

PACS numbers: 62.23.Pq, 68.37.Hk, 68.55.J-, 81.05.uj, 81.15.Pq, 81.16.Mk, 81.65.Kn

## **Laser-Assisted Electrodeposition of Composite Carbon-Containing Nickel Coatings**

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The paper presents the study of the structure, protective and mechanical properties of nickel composite coatings modified with ultradispersed diamonds and electrodeposited under conditions of external stimulation by laser radiation. An analysis of the cathodic polarization curves shows that the presence of dispersed particles with a concentration of 2–15 g/l in the aqueous electrolyte solution leads to a shift in the cathodic potential to the electronegative region by 108–340 mV, respectively, that indicates an increase in charge-transfer resistance. Nickel composite coatings obtained by laser-assisted electrodeposition are characterized by a higher content of ultradispersed diamond particles in the coating (4.35–5.10 wt.%) as compared to the mode of deposition without laser irradiation (2.24–3.15 wt.%). In this case, the proportion of particles of smaller size ( $\cong 0.25$ – $1 \mu\text{m}$ ) increases in the coatings. The more intense penetration of dispersed-phase particles into the emerging coating during the laser stimulation of the electrodeposition process is due to the presence of a temperature gradient, which provides an additional supply of metal ions in the irradiation region. Increased concentration of the dispersed phase in nickel composite coatings promotes formation of a finer crystalline coating structure, enhanced hardness, corrosion resistance, and wear resistance of the coatings.

У даній роботі представлено дослідження структури, захисних і механічних властивостей ніклевих композиційних покриттів, модифікованих ультрадисперсними діамантами, електроосаджених в умовах зовнішнього впливу лазерним випроміненням. Аналіза катодних поляризаційних кривих показала, що наявність у водному розчині електроліту дисперсних частинок із концентрацією у 2–15 г/л приводить до зміщення катодного потенціалу в електронегативну область на 108–340 мВ відповідно, що вказує на збільшення опору передачі заряду. Нікеле-

ві композитні покриття, одержані методом лазерного електроосадження, характеризуються вищим вмістом ультрадисперсних діамантових частинок у покритті (4,35–5,10 мас.%) порівняно зі способом осадження без лазерного опромінювання (2,24–3,15 мас.%). Водночас у покриттях збільшується частка частинок меншого розміру ( $\cong 0,25\text{--}1\text{ мкм}$ ). Більш інтенсивне проникнення частинок дисперсної фази у формівне покриття під час лазерної стимуляції процесу електроосадження зумовлено наявністю температурного градієнту, який забезпечує додаткове надходження йонів металу в область опромінювання. Підвищена концентрація дисперсної фази в ніклевих композиційних покриттях сприяє формуванню більш дрібнокристалічної структури покриття, підвищенню твердості, корозійної стійкості та зносостійкості покриттів.

**Key words:** ultradispersed diamond particles, composite nickel coatings, laser-assisted electrodeposition, structure, mechanical and protective properties.

**Ключові слова:** ультрадисперсні діамантові частинки, композиційні ніклеві покриття, лазерностимульоване електроосадження, структура, механічні та захисні властивості.

*(Received 1 July, 2023)*

## 1. INTRODUCTION

There are many ways to harden the surface of parts in order to increase the service life of mechanisms, parts and friction pairs, among them: thermochemical treatment or various methods of coating. One of the known ways to improve mechanical properties of the surface is its electrolytic modification by deposition of metal films with the required operational parameters, the most important of which are hardness and wear resistance. However, metal and alloy films, in terms of their physicochemical properties, often do not meet the increased requirements of modern technology. The solution to the surface hardening problem is the modification of the metal matrix with particles of the dispersed phase to obtain composite electrolytic coatings (CEC).

It is known that the introduction of solid dispersed particles (ultradispersed diamonds (UDD)) into electrolytic coatings increases their microhardness and wear resistance. The reasons for this are the reduction of crystallite sizes of the deposited metal and the presence of superhard particles in the coating [1–4]. The conducted literature analysis [5–10] showed that the methods of influencing the process of co-deposition of metal films with UDD include the use of ultrasonic or mechanical stirring of the electrolyte solution in the process of electrodeposition. Because of this activation of the electrodeposition process, solid dispersed particles incorporated into

the coating being formed, prevent the growth of the crystalline phase nuclei, which is the reason for the formation of a finer crystalline coating structure.

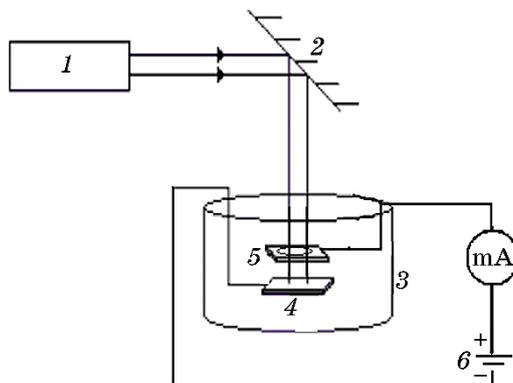
In this paper, we consider a laser-assisted method for the electrodeposition of composite nickel electrolytic coatings. The purpose of this work is to study the effect of laser radiation on the process of co-deposition of metal ions and ultradispersed diamond particles, structure, mechanical and protective properties of electrodeposited composite nickel coatings.

## 2. MATERIALS AND METHODS

Electrodeposition of composite coatings was carried out from sulphate nickel-plating electrolyte of the following composition:  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$  — 300 g/l,  $\text{H}_3\text{BO}_3$  — 30 g/l,  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  — 50 g/l at  $\text{pH} = 5$ . The concentration of UDD ( $C_{\text{UDD}}$ ) in the aqueous electrolyte solution was varied in the range from 2 g/l up to 15 g/l.

Due to the developed surface and the presence of a large number of functional groups, individual nanodiamond particles with an average particle size of 4–5 nm form strong primary aggregates, which, as a rule, act as indestructible parts of nanodiamond powders. UDD particles are prone to spontaneous aggregation among themselves into extremely strong aggregates (40–100 nm) with the subsequent formation of less strong secondary aggregates (up to 1–5  $\mu\text{m}$ ) [1–4].

Electrodeposition was carried out under external exposure to radiation from a  $\text{CO}_2$  gas-discharge laser generating in a continuous mode at a wavelength of 10.6  $\mu\text{m}$  at a laser-radiation power of 25 W (Fig. 1). The temperature of the aqueous electrolyte solution in the near-



**Fig. 1.** Scheme of the test installation: 1—emitting source ( $\text{CO}_2$ -laser); 2—rotary mirror; 3—electrolytic cell; 4—cathode; 5—anode; 6—power supply.

cathode irradiation region increased from 293 K to 351 K. For comparison, the coatings were also deposited using a direct current at a density of  $100 \text{ A/m}^2$ .

The microhardness of the coating was measured on a PMT-3 microhardness tester with an indenter load of 0.196 N. Wear tests of samples were conducted on the friction machine with reciprocating motion of samples with frequency of  $0.5 \text{ s}^{-1}$  and amplitude of 0.15 m in conditions of dry friction against steel under load of 1.7 N. The friction path was parallel to the substrate. Wear resistance was evaluated by weight loss of the coating. X-ray microanalysis was performed using a JSM-64901LV scanning electron microscope (Japan). X-ray phase analysis of the films was conducted on a DRON-2.0 diffractometer using scintillation detection of x-rays. Shooting to determine the phase composition of nickel films was carried out in monochromatized  $\text{CuK}_\alpha$  radiation.

The polarization dependences were recorded in the potentiodynamic mode on a P-5827M potentiostat at a potential sweep rate of 10 mV/s. The measurements were carried out in a three-electrode electrolytic cell. A copper plate was used as the working electrode (cathode). The reference electrode was a silver chloride electrode, and the auxiliary electrode was a platinum electrode.

The viscosity of the aqueous electrolyte solution was determined using a VPZh-4 capillary glass viscometer with an internal capillary diameter of 1.12 mm. A characteristic property of an aqueous nickel-plating electrolyte solution is low sedimentation resistance, leading to uneven distribution of nanodiamond particles in the metal matrix. In order to keep the UDD particles suspended in the electrolyte solution and to prevent settling of particles to the bottom of the electrolytic cell, the aqueous electrolyte solution was stirred with a magnetic stirrer before starting the electrodeposition process.

Accelerated corrosion tests consisted of immersing samples in a 3% sodium chloride solution. The corrosion rate was determined by the gravimetric method (by weight loss of the metal coating). External examination of the samples was carried out daily until the first signs of corrosion appeared and scored on a 10-point scale [11].

### 3. RESULTS AND DISCUSSION OF THEM

In order to determine the optimal modes of electrodeposition of composite coatings of increased hardness and wear resistance, we studied the effect of the concentration of UDD particles ( $C_{UDD}$ , g/L) in an aqueous electrolyte solution on the kinematic viscosity of the solution ( $\nu$ ,  $\text{mm}^2/\text{s}$ ) (Fig. 2).

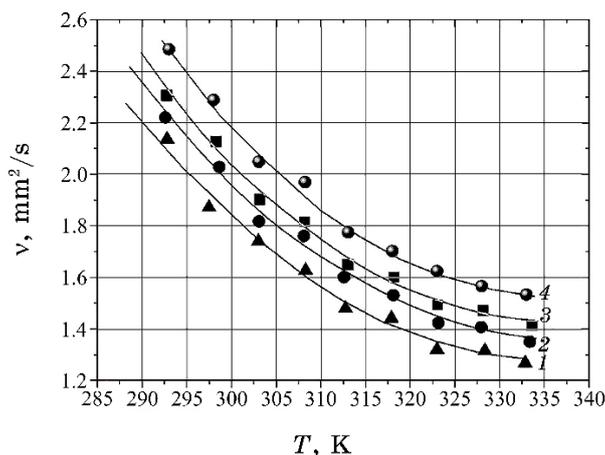


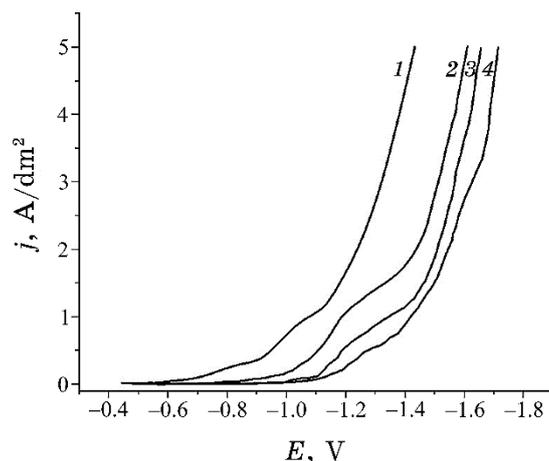
Fig. 2. Dependence of the kinematic viscosity of aqueous nickel-plating electrolyte solution on temperature and concentration of the dispersed phase in the electrolyte [g/l]: 1—0; 2—2; 3—10; 4—15.

From the analysis of the results obtained, it follows that with an increase in the temperature of the aqueous electrolyte solution, the viscosity of the solution decreases, because of which larger UDD particles settle in the lower layers of the electrolyte solution, and their number in the near-cathode region sharply decreases. The increase in concentration of the dispersed phase particles of the finer fraction in the coating formed under the laser-assisted mode of electrodeposition is due to an increase in the flux density of metal ions adsorbed on the surfaces of UDD particles [12, 13], as a result of which the particles of the dispersed phase acquire a positive charge, which promotes electrophoretic co-deposition.

When using laser radiation sources, the main mechanism of laser stimulation of the electrodeposition process is the heating of the metal-electrolyte interface [14, 15]. In Refs. [16–18], the use of laser irradiation of the near-cathode region in the process of electrodeposition of composite coatings contributes to an increase in the cathode current density. Thus, it is of considerable interest to study the effect of laser radiation on the co-deposition of UDD particles and metal ions.

An analysis of the cathodic polarization curves (Fig. 3) showed that the presence of dispersed particles in the aqueous electrolyte solution leads to a shift in the cathodic potential to the electronegative region that indicates an increase in charge transfer resistance.

The increase in the cathodic overpotential during laser-assisted electrodeposition can be explained by the increased, in the direction of laser radiation, flux density of complexes formed because of ad-



**Fig. 3.** Cathodic polarization dependences obtained in sulfuric acid nickel-plating electrolyte: 1—without UDD; 2—with UDD ( $C_{UDD} = 2$  g/l); 3—with UDD ( $C_{UDD} = 15$  g/l); 4—with UDD ( $C_{UDD} = 15$  g/l, laser-assisted mode).

sorption of metal ions on the surfaces of UDD particles. Electropositive charged complex aggregates formed because of the total charge, moving to the cathode surface, block it, thereby, leading to a decrease in the active surface area of the cathode.

Analysis of x-ray patterns of electrolytic nickel coatings (Fig. 4) shows that diffraction maxima corresponding to the diamond phase of carbon overlap with lines corresponding to the crystalline phase of electrolytic nickel that complicates determination of the nanodiamond/nickel ratio in the coating and determines the need for studies of the elemental composition of the coatings. In pure nickel coatings, the preferential orientation of crystallites in the [111] direction is observed (Fig. 4, *a*). The introduction of UDD did not lead to a change in the CEC phase composition, and the diffraction patterns do not show a significant redistribution of the line intensity (Fig. 4, *b*). In composite nickel coatings obtained in the laser-assisted electrodeposition mode, a redistribution of the intensity of the (111) and (220) lines is observed (Fig. 4, *c*), which indicates a change in the conditions of electrocrystallization.

Figure 5 shows the results of x-ray microanalysis of the elemental composition of the coating surface. From the results of x-ray microanalysis of the elemental composition of the coating surface, it follows that the fraction of UDD particles of certain sizes depends on the electrodeposition mode [19, 20]. The average diameter of UDD particles in CEC deposited without laser irradiation was 1.5–2  $\mu\text{m}$ . Composite nickel coatings obtained by laser-assisted electrodeposition are characterized by a higher content of UDD parti-

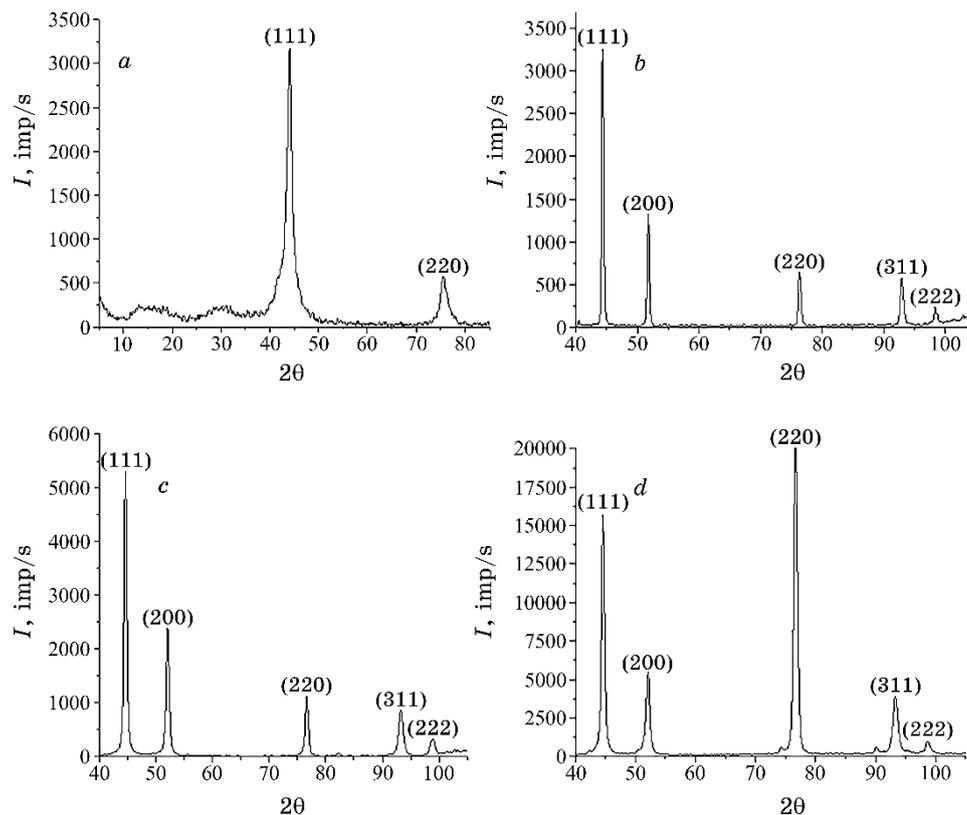
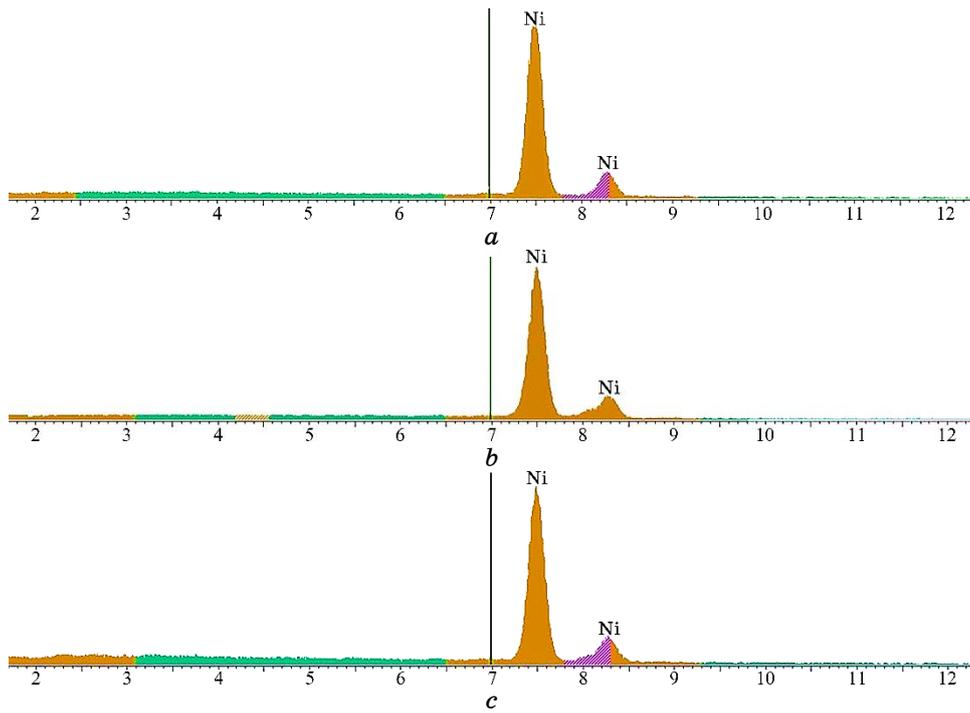


Fig. 4. Diffractograms: (a) UDD powder; (b) Ni (without laser irradiation); (c) Ni+UDD (without laser irradiation); (d) Ni+UDD (laser-assisted mode).

cles in the coating (4.35–5.10 wt.%) as compared to the mode of deposition without laser irradiation (2.24–3.15 wt.%). In this case, the proportion of particles of smaller size  $\cong 0.25\text{--}1\ \mu\text{m}$  increases in the coatings.

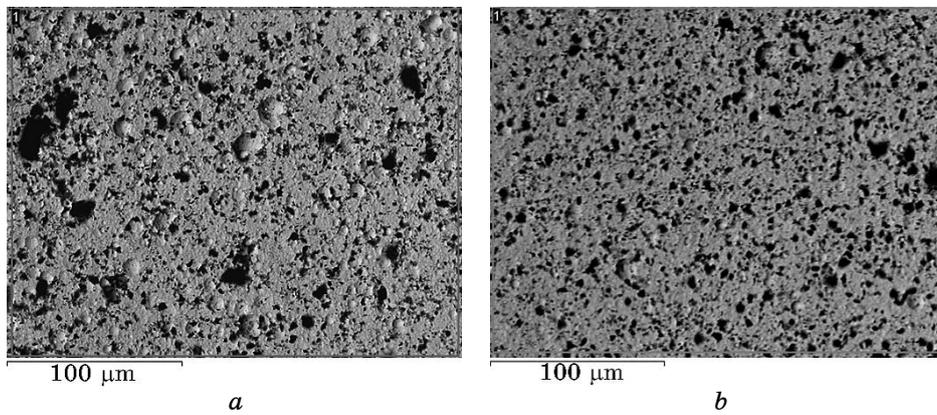
According to the Nernst–Planck equation [21], the increase in disperse phase particle flux density in the aqueous electrolyte solution to the surface of the coating formed during laser-assisted electrodeposition is due to the potential gradient and rise in the diffusion coefficient [22].

The structure and mechanical properties of the resulting composite coating largely depend on the concentration and size of UDD particles in the coating. The results of studies of the fractional composition of UDD particles on the surface of composite electrolytic nickel coatings show that during DC electrodeposition UDD particles of larger size reach the cathode surface. Agglomerates of UDD particles with a size of  $1.5\ \mu\text{m}$  are formed on the CEC surface



**Fig. 5.** X-ray microanalysis: (a) Ni (without laser irradiation); (b) Ni + UDD (without laser irradiation); (c) Ni + UDD (laser-assisted mode).

resulting in formation of coarser crystalline coatings (Fig. 6, a) with microhardness of 1800–1950 MPa.



**Fig. 6.** Surface morphology of the electrolytic nickel composite coatings: (a) direct current without laser irradiation; (b) laser-assisted mode.

The inclusion of smaller UDD particles ( $\cong 0.25\text{--}1\ \mu\text{m}$ ) in the coating composition in the laser irradiation region complicates the surface diffusion of metal adatoms and prevents the growth of nuclei of the crystalline phase that results in formation of a finer crystalline coating structure (Fig. 6, *b*).

Composite coatings are formed more fine-grained that determined microhardness increase from 2500 MPa outside the irradiation area to 3700 MPa in the irradiation area.

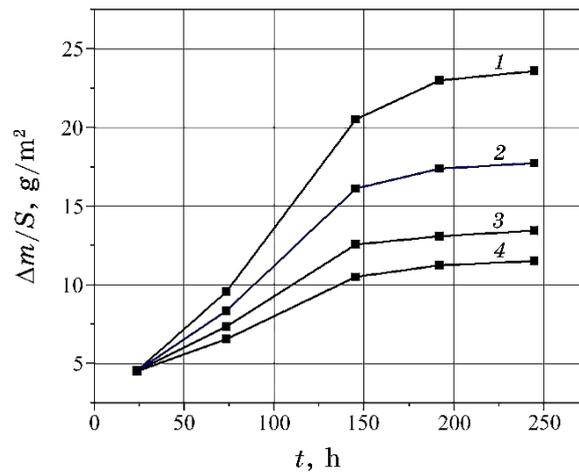
Figure 7 shows the results of the corrosion tests on nickel coatings. It should be noted that the corrosion rate of the samples tested was uniform. However, the change in mass of the carbon-containing nickel coatings over 144 hours is slower than in the pure nickel coatings. This is due to the increased extent of the interlayer boundaries that contain the UDD particles.

The results of the conducted studies make it possible to attribute nickel coatings deposited by means of direct current to the 'Resistant' group with a score of 4, and the intensification of the process of co-deposition of UDD particles under laser irradiation contributes to the production of composite nickel coatings that belong to the 'Extremely resistant' group with a score of 3. This is caused: firstly, by the fact that the UDD particles block the cathode surface thus reducing the area of the active cathode surface that changes the coating growth structure in the cross-section from columnar (Fig. 8, *a*) to microlayer (Fig. 8, *b*); secondly, by an increase in metal ion flux density adsorbed on the UDD particle surfaces, which contributes to a more intense incorporation of UDD particles into the deposited coating. Increased concentration of dispersed phase particles from 2.24 to 4.35 wt.% leads to the formation of fine-grained coatings with fewer pores, which prevents the formation of corrosion centres, in contrast to columnar growth, where the surface of coatings is more heterogeneous.

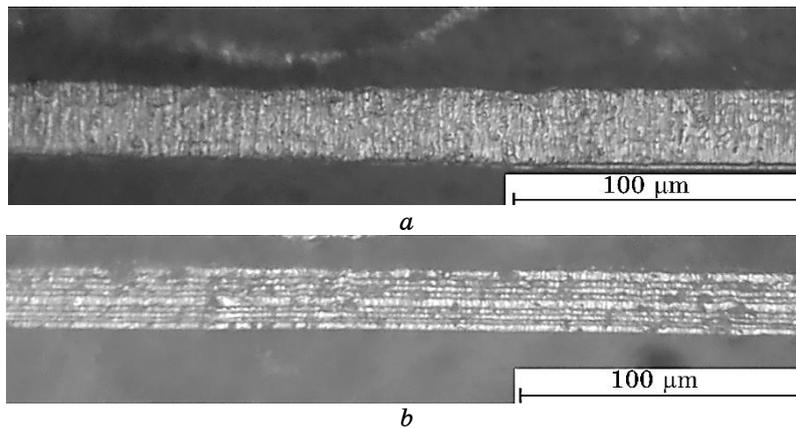
An increase in the UDD content of the nickel films enhances the wear resistance of the coatings. Nickel coatings electrodeposited from the aqueous electrolyte solution without UDD addition lose 10% of their weight after 5 hours of wear. When UDD with 2 g/l concentration were added to the aqueous electrolyte solution, the losses were of 6–8%, and for laser-assisted electrodeposition coatings, they were of 1–2%.

#### 4. CONCLUSION

1. The increase in the concentration of smaller UDD particles ( $\cong 0.25\text{--}1\ \mu\text{m}$ ) in the coating formed under laser-assisted deposition is due to the potential gradient and rise in the diffusion coefficient.
2. The increase in the flux density of complexes formed because of



**Fig. 7.** Dependences of the mass change of electrolytic coatings: 1—Ni (without laser irradiation); 2—Ni+UDD ( $C_{UDD} = 2$  g/l, without laser irradiation); 3—Ni+UDD ( $C_{UDD} = 15$  g/l, without laser irradiation); 4—Ni+UDD ( $C_{UDD} = 15$  g/l, laser-assisted mode).



**Fig. 8.** Structure of electrolytic coatings in cross section: direct current: (a) Ni (without laser irradiation); (b) Ni + UDD (laser-assisted mode).

the adsorption of metal ions on the surfaces of UDD particles leads to an increase in oversaturation at the crystallization front. The formed coating is reached by smaller size UDD particles that block the growth of nuclei of the crystalline phase, which leads to the formation of a more densely packed coating and changes the cross-sectional growth structure from columnar to microlayer.

3. The formation of finer crystalline coatings and change of cross-

sectional growth structure from columnar to microlayer at laser-assisted deposition process resulted in improvement of mechanical and protective properties of carbon-containing nickel coatings (coating microhardness increased from 1800–1950 MPa to 2500–3700 MPa, corrosion resistance increased 2 times, and the wear of coatings decreased 3 times).

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