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APPLIED ELECTROCHEMISTRY AND CORROSION PROTECTION OF METALS

Alkalization of the Near-Cathode Layer in Electrodeposition of Nickel from a Chloride Electrode

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Abstract—Dependences of the pH at which hydrate formation begins and the pH of the near-cathode layer on the electrolysis modes (temperature, cathode current density, pH in the electrolyte bulk) and the dependence of the pH of the near-cathode layer on the distance from the cathode surface in a low-concentration chloride nickel-plating electrolyte were studied.

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The electrochemical deposition of metals is frequently accompanied by simultaneous evolution of hydrogen, which leads to alkalization of the near-cathode space and creates conditions in which highly dispersed sols of hydroxides and basic salts of a metal being electrodeposited can be formed. Changes in the pH of the near-cathode layer, $\mathrm{pH_s}$, affect the mechanism and kinetics of electrode reactions and the quality and structure of the deposit formed.

The formation of colloidal and microheterogeneous particles in electrolytes in deposition of metals and alloys and their effect on the properties of the electroplated coatings obtained and on the metal deposition mechanism have long attracted the attention of electrochemists.

The fundamental aspects of colloid formation in cathodic processes of metal discharge have been analyzed [1–20]. M.N. Polukarov suggested that colloidal and microheterogeneous compounds of a metal being electrodeposited are formed near the cathode in the course of electrolysis. The formation of a metallic coating on the cathode from particles moving toward its surface has been observed in those cases when kinetically stable dispersed systems appear under the electrolysis conditions [2–4]. Electron-microscopic studies have shown that a difficultly soluble hydroxide of a metal being electrodeposited is present on the surface of lustrous deposits [5, 6]. The process of formation of stable colloidal and microheterogeneous compounds of nickel in the near-cathode space of various nickel-plating electrolytes has been studied with an ultramicroscope [7–9]. The authors of [10–13] examined the formation and stability of colloid compounds of nickel in nickel-plating electrolytes.

Studies of the Watts nickel-plating electrolyte with various additives have led to a conclusion that the dispersity of colloidal particles of basic nickel compounds affects the quality of the deposits obtained [14–17]. It was found that the quality of the deposits improved as the dispersity of colloid nickel compounds increased. In addition, it was suggested that the electrodeposited nickel is formed by two simultaneously occurring processes: discharge of nickel ions and reduction of a film of nickel hydroxide to the metal by atomic hydrogen formed as a result of alkalization of the near-cathode space.

V.A. Kaikaris experimentally demonstrated that colloidal compounds of metals can be reduced at the cathode to give a compact plated coating. It was found that, if colloidal particles of compounds of metals being electrodeposited are present and the conditions of the two-factor theory of luster formation are satisfied, a strong luster of the coatings is obtained [18, 19].

According to the two-factor theory of luster formation, the following conditions should be satisfied for lustrous coatings to be obtained: (1) colloidal particles that can be reduced by hydrogen or electrons from the cathode should be formed in the near-cathode layer and (2) forces aligning the reducing colloidal particles in accordance with the shape of the fluid 1–fluid 2 phase surface should be created. In this case, fluid 1 is the bulk of the electrolyte, and fluid 2, an electrolyte layer at 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 fluid-like surface of lustrous coatings.

EXPERIMENTAL

The study was carried out in a low-concentration chloride nickel-plating electrolyte of the following composition (g l^{-1}): nickel chloride hexahydrate 50–100, boric acid 30–40, chloramine B 0.8–1.2; and 1,4-butynediol 04–0.8 ml l^{-1} [21]. The electrolyte was prepared from distilled water and reagents of analytically pure grade.

Polarization dependences were measured using a PI-50-1-1 potentiostat by the potentiodynamic method at a potential sweep rate of 1 mV s^{-1}. All the measurements were made in a YaSE-2 electrochemical cell thermostated with a UTU-4 ultrathermostat. A nickel plate with a 10 × 10 mm working area served as the electrode under study. The nonworking sides of the electrode were insulated with an epoxy compound. The potential of the electrodes under study was measured relative to a silver chloride reference electrode and recalculated to the hydrogen scale.

The current efficiencies CE by nickel and hydrogen were determined under galvanostatic conditions with a P-5848 potentiostat by two methods: gravimetric (with a copper coulometer) and coulometric (with a gas coulometer). The cell for determining the CE by nickel and hydrogen is shown, together with the gas coulometer, in Fig. 1.

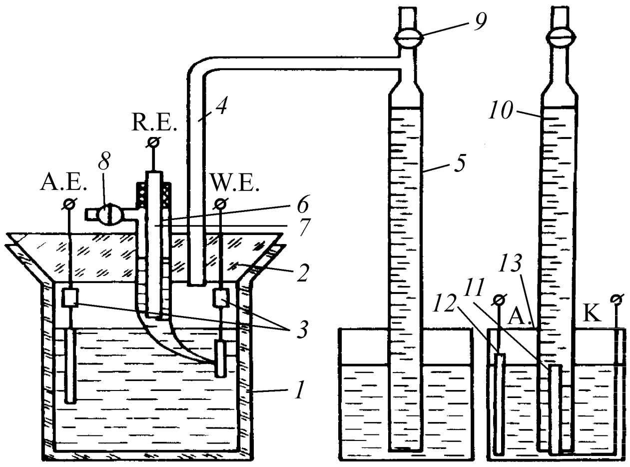

Fig. 1. Schematic of the installation for determining the current efficiency by nickel and hydrogen. For explanations, see text.

The installation comprises a glass vessel *1* with a ground joint and a polymethyl methacrylate cover *2* fitted into this joint. Conductors with holders *3* of the working and auxiliary electrodes and gas-discharge tube *4* connected to a 25-ml burette *5* are built in the cover. The burette is lowered into a vessel with a 100-g l^{-1} potassium hydroxide solution. A glass tube with a Luggin capillary and discharge pipe *6* with reference electrode *7* and valve *8* are also built in the cover. Microscopic channels at places of insertion of the conductors and the gas-discharge tube with the Luggin capillary and the silver chloride electrode are hermetically sealed with an epoxy compound. To preclude gas leakage, the cover is placed on the vessel with the electrolyte under study after the ground joint is preliminarily smeared with a vacuum lubricant. Burette *5* is filled via valve *9* with a potassium hydroxide solution, and the glass tube with the Luggin capillary is filled via valve *8* with the electrolyte under study in such a way that the nose of the silver chloride electrode touches the working electrode. The nickel working electrode is embedded in the epoxy compound, except on its working side.

The current efficiency by hydrogen was calculated upon the electrolysis from the ratio between the volume of hydrogen in burette *5* and in the coulometer constituted by a 25-ml burette *10*, below which a steel cathode with an insulated current drainage *11* is submerged, and steel anode *12*. The electrolyte in the coulometer, poured into vessel *13*, has the form of a 100-g l^{-1} potassium hydroxide solution. The solution in the coulometer and the nickel-plating electrolyte are preliminarily saturated with hydrogen. The volume of hydrogen evolved during the electrolysis was reduced to the standard conditions. The electrolysis duration was determined with a stopwatch. The coulometer was connected in series with the working electrolyzer to "ammeter" terminals of the potentiostat.

The acidity in the near-electrode layer of the electrolyte was measured in relation to the distance to the cathode by the method reported in [22, 23], with a microscopic glass electrode (MGE) used. Such an electrode is similar in shape to the Luggin capillary to whose edge a film of an electrode glass, with a working area diameter of up to 0.5 mm, is welded. The electrolytic key of the reference electrode, which is also similar to the Luggin capillary, is brought to the working surface together with the MSE. The key is filled with a 3% solution of agar-agar, prepared using a saturated potassium chloride solution. The MSE is filled with a 0.1 M hydrochloric acid solution, into which a silver wire coated with silver chloride is submerged. An identical electrode is lowered into the key of the reference electrode. The MSE and the key of the reference electrode are brought to the electrode in the same plane, as close to each other as possible. The pH is measured with an EV-74 versatile ion meter. Prior to measurements, electrolysis is performed for 3–5 min, and at measurement instants, the current in the circuit is switched off.

The pH_s was measured directly at the cathode by the method of a metal-hydrogen electrode [24]. The installation for determining pH_s with a metal-hydrogen nickel electrode includes an ordinary three-electrode cell. The cathode, near which a change in the electrolyte pH is to be measured, simultaneously serves as the metal-hydrogen electrode. A saturated silver chloride electrode is used as reference. A nickel band serves as the anode.

In the galvanostatic mode, the current was set with a PI-50-1 potentiostat combined with a PR-8 programming unit. The curve describing the decay of the potential was recorded with an S8-12 storage instrument.

The acidity of the near-electrode layer was calculated by the formula

$$\mathrm{pH} = E/0.059,$$

where E is the electrode potential (V) found from the potential decay curve in 0.02 s after switching-off the current as a difference between the electrode potential under current and the final value of the potential after switching-off the polarizing current.

The pH was calculated on the assumption that the nickel electrode behaves under these conditions as a hydrogen electrode.

Ultramicroscopic observations were made with an MBI-6 microscope, combined with a dark-field condenser, at magnifications of 63 and 280. A closed cell with a depth of 0.2 mm was used. Nickel wires 0.2 mm in diameter served as electrodes. The ultramicroscopic study was carried out with an MBS-2 microscope at magnifications of 25 and 50. The observations were made in a 30 × 40 × 20 mm cell covered on all sides with a bitumen lacquer, with a slit about 1 mm wide left on one side. The cell was laterally exposed to light from a substage illuminator of a Zigmondi ultramicroscope, in which the voltaic arc was replaced with a 300 W projector lamp. To preclude penetration of IR light into the cell, an IR-nontransparent glass was placed between the condenser and illuminator.

The study of the electrodeposition of nickel from a low-concentration chloride electrolyte demonstrated that compact lustrous nickel deposits are obtained at a temperature of 20°C and pH 1.0 at cathode current densities of 0.5 to 6 A dm^{-2}, with a current efficiency by nickel of 92–94%. Raising the pH of the starting solution to 5.0 enables deposition of high-quality deposits at lower current densities of 0.1 to 2 A dm^{-2}, with a current efficiency of 97–98%. At pH 1.0 and electrolyte temperature of 40°C, high-quality deposits are formed at cathode current densities of 0.5–12 A dm^{-2}.

In the course of electrolysis, the concentration of hydrogen ions in the near-cathode layer sharply decreases and pH_s depends on the pH in the solution bulk, composition and concentration of the electrolyte components, temperature, and cathode current density. Therefore, it is important to study the effect of the cathode current density, solution temperature, and concentration of hydrogen ions in the electrolyte bulk on the extent of alkalization in the near-cathode layer in electrodeposition of nickel from a low-concentration chloride electrolyte.

The fact that the chloride nickel-plating electrolyte contains a buffer additive that hinders coagulation of colloid particles affects the dependence of pH_s on the current density. An additive of this kind must, on the one hand, hinder sharp variation of pH_s with increasing current density and, on the other, serve as a stabilizer of finely dispersed compounds, which precludes their coagulation and enables their discharge to the metal. All these factors result in that coarsely dispersed hydrates and basic salts start to be formed at higher pH_s and, as aconsequence, at higher current densities.

Figure 2 shows how pH_s depends on the cathode current density at different solution temperatures (Fig.2a) and on the pH in the bulk of the chloride electrolyte containing boric acid as a buffering additive (Fig. 2b). It can be seen that, in a low-concentration chloride nickel-plating electrolyte at pH 1.0 in the solution bulk, pH_s is approximately 4.1 at 20°C and 3.7 at 40°C.

As the cathode current density increases, pH_s grows and tends to a certain value at both 20 and 40°C. In electrodeposition from a chloride electrolyte, pH_s approaches a value of 6.2 at pH 1.0 and temperature of 20°C, and 6.1 at pH 1.0 and 40°C. The existence of acertain limiting pH_s value that varies only slightly with increasing current density indicates that difficultly soluble compounds are formed in the electrolyte and

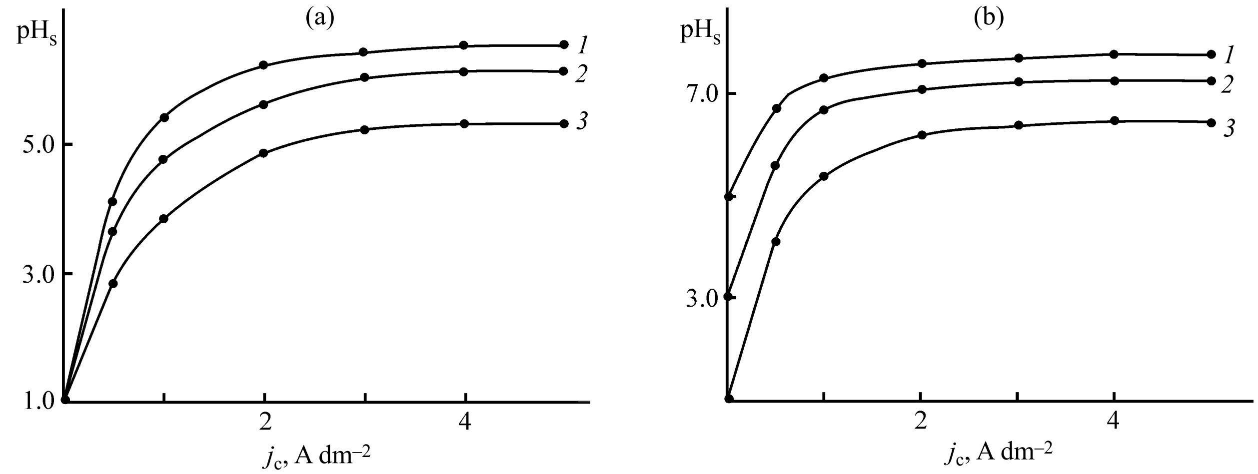

Fig. 2. pH$_s$ vs. the cathode current density j_c in a chloride electrolyte at various (a) temperatures and (b) pH values. Electrolyte composition (g l^{-1}): nickel chloride hexahydrate 100, boric acid 40, chloramine B 1; 1,4-butinediol 0.5 ml l^{-1}; the same for Figs. 4 and 5. (a) Temperature (°C): (*1*) 20, (*2*) 40, and (*3*) 60; pH 1.0. (b) pH: (*1*) 5.0, (*2*) 3.0, and (*3*) 1.0; $T = 20$°C.

hinder further rise in pH.

A comparison of the working ranges of the cathode current densities with the dependence of pH$_s$ on the cathode current density demonstrated that high-quality deposits start to be formed at current densities at which pH$_s$ is approximately equal to the hydration pH$_h$. For a chloride nickel-plating electrolyte at a boric acid concentration of 40 g l^{-1}, pH$_h$ is approximately 3.6 at 20°C (Fig. 3) and 3.4 at 40°C. For a chloride nickel-plating electrolyte of the same composition without an additive, pH$_h$ is approximately 4.1 at 20°C and 3.6 at 55°C [25]. It was found using the potentiometric titration method that, as the boric acid concentration is raised from 0 to 40 g l^{-1}, the pH$_h$ in the above electrolyte decreases from 4.8 to 3.6 at the electrolyte temperature of 20°C (Fig. 3).

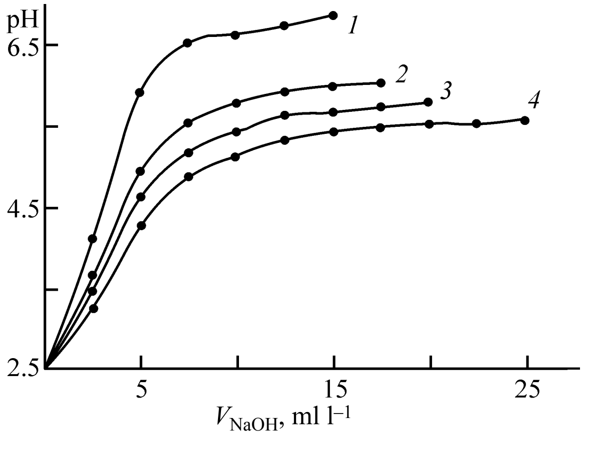

Fig. 3. pH of the electrolyte vs. the volume V_{NaOH} of sodium hydroxide (100 g l^{-1}) introduced into the chloride electrolyte with varied content of boric acid. Electrolyte composition (g l^{-1}): nickel chloride hexahydrate 100 and chloramine B 1; 1,4-butinediol 0.5 ml l^{-1}. Content of boric acid (g l^{-1}): (*1*) 0, (*2*) 10, (*3*) 30, and (*4*) 40; $T = 20$°C.

Thus, in the low-concentration nickel-plating electrolyte, there are all conditions for finely dispersed hydroxides and basic compounds of nickel to be formed. Their main distinction from systems formed in ordinary, widely industrially used sulfate and sulfate-chloride nickel-plating electrolytes consists in a finer dispersity, which follows from ultramicroscopic observations, and in stability, because the chloride electrolyte contains no multiply charged sulfate ions exhibiting a widely known coagulating effect on colloids.

Also, the dependence of the electrolyte pH on the distance from the cathode was studied (Fig. 4). It can be seen from the dependences of pH$_s$ on the distance to the cathode at different current densities that, as the cathode current density is raised from 0.5 to 6 A dm^{-2} in a chloride electrolyte at pH 1.0 and temperature of 20°C, pH$_s$ increases from 3.7 to 6.1 and becomes almost equal to the pH value in the electrolyte bulk only at a distance of 1.7 mm from the cathode (Fig. 4a). As the cathode current density is raised from 0.5 to 12 A dm^{-2} at pH 1.0 and temperature of 40°C, pH$_s$ increases from 3.4 to 6.0 and becomes equal to that in the electrolyte bulk at a distance of about 1.5 mm from the cathode (Fig. 4b).

As the electrolyte temperature is raised from 20 to 40°C, the luster of nickel coatings becomes more pronounced. This is presumably due to a rise in the degree of hydrolysis of the electrolyte and to the formation of a layer with increased dispersity of colloid particles at the cathode. However, at temperatures exceeding 70°C, organic additives stabilizing finely dispersed systems may decompose, which leads to disintegration of these systems and to a sharp decrease in the extent of luster of the nickel coatings being formed.

If, in addition, pH_s substantially exceeds pH_h, this may lead to formation of coarsely dispersed hydroxides and basic compounds of nickel and to the resulting disintegration of the phase surface of the more viscous layer (fluid 2) at the electrode surface. In this case, the second factor favoring a stronger luster of electroplated coatings disappears. Also, the hydrodynamic mode at the surface of a growing lustrous coatings is disturbed [18].

Because in the course of nickel electrodeposition, the near-cathode layer is alkalized and finely dispersed nickel compounds are formed, which can be reduced at the cathode together with nickel cations, it would be expected that unreduced molecules of nickel compounds contained in a dispersed particle can be incorporated into the nickel coating. For electrolytes in which nickel ions are discharged simultaneously with the reduction of finely dispersed nickel compounds, the following behavior is observed. Until the corresponding potential is reached and conditions for discharge of nickel-containing finely dispersed particles are created, they can be incorporated into the coating without being discharged and then, upon a shift of the potential into a more electronegative region, their more complete discharge begins. As reducing agents can serve both electrons from the cathode and(or) the evolving hydrogen. Such a mechanism involving finely dispersed compounds of the metal being electrodeposited may strongly affect the properties of the coatings being obtained. This is confirmed by the hump-shaped dependence of the microhardness, internal stresses, and luster on the cathode current density, by X-ray phase analyses [26], and by dependences of the overall current efficiency on the potential.

Figure 5 shows overall values of the cathode CE by nickel and hydrogen with a polarization characteristic of the process at the cathode in a chloride electrolyte. Beginning from low current densities, the overall CE by nickel and hydrogen exceeds 100% and reaches a maximum at potentials of about –(0.740–0.770) V at both 20 and 40°C. The maximum overall CE is approximately 104% at 40°C and 103% at 20°C.

The obtained dependences of pH_s on the cathode current density, solution temperature, and acidity of the

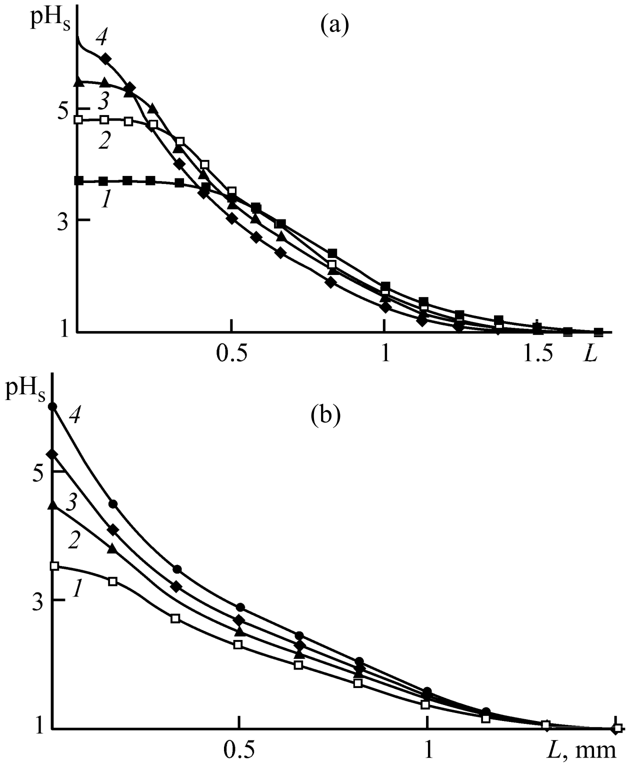

Fig. 4. pH_s vs. the distance L from the cathode into the electrolyte bulk at different cathode current densities at temperatures of (a) 20 and (b) 40°C. j_c (A dm^{-2}): (a) (*1*) 0.5, (*2*) 2.0, (*3*) 4.0, and (*4*) 6.0; (b) (*1*) 0.5, (*2*) 4.0, (*3*) 8.0, and (*4*) 12.0; pH 1.0; the same for Fig. 5.

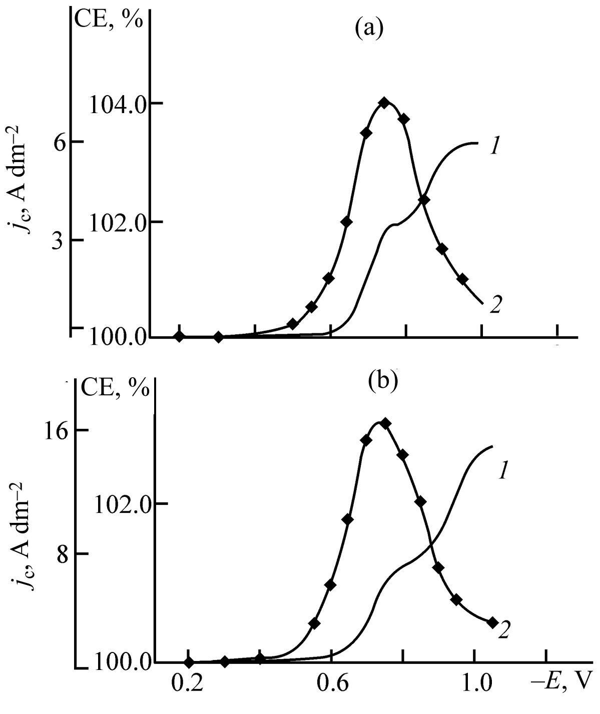

Fig. 5. (*1*) Current density j and (*2*) overall current efficiency CE by nickel and hydrogen vs. the electrode potential E in a chloride electrolyte at temperatures of (a) 20 and (b) 40°C.

starting electrolyte can be used to find electrolysis modes in which lustrous nickel-based deposits are formed.

Directly obtained data on pH_s and pH_h enable more certain conclusions about the role played by finely dispersed particles based on a metal being electrodeposited in the process of formation of lustrous coatings. Presence of finely dispersed particles in the near-cathode layer is presumably a necessary condition for lustrous coatings to be obtained.

The importance of the electrolyte acidity in electrodeposition of metals is a common knowledge. Particularly important is the variation of acidity in the near-cathode layer. It is impossible to purposefully develop new promising electrolytes and obtain deposits with prescribed composition and properties without taking into account the variation of pH_s in electrodeposition of metals.

Some theories of deposition of lustrous electroplated coatings [15, 18] are based on the assumption that the process can only occur after a certain steady-state pH_s value is reached, with the mechanical properties of these coatings also dependent on presence of finely dispersed hydroxide compounds or basic salts formed in the near-cathode layer of the electrolyte as a result of its alkalization [27].

CONCLUSIONS

(1) It was shown that, in a low-concentration chloride nickel-plating electrolyte, there are, irrespective of the electrolysis modes, all conditions for finely dispersed hydroxides and basic salts of nickel to be formed in the near-cathode layer, with lustrous coatings deposited after pH_s reaches pH_h. At 20°C, pH_h is approximately 3.6, and pH_s at pH 1.0 in the electrolyte bulk is approximately 3.7 and 6.1 at cathode current densities of 0.5 and 6 A dm^{-2}, respectively.

(2) The dependence of pH_s on the distance to the cathode surface was studied in different electrolysis modes. It was demonstrated that, in the working range of cathode current densities at pH 1.0 in the electrolyte bulk, pH_s becomes equal to the pH in the bulk of the electrolyte at distances of 1.7 and 1.5 mm at 20 and 40°C, respectively.

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