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TECHNICAL ARTICLE



Model of Dispersed Phase Particle Distribution in a Composite Electrolytic Coating

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Abstract

A model is proposed to evaluate distribution of dispersed phase particles in a composite metal coating. This model is based on calculation of degree of surface occupation by particles and their distribution in volume. Effective parameters applied for electrolytic composites evaluation at the microscale level were formulated, and method for the parameters evaluation was set out. It was shown that density of distribution and portion of particles with certain size in a coating depend on electrodeposition modes. Generation of higher-fine crystalline close-packed structures of coatings in conditions of pulse relative duration increase from 2 to 50 and unchanged current frequency 50 Hz is caused by both increase of oversaturation at the crystallization front that results in higher non-equilibrium process of crystallization and also by passivation effect of UDD particles on the surface which is formed. Non-equilibrium conditions of crystallization give rise to more intensive penetration of disperse phase particles with smaller size ($\sim 0.25-1~\mu m$) into growing coating, decrease of microlayers thickness from 4 to 2 μm and increase of UDD particles concentration from 1.43 to 2.47 mas.%.

Keywords Composite electrolytic coating · Ultra-dispersed diamond particles · Degree of surface occupation · Density of distribution

Introduction

Electrolytic coatings application represents one of the methods used for metalwork protection against corrosion and abrasion wear during the operation. One promising method of improvement of coatings performance properties involves composite electrolytic coatings (CEC) technology realized by co-deposition of metal substrate and reinforcing dispersed particles of the second phase. Growing interest to composite materials in these days is generated by opportunity for making materials which exhibit unique physicochemical properties [1–7]. By adding of detonation-synthesized nanodiamonds into aqueous nickel-plating and iron-plating electrolyte solution, the forming coatings receive 2–2.5 times increased microhardness, 3–6 times improved wear resistance, 3–4 times reduced porosity [1], and this addition provides significant effect on microstructure [2], tribological

Application of systems analysis to solving the task of improvement of CEC functional properties which lies in modification of metal matrix with UDD particles and application of unsteady modes of electrodeposition (pulse current [10] and programmable pulse current [11]) gave rise to nickel coatings microhardness from 4.2 to 6.5 GPA, and wear resistance increase in 3–3.5 times.

Structure and properties of composite electrolytic coatings depend on a nature and size of carbon nanomaterials, their concentration in a coating and interaction with a metal matrix. Therefore, special attention is given to monitoring and control of carbon nanomaterial concentration in a CEC. This problem cannot be solved without study of mechanism of formation of carbon-containing composite metal coatings structure. Gained knowledge would give an opportunity to control process of codeposition of nanocomposite materials and produce a coating with tailor-made functional properties. There are several publications [12–14] which deal with study of mechanism of codeposition of nanodiamond with a metal matrix. The authors



properties [3–7] of composites and their corrosion resistance [5–8]. Particular attention is given to CEC comprising reinforcing particles relating to class of super-hard materials such as ultra-dispersed diamond (UDD) [6, 9].

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defined three stages of CEC growth process: dispersed phase particles and metal ions motion from electrolyte bulk into near-electrode layer; ultra-dispersed particles and ions transportation from near-electrode layer on a cathode; and refill deposition of particles arrived to cathode surface.

Structure of composite coatings has the form of alternating volumes featured with different properties on a microscale level. So, parameters of CEC evaluation on microscale level for description of composite material microstructure make possible to simplify task of making a CEC with tailor-made properties.

Such tasks can be solved based on construction of models of filling material distribution in a matrix. It is necessary to note that CEC may attain their maximum properties subject to certain concentration of dispersed phase or distance between particles in the coating that are specified by electrodeposition mode [15, 16]. So, application of pulsed electrodeposition modes [15] gave us an opportunity to provide control over the structure and properties of nickel coatings within much wider range and increase UDD particles distribution density in a coating. Moreover, we developed a program for the layer-by-layer deposition of composite nickel coatings [16], and by using this process microlayer coatings being gradient in view of UDD particles concentration were obtained. That effect resulted in coatings wear resistance increase and less consumption of dispersed nanodiamond particles.

In view of surface of coating, CEC can be evaluated with a parameter like ratio between surface occupied by dispersed phase and surface across which the particles are distributed. However, research showed that concentration of dispersed phase and degree of surface occupation with particles do not provide complete description of dispersed phase distribution pattern in a coating and distance between particles vary both in coating volume and on coating surface. Therefore, development of effective parameters for evaluating the electrolytic compositions at the microlevel and formulation of methodology for their determination represent a topical task. The purpose of this study lies in construction of a mathematical model applied for evaluation of the dispersed phase particles distribution in a composite metal coating. The model is based on calculation of degree of surface occupation with particles and their distribution in the volume. Application of this model to predicting the content of dispersed phase particles in a composite metal coating forms another task of the study.

Calculation of Characteristics of Dispersed Phase Particles Microdistribution in Composite Electrolytic Coating

The model foundation is built on the assumption that particles look like sphere with the size (diameter) d_i and volume



and in the surface of coating particles are of disk shape with an area of

$$s_i = \frac{\pi d_i^2}{4}. (2)$$

Distribution of particles with the size of d_i in coating can be simulated by way of dispersed phase particles surrounding with metal atoms till mutual contact (Fig. 1). In this case, on the surface particle with the diameter of $d_i + l_i$ and its surrounding metal atoms occupies area

$$s_{\rm d} = \frac{\pi}{4} \left(d_i + l_i \right)^2 = s_i \left(1 + \frac{l_i}{d_i} \right)^2.$$
 (3)

If n particles with the diameter of d_i are located on segment L of surface straight line, then their average diameter makes

$$\bar{d} = \sum_{i=1}^{n} d_i / n,\tag{4}$$

and average distance between them makes

$$\bar{l} = \left(L - \sum_{i=1}^{n} d_i\right) / n. \tag{5}$$

To obtain average value of area of the particle surrounded by metal atoms let us replace the values in expression (1) by their average values from Eqs. (2) and (3):

$$\bar{s}_{d} = \frac{\pi}{4} \left[\sum_{i=1}^{n} d_{i} / n + \left(L - \sum_{i=1}^{n} d_{i} \right) / n \right]^{2} = \bar{s} \cdot \left(L_{n} / \sum_{i=1}^{n} d_{i} \right)^{2}, \tag{6}$$

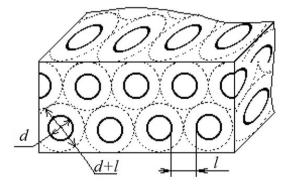


Fig. 1 Model of uniform packing of dispersed phase particles surrounded by metal atoms in a composite electrolytic coating



where \bar{S} —average area of dispersed phase particle on the surface, $L_{\rm n} = \frac{L}{n} = d_i + l_i$ —segment of straight line occupied by the particle surrounded by metal atoms. Total area of n particles surrounded by metal atoms at the sector of straight line of the surface makes

$$\bar{S}_{d} = S \cdot \left(L_n / \sum_{i=1}^n d_i \right)^2, \tag{7}$$

where $S = n \cdot \bar{s}$ —total area occupied by the particles themselves without surrounding metal atoms.

Thus, one of the effective parameters for estimating distribution of dispersed phase on a coating surface can be formed from the ratio between surface \bar{S}_d occupied by particles surrounded by metal atoms and surface S_L which they are distributed on.

$$\sigma = \frac{\bar{S}_{d}}{S_{L}} = \frac{S}{S_{L}} \cdot \left(L_{n} / \sum_{i=1}^{n} d_{i} \right)^{2}. \tag{8}$$

Parameter σ describes density of particles distribution on a coating surface and can be expressed as a percentage.

Let us consider the case when $n_x = \frac{L}{d}$ and $n_y = \frac{L}{d}$ identical particles are densely arranged along two selected Cartesian coordinates X and Y (Fig. 2a). Density of particles distribution on the surface

$$\sigma = \left(n_x \cdot n_y \cdot \frac{\pi d^2}{4}\right) / L^2 = \left(\frac{L^2}{d^2} \cdot \frac{\pi d^2}{4}\right) / L^2 = \frac{\pi}{4}. \quad (9)$$

With this distribution, each particle is surrounded by four others and density of such distribution of particles on the surface

$$\sigma = \pi/4 \approx 0.785. \tag{10}$$

Let us consider the case when $n_x = \frac{L}{2L^d}$ particles are located in direction of X axis, and $n_y = \frac{L}{d(1+\sqrt{3}/2)}$ particles in form

of three contiguous particles are located along the *Y* axis (at a distance of d + h, where $h = d\frac{\sqrt{3}}{2}$) (Fig. 2b). Density of particles distribution on the surface

$$\sigma = \left(N_x \cdot N_y \cdot \frac{\pi d^2}{4}\right) / L^2 = \left(\frac{2L^2}{d^2 \left(1 + \frac{\sqrt{3}}{2}\right)} \cdot \frac{\pi d^2}{4}\right) / L^2 = \frac{\pi}{2 + \sqrt{3}}.$$
(11)

With this distribution, each particle is surrounded by the six others and density of such particles distribution on the surface

$$\sigma = \frac{\pi}{2 + \sqrt{3}} \approx 0.842. \tag{12}$$

If number of the nearest particles surrounding one particle on the surface (so-called surface coordination number) is denoted as N_S then linear relationship between N_S and density of their distribution on the surface S can be identified by two points (10) and (12) by way of linear interpolation of system of equations such as

$$N_{\sigma_i} = a\sigma_i + b \text{ or } \begin{cases} 6 = 0.842a + b \\ 4 = 0.785a + b \end{cases}$$
 (13)

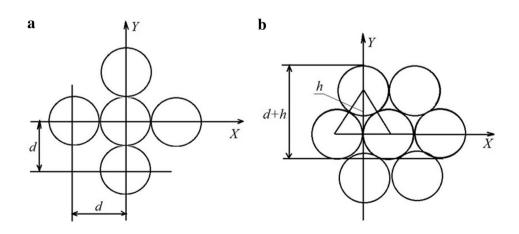
By solving the system of Eq. (13), coefficients *a* and *b* are calculated and next linear equation is obtained

$$N_{\rm S} = 35, \ 1\sigma_i - 23, 5 = 35.1 \frac{S}{S_{\rm L}} \cdot \left(L_n / \sum_{i=1}^n d_i \right)^2 - 23.5.$$
 (14)

Thus, surface coordination number N_S can be treated as another effective parameter which characterizes distribution of dispersed phase on the surface of composite coating.

Let us consider distribution of particles with a size of d_i and volume $V_d = \frac{4}{3}\pi \left(\frac{d_i}{2}\right)^3$ in the occupied volume V of the coating under condition of dense packing of particles. In this

Fig. 2 Model of uniform distribution of identical and disk-shaped particles on CEC surface surrounded by the four nearest particles (a) and the six ones (b)





case, particle with a diameter of d + l surrounded by metal atoms has volume

$$V_{d+l} = \frac{4}{3}\pi \left(\frac{d+l}{2}\right)^3 = \frac{4}{3}\pi \left(\frac{d}{2}\right)^3 \cdot \left(1 + \frac{l}{d}\right)^3 = V_d \cdot \left(1 + \frac{l}{d}\right)^3. \tag{15}$$

Volume of dispersed phase V_p , consisting of N particles distributed in the coating with the volume V

$$V_{\rm p} = N \cdot \frac{4}{3}\pi \left(\frac{d}{2}\right)^3 = N \cdot V_d. \tag{16}$$

Volume of dispersed phase surrounded by metal atoms will be determined by the equation

$$\bar{V}_{p} = N \cdot V_{d} \cdot \left(1 + \frac{l}{d}\right)^{3} = V_{p} \cdot \left(1 + \frac{l}{d}\right)^{3}. \tag{17}$$

Formulae for estimating a packing density (filling) of dispersed phase particles in the volume of composite coating

$$P_{\rm V} = \frac{V_{\rm p}}{V}.\tag{18}$$

Test Procedure

Composite coatings were electroplated on a low-carbon steel substrate from sulfate nickel-plating electrolyte which had the following composition: Ni₂SO₄·7H₂O—300 g/l, H_3BO_3 —30 g/l, Na_2SO_4 ·10 H_2O —50 g/l, at pH 5 and temperature 293...298 K. A pure nickel plate was used as an anode, which made it possible to maintain concentration of the basic metal salt unchanged and had positive effect on repeatability of experiments. To keep uniformity of electric field generated by flux of charged ions, the electrodes were arranged parallel to each other. Concentration of UDD particles in electrolyte aqueous solution made 2 g/l. In order to keep nanodiamond particles in a suspended state in the volume of electrolyte solution and to prevent particles from settling on the bottom of electrolytic cell, a magnetic mixer was used for stirring the aqueous electrolyte solution. Electrodeposition process is shown schematically in Fig. 3. At the initial moment of time, UDD particles float in their suspended state in the volume of electrolyte. Electrolytic cell comprises cathode, anode and aqueous electrolyte solution containing Ni²⁺ ions and UDD nanoparticles.

Electrodeposition was carried out at temperature 293–298 K, with rectangular current pulse (Fig. 4) at frequency (f) 50 Hz, pulse length (t_p) from 10 to 0.4 ms, relative pulse duration (Q—period (T) to pulse duration ratio) from 2 to 50, average current density (j_{av}) 100 A/m² and amplitude current density (j_{max}) from 200 to 5000 A/m². To perform comparison, composite nickel coatings were produced with

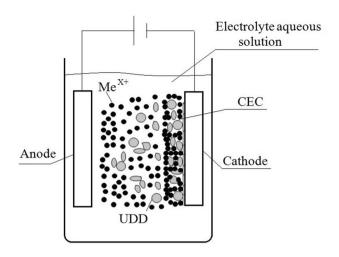


Fig. 3 Electrodeposition flow chart

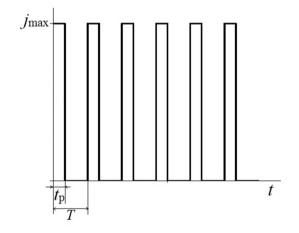


Fig. 4 Pulse current waveform used for CEC deposition

usage of the same aqueous electrolyte solution subject to DC application at density 100 A/m^2 . Value of cathode overvoltage (oversaturation) (η) was determined as difference between current and equilibrium values of potential [6, 17].

Microstructure and detailed element composition were analyzed with use of scanning electronic microscope JSM-64901LV (Japan) and energy-dispersive spectrometer INCA PENTAx3 (OXFORD Instruments). Microstructure of coatings in cross section was analyzed with use of optical microscope Neophot-21. Face metallographic samples were made by mechanical polishing. To demonstrate the structure of cross section, nickel films were etched chemically in 50% nitric acid solution during 10–15 s.



Results and Analysis

Picture of surface of composite electrolytic nickel coating comprising UDD articles at concentration 2 g/l is shown in Fig. 5. It can be seen from Fig. 5 that particles are non-uniformly distributed on the composite coating surface and besides they built conglomerates with various size and density.

To calculate average size of particles, we used method grounded on analyzing a distribution of length of chords on a coating surface (chord method) [18]. When using the chord method, cut right lines were applied on a microstructure image. These lines were parallel to upper bound of vision area and equally mutually spaced in order to ensure representativeness of an area under treatment. Length of chords cut by profile lines of particles sections on the cut right lines was measured, and then, length values were split in size

groups. Particles which were in direct contact with each other were measured separately if dihedron at the border of particles contact with each other and matrix made $\theta \le 90^\circ$. Otherwise, conglomerate was treated as a single particle. Length of average chord in plane of metallographic sample was calculated by formula

$$\bar{l}_{s} = \sum_{i=1}^{n} l_{i} n_{i} / \sum_{i=1}^{n} l_{i}$$
(19)

where l_i and n_i —average chord and number of sections of particle from the *i*th group on the unit surface area. Lines of grid placed over the image crossed particles and their conglomerates in different points. Therefore, areas of particles and conglomerates in points of crossing the grid lines were summed up instead of summing the equivalent diameters of particles.

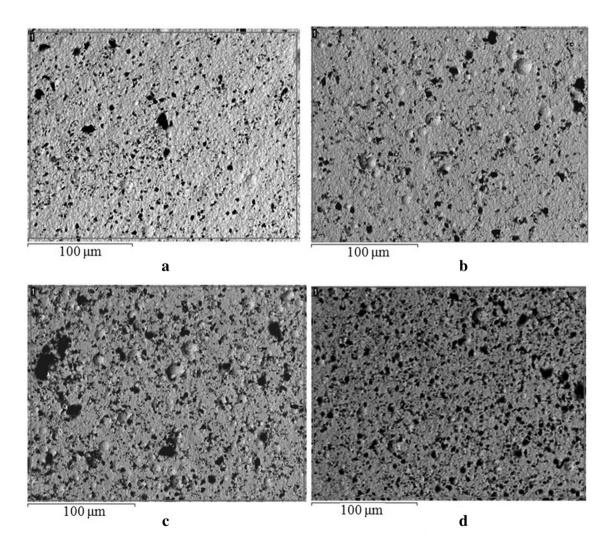


Fig. 5 Surface of composite nickel coating: (a)—direct current ($j=100 \text{ A/m}^2$); pulse current (f=50 Hz, $j_{av}=100 \text{ A/m}^2$), (b)—Q=2, (c)—Q=25, (d)—Q=50



Proceeding from inputs presented in Table 1 and assumptions made herein values of degree of surface occupation (σ), surface coordination number ($N_{\rm S}$) and were obtained filling density of particles in the volume ($P_{\rm V}$).

Experimental values of particles distribution density on the coating surface (σ) (Table 1) for the DC deposition mode correlate with the results of calculations according to the mathematical model of particles uniform distribution on the CEC surface surrounded by the four nearest particles (Fig. 2a). Good correlation of experimental values σ for the pulsed current deposition mode with the results of calculation according to model of close packing of particles on the surface of CEC surrounded by the six nearest particles (Fig. 2b) testifies that under higher non-equilibrium conditions of deposition, smaller UDD size particles penetrate in the growing coating.

Correctness of the developed mathematical model which describes distribution of the dispersed phase particles over the volume of composite coating was verified by way of comparison of test results obtained as a part of the study of dispersed phase particles concentration in the coating ($C_{\rm UDD}$, mas.%) by applying a microspectral analysis with calculations results as for particles distribution density over the volume ($P_{\rm V}$,%) (Table 1).

Comparison of the coatings elemental composition ($C_{\rm UDD}$, mas.%) research results obtained by applying a microspectral analysis with the results of evaluation of the particles distribution density over the volume ($P_{\rm V}$, %) (Table 1) gives a reasonable correlation according to the following formulae

$$\begin{split} C_{\text{UDD}} &= \frac{m_{_{\text{UDD}}}}{m_{_{\text{UDD}}} + m_{_{\text{Ni}}}} \cdot 100\% = \frac{\rho_{_{\text{UDD}}} \cdot V_{_{\text{UDD}}}}{\rho_{_{\text{UDD}}} \cdot V_{_{\text{UDD}}} + \rho_{\text{Ni}} \cdot V_{\text{Ni}}} \cdot 100\% \\ &= \frac{\rho_{_{\text{UDD}}} \cdot P_{_{\text{V}}}}{\rho_{_{\text{UDD}}} \cdot P_{_{\text{V}}} + \rho_{_{\text{Ni}}} \cdot \left(1 - P_{\text{V}}\right)} \cdot 100\%, \end{split} \tag{20}$$

where $m_{_{\rm UDD}}$ —mass of UDD particles in a coating, $m_{_{\rm Ni}}$ —nickel coating mass, $\rho_{_{\rm UDD}}$ —density of UDD particles, $\rho_{_{\rm Ni}}$ —nickel density, $V_{_{\rm UDD}}$ —UDD particles volume in a coating expressed in terms of particles occupation density in a coating volume ($P_{\rm V}$), $V_{_{\rm Ni}}$ —nickel coating volume expressed in terms of UDD particles occupation density in a coating volume as $(1-P_{\rm V})$.

Evaluation of density of particles distribution in volume $(P_{\rm V})$ is grounded on the results of testing the CEC microlayers in cross section (Fig. 6) [19–21].

The major part of UDD particles in the coating is traced in the form of dark inclusions (Figs. 5 and 6). Micrographs of CEC metallographic samples (Fig. 6) show light layers, containing predominant nickel with minimum content of UDD particles inclusions, which alternate with dark layers enriched with UDD particles.

Generation of microlaminated ECC growth structure is caused by passivating effect of ultra-dispersed diamond particles on the surface which is formed.

Calculation shows that coating microlayer is built within period ~ 580 s at advance speed of front of coating growth ~ 3 nm/s. During coating deposition with a total thickness 20–25 μ m DC process provides formation of 7–8 layers ~ 4 μ m thickness each (Fig. 6a), whereas AC process provides formation of 12–13 layers ~ 2 μ m thickness each (Fig. 6b). This outcome is confirmed by results of metallographic examination of structure of coatings growth in cross section.

Microlayer thickness loss from 4 to 2 μ m in case of the direct current deposition mode change over to the pulsed mode of electrodeposition is caused by non-equilibrium nature of a deposition process and increase in the rate of UDD particles supply to the cathode surface during the current pulse time. For the pulsed electrodeposition modes of (Fig. 6b), UDD particles supply to the cathode surface is

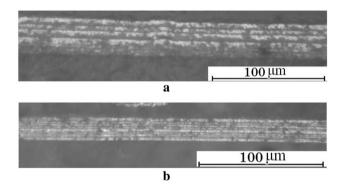


Fig. 6 Structure of composite nickel coating in cross section: (a)—direct current ($j=100 \text{ A/m}^2$), (b)—pulse current (f=50 Hz, Q=50, $j_{av}=100 \text{ A/m}^2$)

Table 1 Effective parameters to evaluate distribution of dispersed phase on coating surface and in coating volume

Deposition mode					C_{UDD} , mas.%	\bar{l} , μm	$\frac{S}{S}$, %	σ , %	$N_{\rm S}$	$P_{ m V},\%$
	$j_{\rm av}$, A/m ²	j_{max} , A/m ²	f, Hz	Q			L			
Direct current	100	100			1.43	8.04	10.8	75.1	2.9	3.1
Pulse current	100	5000	50	2	1.71	6.64	11.3	78.4	4.0	3.7
				25	2.14	5.89	11.9	80.2	4.7	4.6
				50	2.47	4.69	12.4	83.6	5.8	5.3



more uniform than in the direct current electrodeposition mode (Fig. 6a), that is demonstrated by regular thickness of microlayers.

So, composite electrolytic coatings and distribution of dispersed phase in the coating can be characterized by surface and volumetric relative parameters. Data presented in Table 1 and images of surface and cross section of composite electrolytic coating (Figs. 5 and 6) allowed to describe in details distribution of dispersed phase particles in composite substance as compared to the method which uses only concentration and average distance between particles.

Analysis of obtained data about distribution of dispersed phase on the surface and in the volume of composite electrolytic coatings showed that nickel-based CEC deposited at hard mode of pulse current (f=50 Hz, Q=50) are characterized by high values of package density $P_{\rm V}$ and degree of surface occupation with particles exceeds by 15% the degree obtained for the DC-produced nickel-based CEC.

To analyze distribution of particles of dispersed phase by size on the surface of composite electrolyte nickel coatings, statistical processing of test results of UDD particles concentration in CEC was performed. To establish functional relationship between concentration and size (diameter) of particles, a software STATISTICA [22] was used to perform this statistical analysis.

Figure 7 shows approximating curve of experimental data bar graph for UDD particles fractional composition on the surface of composite electrolyte nickel coatings. Average size of UDD particles made $1.5-2 \mu m$.

As a result of performed calculations, analytical form of function of particles distribution by their size was obtained

$$n = a \cdot d^2 \cdot \exp(-c \cdot d^2) + b, \tag{21}$$

where n—concentration of dispersed phase particles expressed in form of number of particles with size d_i to total number of particles in composite material (%),a, b, c—approximation constants.

Comparison of distribution function with test bar graph showed that calculated curves satisfactorily describe experimental distribution by size at parameters values: $a = (14 \div 70) \ \mu m^{-2}$, $c = (0.22 \div 0.80) \ \mu m^{-2}$, $b = (1.0 \div 2.5)\%$. It follows from distribution function that subject to certain values of particles, size function n = f(d) reaches its maximum value which corresponds to the most probable size of particles $(d_B, \mu m)$

$$d_{\rm B} = \sqrt{\frac{1}{c}} \tag{22}$$

and it can be found from extremum of distribution function (21).

It follows from the results of micro X-ray spectral analysis of coatings surface element composition [23, 24] that

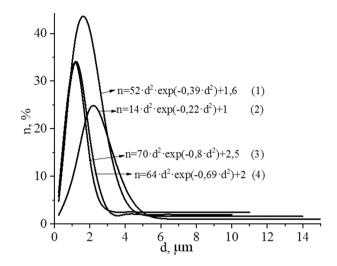


Fig. 7 Function of degree of surface occupation with UDD particles (n, %) dependence from particle size (d) in composite electrolyte nickel coatings deposited with application of: (1) direct current $(j=100 \text{ A/m}^2)$; pulse current $(f=50 \text{ Hz}, j_{av}=100 \text{ A/m}^2)$; (2) Q=2; (3) Q=25; (4) Q=50

portion of particles with certain size depends on mode of electrodeposition. Composite nickel coatings produced with application of pulse current are characterized by higher density of UDD particle distribution in the coating. Besides, degree of surface occupation with UDD particles at pulse deposition is approximately 2 times higher as compared to the composite nickel coatings produced with application of direct current. At that, increase of current relative pulse duration from 2 to 50 and unchanged current frequency (50 Hz) results in increase of percentage of particles with less size $d \sim 0.25-1 \mu m$ (Fig. 7).

Intermittent nature of the pulse current and increase of current relative pulses duration contribute to more intensive penetration of smaller size dispersed phase particles into the growing coating (Fig. 7). It happens due to high instantaneous current densities in pulses (5000 A/m²) and consequently due to nickel ions discharge at higher values of the cathodic overvoltage (η = 1.3 V) as compared to the DC deposition mode (η = 0.9 V). Increase of oversaturation at the crystallization front promotes to increase of the nucleation rate and reduction of their growth rate, formation of more fine-grained, close-packed coating with the more uniform distribution of UDD particles in the coating.

Conclusions

 Mathematical model which describes occupation of composite electrolytic coating surface with particles of dispersed phase and particles distribution in volume of the surface was developed. Composite electrolytic coat-



- ing and distribution of dispersed phase particles over the CEC were characterized by surface parameters (fraction of the surface covered with dispersed phase particles $\frac{S}{S_L}$; average distance between particles \bar{l} ; density of particles distribution on the composition surface σ ; surface coordination number of particles distribution $N_{\rm S}$) and volumetric characteristics (distribution density of particles in the volume $P_{\rm V}$).
- 2. Structure of electrolyte nickel coatings under state of ultra-dispersed diamond particles packing in a metal matrix was estimated by the surface coordination number. Linear dependence of this parameter on the main characteristics of the package was deduced. It was shown that composite electrolytic nickel coatings deposited under a hard pulsed current mode ($j_{\text{max}} = 5000 \text{ A/m}^2$, f = 50 Hz, Q = 50) are characterized by high values of both particle distribution density on the surface and coordination number.
- 3. Concentration functional dependence on the particles size (diameter *d*) in a coating was defined. Growth of smaller size particles (*d*~0.25–1 μm) concentration in a coating at pulsed deposition mode is caused by higher non-equilibrium crystallization conditions (maximum overvoltage value makes 1.3 V). With increase of the oversaturation at the crystallization front, smaller-in-diameter UDD particles arrive at the growing coating and these particles block also growth of crystalline phase nuclei that leads to formation of highly close-packed coating.

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