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FUNCTIONAL COATINGS AND SURFACE TREATMENT

Structure and Properties of Composite Nickel Coatings Deposited by Means of Programmable Pulsed Current under Laser Irradiation

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Abstract—A method for the formation of composite electrolytic coatings in the process of electrodeposition in an electrolyte with ultradisperse diamond (UDD) particles in the programmable pulsed current regime under simultaneous laser irradiation has been developed. This method provides the layer-by-layer deposition of gradient nickel coatings 15–20 μm in thickness with a variable content of UDD particles along their depth. The amount of UDD particles is minimal (0.10–0.13 at %) in the layers deposited in the initial period of this process, whereas the concentration of UDD particles in the layers formed at the later process stages grows to 0.19–0.26 at %. The concentration gradient of UDD particles along the depth improves the adhesion properties and wear resistance of coatings and provides a 16% decrease in the consumption of UDD particles with a local increase in the concentration of UDD particles in a coating to 0.32 at %.

Keywords: programmable pulsed current, laser-stimulated electrodeposition, composite nickel coatings, ultradisperse diamond particles, structure, mechanical properties

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INTRODUCTION

In recent years, a great amount of attention has been paid to the improvement of electrolytic metal coatings by mixing the aqueous solutions of electrolytes with different disperse particles, which intrude into a coating and thereby increase its physicochemical properties [1–7]. The studies are aimed both at the search for ways to intensity the coprecipitation of metals and the dispersion of particles and at the stabilization of these processes to form coatings with specified properties. Among them are the studies of the effect produced by reversed and asymmetrical current and the superimposition of pulsed current, ultrasound, a magnetic field, and external laser radiation [2, 8–19]. A complex solution for the problem of improving the functional properties of the surface seems to be the modification of the metallic matrix with ultradisperse diamond (UDD) particles to form nickel-based composite electrolytic coatings (CECs) in unsteady-state electrolysis regimes under laser irradiation in the process of electrodeposition.

The widespread application of nickel-based CECs [3, 5, 8, 9–19] is due to both the physicochemical properties of electrolytic nickel, such as its high hardness and wear resistance and ability to protect the basic metal from corrosion and provide its highly decorative finish, and the easy coprecipitation with most disperse particles of different nature.

EXPERIMENTAL

The electrodeposition of composite coatings was performed onto a low-carbon steel substrate at pH of 5 and a temperature of 293–298 K from the sulfate nickel-plating electrolyte with the following composition (g/L): $Ni_2SO_4 \cdot 7H_2O$, 300; H_3BO_3, 30; $Na_2SO_4 \cdot 10H_2O$, 50. The composite nickel coatings were deposited using programmable pulsed current with equal unipolar current pulse burst times t_b = 36 min, frequency f = 50 Hz, average current density j_{av} = 100 A/m^2, and the following sequential burst-to-burst change in the pulse ratio Q: 2 for burst I, 12 for burst II, 25 for burst III, 38 for burst IV, and 50 for burst V. The pulse duration time t_p was varied from 10 to 0.4 ms at a constant period T = 20 ms. The concentration of UDD particles (C_{UDD}) in the aqueous electrolyte solution was 2 g/L. To intensify the process, the electrodeposition of composite electrolytic coatings was performed on a laser electrolytic setup (Fig. 1) constructed on the basis of a gas-discharge CO_2 laser with a power of 25 W (l = 10.6 μm) in the continuous generation regime. The temperature of the aqueous elec-

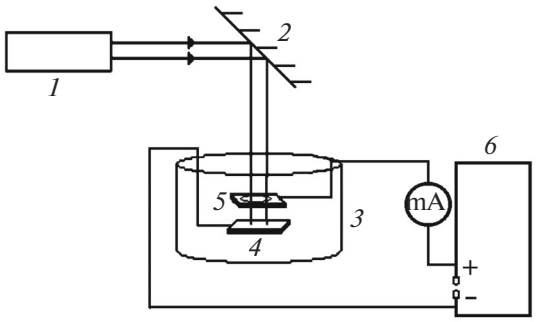

Fig. 1. Diagram of experimental setup: (*1*) laser radiation source (CO_2 laser), (*2*) deflecting mirror, (*3*) electrolytic cell, (*4*) cathode, (*5*) anode, (*6*) power supply.

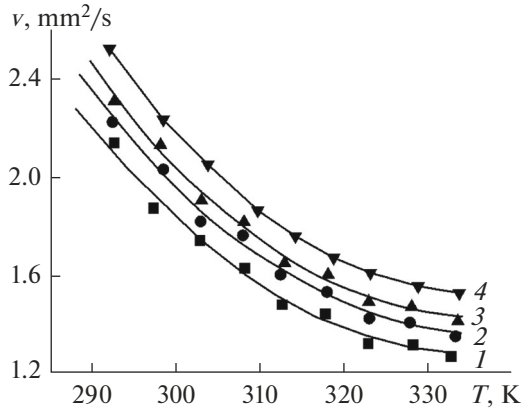

Fig. 2. Kinematic viscosity of the aqueous nickel-plating electrolyte solution versus temperature at a disperse phase concentration in the electrolyte of (*1*) 0, (*2*), 2, (*3*) 10, and (*4*) 15 g/L.

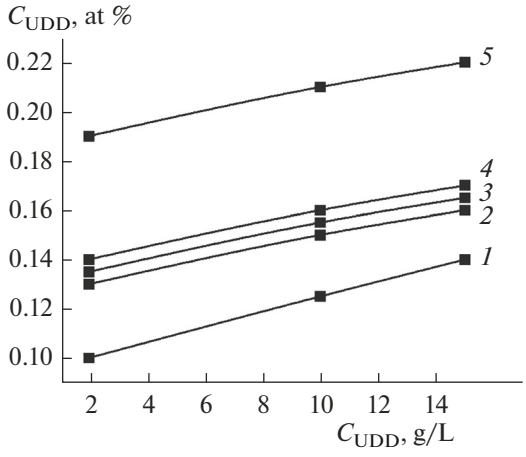

Fig. 3. Amount of ultradisperse diamond (UDD) particles in the composite material (at %) versus disperse phase concentration in the electrolyte solution (g/L): (*1*) direct current, (*2*)–(*5*) pulsed current (j_{av} = 100 A/m^2, f = 50 Hz) at a pulse ratio Q = (*2*) 2, (*3*) 12, (*4*) 25, and (*5*) 50.

trolyte solution in the near-cathode region of irradiation grew to 351 K.

The microhardness of a coating was measured on a PMT-3 microhardness meter at an indentor load of 0.196 N. The wear tests of specimens were carried out on a friction machine with the reciprocal motion of specimens with a frequency of 0.5 s^{-1} and an amplitude of 0.15 m under the conditions of dry friction against steel 45 (GOST (State Standard) 1050-74) at a load of 1.7 N (GOST 23.204-78). The friction path was parallel to the substrate. The wear resistance was estimated from the coating mass loss.

The X-ray spectral microanalysis of specimens was performed on a JSM-64901LV scanning electron microscope. The phase composition of films was determined on a DRON-2.0 X-ray diffractometer in monochromatized MoK_α radiation. Polarization curves were recorded in a three-electrode electrolytic cell in the potentiodynamic regime on a P-5827M potentiostat at a potential sweep rate of 10 mV/s. The working electrode (cathode) was a copper plate, the reference electrode was a silver/silver chloride electrode, and the auxiliary electrode was a platinum electrode. The aqueous electrolyte solution was stirred with a magnetic agitator to retain UDD particles in the suspended state in the electrolyte solution volume and prevent their sedimentation on the bottom of the electrolytic cell.

The viscosity of the aqueous electrolyte solution was determined on a VPZh-4 capillary glass viscometer with the diameter of the internal capillary of 1.12 mm.

RESULTS AND DISCUSSION

To determine the optimal regimes for the electrodeposition of composite coatings with increased hardness and wear resistance, the effect of the concentration of UDD particles in the electrolyte and the temperature of the aqueous electrolyte solution on its kinematic viscosity ν (Fig. 2) and the content of UDD particles in the composite (Fig. 3) was studied.

It follows from the analysis of the results that the kinematic viscosity of the electrolyte solution grows from 2.14 × 10^{-6} to 2.49 × 10^{-6} m^2/s with an increase in the concentration of UDD particles in the aqueous electrolyte solution from 0 to 15 g/L at its constant temperature T = 293 K, thus making more probable the intrusion of particles with a larger diameter into the coating. When the process temperature is decreased, the probability of the intrusion of coarser particles into the coating also grows, especially at high current densities. When the temperature of the aqueous electrolyte solution increases from 293 to 333 K, its viscosity decreases by 1.6 times, so coarser particles precipitate in the lower layers of the electrolyte solution, and their amount in the near-cathode space

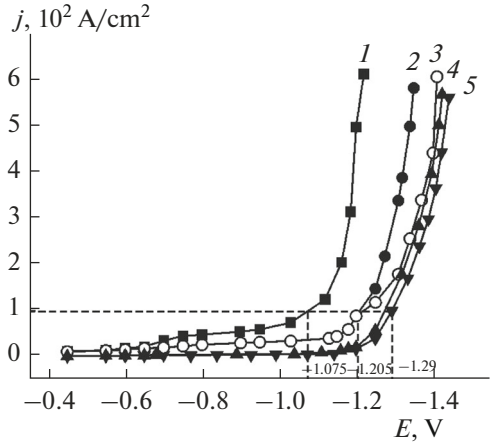

Fig. 4. Cathodic polarization curves taken in the nickel-plating sulfate electrolyte (*1*) without UDD, (*2*) with UDD, (*3*) with UDD and mechanical mixing (44.2 rps), (*4*) with UDD and laser irradiation, and (*5*) with UDD, laser irradiation, and mechanical mixing (44.2 rps).

abruptly decreases, and the particles of a finer fraction intrude into the coating.

The cathode polarization curves at different concentrations of UDD particles in the aqueous nickel-plating electrolyte solution are shown in Fig. 4. As can be seen, the presence of disperse particles in the aqueous electrolyte solution leads to the shift of the cathode potential into the electronegative region. Thus, the shift of the cathode potential into the electronegative region is 130 mV at an increase in the concentration of UDD particles from 0 to 2 g/L and 215 mV in the laser-stimulated electrodeposition regime, thus indicating an increase in the charge-transfer resistance.

An increase in the cathode overpotential in the laser-stimulated electrodeposition regime can be explained by a growth in the flow of metal ions in the direction of laser radiation and their adsorption on the surface of UDD particles. The formed electropositively charged complex aggregates, whose size may exceed 100 nm, move toward the cathode surface and block it, thus leading to a decrease in the cathode active surface area, i.e., its passivation.

To investigate the effect of disperse phase particles and laser radiation on the structure of composite coatings, X-ray diffraction studies of coating specimens were conducted (Fig. 5). No traces of diamond in the

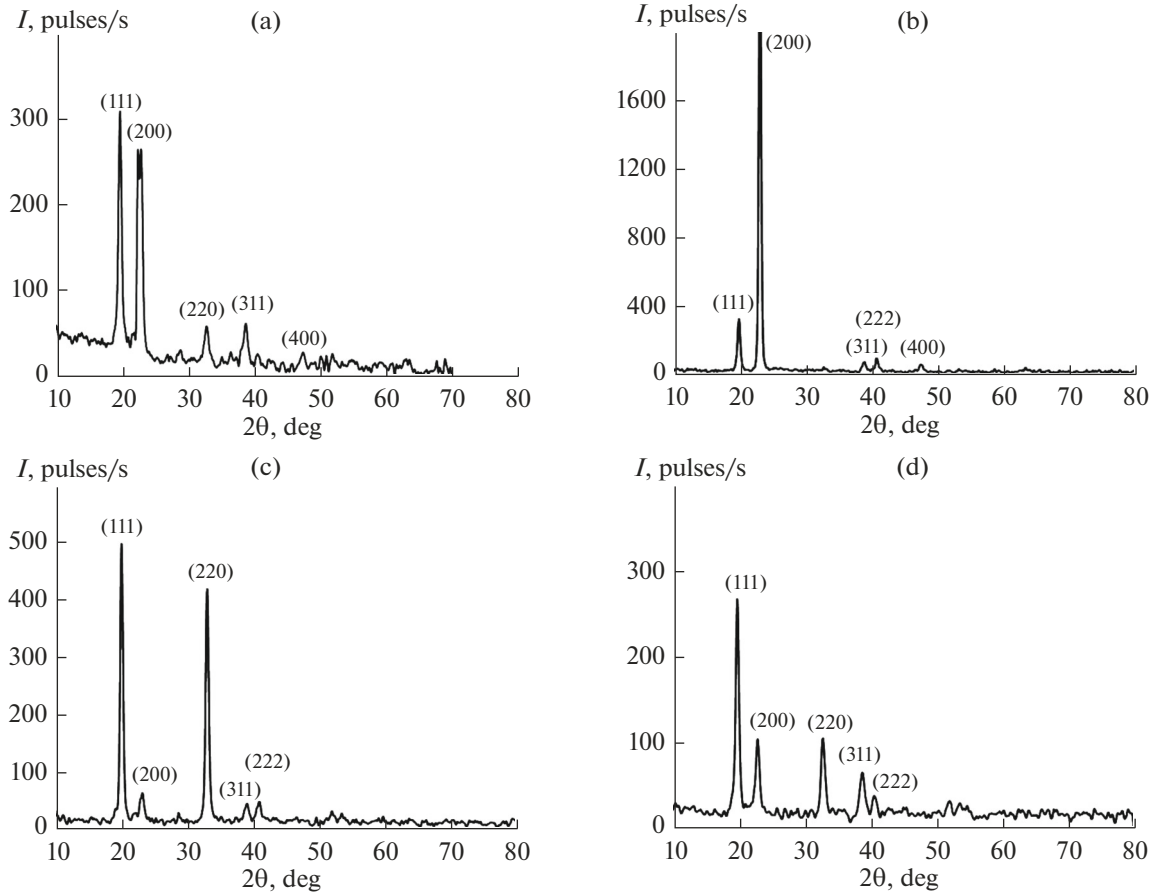

Fig. 5. X-ray diffraction pattern of the composite electrolytic coatings formed by means of laser-stimulated deposition: (a) direct current ($j = 100$ A/m^2); (b, c) pulsed current ($j_{av} = 100$ A/m^2, $f = 50$ Hz) with a pulse ratio $Q =$ (b) 2 and (c) 50; (d) programmable pulsed current ($j_{av} = 100$ A/m^2, $f = 50$ Hz, $Q = 2$–50).

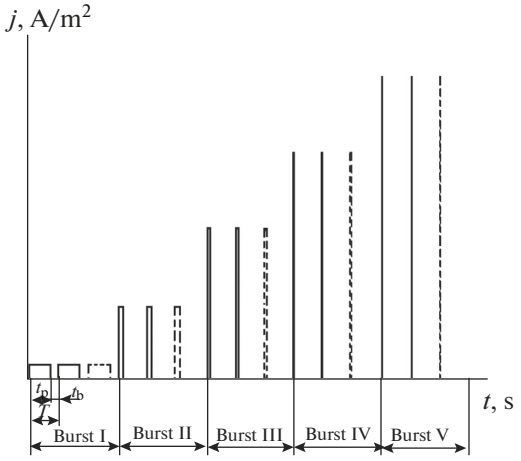

Fig. 6. Diagram of programmable pulsed current.

coatings are revealed in the presented X-ray diffraction patterns, which seems to be due to the fact that the diffraction maxima corresponding to the diamond phase of carbon are superimposed onto the lines corresponding to the crystalline phase of electrolytic nickel, and, in addition, the content of UDD particles in the nickel coating is less than 1%.

When UDD particles are used as a disperse phase, the type of crystal lattice of the coating material remains unchanged, but the predominant crystal growth directions change.

The composite coatings deposited by means of pulsed current with average density j_{av} = 100 A/m^2, pulse repetition frequency f = 50 Hz, and pulse ratio Q = 2 have a pronounced [100] texture (Fig. 5b). In the X-ray diffraction patterns of the specimens deposited by means of pulsed current with current pulse ratio Q = 50 (Fig. 5c) and programmable pulsed current (Fig. 5d), the redistribution of intensities between the diffraction peaks corresponding to the reflections from the (111) and (220) planes is observed, thus indicating the formation of composite electrolytic nickel with a [110]-type axial structure in the coating.

On the basis of the results obtained, a program of pulsed unipolar current (Fig. 6) for the deposition of composite nickel coatings 15–20 μm in thickness with a gradient content of UDD particles was developed.

The results of the X-ray spectral microanalysis of the elemental surface composition and the metallographic structural studies of cross sections have demonstrated that the composite nickel coating microlayers with a minimum content of UDD particles in the metallic matrix (0.10–0.13 at %) are deposited in the repetition time of bursts I–II of current

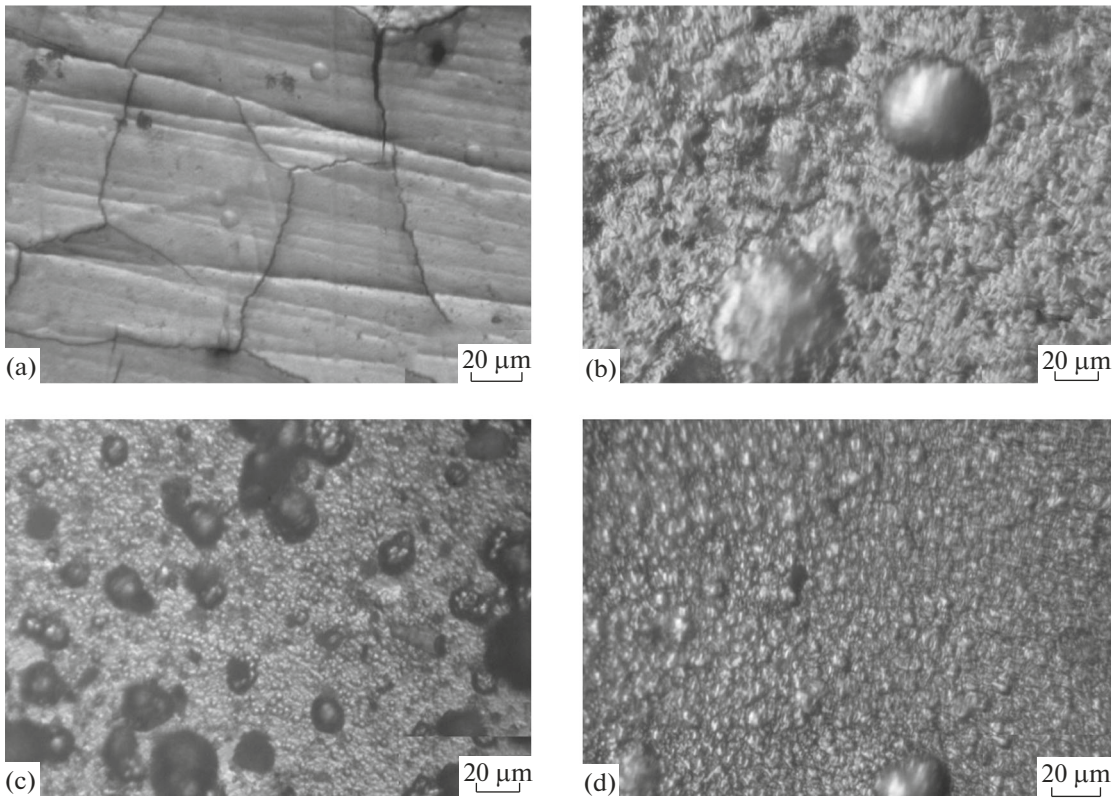

Fig. 7. Surface morphology of the composite electrolytic coatings: (a) direct current (j = 100 A/m^2); (b, c) pulsed current (j_{av} = 100 A/m^2, f = 50 Hz) at a pulse ratio Q = (b) 2 and (c) 50; (d) programmable pulsed current (j_{av} = 100 A/m^2, f = 50 Hz, Q = 2–50).

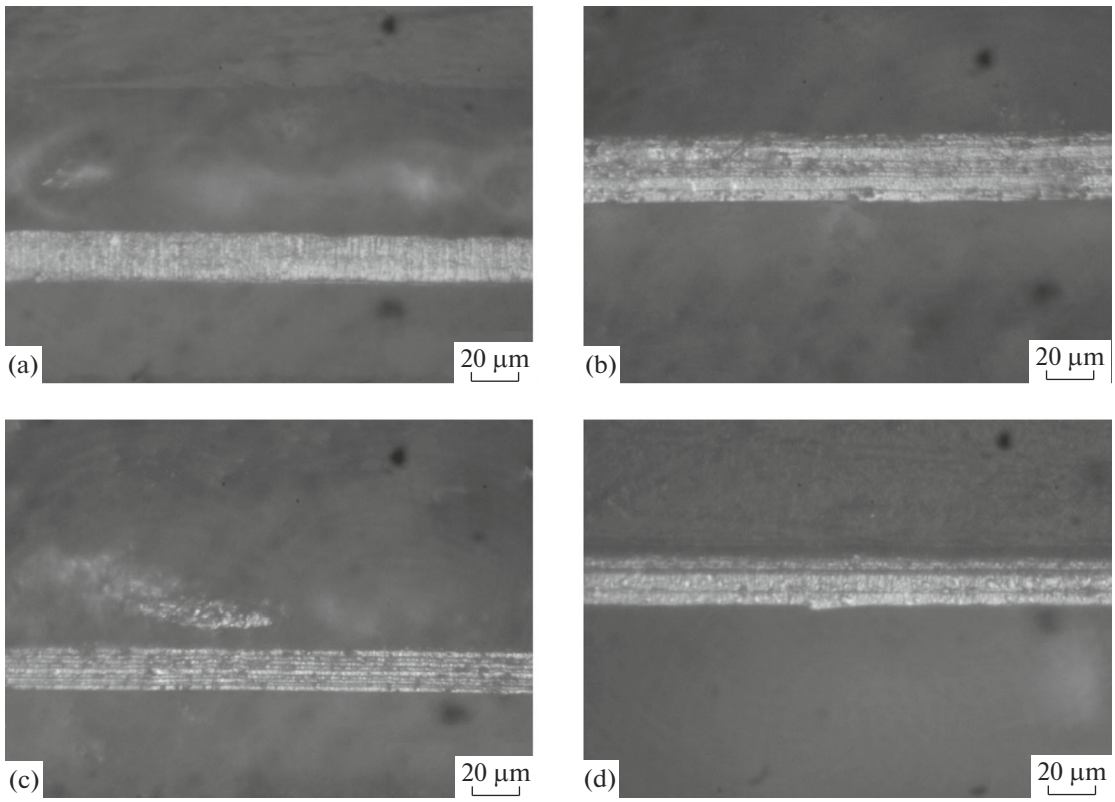

Fig. 8. Structure of the composite electrolytic coatings in the cross section: (a) direct current (j = 100 A/m^2); (b, c) pulsed current (j_{av} = 100 A/m^2, f = 50 Hz) at a pulse ratio Q = (b) 2 and (c) 50; (d) programmable pulsed current (j_{av} = 100 A/m^2, f = 50 Hz, Q = 2–50).

pulses with a duration time of 10–1.7 ms and a density of 200–1200 A/m^2, thus increasing the metal–substrate adhesion strength. The surface morphology of the composite electrolytic coatings deposited in such regimes (Fig. 7b) is characterized by the absence of microcracks typical of pure electrolytic nickel coatings (Fig. 7a).

A columnar growth structure is formed in the cross section of the first coating layers (Fig. 8d) deposited in the repetition time of bursts I–II of current pulses as in the laser-stimulated regime of deposition at a constant current (Fig. 8b).

A discrete character of pulsed current, an increase in the pulse ratio, and the effect of laser radiation promote the deposition of composite nickel coating microlayers with a maximum content of UDD particles (0.26–0.32 at %) in the repetition time of bursts III–V of current pulses with a duration time of 0.8–0.4 ms and a density of 2500–5000 A/m^2. The more intense penetration of disperse phase particles into the formed coating is due, first, to high instantaneous densities of current in pulses (j_{max} = 5000 A/m^2) and, consequently, the reduction of nickel ions at higher cathode overpotentials (~1.00 V) and, second, to an increase in the velocity of motion of metal ions in the direction of laser radiation and their adsorption on the surface of UDD particles, which favors electrophoretic codeposition.

It should be noted that the inclusion of UDD particles in the coating complicates the surface diffusion of metal adatoms and hampers the growth of crystalline phase nuclei, being a reason for the formation of a finer crystalline structure of coatings (Fig. 7d).

The study of side micrographic sections has shown the formation of microlayers with a sharply pronounced layered structure of growth in a cross section (Fig. 8d) along with a columnar growth structure due to the passivating effect of UDD particles on the surface of a formed coating.

An increase in the content of UDD particles in the coating formed in the zone of laser irradiation leads to the growth of the hardness and wear resistance of the composite electrolytic coating. Measurements have shown that the microhardness of the coatings deposited by means of programmable pulsed current grows from 2000–2500 to 3500–4200 MPa, whereas their wear decreases to 2.5%. The use of laser irradiation for the electrodeposition of composite nickel coatings by means of programmable pulsed current enables the local concentration of UDD particles in a coating to grow from 0.19 to 0.32 at %, thus leading to an increase in the microhardness to 6400–6500 MPa and a

decrease in the wear resistance of coatings to 1.5% in comparison with the composite electrolytic coatings formed without laser stimulation of the deposition process.

CONCLUSIONS

It has been demonstrated that the use of programmable pulsed current with simultaneous laser irradiation in the process of electrodeposition enables the layer-by-layer formation of gradient composite nickel coatings 15–20 μm thick, in which the content of UDD particles grows in each subsequent layer.

The developed methods for the deposition of gradient composite coatings, first, provides the improvement of the adhesion properties and wear resistance of coatings; second, decreases the consumption of added UDD particles; and, third, increases the local concentration of UDD particles in a coating.

CONFLICT OF INTERESTS

The authors declare that they have no conflict of interest.

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