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BRIEF COMMUNICATIONS

Electrodeposition and Properties of Composite Coatings Based on Nickel

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Abstract—Composite electrochemical platings based on nickel and containing graphite bisulfate as a dispersed phase were obtained. Their electrodeposition and tribological characteristics were studied and compared with those of electrolytic nickel deposits free from a disperse phase.

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Composite electrochemical platings (CEPs) have received acceptance owing to the fact that they improve operation properties of metal surfaces (hardness, wear hardness, and corrosion resistance). Unlike classical electrochemical platings, CEPs are obtained with the use of electrolytes-suspensions containing dispersion particles of various sizes and types [1–4].

The efficiency of CEP application in many respects is defined by the nature of a dispersed phase. Graphite and its derivatives are of interest as dispersed materials for composite coatings [4–7]. Graphite has a layered structure. Interstitial graphite compounds (IGC) are obtained by penetration of various molecules or ions in the interlayer space of their crystal lattice [8]. The reaction of graphite with sulfuric acid in the presence of strong oxidizing agents yields graphite bisulfate with a composition described by the formula $C_{24}^+(HSO_4)-2H_2SO_4$ [9].

There are chemical and electrochemical methods of the IGC synthesis [10]. The chemical method is technologically simple, but the resulting product is inhomogeneous. The electrochemical synthesis allows obtaining high-purity IGC with a specified composition.

The aim of the present work was to obtain CEPs on the basis of nickel with graphite bisulfate and to study the process of their precipitation and tribological properties of forming coatings. In the work we used graphite bisulfate synthesized by the electrochemical method.

EXPERIMENTAL

Composite electrochemical platings based on nickel-graphite bisulfate were precipitated from an electrolyte of the composition (g l^{-1}): NiSO₄·7H₂O, 220; NiCl₂·6H₂O, 40; CH₃COONa, 30; and graphite bisulfate 10. Particle sizes of the disperse phase were up to 10 µm.

Graphite bisulfate was synthesized by the anodic oxidation of dispersed powder graphite GSM-1 in the potentiostat regime at room temperature. Dispersed graphite served as a working electrode, and 12Kh18N10T steel was a counter electrode. A 5.32 M solution of H_2SO_4 (special-purity grade) served as an electrolyte. Graphite particles were tightened to a current lead by a sliding piston, which moved during the interstitial reaction, increasing the volume of a suspension electrode. It allowed us to hold a constant pressure of tightening graphite during the whole process.

Electrodeposition of CEPs was carried out on a steel base (steel 45) at room temperature with permanent stirring of a solution. Pure nickel was deposited from the electrolyte of the above composition without adding graphite bisulfate. Adhesion of the resulting coatings was estimated by applying a net of scores (GOST 9.302-79).

Sliding friction coefficient f of electrodeposited coatings was determined according to the scheme given in [11] and was calculated by the formula

$$f = \frac{F_{\rm fr}}{P} = \tan \alpha,$$

where $F_{\rm fr}$ is force of sliding friction; *P*, force corresponding to the pressure which a counterbody put on a test surface.

A steel sample was used as a counterbody. Its weight in all experiments was 1 g.

Electrochemical measurements were carried out on a P-30S pulsing potentiostat. Potentials were set in relation to the saturated silver-chloride reference electrode and reduced to the hydrogen scale.

Potentiodynamic polarization curves of nickel precipitation show that the addition of a dispersed phase of graphite bisulfate to the nickel-plating electrolyte facilitates the cathode process (Fig. 1). In the presence of dispersion particles nickel is precipitated at less negative potentials. Currents of the CEP electrodeposition increase as compared to nickel coatings without a dispersed phase, which points to an increase in the cathode process rate.

Transfer of dispersion particles to the cathode can be carried out not only due to intermixing of the electrolyte, but also proceed through a stage of adsorption of deposited metal cations on their surface [2]. Having received such charge, particles are transferred to the cathode and there are overgrown with uncharged metal. The ions adsorbed on particles participate in the bridging binding of a dispersed phase with a cathode surface. This binding attenuates a disjoining pressure of a liquid interlayer between a particle and the cathode, thus strengthening adhesion [12]. Dispersion particles play a role of crys-



Fig. 1. Potentiodynamic polarization curves of nickel precipitation obtained in an electrolyte of nickel-plating (1) without addition and (2) with addition of graphite bisulfate. (*i*) current density, A cm⁻², (*E*) potential, V.

tallization centers on the cathode surface, defining the further growth of the electrolytic deposit.

When nickel coatings are precipitated in the galvanostatic mode, potentials are shifted to the positive side as graphite bisulfate is added in the nickel-plating electrolyte (Fig. 2), which confirms the data of potentiodynamic experiments. The polarization capacity C was calculated from the data of galvanostatic measurings by the expression

$$C = \frac{i}{\partial E/\partial t},$$

where *i* is current density, A cm⁻²; *E*, potential, V; and *t*, time, s.

Values of polarization capacity decrease on passing from nickel coatings to CEP nickel-graphite bisulfate (see the table). It is attributable to the fact that the size of a double electrical layer increases when dispersion particles penetrate in it. Similar changes should affect the state and properties of the surface of the studied coatings.

The sliding friction coefficient f is one of the most important characteristics of metal surfaces. Values of f for nickel-graphite bisulfate CEP twice decrease compared to nickel electroplating (see the table). It is connected with the fact that graphite bisulfate particles penetrating into coatings on the electrodeposition fulfill a function of a dry lubrication (the experiment was carried out under dry friction conditions). Decrease in the friction coefficient of the studied composite coatings, as compared with pure nickel, is obviously defined by a layer structure of the



Fig. 2. Galvanostatic curves of nickel precipitation (1) without addition and (2) with addition of graphite bisulfate at $i_c = 4$ A dm⁻². (*E*) potential, V; (*t*) time, s.

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<i>i</i> , A dm ⁻²	$C imes 10^3$, Φ cm ⁻²		f	
	nickel	CEP	nickel	CEP
2	22.3	12.8	_	_
3	40.1	16.2	_	_
4	52.9	22.3	_	_
5	67.4	27.8	_	_
6	79.7	33.4	0.38	0.16
7	92.8	38.0	0.34	0.15
8	107.3	41.8	0.34	0.14
9	119.9	47.0	0.33	0.14
10	133.2	52.0	0.30	0.13

Polarization capacity and coefficients of sliding friction of nickel coatings at various cathode current density

dispersed phase.

Coefficients of sliding friction of composite coatings nickel-graphite bisulfate also decrease as a coating thickness increases ($i = 10 \text{ A dm}^{-2}$):

Coating thickness, µm	10	20	30	40
Friction coefficient	0.24	0.20	0.17	0.13

This phenomenon seems to be connected with increasing insertions of dispersion particles in a coating during its growth in thickness, and also with their more uniform distribution over the electrodeposit surface.

CONCLUSION

It has been found that the addition of a dispersed phase of graphite bisulfate to the nickel-plating electrolyte facilitates the electrodeposition process and promotes formation of composite coatings. Penetrating in nickel electrodeposits, graphite bisulfate renders defining effect on their tribological properties.

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