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## **Kinetic regularities of the formation of composite electrolytic coatings containing ultradispersed diamond particles**

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The paper formulates the problem of joint electrolytic co-deposition of metal ions and ultradispersed diamond particles into a metal matrix. It presents the developed mathematical model that describes the mechanism and kinetics of the cathode process, mass transfer of metal ions and ultradispersed diamond particles. A satisfactory correlation with experimental data was obtained. The contribution of the thermal action of laser radiation to the intensification of the process of co-deposition of dispersed particles and metal ions was determined. It was found that the more intense penetration of dispersed phase particles into the forming 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. Based on the theoretical and experimental studies, we established the regularities of the influence of the number and size of nanoparticles on the strengthening properties of composite metal coatings. It was found that an increase in the temperature of an aqueous electrolyte solution in the cathode region during a laser-stimulated deposition process leads to an increase in the flux density of ultradispersed diamond particles, and, as a result, to an increase in the concentration of the dispersed phase in nickel composite coatings, which contributes to the formation of a finer crystalline structure of coatings, an improvement in adhesion, strength properties and increased wear resistance of coatings.

**Keywords:** ultrafine diamond particles, electrodeposition, laser stimulation of the electrodeposition process, composite electrolytic coatings, mechanical properties.

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### **Introduction**

Obtaining composite electrolytic coatings (CEC) is the most important area of solid state physics. In the process of applying CEC, it is possible to obtain coatings that differ significantly from classical galvanic coatings in terms of their operational characteristics.

Electrolytic co-deposition (ECD) is used in industries such as automotive, construction, power generation, as well as in the aerospace and oil and gas sectors. Using the ECD process, it was possible to obtain coatings from both soft magnetic materials for the production of sensors [1, 2] and hard magnetic materials [3, 4]. CECs are widely used as wear-resistant coatings, low-friction coatings, coatings for tools with high hardness, coatings for abrasive tools [5], a component for precipitation hardening of alloys, as well as for protection against oxidation and high-

temperature corrosion [6, 7].

Earlier, the authors of this work found that the presence of nanodiamond particles in metal composite electrolytic coatings significantly affects the microstructure, protective and mechanical properties of coatings, which manifests itself in their high hardness, wear resistance and corrosion resistance [8-10].

The unique physicochemical properties of electrodeposited metal coatings largely depend on the concentration of carbon nanomaterial (CNM) particles in the metal matrix. Therefore, in recent years, special attention is paid to the control and management of the content of CNM particles in composite metal coatings. The solution to this problem is impossible without studying the mechanism of formation of the structure of carbon-containing composite metal coatings. However, the process of co-deposition of metal ions and CNM

particles on a substrate remains not fully understood.

The purpose of this work is to develop a mathematical model describing the transfer of ultradispersed diamond (UDD) particles and metal ions in the volume of an electrolytic bath and the kinetics of the process of co-deposition of metal ions and UDD particles on the cathode, as well as to establish the influence of the thermal factor during a laser-stimulated electrodeposition process on the size and concentration of nanoparticles in the metal matrix and on the strengthening properties of composite electrolytic coatings.

## I. Materials and methods

Composite electrolytic coatings were obtained from an aqueous solution of nickel-plating electrolyte of the following composition:  $\text{Ni}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$  - 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 pH-5, temperature 293 K and current density 100 A/m<sup>2</sup>. UDD nanoparticles were used as a dispersed phase (DP). Particle sizes – 0,04-15 microns.

In order to intensify the process, the electrodeposition of the CEC was also carried out on a laser-electrolytic facility based on a gas-discharge  $\text{CO}_2$ -laser with a power of 25 W and continuous mode lasing at 10.6  $\mu\text{m}$  wavelength. The temperature of the aqueous electrolyte solution in the cathode irradiation region increased from 293 K to 351 K [11].

The cathode was a copper substrate (1,8 × 1,8 cm<sup>2</sup>), which was mechanically polished, chemically treated in a 3% nitric acid solution, and degreased with Vienna lime. A pure nickel plate was used as the anode, which made it possible to maintain the concentration of the basic metal salt unchanged and had a positive effect on the repeatability of the experiments. For the uniformity of the electric field created by the flow of charged ions, the electrodes were placed parallel to each other. The concentration of UDD particles ( $C$ , g/l) in the aqueous electrolyte solution was 2 g/l.

The viscosity of aqueous electrolyte solutions was determined using a VPZh-2 capillary glass viscometer with an inner capillary diameter of 0,73 mm in accordance with GOST 8.265-77.

Due to the developed surface and the presence of a large number of functional groups, individual nanodiamond (ND) 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. ND particles are prone to spontaneous aggregation among themselves into extremely strong aggregates (40-100 nm) with the subsequent formation of less durable secondary ones (up to 1-5  $\mu\text{m}$ ) [12–14].

To determine the average particle size, we used a method based on the analysis of the distribution of chord lengths on the coating surface (chord method) [15].

The microstructure and elemental composition of the coating surface were investigated using a JSM-64901LV scanning electron microscope (Japan) with an INCA PENTAx3 energy dispersive spectrometer (OXFORD Instruments).

The microhardness of the coatings ( $H_\mu$ , MPa) was measured on PMT-3 device with indentation load of

0,1 N. The microhardness was measured along the sample diagonal. The wear tests of the samples were carried out on a friction machine with a reciprocating motion of the samples with a frequency of 0,5 s<sup>-1</sup> and an amplitude of 0,15 m under conditions of dry friction on steel. The adhesion strength of copper base coatings was determined by the repeated bending method. The tensile strength of electrolytic metal films was tested on a tensile testing machine MI-44. The tensile strength of the samples was evaluated by the ratio of the longitudinal force to the cross-sectional area of the sample.

## II. Problem statement

The electrodeposition process is shown schematically in Fig. 1. At the initial moment of time, the particles of the nanocarbon material are in suspension in the electrolyte volume. The electrolytic cell consists of a cathode, an anode, and an aqueous electrolyte solution containing  $\text{Ni}^{2+}$  ions and spherical UDD nanoparticles of radius  $r$  with a concentration  $C_{\text{CNM}}$ .

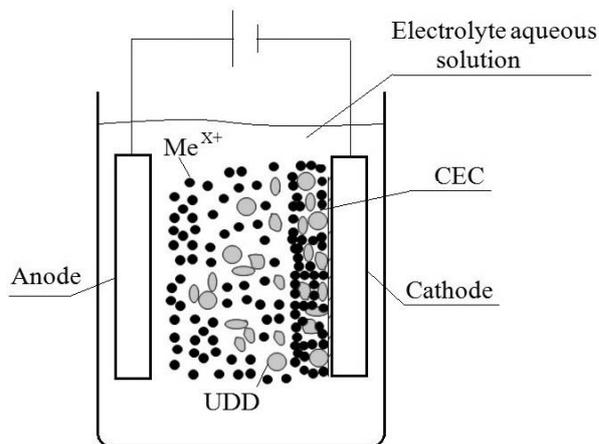


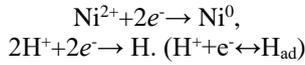
Fig. 1. Scheme of electrodeposition process.

The kinetics of the cathodic process is determined by the concentration of metal ions and DP particles near the cathode surface, which are known only at the initial moment of the electrodeposition process. In a stirred electrolyte solution, they are equal to the corresponding concentration values in the volume of the electrolyte solution. However, at the initial moment of deposition, the concentration values at the cathode-electrolyte interface change. Near the cathode surface, a mass transfer layer is formed, over the entire thickness of which the concentration of metal ions changes. When constructing a model of the problem under consideration, we make the following assumptions:

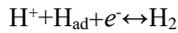
- Outside the mass transfer layer, the concentrations of metal ions and DP particles do not change and are equal to the values of the concentrations in the volume of the electrolyte solution;
- Due to the small size of the DP particles and the vertical arrangement of the electrodes, the influence of the forces of Archimedes and gravity can be neglected.

### III. Simulation of the process of joint electrolytic deposition of metal ions and UDD particles

When nickel is electrodeposited from a sulfate electrolyte solution at the cathode, the reactions of reduction of nickel ions and hydrogen evolution take place:



The stage of the discharge of hydrogen ions is followed by the removal of adsorbed hydrogen atoms from the cathode surface by their electrochemical desorption



or chemical recombination



The total cathode stream is equal to the sum of the streams of each of the reactions. The equation for the total cathode stream involved in mass transfer can be written as follows

$$j = j_F + j_H + j_{\text{CNM}}, \quad (1)$$

where  $j_F$  – partial current density of the metal ion discharge;  $j_H$  – partial current density of the hydrogen ion discharge;  $j_{\text{CNM}}$  – partial current density that ensures the transfer of CNM particles.

To establish the mechanism of incorporation of DP particles into the forming coating, it is necessary to estimate the particle flux density. According to the Nernst-Planck equation [16], the transfer of ions and carbon nanoparticles in an aqueous electrolyte solution is determined by two factors: the unevenness of their distribution, i.e. concentration gradient, and the electric field effect

$$J = -D \frac{dc}{dx} - \frac{D}{RT} ZFc \frac{d\varphi}{dx} = -D \left( \frac{dc}{dx} + \frac{ZFc}{RT} \frac{d\varphi}{dx} \right), \quad (2)$$

Where  $D$  - diffusion coefficient ( $\text{m}^2/\text{s}$ ).

In the case when the radius of the diffusing particle is much larger than the radius of the molecule of the liquid itself, the diffusion coefficient can be estimated from the Stokes-Einstein relation [17]

$$D \cong \frac{kT}{6\pi\eta \cdot r}, \quad (3)$$

where  $r$  – particle radius,  $\eta$  – coefficient of internal friction (dynamic viscosity) of the aqueous electrolyte solution.

Taking the electric field to be uniform and taking into account that

$$\frac{ZFc}{RT} \frac{d\varphi}{dx} = \frac{ZFc}{RT} \frac{\Delta\varphi}{l} = \frac{\psi}{l} c, \quad (4)$$

where  $\Delta\varphi$  – potential difference in electrical double layer (EDL),  $l$  – EDL thickness ( $l = \sqrt{Dt}$ , where  $t$  – deposition process time),  $\psi = \frac{ZF}{RT} \Delta\varphi$  – auxiliary quantity (dimensionless potential), we obtain the Nernst-Planck equation in the form

$$J = -D \left( \frac{dc}{dx} + \frac{\psi}{l} c \right). \quad (5)$$

The solution to equation (5) has the form [18]

$$J = \frac{D\psi}{l} \frac{c_0 - e^{\psi} c_l}{e^{\psi} - 1}, \quad (6)$$

where  $c_0$  and  $c_l$  – concentration of metal ions and CNM particles in the volume of an aqueous electrolyte solution and near the cathode surface, respectively.

Equation (6) establishes a relationship between the flux density of metal ions and CNM particles with two quantities:

1) concentration of metal ions and CNM particles in an aqueous electrolyte solution; 2) electric field.

In order to establish the mechanism of transfer and co-deposition of CNM particles, let us analyse a particular case of equation (6):

1)  $\psi = 0$  which means either  $Z = 0$  (neutral particles), or the absence of an electric field ( $\Delta\varphi = 0$ ), or both. After mathematical transformations, we get

$$J = \frac{D}{l} (c_0 - c_l), \quad (7)$$

This model (Model 1) takes into account only the diffusion mechanism of the process of joint electrolytic deposition of metal ions and UDD particles.

2) the same concentration of carbon nanoparticles in the volume of the aqueous electrolyte solution ( $c_0$ ) and at the cathode surface ( $c_l$ ), i.e. in the presence of an electric field.

$$J = -\frac{D\psi}{l} c \quad \text{or} \quad J = -D \frac{ZF}{RT} \frac{\Delta\varphi}{l} c. \quad (8)$$

Model 2 considers the transfer of CNM particles in an aqueous electrolyte solution under the effect of electric field. The calculations of the CNM particle flux density took into account that during the deposition of nickel from simple sulfuric acid aqueous solutions of electrolytes, an overvoltage of 0.5 V is maintained at the cathode [19-21].

The corresponding data calculated by us according to (3) and (7) for model 1 and according to (3) and (8) for model 2 for particles ranging in size from 10 nm to 0.1  $\mu\text{m}$  are shown in Table.

Analysis of the calculation results for mathematical models of the process of joint electrolytic deposition of metal ions and UDD particles (Table 1) showed that the main factor affecting the transfer of CNM particles in the aqueous electrolyte solution is the potential gradient. Calculation by formula (6) showed that the contribution of the concentration gradient to the particle flux density is insignificant. The experimentally obtained value of the UDD particle flux density for the DC deposition mode ( $J = 5.8 \cdot 10^{-7} \text{ kg/m}^2 \cdot \text{s}$ ) correlates with the calculation results of the mathematical model 2 (Table) for particles with a size of  $\sim 1 \mu\text{m}$ .

Consequently, the transfer of CNM particles occurs mainly not by the diffusion mechanism, but under the effect of an electric field. Also, earlier in the work [22-24], we found that the transfer of CNM particles from the volume of an aqueous electrolyte solution to the cathode surface is possible due to the acquisition of a positive charge by the CNM/M complex (where M is a metal).

**Table 1.**

Flux density of UDD particles in an aqueous solution of nickel plating electrolyte and their concentration in a composite electrolytic coating

<i>r</i> , μm	<i>D</i> , m <sup>2</sup> /s	<i>l</i> , μm	Model			
			1		2	
			<i>J</i> , kg/m <sup>2</sup> ·s	<i>C</i> , wt%	<i>J</i> , kg/m <sup>2</sup> ·s	<i>C</i> , wt%
100	10 <sup>-15</sup>	2.7	4.7·10 <sup>-10</sup>	0.002	1.5·10 <sup>-8</sup>	0.056
10	10 <sup>-14</sup>	8.5	1.5·10 <sup>-9</sup>	0.006	4.6·10 <sup>-8</sup>	0.17
1	10 <sup>-13</sup>	27	4.7·10 <sup>-9</sup>	0.02	2.9·10 <sup>-7</sup>	1.08
0.1	10 <sup>-12</sup>	85	1.5·10 <sup>-8</sup>	0.035	9.3·10 <sup>-7</sup>	3.38
0.01	10 <sup>-11</sup>	270	4.7·10 <sup>-8</sup>	0.11	1.5·10 <sup>-6</sup>	5.2

The flux density of DP particles is determined by the charge of metal cations adsorbed on the particle surface, which, due to the positive charging of the particles, promotes electrophoretic co-deposition. In [22-24], we showed that a charge greater than +2*e* (*e* – electron charge) is not retained on a CNM particle, since when several metal ions are successively attached to a CNM particle, their binding energy decreases. At an electrokinetic potential of ±30 mV, corresponding to a good stability of the colloidal system [25] (no particle coagulation), an elementary charge of 1.6·10<sup>-19</sup> C can be adsorbed by a particle of ~1.5-2 μm.

To determine the concentration of the dispersed phase in the coating (in wt%) (Table) by the expression

$$C = \frac{m_{\text{CNM}}}{m_{\text{CNM}} + m_{\text{Ni}} \cdot \text{CE}} \cdot 100\% \quad (10)$$

based on the results of calculating the flux density of UDD particles (Table 1), the following were estimated: CNM mass (*m*<sub>CNM</sub>) and nickel mass (*m*<sub>Ni</sub>), taking into account the metal current efficiency (CE).

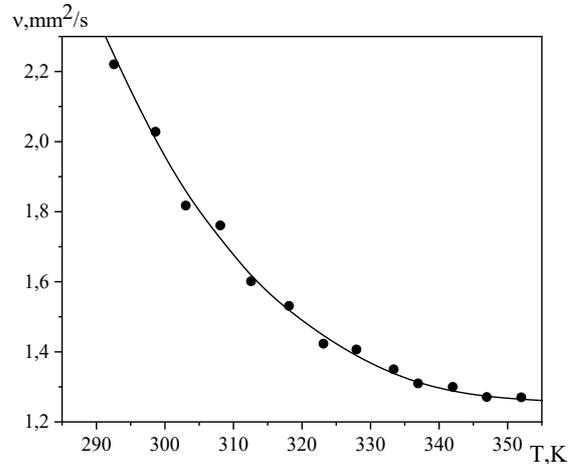
Comparison of the results of studying the elemental composition of coatings and the results of evaluating the concentration of the dispersed phase in the coating (in wt%) using formula (10) gives a satisfactory correlation with the mathematical model 2 (Table) for particles of ~ 1 μm.

When using laser sources, the main mechanism of laser stimulation of the electrodeposition process is the metal/electrolyte interface heating [26]. In [27], when using laser irradiation for the electrodeposition of composite coatings, we observed increased electrodeposition current densities due to mixing and an increase in temperature. Thus, it is of considerable interest to study the thermal effect of laser radiation on the process of co-deposition of CNM particles.

Fig. 2 shows the results of studying the dependence of the kinematic viscosity (*v*, mm<sup>2</sup>/s) on the temperature (*T*, K) of an aqueous solution of nickel-plating electrolyte at UDD particle solution concentration of 2 g/l.

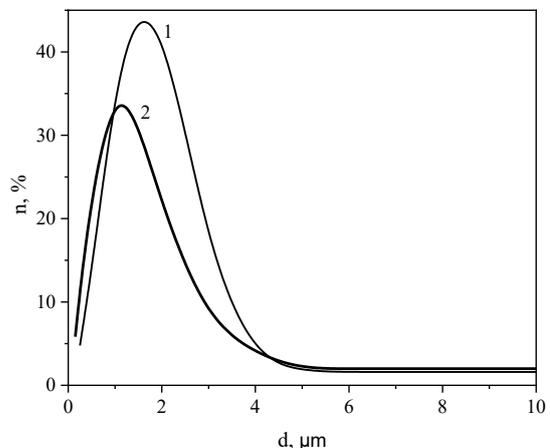
The analysis of the obtained results show that an increase in the temperature of the aqueous electrolyte solution from 293 K to 351 K reduces the solution viscosity by 1.7 times. As a result, the larger UDD particles settle in the lower layers of the electrolyte solution, their amount in the cathode space decreases sharply and particles of a finer fraction are included in the coating.

To analyse the size distribution of dispersed phase particles on the surface of composite electrolytic nickel coatings, we carried out statistical processing of the results of studies of the UDD particle concentration in CEC. To establish the functional dependence of the concentration on the particle size (diameter), we used the software package for statistical analysis STATISTICA 12 [28, 29].



**Fig. 2.** Dependence of kinematic viscosity on the temperature of an aqueous solution of nickel plating electrolyte.

Fig. 3 shows the approximating curves of the experimental histograms of the fractional composition of UDD particles on the surface of composite electrolytic nickel coatings.



**Fig. 3.** Dependence of the degree of filling of the CEC surface with UDD particles (*n*, %) on their size (*d*) and the mode of deposition at direct current (*j*=100 A/m<sup>2</sup>): (1) without laser irradiation; (2) with laser irradiation.

The results of X-ray microanalysis of the coating surface elemental composition (Fig. 3) show that the fraction of particles of certain sizes depends on the electrodeposition mode. Composite electrolytic nickel coatings obtained by laser stimulation of the deposition process are characterized by a higher concentration of particles in a coating of smaller size  $d \sim 0.1-1 \mu\text{m}$  (Fig. 3).

The experimentally obtained value of the UDD particle flux density for the DC deposition mode under laser irradiation and the result of evaluating the concentration of the dispersed phase in the coating in the irradiated region correlate with the calculation results of the mathematical model 2 (Table 1) for particles of  $\sim 0.1 \mu\text{m}$ .

More intense penetration of the dispersed phase particles into the forming coating during the laser stimulation of the electrodeposition process is due to the presence of the temperature gradient. The temperature rise of the aqueous electrolyte solution in the cathode region during the laser-stimulated deposition process leads to the increased diffusion coefficient, which provides an additional supply of metal ions to the surface of the emerging composite coating in the irradiation region. In addition, it is known [30] that dielectrics, which include CNM particles introduced into the electrolyte solution, are involved in the irradiation region during laser irradiation, which leads to the increased UDD concentration in the coating.

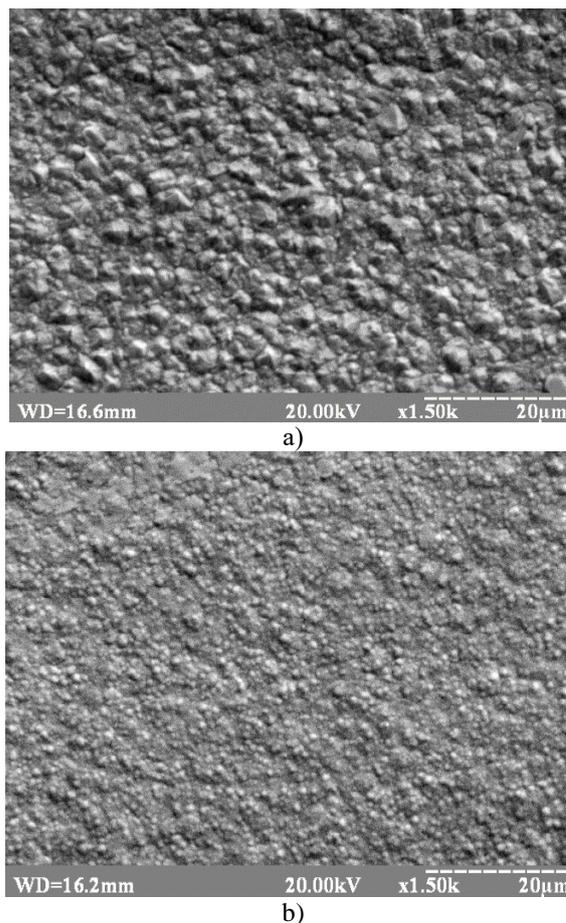
The structure and mechanical properties of the emerging composite coating largely depend on the concentration and size of UDD particles in the coating. The results of studies of the fractional composition of UDD particles on the surface of composite electrolytic nickel coatings show that, during DC electrodeposition, larger UDD particles reach the cathode surface (Fig. 3 (1)). On the ECC surface, the agglomerates of UDD particles of  $1.5 \mu\text{m}$  are formed, which leads to the formation of coarse-crystalline coatings (Fig. 4 a), the microhardness of which is 1800-1950 MPa.

The inclusion of smaller UDD particles ( $\sim 0.1-1 \mu\text{m}$ ) in the coating composition in the laser irradiation region complicates the surface diffusion of metal adatoms and prevents the growth of crystalline phase nuclei, which is the reason for the formation of a finer crystalline structure of the coatings (Fig. 4b). Composite coatings are formed more fine-grained, which determined an increase in microhardness from 2500 MPa outside the irradiation region to 3700 MPa in the irradiation region (Fig. 5).

The increased content of UDD in nickel films improves the wear resistance of the coatings. Nickel coatings electrodeposited from an aqueous electrolyte solution without the addition of UDD, after 5 hours of wear, lose 10% of their weight, when added to an aqueous solution of UDD electrolyte with a concentration of 2 g/l – 6-8%, and the coatings obtained by laser-stimulated electrodeposition - 1-2%.

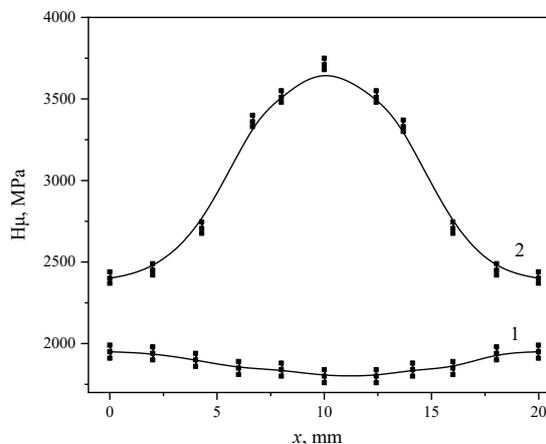
Adhesion tests of the nickel coatings with a thickness of 15-20 microns by  $180^\circ$  bending of the samples (until fracture) showed that on the samples electrodeposited at direct current without inclusions of CNM particles, the coatings peeled off along the entire fracture line. On CEC samples, electrodeposited under laser irradiation, the coatings do not crack or peel off when the copper base is

bent until fracture.



**Fig. 4.** Surface morphology of composite electrolytic nickel coatings: a–direct current without laser irradiation; b–direct current with laser irradiation.

The measured strength values for composite electrolytic nickel films obtained at direct current without laser irradiation are 580 MPa with a coating thickness of 18-20  $\mu\text{m}$ , which exceeds the strength of electrolytic nickel coatings by 20%. The use of laser irradiation in the deposition process made it possible to increase the ultimate strength of the CEC up to 660 MPa.



**Fig. 5.** Dependences of the microhardness of the surface of composite electrolytic nickel coatings on the sample diagonal coordinate  $x$ : 1 – direct current without laser irradiation; 2 - direct current with laser irradiation.

## Conclusions

1. The developed mathematical model describes the mechanism and kinetics of the cathode process, the mass transfer of metal ions and ultradispersed diamond particles. It was found that the main factor affecting the transfer of CNM particles in an aqueous electrolyte solution is the potential gradient. A satisfactory correlation was obtained between the experimental data on the UDD particle flux density and the dispersed phase concentration in the coating with the results of calculations of the mathematical model 2 (Table 1) for particles with a size of  $\sim 1 \mu\text{m}$ .

2. Studies were conducted on the thermal effect of laser radiation on the process of co-deposition of CNM particles. It was found that CECs obtained with laser stimulation of the deposition process are characterized by a higher concentration of particles in a coating of a smaller size of 0.1-1  $\mu\text{m}$  due to the presence of a temperature

gradient, which provides an additional supply of metal ions in the irradiation region.

3. In the laser-stimulated process of CEC electrodeposition, the emerging coating is reached by UDD particles of a smaller diameter, which block the growth of the crystalline phase nuclei, resulting in the formation of a more close-packed coating, improved adhesion and strength properties, as well as increased wear resistance of the coatings.

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## Кінетичні закономірності формування композиційних електролітичних покриттів, що містять частинки ультрадисперсного алмазу

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Сформульована задача сумісного електролітичного осадження іонів металу та частинок ультрадисперсного алмазу в металеву матрицю. Розроблено математичну модель, що описує механізм та кінетику катодного процесу, масоперенесення іонів металу та частинок ультрадисперсного алмазу. Отримано задовільну кореляцію з експериментальними даними. Визначено внесок теплової дії лазерного випромінювання в інтенсифікацію процесу співосадження частинок дисперсної фази та іонів металу. Встановлено, що більш інтенсивне проникнення частинок дисперсної фази у покриття, що формується у процесі стимуляції процесу електроосадження лазерним випромінюванням, обумовлене присутністю температурного градієнту, що забезпечує додаткове підведення іонів металу в області опромінювання. На підставі теоретичних та експериментальних досліджень встановлено закономірності впливу кількості та розміру наночастинок на зміцнюючі властивості композиційних металевих покриттів. Встановлено, що підвищення температури водного розчину електроліту у прикатодній області при лазерно-стимульованому процесі електроосадження призводить до збільшення густини потоку частинок ультрадисперсного алмазу, та, як наслідок, до збільшення концентрації дисперсної фази у нікелевих композиційних покриттях, що сприяє формуванню більш дрібнокристалічної структури покриттів, поліпшенню міцності, адгезійних властивостей та підвищенню зносостійкості покриттів.

**Ключові слова:** частинки ультрадисперсного алмазу, електроосадження, лазерне стимулювання процесу електроосадження, композиційні електролітичні покриття, механічні властивості.