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Electrodeposition of nickel and composite nickel-fullerenol coatings from low-temperature sulphate-chloride-isobutyrate electrolyte

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Abstract

It is investigated low-temperature electrolyte with addition of isobutyric acid as an alternative to standard electrolyte with addition of boric acid (Watts's type). It is found that sulphate-chloride-isobutyric electrolyte has a high buffer capacity and allows receiving coatings with low microhardness (170-200 HV). Addition of fullerenol in electrolyte leads for getting more corrosion resistance coatings, improving structure and enhancing microhardness.

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1. Introduction

Electrolytic deposition of nickel coatings is one of the most common processes in electroplating. There is an increased attention to its study which caused a huge number of industrial applications of nickel, such as electrodeposition of protective, functional and decorative coatings¹, catalytically active coatings for hydrogen evolution, the use of nickel as a part of an alloy^{2,3} or metal-bond to composite electrolytic coatings (CEC)⁴⁻⁶.

There are different requirements to nickel coatings depending on its use. One of the main properties of electrolytes for CEC is getting thick and uniform coating over the entire surface. Thus, in this case is important the selection of

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an electrolyte with high throwing power, stability of the composition (high buffer capacity) and the high operating current density.

An important component in the nickel electrolyte is a substance which maintains a constant pH in the volume of electrolyte and in the cathode layer. H_3BO_3 is traditionally used as such additive. However, it seeks alternative to boric acid due to restrictions on the industrial use of boric acid (the third hazard class) in 2004 in several European countries as well as in Japan^{7,8}. Galvanics search for more efficient, environmentally friendly additives in the nickel electrolyte. In addition, experimental data on the pH in the cathode layer of nickel sulfate solutions with boric acid confirm low buffering capacity in the nickel plating electrolytes⁹. As part of an equivalent buffering there are considered a number of carboxylic (acetic^{10,11}), hydroxycarboxylic (lactic¹², tartaric¹³, citric^{8,14}, malic⁹), amino (aminoacetic¹⁵) and dicarboxylic (succinic^{9,16}, glutaric^{9,13}, adipic⁹) acids. For various mixtures a range of buffering is generally within ± 1 pK. These carboxylic acids have a pK value of about 4 and are effective buffers in the range from 3 to 5. It is void the formation of nickel hydroxide.

Application of CEC in some cases allows to provide new properties of the surface: the coatings increase the mechanical strength, improve corrosion resistance, wear resistance, heat resistance^{5,17,18}. An important parameter in this case is the selection of the number and size of the dispersed phase and the conditions of electrolysis.

As materials of the dispersed phase in the electrodeposition of CEC are used carbon-containing components: ultrafine diamonds¹⁷, fullerene¹⁸, as well as numerous oxides, carbides and borides. Fullerene introduction makes surface smoother, improves corrosion properties and reduces the friction coefficient¹⁸. However, the extensive use of lightweight fullerenes is often hampered by their almost complete incompatibility with water and aqueous suspensions¹⁹.

Thus, the main directions of improving the process of nickel electrodeposition are finding alternative to boric acid buffer additives, lowering the operating temperature of the electrolyte in order to save electricity²⁰, the development of CEC on base of nickel plating.

This paper presents the results of studies on the structure and properties of nickel and nickel composite coatings electrodeposited from low-temperature sulphate-chloride-isobutyrate electrolytes.

2. Experimental

The object of the study was the electrolyte of the following composition, $\text{g}\cdot\text{dm}^{-3}$: No. 1 – $\text{NiSO}_4\cdot 7\text{H}_2\text{O}$ 100; $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$ 20, isobutyric acid ($(\text{CH}_3)_2\text{CHCOOH}$) 16; No. 2 – $\text{NiSO}_4\cdot 7\text{H}_2\text{O}$ 210; $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$ 35, $(\text{CH}_3)_2\text{CHCOOH}$ 32; No. 3 – $\text{NiSO}_4\cdot 7\text{H}_2\text{O}$ 220; $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$ 40, $(\text{CH}_3)_2\text{CHCOOH}$ 48. All electrolytes included glycerin 0,60 – 0,65 $\text{g}\cdot\text{dm}^{-3}$, pH = 2 – 4; $t = 20 - 25^\circ\text{C}$. As dispersed phase was used fullereneol $\text{C}_{60}(\text{OH})_{24\pm 7}\text{O}_{1\pm 3}$ of Fullereneol-d grade («Innovations of Leningrad institutes and companies») at a concentration of $2\cdot 10^{-3}$ to $2\cdot 10^{-4}$ g/dm^3 . As fullereneol is water soluble, so stirring was not necessary.

For the preparation of solutions and electrolytes were used reagents of p.a. purity grade.

Cathodic current efficiency (CE) of nickel was determined gravimetrically. Coatings were prepared in galvanostatic mode with a stabilized power supply B5-47. The study of electrochemical processes was performed in a conventional three-electrode cell in the potentiostatic mode using Potentiostat PI-50-1.1 supplied with the programmer PR-8. Pre-treatment of the steel comprises the steps of chemical degreasing (Na_3PO_4 , Na_2CO_3 , NaOH) and activation (H_2SO_4) with intermittent washing. Buffering properties were determined by potentiometric titration. Determination of the scattering power is conducted in accordance with GOST 9.309-86 in Moller cell. The morphology of freshly precipitated coatings was evaluated on the basis of SEM micrographs taken with a scanning electron microscope JEOL JSM- 5610 LV. Microhardness was determined by the PMT-3 with a thickness of coatings 20 microns and a load of 100 g.

3. Results and discussion

Comparison of polarization curves which were obtained from nickel electrolyte with different content of isobutyric acid (Fig. 1) shows that the cathodic polarization decreases by adding acid. It can be associated with an increasing in buffering in solution. It is known that resistance of electrolyte to changing of pH during electrolysis is a critical parameter for deposition of metal without inclusion of hydroxide basic salts or hydrogen incorporation. By

potentiometric titration it was found that increasing of isobutyric acid concentration from 32 to 48 g dm⁻³ considerably increases buffer capacity of electrolyte and allow electrodepositing coatings in a longer period of time (Fig. 2).

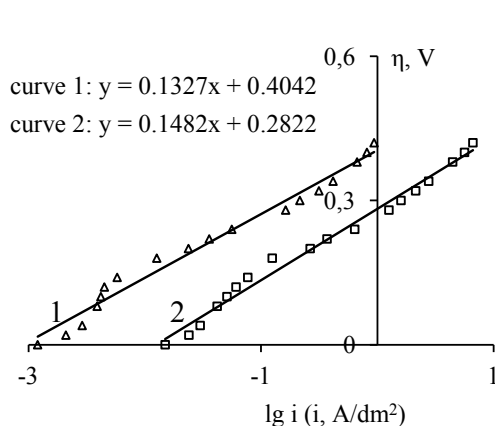


Fig. 1. Cathodic polarization curves characterizing the behavior of the steel electrode in an electrolyte: 1 - No. 1, 2 - No. 2

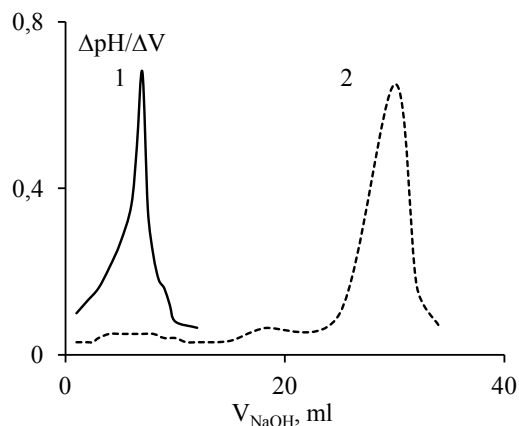


Fig. 2. The integral curves of potentiometric titration of nickel plating electrolyte: 1 - No. 2, 2 - No. 3

Coatings of all the compositions are light gray with little luster. In the diluted composition (No. 1) the current efficiency reaches 93 % at a current density of 1 A/dm², whereas in more concentrated compositions (No. 2, No. 3) the current efficiency does not exceed 75 % (Fig. 3). At pH values more than 4.5 A/dm² it is observed black edges of the samples.

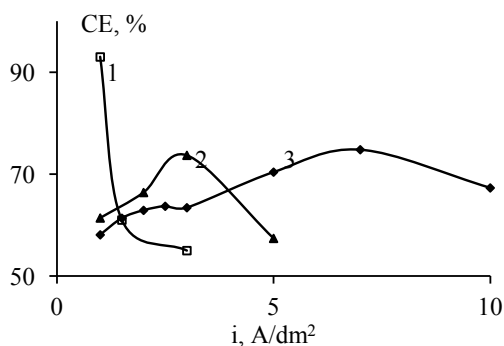


Fig. 3. The dependence of current efficiency on the current density in the nickel-plating electrolyte: 1 – No. 1; 2 – No. 2; 3 – No. 3

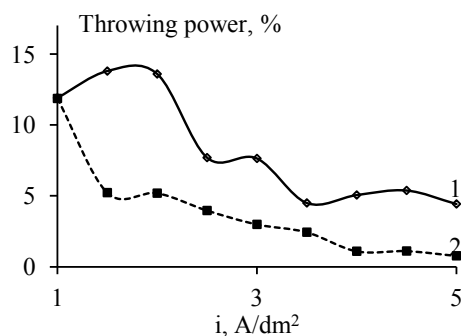


Fig. 4. Dependence of the throwing power of current and metal on the current density in the nickel electrolyte No. 3 (1 – throwing power by current, 2 – throwing power by metal)

It is hard to obtain roughness and uniform nickel coatings on complicated detail because of low value of throwing power in nickel plating electrolytes. It is investigated that meaning of throwing power of electrolytes with addition of isobutyric acid by current and metal (Fig. 4) with increasing current density until 5 A/dm² is reduced to 3-8 %, therefore, it is advisable to use such electrolyte at a low current density of 1–1.5 A/dm².

SEM micrographs showing surface morphologies of pure nickel and nickel composite coatings are presented in Fig. 5.

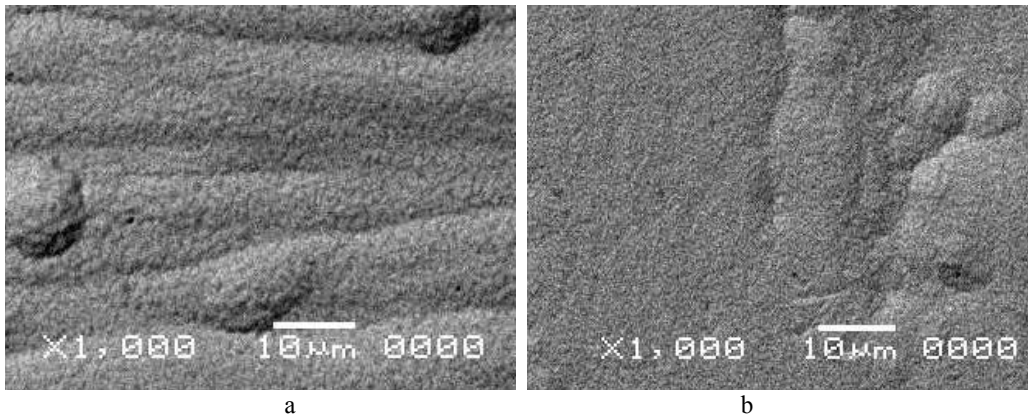


Fig. 5. (a) Nickel coatings photomicrographs obtained from electrolyte No. 3 at pH 2.5 and $i = 1.5 \text{ A/dm}^2$; (b) 0.002 g/dm^3 fullereneol

Nickel coating microstructure (Fig. 5 a) has smooth topography. It is formed grain oval with clearly defined edges and visible grain size of 0.5-1 microns. Introduction of fullereneol to electrolyte provides a coating with a smooth terrain (Fig. 5, b). Milling of nickel coating modifies the properties of the resulting composite material.

The variation of microhardness Ni-fullereneol composite coatings as a function of fullereneol nanoparticle content in the electrolytic bath is presented in Fig. 6. The microhardness of the nickel coatings produced from electrolytes is in the range of 170-220 HV. Fullereneol adding allows to make structure of coating harder in 1,5 times. The hardness of composite coatings is mainly determined by the microstructure of matrix. Since all the coatings have smaller grain (Fig. 5), the increasing hardness of the Ni-fullereneol composite coatings with increasing fullereneol content in the electrolyte bath seem to be primarily due to enhanced dispersion strengthening effect⁵.

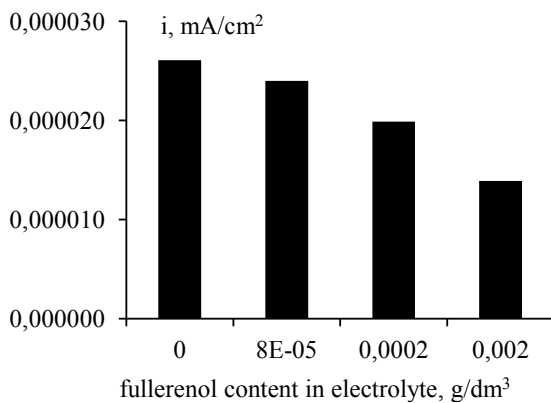


Fig. 6. Dependence of fullereneol amount on the corrosion current in the electrolyte No. 3

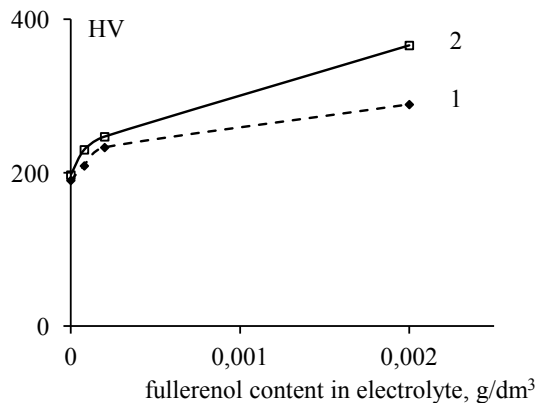


Fig. 7. Dependence of microhardness on the current density in the electrolyte 1 - No. 2, 2 - No. 3

The introduction of fullereneol increases the corrosion resistance of the composite coating (Fig. 7). The corrosion behavior of composite nickel-fullereneol coatings depend remarkably upon the interconnection of fullereneol particles. We interpret the change of corrosion resistance with the change of structural properties of the electrodeposited coatings.

4. Conclusions

It is developed a composition which has high buffer capacity and can be an alternative to Watts's electrolyte without addition of boric acid. Obtained data show that the low temperature electrolyte with isobutyric acid is forming quality coatings with microhardness 200 HV. It is shown that the introduction fullerene into the electrolyte leads to milling of coatings, roughness of surface, allows to make structure of coating harder in 1,5 times and increases the corrosion resistance in chloride atmosphere.

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