitations in the working range of potentials.

Comparing the working intervals of the cathode current densities and the dependence of the pH$_s$ value on the cathode current density, one can notice that high-quality deposits start to be formed at current densities at which pH$_s$ reaches pH$_h$. The latter value for a chloride nickel-plating electrolyte of the same composition, but without an additive, is approximately 4.1 at a temperature of 20°C and 3.6 at 55°C [9].

As can be seen in Fig. 4, pH$_s$ increases with the cathode current density and tends to a certain limiting value at both 20 and 60°C. In electrodeposition at pH 1.0 from the electrolyte under development, pH$_s$ tends to 6.1 at 20°C, which coincides with the data of [10], and to 5.0 at 60°C. It follows from the dependences obtained that, even at j = 1 A dm^{-2}, pH$_s$ reaches a value at which basic

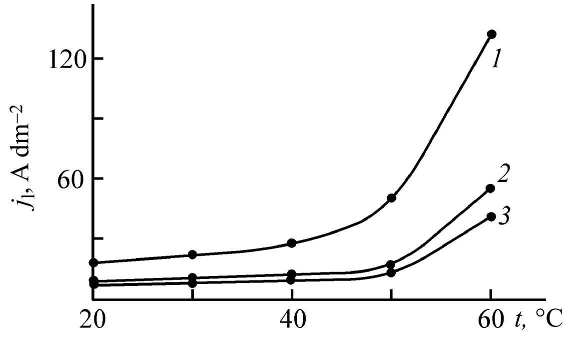

Fig. 3. Limiting working cathode current density j_l vs. the temperature t of the chloride electrolyte. pH: (*1*) 1.0, (*2*) 3.0, and (*3*) 5.0.

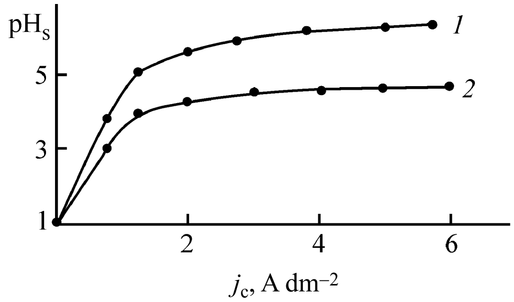

Fig. 4. pH$_s$ vs. the cathode current density j_c at chloride electrolyte temperatures of (*1*) 20 and (*2*) 60°C.

nickel compounds are formed, which favors formation of colloid particles of nickel compounds in the near-cathode layer, and just at $j > 1$ A dm^{-2} high-quality deposits are obtained at both 20 and 60°C.

The effect of the concentration and type of buffering additives on the limiting current densities in the chloride nickel-plating electrolyte was studied in [11–13]. It was shown that the limiting current densities increase with the concentration of buffering additives. For example, the limiting current density grows as follows: as the concentration of an acid is raised from 10 to 60 g l^{-1}, by a factor of 1.6 for aminoacetic acid, 1.9 for sulfosalicylic acid, and 2.2 for sulfamic acid; by a factor of 1.7 as the concentration of boric acid is raised from 20 to 40 g l^{-1}, by a factor of 1.5 for ammonium chloride, etc. An increase in the concentration of buffering additives leads to a decrease in pH$_s$ [14].

It is known [15, 16] that, in electrodeposition of nickel, the near-cathode layer is alkalinized and there appear conditions for formation of finely dispersed nickel compounds, whose presence is confirmed by electron microscopy. Nickel hydroxide is present in the coatings, and the sensitive method of radioactive isotopes quantitatively demonstrated that galvanic nickel deposits contain hydroxide compounds [17, 18]. The involvement of finely dispersed nickel compounds in the cathode process is also indicated by the fact that the limiting current density in the potentiodynamic characteristics of the cathode process becomes two times lower in the case of electrolysis with a cathode coated with an agar-agar gel, which is a filter for finely dispersed nickel compounds.

It is believed that the increase in the limiting diffusion current in electrolyte solutions with temperature is a common feature. In chloride electrolytes, the limiting working current density is an order of magnitude higher in this case, which points to a specific mechanism of reduction of nickel ions in these solutions [1, 2].

The fact that the output capacity of nickel plating is at a maximum at pH 1.0 and temperature of 60°C can be understood as follows. In this case, a reducible finely dispersed system of nickel compounds appears in the near-cathode layer. This system has the optimal parameters for appearance of equilibrium and nonequilibrium electrosurface phenomena in the difficultly stirrable part of the diffusion layer, which include the optimal dispersity, composition, and homogeneity of the system, its certain stability, interparticle distances in the system, etc. According to the data of [19, 20], the layer of stabilized colloids and fine suspensions, formed near the cathode surface, is a typical capillary system, i.e., a capillary-porous formation with a solid, but not rigid skeleton pierced by a system of pores filled by the electrolyte solution. These pores have an arbitrary shape and structure, which vary in the course of time because of the continuous involvement of the pore-forming substance (nickel hydroxide in the given case) in the electrochemical processes. Various electrosurface phenomena arise in such a layer under the action of the electric field of the cathode (e.g., electrophoresis, electroosmosis, dipolophoresis, diffusiophoresis), and just these phenomena are the reason why the deposition of metals and alloys is accelerated.

For electrolytes in which nickel ions are discharged simultaneously with the reduction of finely dispersed nickel compounds, the following behavior is observed. While the discharge potential is not reached and conditions for discharge of nickel-containing finely dispersed particles at the cathode are not created, these compounds can be incorporated into the coating without being discharged. When, however, the potential shifts to a more electronegative region, their more complete discharge begins. Electrons from the cathode and(or) evolving hydrogen can serve as reducing agents. Such a mechanism involving finely dispersed compounds of the metal being electrodeposited can strongly affect the properties of the coatings obtained.

Important parameters of nickel coatings are luster, microhardness, internal stresses, adhesion, corrosion resistance, uniformity of distribution over the surface of intricately shaped articles, and porosity. In view of the specific mechanism of reduction of finely dispersed nickel compounds at the cathode, compared with nickel discharge from ions, it would be expected that unreduced molecules of nickel compounds contained in a dispersed particles will be incorporated into a nickel coating, especially at low current densities. This can change the coating properties.

As the cathode current density increases from 5 to 10 A dm^{-2} at the electrolyte temperature of 60°C, the microhardness of the coatings first increases and then starts to decreases and does so up to a cathode current density of 10 A dm^{-2} (Fig. 5). The same run of the dependence is observed at 20°C.

For the conventional electrolytes, in which discharge of a metal occurs from its ions, such a dependence is unusual. However, for the electrolyte whose high performance is accounted for by a specific mechanism

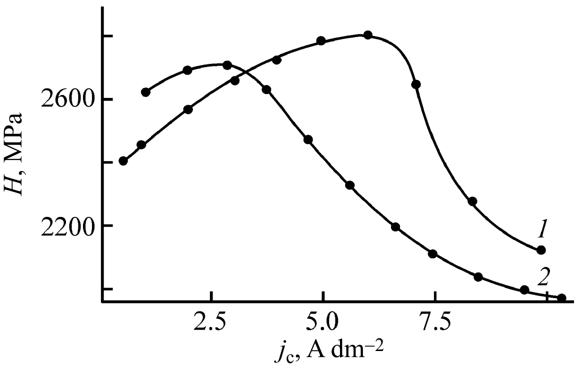

Fig. 5. Microhardness H of nickel coatings vs. the cathode current density j_c. Chloride electrolyte; the same for Figs. 6–8. Deposition temperature (°C): (*1*) 20 and (*2*) 60; the same for Fig. 6.

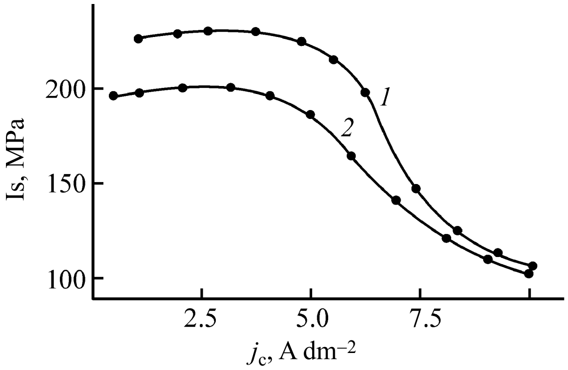

Fig. 6. Internal stresses Is of nickel coatings vs. the cathode current density j_c. Coating thickness 12 μm.

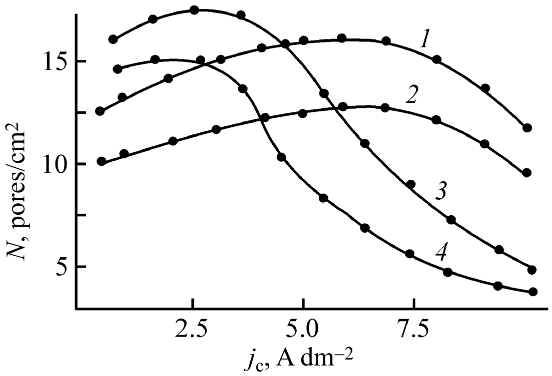

Fig. 7. Porosity N of nickel coatings vs. the cathode current density j_c. Deposition temperature (°C): (*1, 2*) 20 and (*3, 4*) 60. Coating thickness (μm): (*1, 3*) 0.5 and (*2, 4*) 1.0.

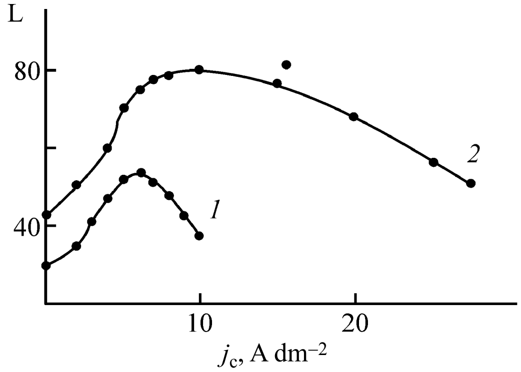

Fig. 8. Luster L of nickel coatings vs. the cathode current density j_c. Deposition temperature (°C): (*1*) 20, (*2*) 40.

of reduction of finely dispersed compounds of the electrodeposited metal, together with its ions, such a dependence of the coating microhardness on the current density indirectly confirms the specificity of the cathode process. If the reduction potential of finely dispersed particles is not reached, or if it is already reached, but the reduction is incomplete because of the polydispersity of the particles, then the amount of inclusions in the coating increases. This changes the structure-sensitive properties. If the potential of complete reduction of finely dispersed nickel compounds is reached and these compounds are monodisperse, the amount of inclusions of unreduced particles in a coating becomes smaller and, therefore, the microhardness decreases.

The dependence of the Is of nickel coatings on the current density and electrolyte temperature is shown in Fig. 6. The measurements were made at the instant when the electrolysis was terminated. Tensile stresses were observed. The type of the dependence of such a structure-sensitive parameter as Is confirms what was stated above about changes in the microhardness of coatings formed in electrolytes containing finely dispersed compounds of a metal being electrodeposited. A similar dependence is observed for the porosity (Fig. 7).

The dependence of the luster on the cathode current density is shown in Fig. 8.

The maximum luster of the nickel coatings is observed at approximately the same current densities as the maximum microhardness and Is. This points to pronounced changes in the electrolyte layer adjacent to the cathode in these electrolysis modes.

According to the two-factor theory of luster formation [21], two conditions should be satisfied for obtaining lustrous coatings: (1) finely dispersed particles of the type [MA] (where M is a metal ion, and A, anion) that can be reduced by hydrogen or electrons from the cathode should be formed in the near-cathode layer and (2) forces should be created that align the finely dispersed particles being reduced with the shape of the liquid 1–liquid 2 phase boundary. Here, liquid 1 is the electrolyte in its bulk, and liquid 2, that near the cathode, where the viscosity is increased because of the presence of dispersed particles.

It is the surface tension forces at this boundary that create a liquid-like surface of lustrous coatings.

As the working current density increases, the pH value in the near-cathode layers increases because of the simultaneous, with nickel deposition, hydrogen evolution. At a pH exceeding a certain value (depending on temperature and composition and concentration of components in the electrolyte), the pH_h of nickel is reached. This leads to formation of too coarse particles of hydroxides and basic salts and to disintegration of the phase surface of the more viscous layer (liquid 2) at the electrode surface. This eliminates the second factor favoring the formation of lustrous coatings [21]. The hydrodynamic mode at the surface of a growing lustrous coating is disturbed [22]. A specific hydrodynamic mode is created by electrosurface phenomena in the mobile system of pores at the cathode in the case of a simultaneous reduction of finely dispersed particles of compounds of a metal and its ions.

An X-ray structural analysis of coatings deposited from a chloride electrolyte at pH 1.0, temperature of 20°C, and current densities of 1 and 10 A dm^{-2} demonstrated that the γ-NiOOH, $Ni(OH)_2$ phase is present in the coatings [3]; however, the number of reflections at 10 A dm^{-2} is considerably lower. This also confirms that finely dispersed nickel compounds start to be reduced at the cathode as the reduction potential of nickel hydroxide (–0.720 V) [7] is reached.

The adhesion of nickel coatings deposited from a chloride electrolyte to steel, copper, and copper alloys supports satisfies GOST (State Standard) 9.302–88.

CONCLUSIONS

(1) The mass-transfer rate increases by a factor of 6.2 within the temperature range 20–50°C, and by a factor of 21.4 as temperature increases from 50 to 60°C.

(2) The calculated temperature dependences have high values: approximately 4.8 % deg^{-1} for the temperature range 50–60°C and pH 1.0, and 5.6 % deg^{-1} for pH 5.0.

(3) Introduction of 1,4-butynediol into the chloride nickel-plating electrolyte has no effect on the mass-transfer rate.

(4) The pH_h of nickel is reached in the near-cathode layer in the working range of current densities at both 20 and 60°C, and finely dispersed nickel compounds are formed, which are involved in the acceleration of the electrodeposition of nickel from a chloride electrolyte.

(5) As the cathode current density increases, the microhardness, internal stresses, porosity, and luster pass through a maximum.

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