Mechanism of incorporation of carbon nanomaterial particles in composite electrolytic metal coating

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The problem of joint electrolytic deposition of metal ions and ultradispersed diamond particles into a metal matrix is formulated. The mathematical model describing the mechanism and kinetics of the cathodic process, the mass transfer of metal ions and carbon nanomaterial particles is developed. It has been established that transfer of particles of the dispersed phase occurs mainly not by the diffusion mechanism but under the influence of an electric field.

Keywords*: ultradispersed diamond particles, electrodeposition, composite electrolytic coatings.*

Introduction

The creation of composite electrolytic coatings (CEC) is one of the current areas of solid state physics. The principle of obtaining CEC is based on the fact that, together with metals, particles of the dispersed phase co-precipitate from aqueous electrolyte solutions. Included in coatings, particles significantly improve their performance properties (hardness, wear resistance, corrosion resistance) and give them new qualities (antifriction, magnetic, catalytic) [1—6]. Due to this, CECs are widely used in various industries, and the development of new types of composite coatings and the search for ways to control their properties is an important scientific and applied task.

The efficiency of using CEC is largely determined by the nature of the dispersed phase. Particles of ultradispersed diamond, which belong to the class of superhard materials, are of particular interest as modifiers of composite electroplating coatings [7—11].

The unique physicochemical properties of electrodeposited metal films largely depend on the concentration of carbon nanomaterial (CNM) particles in the metal matrix. Therefore, the control and management of CNM particle content in composite metal films has recently attracted particular attention. The solution to such a problem is impossible without studying the mechanism of structure formation of carbon-containing composite metal coatings.

The purpose of this work is to develop a mathematical model that describes the transfer of CNM particles and metal ions in the volume of the electrolytic bath, as well as the kinetics of the co-precipitation process of metal ions and CNM particles on the cathode.

Materials and methods

Composite metal coatings were deposited from an aqueous electrolyte solution of the following composition, in g/l: $NiSO_4 \cdot 7H_2O$ — 300, H_3BO_3 — 30, $Na_2SO_4 \cdot 10H_2O$ — 50, pH — 5,0.

UDD nanoparticles were used as the dispersed phase. The UDD concentration in the aqueous electrolyte solution was 2 g/L. The size of UDD particles are 0.04—15 μm. 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 non-destructive parts of nanodiamond powders. ND particles are prone to spontaneous aggregation among themselves into very strong aggregates (40—100 nm) followed by the formation of weaker secondary aggregates (up to 1—5 μm) [12, 13].

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 microstructure and elemental composition of the coating surfaces were studied using a JSM-64901LV scanning electron microscope (Japan) with an INCA PENTAx3 energy dispersive spectrometer (OXFORD Instruments). The software package for statistical analysis STATISTICA 12 [14] was used to determine the functional dependence of the concentration on the size (diameter) of the particles.

The electrodeposition process is schematically shown in fig. 1. An electrolytic cell consists of a cathode, an anode, and an aqueous electrolyte solution containing Ni^{2+} ions and CNM particles.

To keep the CNM particles in a suspended state in the volume of the aqueous electrolyte solution and to prevent them from settling to the bottom of the electrolytic cell, the electrolyte solution was stirred using a magnetic stirrer.

The kinetics of the cathode process is determined by the concentration of metal ions and CNM 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

Fig. 1. Electrodeposition process flow diagram.

solution. But at the initial moment of deposition, the concentrations at the cathode-electrolyte interface change. A mass transfer layer is formed near the cathode surface and the concentration of metal ions changes along its entire thickness. When constructing the model of the problem under consideration, we make the following assumptions:

metal ion and CNM particle concentrations do not change outside the mass transfer layer and are equal to the concentrations in the electrolyte solution volume;

in view of small size of CNM particles and the vertical arrangement of the electrodes, the influence of the Archimedes forces and gravity can be neglect.

Results and discussion

Analysis of cathodic polarization curves (fig. 2) showed that the presence of dispersed particles in an aqueous electrolyte solution leads to a shift in the cathode potential to the electronegative region, which indicates an increase in the charge transfer resistance.
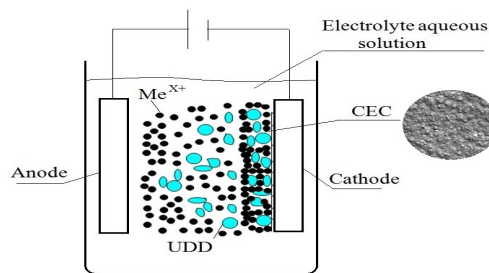
To establish the mechanism for the incorporation of the dispersed phase particles in the coating being formed, it is necessary to estimate the particle flux density. The most optimal mathematical expression for describing this physical process is the Nernst-Planck equation. The interest in studying the Nernst—Planck equation from an applied point of view is due to its applicability to the description of transport phenomena in various media.

According to the Nernst—Planck equation [15], the transfer of ions and carbon nanoparticles in an aqueous electrolyte solution is determined by two factors: their distribution unevenness, i. e. concentration gradient, and the influence of electric field

$$J = -D\frac{dc}{dx} - \frac{D}{RT}ZFc\frac{d\varphi}{dx} = -D\left(\frac{dc}{dx} + \frac{ZFc}{RT}\frac{d\varphi}{dx}\right), \qquad (1)$$

where D — diffusion coefficient (m^2/s); R — universal gas constant; T — absolute temperature, Z — ion charge; F — Faraday number.

In the case when the radius of the diffusing particle is much larger than the radius of the molecule of liquid itself, the diffusion coefficient can be estimated from the Stokes—Einstein relation [16]

$$D \cong \frac{kT}{6\pi\eta \cdot r}, \qquad (2)$$

where r — radius of the particle; η — internal friction coefficient (dynamic viscosity) of the aqueous electrolyte solution.

Assuming the electric field to be homogeneous and considering that

$$\frac{ZFc}{RT}\frac{d\varphi}{dx} = \frac{ZFc}{RT}\frac{\Delta\varphi}{l} = \frac{\psi}{l}c, \qquad (3)$$

where $\Delta\varphi$ — potential difference in double electric field (DEF); l — DEL thickness ($l = \sqrt{Dt}$, where t — time of the deposition process); $\psi = \frac{ZF}{RT}\Delta\varphi$ — auxiliary quantity (dimensionless potential), we obtain the Nernst—Planck equation in the form

$$J = -D\left(\frac{dc}{dx} + \frac{\psi}{l}c\right). \qquad (4)$$

Solution of the equation (4) has the form

$$J = \frac{D\psi}{l}\frac{c_0 - e^{\psi}c_l}{e^{\psi} - 1}, \qquad (5)$$

where c_0 and c_l are concentrations of metal ion sand CNM particles in the volume of the aqueous electrolyte solution and near the cathode surface respectively.

Equation (5) relates the fluxdensity of metalions and CNM particle swith two quantities:
I) concentration of metalions and CNM particles in the aqueous electrolytes olution;
II) electricfield. In ordertodetermine the mechanism of transferandco-precipitation of CNM particleslet us analyseaparticularcase of the equation (5):
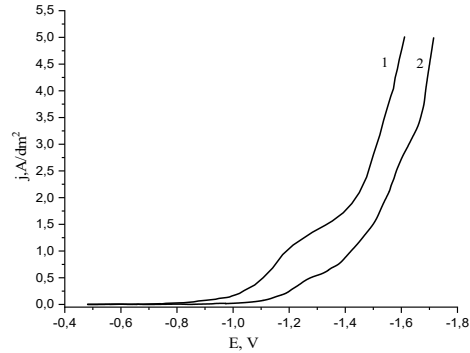

Fig. 2. Cathodic polarization dependences obtained in sulphuric nickel plating electrolyte: 1 — without UDD; 2 — with UDD.

I) $\psi = 0$, which meanseither $Z = 0$ (neutralparticles) ornoelectricfield ($\Delta\varphi = 0$), or both. After mathematical transformations we obtain

$$J = \frac{D}{l}(c_0 - c_l) .$$ (6)

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

II) the same concentration of carbon nanoparticles in the volume of the aqueous electrolyte solution (c_0) and near the cathode surface (c_l), i. e. $c_0 = c_i = c$ in the presence of electric field.

$$J = -\frac{D\psi}{l}c \text{ or } J = -D\frac{ZF}{RT}\frac{\Delta\varphi}{l}c .$$ (7)

Model II considers the transfer of CNM particles in the aqueous electrolyte solution under the action of an electric field. In calculations of the flux density of CNM particles, it was taken into account that an overpotential of 0,5 V is maintained on the cathode during the deposition of nickel from simple sulphuric acid aqueous electrolyte solutions [17].

As a result of the simulation, we obtained the dependences of the flux density of UDD particles in an aqueous solution of nickel plating electrolyte and their concentration in the composite electrolytic coating on the size of DF particles, which is shown in fig. 3.

To determine the concentration of the dispersed phase in the coating (in % (wt.)) (fig. 3 (2)) by the expression

$$C = \frac{m_{CNM}}{m_{CNM} + m_{Ni} \cdot CE} \cdot 100\%$$ (8)

from the results of calculation of the flux density of UDD particles (fig. 3 (1)), the CNM mass (m_{CNM}) and the nickel mass (m_{Ni}) were estimated, taking into account the metal current efficiency (CE).

To analyze the size distribution of particles of the dispersed phase on the surface of composite electrolytic nickel coatings, statistical processing of the results of studies of the UDD particles concentration in CEC was carried out.

Figure 4 shows the approximating curves of experimental histograms of the fractional composition of UDD particles on the surface of composite electrolytic nickel coatings. The average diameter of UDD particles was 1—2 µm.

The calculations resulted in the analytical form of the particle size distribution function in the coating

$$n = a \cdot d^2 \cdot \exp(-c \cdot d^2) + b ,$$ (9)

where n (%) — concentration of particles of the dispersed phase, expressed in terms of the number of particles of size d_i to the total number of particles in the composite volume; a, b, c — approximation constants. Distribution function shows that for certain particle size values the function $n = f(d)$ has a maximum that corresponds to the most probable particle size (d_P, µm)

$$d_P = \sqrt{\frac{1}{c}}$$ (10)

and is derived from the extremum of distribution function (10).

Comparison of the results of studying the elemental composition of coatings (figs. 4) and the results of estimating the concentration of the dispersed phase in the

coating (in % (wt.)) according to formula (8) gives a satisfactory correlation with the mathematical model II (fig. 3, *b*) for particles with a size of ~1 μm.

Analysis of the results of calculations of mathematical models of the process of co-deposition of metal ions and UDD particles (fig. 3) showed that the main factor influencing the transfer of CNM particles in an aqueous electrolyte solution is the potential gradient. The calculation by formula (5) showed that the contribution of the concentration gradient to the particle flux density is insignificant. The experimentally obtained value of the flux density of UDD particles ($J = 5{,}8 \cdot 10^{-7}$ kg/m$^2 \cdot$s) correlates with the results of calculations of the mathematical model II (fig. 3, *b*) for particles ~1 μm in size.

Consequently, the transfer of CNM particles occurs mainly not by the diffusion mechanism, but under the action of an electric field. It can be assumed that the formed CNM-metal complexes, as a result of the
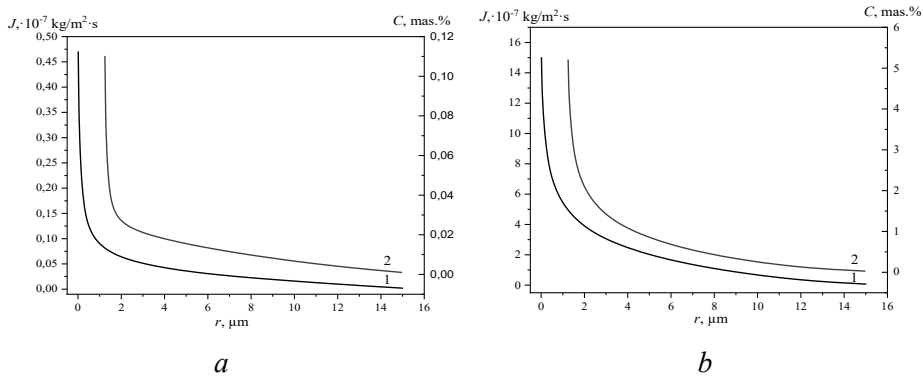

a   *b*

Fig. 3. Dependences of the flux density of UDD particles in the aqueous solution of nickel plating electrolyte (1) and their concentration (2) in the composite electrolytic coating on the particle size: *a* — Model I; *b* — Model II.

Fig. 4. Dependences of the degree of surface coverage with UDD particles (n, %) on the particle size (d) in composite electrolytic nickel coatings.

$$n = 52 \cdot d^2 \cdot \exp(-0{,}39 \cdot d^2) + 1{,}6$$
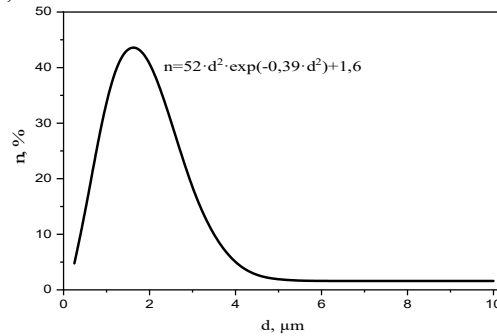
adsorption of metal atoms on the surface of a CNM particle, gain a charge in the electrolyte solution and move towards the cathode under the action of an electric field created by the potential difference between the anode and the cathode.

Fig. 5 shows the surface images of the electrolytic nickel coating. From the SEM micrograph of the nickel coatings shown in fig. 5, it follows that the grain sizes of the coatings change depending on the deposition conditions. Studies of the fine structure of the coatings showed a decrease in crystallite size from 104 nm for pure nickel (fig. 5, *a*) to 85 nm for the composite nickel coating (fig. 5, *b*).

The inclusion of UDD particles in the coating composition complicates the surface diffusion of metal ad-atoms and prevents the growth of nuclei of the crystalline phase. As a result, composite coatings form finer grains and the cross-sectional coating growth structure changes from columnar (fig. 6, *a*) to microlayered one (fig. 6, *b*).

Thus, the addition of CNM particles to the aqueous electrolyte solution leads to an increase in supersaturation at the crystallization front, thereby enhancing the nucleation rate and reducing the nuclei growth rate, and contributing to the formation
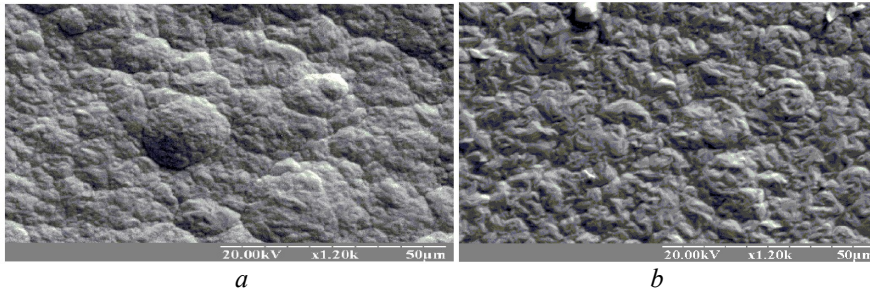

Fig. 5. SEM micro-photographs of the surface: *a* — nickel coating, *b* — composite nickel coating.
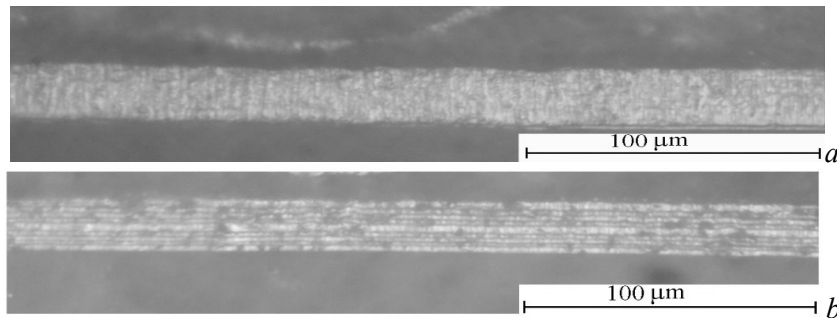

Fig. 6. Cross-sectional structure of electrolytic coatings: *a* — nickel coating, *b* — composite nickel coating.

of a finer-grained, close-packed coating. The inclusion of UDD particles in the nickel coating changes the growth structure in the cross section from columnar to microlayered, which is caused by the passive action of the particles of the dispersed phase on the surface being formed.

Conclusions

The mathematical model describing the mechanism and kinetics of the cathode process, the mass transfer of metal ions and ultradispersed diamond particles is developed. It is found that the transfer of CNM particles occurs mainly not by the diffusion mechanism, but under the influence of an electric field.

An increase in the cathode overpotential indicates a decrease in the active surface area of the cathode by UDD particles, which are transported in an aqueous electrolyte solution under the action of an electric field.

The UDD particles, reaching the cathode surface, block the growth of nuclei of the crystalline phase, which leads to the formation of a more densely packed coating and changes the growth structure in the cross section from columnar to microlayered one.

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Механізм включення частинок вуглецевого наноматеріалу в композиційне електролітичне металеве покриття

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Методом електроосадження з водного розчину електроліту нікелювання, що містить частинки ультрадисперсного алмазу, отримано композиційні металеві покриття. Результати досліджень катодних поляризаційних залежностей свідчать про збільшення опору перенесення заряду у водному розчині електроліту внаслідок можливої адсорбції іонів металу на поверхні частинок ультрадисперсного алмазу. Сформульовано задачу спільного електролітичного осадження іонів металу та частинок ультрадисперсного алмазу в металеву матрицю. Розроблено математичну модель, яка описує механізм та кінетику катодного процесу, масоперенесення іонів металу та частинок вуглецевого наноматеріалу. Отримано задовільну кореляцію з експериментальними даними. В результаті моделювання отримано залежності густини потоку частинок ультрадисперсного алмазу у водному розчині електроліту нікелювання та їх концентрації в композиційному електролітичному покритті від розміру частинок дисперсної фази. Встановлено, що перенесення частинок дисперсної фази відбувається в основному не за дифузійним механізмом, а під дією електричного поля. Дослідження тонкої структури покриттів показали зменшення розмірів кристалітів від 104 нм для нікелю чистого до 85 нм для композиційного нікелевого покриття. Включення частинок ультрадисперсного алмазу до складу покриття ускладнює поверхневу дифузію адсорбованих на катоді атомів металу і перешкоджає зростанню зародків кристалічної фази, в результаті чого композиційні покриття формуються більш дрібнозернистими, а структура покриття у поперечному перерізі змінюється від стовпчастої до мікрошарової.

Ключові слова: частинки ультрадисперсного алмазу, електроосадження, композиційні електролітичні покриття.