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APPLIED ELECTROCHEMISTRY AND CORROSION PROTECTION OF METALS

Influence of the Composition of Dilute Nickel-Plating Electrolytes on the Physicomechanical Properties of Electroplated Coatings

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Abstract—The influence of the composition of dilute nickel-plating electrolyte containing luster-forming additives on the leveling, plasticity, and internal stresses of coatings being electroplated was studied. The possibility of combining nickel sulfate, sodium chloride, and boric acid as the main composition of a dilute nickel-plating electrolyte was analyzed.

Technological solutions that would make lower the expenditure of nonferrous metals, such as nickel, tin, copper, and their alloys, are sought for in order to further develop the galvanic industries. Compositions of bright-nickel-plating electrolytes ensuring a common plating rate of 0.8–1.2 $\mu m\ min^{-1}$ at the concentrations of salts of a metal being deposited lowered by a factor of 2–2.5 (with a total nickel concentration of up to 30–35 $g\ l^{-1}$) have been suggested [1–4]. The rate of nickel plating depends not only on the anionic composition of an electrolyte [5], but also on the luster-forming formulations used. The nature and cathodic behavior of luster-forming additives may lead to a redistribution of the rates of nickel deposition and hydrogen evolution in favor of the latter process. In this case, formation of nickel hydroxide compounds in a near-cathode layer and their inhibiting effect on nickel electrodeposition become more likely, and the microstructure of the resulting coatings is changed. The considerable increase in the hydrogenation of the deposits deteriorates the physicomechanical properties of the coatings obtained [6–8]. To improve the main characteristics of the bright-nickel-plating process, acetylene compounds are used in combination with ethylene and organosulfur additives [9].

The aim of this study, was to assess the influence exerted by the composition of a dilute nickel-plating electrolyte containing luster-forming additives based on β-oxyethyl cinnamide (OECAM) on the physicomechanical properties of the coatings being deposited.

EXPERIMENTAL

The study was performed in nickel-plating electrolytes containing ($g\ l^{-1}$): no. 1: 140 $NiSO_4 \cdot 7H_2O$, 30 $NiCl_2 \cdot 6H_2O$, and 30 H_3BO_3; no. 2: 33 $NiSO_4 \cdot 7H_2O$, 120 $NiCl_2 \cdot 6H_2O$, and 30 H_3BO_3; no. 3: 150 $NiSO_4 \cdot 7H_2O$, 50 NaCl, and 30 H_3BO_3. The electrolytes prepared were subjected to selective purification. Chemically and analytically pure reagents were used in the experiments. OECAM was synthesized and purified[1] mp 87°C. 2-butyne-1,4-diol (YN) was twice recrystallized from chloroform, mp 58°C; 2-butene-1,4-diol (EN) was purified chromatographically, mp 113°C at a pressure of 5 mm Hg. Saccharin was recrystallized from ethanol, mp 225–226°C. The temperature of the experiment was 50°C and pH 4.0. The pH value of the electrolytes was measured with an LPU-01 pH-meter and adjusted with hydrochloric acid or sodium hydroxide.

The microleveling power was determined by measuring profilograms of a titanium substrate with triangular grooves cut to a depth of about 4 μm (angle 120°). The microleveling factor B (%) was calculated from data on the average depth of the grooves before and after the nickel plating with the use of the formula:

$$B = \frac{h_1 - h_2}{h_1} \times 100, \qquad (1)$$

where h_1 and h_2 are the depths of the substrate grooves (μm) before and after the deposition of a coating, respectively.

The plasticity of the coatings was evaluated by their ultimate tensile elongation, measured with a spiral elastometer.[2] Plates with coatings (170 × 10 mm in size and 1 mm thick) were placed on the elastometer having the form of a spiral template with a step-

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[1] At the Department of Organic Chemistry, Vilnius University.

[2] Designed at the Institute of Chemistry.

Limiting current density i_c in a Hull cell for various nickel plating electrolytes for bright nickel plating

Electrolyte	Electrolyte no.	Luster-forming additive, g l^{-1}	i_c, A dm^{-2}
Sulfate	1	Saccharin, 1.5; OECAM, 0.5; YN, 0.05	1.9
Chloride	2	The same	2.8
	3	″	2.0
	2	Saccharin, 1.5; YN, 0.08; EN, 0.16	3.2

wise changing radius of curvature. The critical elongation, at which coatings cracked, was determined with a special paste containing *o*-phenanthroline chloride indicator, which could reveal an uncoated steel substrate.

The elongation *l* (%) was calculated by the formula

$$l = [d/(2r + d)] \times 100, \tag{2}$$

where *d* is the thickness of a plate with a coating (mm), and *r*, the radius of curvature at the critical point of the spiral surface.

The internal stresses (IS) in the nickel coatings were measured by the method of a flexible cathode with a device that could measure the cathode curvature after its being coated in a stirred electrolyte [10].

It is known that chloride nickel-plating electrolytes ensure a higher rate of nickel deposition, compared with sulfate electrolytes [5]. Introduction of sodium salts as supporting additives, which are used to improve the throwing power of nickel-plating electrolytes [6], makes lower the electrodeposition rate. The table lists the electrolyte formulations and estimates of the nickel-plating rates, found by the fast method [5] with a Hull cell. The formulation suggested is similar to the technological solution of [9], which consists in that small concentrations of YN are used in combination with an ethylene compound, EN, with the key role played by the competition of acetylene and ethylene groups in hydrogenation. β-Oxyethyl cinnamide is described by the formula $C_6H_5CH{=}CH{-}CONHCH_2CH_2OH$ and, unlike EN, contains a phenyl radical and nitrogen. A comparative study of the known bright-nickel-plating electrolyte based on a mixture of YN and EN [9] in an untypical formulation of a dilute electrolyte no. 2 demonstrated that the rates of metal plating in a dilute chloride solution differ only slightly for the additives used.

The coatings obtained in a chloride electrolyte have a factor of 1.5–2.0 lower internal compression stresses over the entire range of the current densities i_c (Fig. 1a).

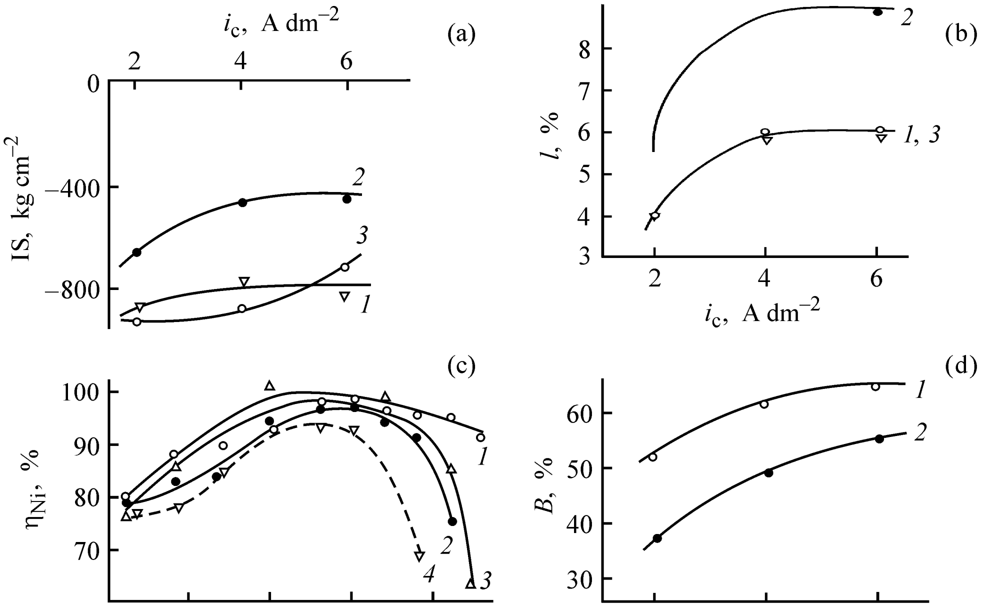

Fig. 1. (a) Internal stresses IS, (b) plasticity *l*, (c) current efficiency η_{Ni}, and (d) microleveling factor *B* vs. the current density i_c in various nickel-plating electrolytes. Temperature 50°C and pH 4.0. (a, b, d) Digits at curves are the electrolyte numbers; Additive to the electrolytes (g l^{-1}): saccharin 1.5, OECAM 0.5, and YN 0.05. (c) Electrolyte (g l^{-1}): (*1*) no. 2; (*2*) no. 2 + saccharin, 1.5; (*3*) $NiCl_2 \cdot 6H_2O$, 27; Na_2SO_4, 70; H_3BO_3, 30; and (*4*) no. 1 + saccharin, 1.5.

The plasticity of a lustrous nickel coating formed under the same conditions reaches a value of 9% (Fig. 1b), which is very high, compared with that obtained previously (up to 6%) for the technological solutions suggested in [9]. It should be noted that sufficiently plastic deposits (6%) are also obtained from dilute nickel-plating electrolyte nos. 1 and 3 (Fig. 1b). Presumably, the possible reason for the smaller elongation is the lower current efficiency by nickel in sulfate electrolytes, compared with chloride electrolytes. A similar effect is produced by sodium ions (Fig. 1c). In this case, a stronger alkalization of the near-cathode space is observed and the amount of impurities incorporated into the nickel deposit is larger. The best leveling power is observed for sulfate electrolyte no. 1 (Fig. 1d). This may be due to different catalytic activities of the renewed nickel surface in reactions of cathodic conversion of ethylene and acetylene compounds. Therefore, the choice of the electrolyte composition depends on whether a higher plasticity or leveling is required for a particular coating.

The data in the table indicate that the rates of nickel plating in dilute nickel-plating electrolytes, sulfate electrolyte no. 1 and chloride electrolyte no. 3, are nearly the same and the coatings obtained from these electrolytes have the same internal stresses and plasticities (Figs. 1a, 1b). This shows that nickel sulfate, sodium chloride, and boric acid can be combined in the formulation of a dilute nickel-plating electrolyte based on OECAM if nickel chloride is completely replaced with sodium chloride.

CONCLUSION

A study of the influence exerted by the composition of a dilute nickel-plating electrolyte containing β-oxyethyl cinnamide as luster-forming additive on the physicomechanical properties of the coatings deposited demonstrated that nickel sulfate, sodium chloride, and boric acid can be used in combination in the formulation of a dilute nickel-plating electrolyte.

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