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Convection–Diffusion Model for the Synthesis of PVD Coatings and the Influence of Nanolayer Parameters on the Formation of Fractal and Hierarchical Structures

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Abstract: The study proposes a model for the deposition of coatings, which takes into account the stochastic nature of the deposition process and is built considering the influence of the parallel convection and diffusion processes. The investigation has found that the dispersion of the motion direction of deposited particles in front of a substrate increases, which indicates a growth of the randomness in the trajectories of the particles being deposited. The obtained formulas indicate the fractal nature of the deposition process. During the formation of the multilayer coating structure, mismatched fractal structures of the layers overlap each other and thus the clustering effect is largely leveled out. The value of the nanolayer λ period has a significant influence on the fractal structure of the coating and the formation of feather-like hierarchical structures in it.

Keywords: hierarchical structure; multilayer PVD coating; stochastic process; convection and diffusion

1. Introduction

The process of the coating deposition is very complex and undoubtedly stochastic [1–7]. Accordingly, the modeling of the coating deposition process is also a complex and many-sided challenge, and in some cases, a probabilistic approach is required to meet this challenge [3–7]. Initially, one of the key tasks for the modeling of the processes under consideration was to predict a thickness of a coating, including a coating deposited on a complex-shape surface. To meet the above challenges, physical and geometric methods were applied, which made it possible to achieve the certain prediction accuracy. In particular, the studies proposed the coating thickness uniformity model [8,9], the cosine analytical and generic computational model [10], and the inverse power law relationship between thickness and source-to-substrate distance was considered [11]. Recent studies also applied true line-of-sight models, based on the inverse square law and also taking into account the effect of shadow

masks [12]. In [13], the computational level set method was also applied for tracking topographic change of a surface.

The traditional approaches to the modeling of mass transfer processes, in particular, the coating deposition processes, have significant limitations when described in micro- and mesosystems [14,15]. In connection with the above, the processes are often modeled on micro- nano- and atomic levels, due to the integration of systems with a large number of particles, the motion of which is described, in particular, by equations of molecular dynamics of Newtonian mechanics. A significant problem of these methods is the existing limitation of the maximum number of particles in a system due to the limit of computing power.

Approaches of molecular dynamics are used to model the deposition process [16]. By simulating the interaction of individual atoms, this method makes it possible to predict the morphology, thermal and electronic properties, and also internal stresses of the coating being deposited. When the above method is applied, the forces of interatomic interaction are presented in the form of classical potential forces. The configuration sets obtained in the course of the calculations using the method of molecular dynamics are distributed in accordance with a certain statistical distribution function, for example, a one corresponding to microcanonical distribution. The exact information concerning the trajectories of system particles at large time intervals is not necessary to obtain results of a macroscopic (thermodynamic) nature [17]. The principals of molecular dynamics can be applied to simulate the coating deposition process using dynamic equations and pressure and temperature boundary conditions for substrate and coating surfaces, taking into account the results of the preliminary study of stresses in the coating.

In particular, to model the coating deposition process, the Particle-in-Cell Monte Carlo simulation method [3,4], with both modeling options of simpler 2D [5] and more complex 3D [6–8], requiring advanced computing power, is applied. During the comparison of 2D and 3D models, it was found that the main difference between two-dimensional and three-dimensional options of modeling was consideration of the effect of propagating plasma waves that had a significant influence on the properties of particle transport in discharges limited by a magnetic field. Two-dimensional modeling provides useful qualitative information about the general trends and mechanisms of magnetron discharges, while three-dimensional modeling makes it possible to quantitatively describe the electron transfer and current–voltage characteristics [18]. Based on the results of 2D modeling using the Monte Carlo algorithm, the formation of a coating with feather-like hierarchical structure was demonstrated in [19]. The results of the study focused on the development of a columnar coating structure have proved that the average distance between columns first increases sharply and then stabilizes due to cessation of the growth and regeneration of the structure. The Monte Carlo methods were applied for 2D modeling of the process of micropore formation in a coating, given the stochastic nature of the process [20]. Approaches of computational fluid dynamics were also applied, they give a much rougher description of the process, but at the same time contribute to a noticeable reduction in the amount of calculations, thus making it possible to introduce modeling in the 3D geometry with high-scale detailing [21,22]. A more detailed analysis of various methods for modeling the coating deposition process can be found in [23]. Thus, the most accurate and complete simulation of the deposition process should take into account the stochastic nature of this process and consider the molecular level, because a coating is formed precisely at this level. Several studies [24–26] consider a cluster, hierarchical structure of the coating, deposited through various methods, and the influence of the deposition process parameters on the formation of such structure. However, the influence of the parameters of the nanolayer coating structure on the formation of hierarchical structures in the coating requires an additional study.

2. Materials and Methods

The filtered cathodic vacuum arc deposition (FCVAD) [27–36] technology was applied to deposit the Ti–TiN–(Ti,Cr,Al)N coatings. A VIT-2 unit, (IDTI RAS—MSTU STANKIN, Moscow, Russia), equipped with two arc evaporators with a pulsed magnetic field and one arc evaporator with filtering

of the vapor-ion flow, was used to deposit the coatings. In addition, the system was equipped with a source of pulsed bias voltage supply to a substrate, a dynamic gas mixing system for reaction gases, a system for automatic control of pressure in the chamber and a process temperature control system, and a system for stepless adjustment of planetary gear rotation [27–30,35–42]. The nanolayer structure of the coating provides high hardness at elevated temperatures and high oxidation resistance [27–31,37,38]. A three-layer structure of the coating was assumed [27–31].

The parameters for the process of coating deposition are presented in Table 1.

Table 1. Parameters of stages of the technological coating deposition process.

Process	p_N (Pa)	U (V)	I_{Ti} (A)	I_{Al} (A)	I_{Cr} (A)
Pumping and heating of vacuum chamber	0.06	+20	75	120	65
Heating and cleaning of products with gaseous plasma	2.0	100 DC/900 AC $f = 10$ kHz, 2:1	85	80	-
Deposition of coating	0.42	−800 DC	75	160	55
Cooling of products	0.06	-	-	-	-

Note: I_{Ti} = current of titanium cathode, I_{Cr} = current of Cr cathode, I_{Al} = current of aluminum cathode, p_N = gas pressure in chamber, U = voltage on substrate.

An analysis of the microstructure and nanostructure of the samples was studied using JEM 2100 (JEOL, Tokyo, Japan) high-resolution transmission electron microscope (TEM) with an accelerating voltage of 200 kV.

3. Results

3.1. Convection–Diffusion 2D Model for the Stochastic Coating Deposition Process

The creation of a wear resistant layer of the coating combines two parallel processes: convection and diffusion. Convection causes the rectilinear motion of particles from a cathode to the surface on which a coating is to be deposited, while diffusion gives rise to the consideration of random factors influencing particle trajectories, as a result of which the density of the substance being deposited becomes inhomogeneous, and the process represents the diffusion limited by the clustering or, alternatively, the clustering limited by the diffusion. A 2D model of the coating deposition process was considered, according to which the area where particles were deposited was plane (Figure 1). This assumption can be quite logically extended to a 3D model, because the flow of the particles moving through the fixed plane parallel to the Oxz plane is quasi-isotropic. The typical linear size of the deposition area is about L . The particles are emitted from the line of $y = b$ and are deposited on the line of $y = a$.

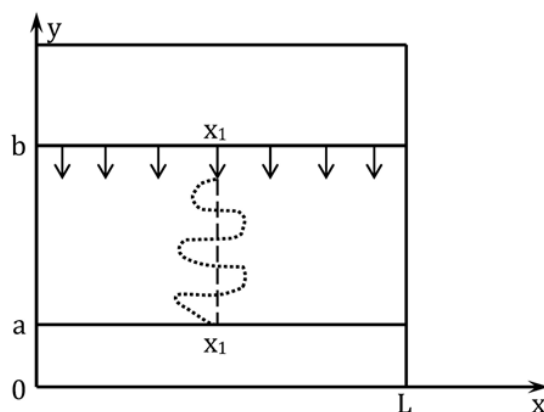


Figure 1. 2D model of the cross-section of the area perpendicular to the plane in which the particles emitted from the cathode in the direction of the substrate are being deposited.

In case if no diffusion occurs, a particle leaving a point with the coordinate (x_1, b) enters a point with the coordinate (x_1, a) , while moving along a straight line connecting these points. In case of diffusion, a particle is moving from the point (x_1, b) to the point (x_1, a) along a random trajectory, and the probability of its getting into point (x_1, a) is not equal to 1 (Figure 2). Let it be assumed that at $t = 0$, the particle with the coordinate (x_1, b) begins to move along the straight line connecting it with the point with the coordinate (x_1, a) . The one-dimensional process with $y = y(t)$ for constant $x = x_1$ is first considered.

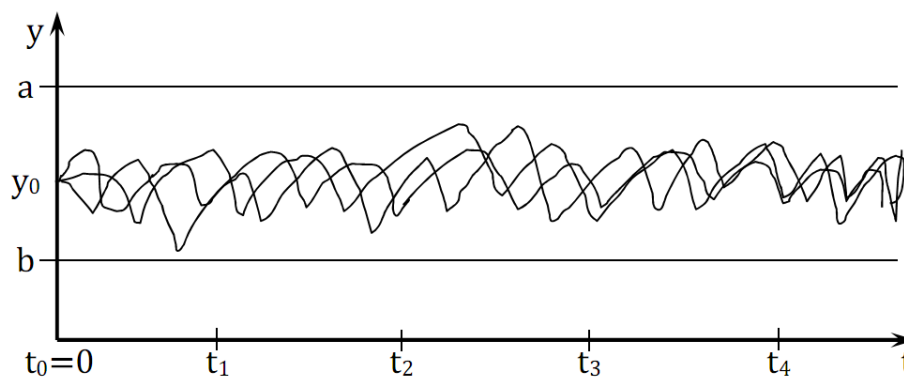


Figure 2. Diagram reflecting random particle trajectories (random walks) moving from the point (x_1, b) to the point (x_1, a) .

Let at time $t = t_0$ the particle has coordinates of $y = y_0$ ($a < y_0 < b$), $x = x_1$ ($0 < x_1 < L$). The probability density $f(y)$ and likelihood $P(y)$ of this event are as follows:

$$f(y) = \delta(y - y_0), \quad \int_a^b f(y) dy = P(y = y_0) \quad (1)$$

When $t > t_0$, the coordinate $y = \xi(t)$ is a random time function, then its probability density can be written in the following form [43]:

$$f(y) = \langle \delta(y) \rangle \quad (2)$$

where the brackets $\langle \rangle$ denote the averaging over realizations.

Let us assume that $\xi(t)$ satisfies a Langevin equation of the Brownian-motion type.

$$\begin{aligned} \frac{d\xi}{dt} &= v(\xi, t) + f(\xi, t), \quad \xi(0) = y_0 = \xi_0 \\ \langle f(\xi, t) \rangle &= 0, \quad B(\xi, t, \xi', t') = \langle f(\xi, t) f(\xi', t') \rangle = 2\delta(t - t') F(\xi, \xi', t) \end{aligned} \quad (3)$$

where $B(\xi, t, \xi', t')$ is a correlation function.

By (3), the differentiation of (2) with respect to t yields an equation for the probability density function of the particle's position:

$$\begin{aligned} \frac{\partial f_t}{\partial t} + \frac{\partial}{\partial y} [v(y, t) + A(y, t)] f_t(y) - \frac{\partial^2}{\partial y^2} [F(x, y, t) f_t(y)] &= 0 \\ A(y, t) &= \frac{\partial}{\partial y} F(y, y', t) \Big|_{y'=y} \end{aligned} \quad (4)$$

The Fokker-Planck-Kolmogorov differential Equation (4) should be solved with the initial condition (1). The physical meaning of the Equation (4) is in description of the stochastic processes for the motion of the coating's deposited particle in the gas phase from the cathode to the substrate. The coefficients in the equation at $f_t(y)$ are the particle transport and diffusion parameters, respectively. According to the Formulas (3) and (4), the equation terms with parameters A and F are specified by fluctuations of the field $f_t(y, t)$, affecting $v(\xi, t)$, which is a deterministic function describing the convective particle

transport. If $f_t(y, t) = f(y)$, i.e., is constant in time, then A and F are also constant in time, which corresponds to the constant diffusion coefficient F and convection $A = 0$. Cases when $f(y, t)$ is non-stationary require a model specification.

The real process of the layer-by-layer formation of a coating is of stochastic nature due to the fact that the layer of particles which started their motion from a source plane does not remain planar, while the particles interact with each other and cannot simultaneously form microclusters during the deposition, with correlations formed between them. Such microconglomerates, being deposited on the substrate, will be considered as nuclei of clusters in the coating layer, which introduce randomness into the deposition process and make the coating structure heterogeneous, fractal. Depending on the mentioned random factors, the deposition time is a random variable for different particles.

Figure 3 exhibits an initial view of the surface of the Ti–TiN–(Ti,Cr,Al)N coating with a pronounced cluster structure.

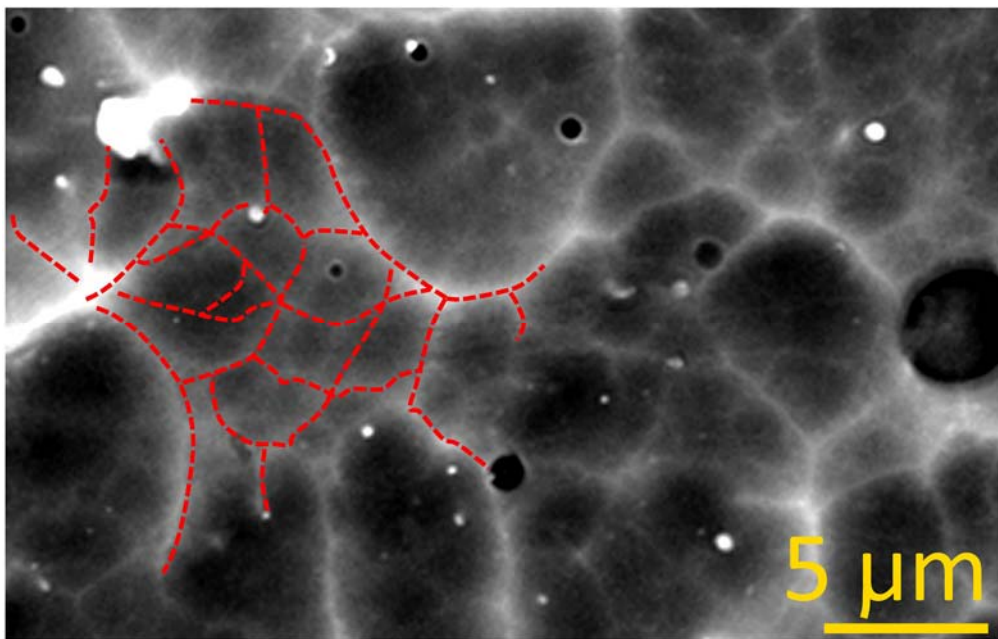


Figure 3. Cluster structure of the surface of the Ti–TiN–(Ti,Cr,Al)N coating after deposition.

The model of a random process reaching the boundaries of its variation area makes it possible to estimate the probability of this event and the average time required for that [43]. Let $P(y_0, t)$ denote the probability of the event that the random process will reach the boundary a or b with the initial condition of $P(y, 0) = 0$ and the boundary conditions of $P(a, t) = P(b, t) = 1$, then $P(y_0, t)$ satisfies the equation [43]:

$$\begin{aligned} \frac{\partial P(y_0, t)}{\partial t} &= K_1(y_0) \frac{\partial P}{\partial y_0} + \frac{1}{2} K_2(y_0) \frac{\partial^2 P}{\partial y_0^2} \\ K_1(y_0) &= v(y_0) + \frac{AF F'}{4}, \quad K_2(y_0) = \frac{AF^2}{2}, \quad F' = \frac{dF}{dy_0} \end{aligned} \quad (5)$$

The drift coefficient K_1 and the diffusion coefficient K_2 are to be specified for every model. As is known [43], the Equation (5) can be solved only for some particular models. When the initial and boundary conditions are formulated, the probability to reach the boundary increases. Figure 4 exhibits in graphic form the probabilities P —to reach the boundary and $\bar{P}$ —not to reach the boundary when the normalization condition is satisfied.

$$P + \bar{P} = 1 \quad (6)$$

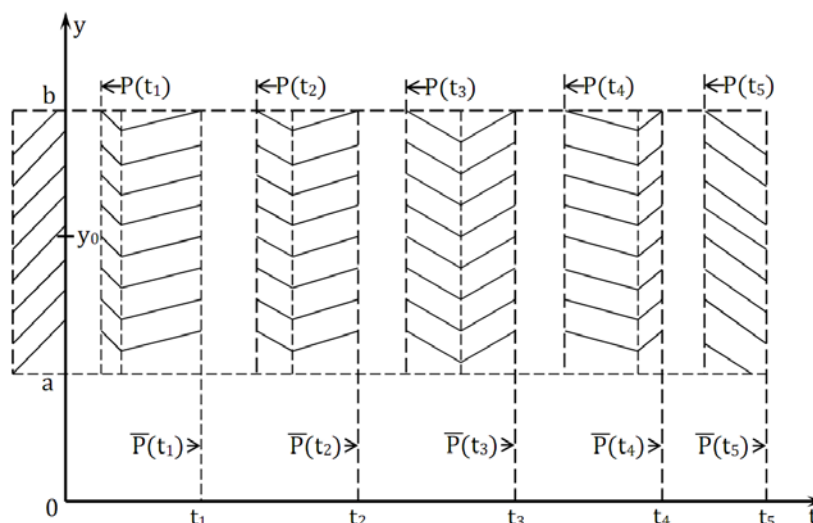


Figure 4. Graphic form depicting the probabilities P —to reach the boundary and $\bar{P}$ —not to reach the boundary.

At Figure 4, $P + \bar{P} = 1$ is the normalization condition:

$$P_i = \frac{S_i}{S}, \quad \bar{P}_i = 1 - \frac{S_i}{S} = \frac{\bar{S}_i}{S}, \quad i = 1, 2, \dots \quad (7)$$

S_i is the area of the rectangle $P(t_i)$,

$\bar{S}_i$ is the area of the rectangle $\bar{P}(t_i)$.

Thus, $P(t_i)$ describes a change in the rectangle, which area is numerically equal to the probability of reaching the boundary (of the substrate), while $\bar{P}(t_i)$ describes a change in the rectangle, which area is numerically equal to the probability of not reaching the boundary.

The time it takes for a particle to reach the substrate is a random variable over a set of realizations. Then to calculate the average time to reach $\langle t \rangle$, a formula for mathematical expectation can be used as follows:

As far as $P(y_0, t) = 1 - \bar{P}(y_0, t)$, then

$$\begin{aligned} \langle t \rangle &= T = \int_0^\infty t \frac{\partial P(y_0, t)}{\partial t} dt = - \int_0^\infty t \frac{\partial \bar{P}}{\partial t} dt = \left\{ \begin{array}{l} \text{integration by parts} \\ t=K, \frac{\partial P}{\partial t} = \partial v \end{array} \right\} \\ &= t \bar{P}|_0^\infty + \int_0^\infty \bar{P}(y_0, t) dt = \int_0^\infty \bar{P}(y_0, t) dt, \text{ as far as } t \bar{P}(y_0, t)|_{t=\infty} \\ &= 0, \quad t \bar{P}(y_0, t)|_{t=0} = 0 \end{aligned} \quad (8)$$

Given (5), an equation for $T(y_0, t)$ can be derived from (7), as follows:

$$\langle t \rangle = T = \int_0^\infty t \frac{\partial P(y_0, t)}{\partial t} dt = K_1 \int_0^\infty t \frac{\partial P}{\partial y_0} dt + K_2 \int_0^\infty t \frac{\partial^2 P}{\partial y_0^2} dt \quad (9)$$

Integration by parts:

$$\int_0^\infty t \frac{\partial P}{\partial t} dt = t P|_0^\infty - \int_0^\infty P(y_0, t) dt = -1 \quad (10)$$

$$\int_0^\infty t \frac{\partial P}{\partial y_0} dt = \frac{d}{dy_0} \int_0^\infty t P dt = \frac{dT}{dy_0} \quad (11)$$

$$\int_0^{\infty} t \frac{\partial^2 P}{\partial y_0^2} dt = \frac{d^2}{dy^2} \int_0^{\infty} t P dt = \frac{d^2 T}{dy^2} \quad (12)$$

Through adding, we get:

$$K_2(y_0) \frac{d^2 T}{dy_0^2} + K_1(y_0) \frac{dT}{dy_0} + 1 = 0 \quad (13)$$

The boundary conditions for (13) are:

$$T = 0 \text{ at } y_0 = a \text{ or } y_0 = b \quad (14)$$

The form of solution for (13) depends on the form of the coefficients $K_1(y_0)$, $K_2(y_0)$, i.e., the form of the equation of motion. If the drift and diffusion coefficients are constant, then the source of particles coincides with the y -axis, i.e., $y_0 = 0$, and the real and imaginary substrates are located symmetrically: $a = -b$, then

$$T = \frac{b}{K_1} \operatorname{th} \left(\frac{K_1}{K_2} b \right) \quad (15)$$

Function graph (15) is depicted in Figure 5.

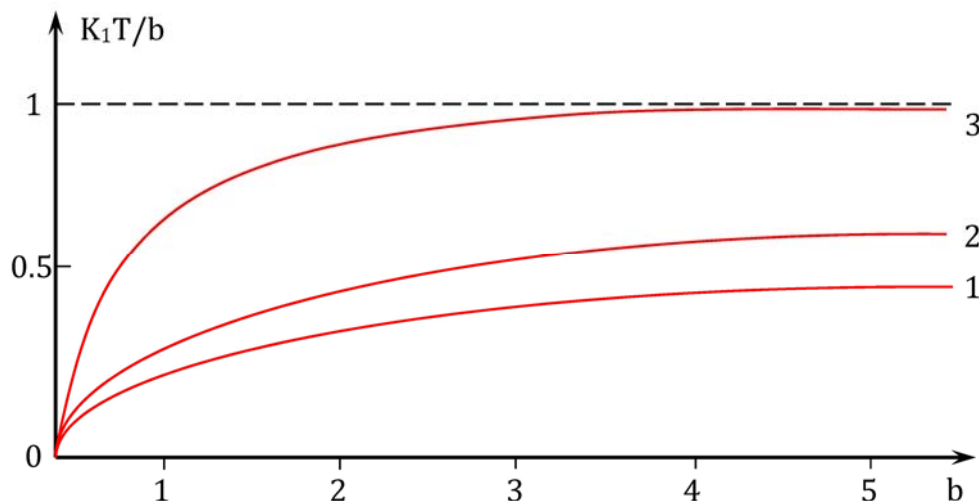


Figure 5. Dimensionless relationship for T and b at various values of K_1/K_2 . 1: $K_1/K_2 = 10$, 2: $K_1/K_2 = 1$, 3: $K_1/K_2 = 0.1$

Figure 5 depicts the dimensionless relationship for T and b at various values of K_1/K_2 . b is the distance from the cathode to the substrate surface (in conventional units).

Figure 5 proves that the larger the drift coefficient K_1 is, the shorter time to deposition is, while the larger the diffusion coefficient K_2 is, the longer the time to deposition is. A model of coating synthesis during the layer-by-layer deposition of particles on a substrate was considered. Under the ideal conditions, a layer of particles emitted by a plane source is deposited on a substrate as a layer, and then the layer thickness $h(t)$ is a deterministic function. Under the real conditions, the coating thickness is a random function, as mentioned above, and it can be represented as follows:

$$H(t) = h(t) + v(t), \quad \langle v \rangle = 0, \quad \langle v(t)v(t_1) \rangle = \frac{N_0}{2} \delta(t - t_1) \quad (16)$$

where $v(t)$ is a random function of white-noise type.

After cooling down, a layer transforms, and the layer thickness at the time t is a certain random process, represented in the following form:

$$H_{\text{KOH}}(t) = h_{\text{KOH}}(t) + v_{\text{KOH}}(t) \quad (17)$$

The coating synthesis process should end when $H_{\text{KOH}}(t) = Q$ is reached. The probability that the $H_{\text{KOH}}(t)$ function would reach the given thickness Q during the time t was considered. The quality of the coating is determined by the fact that its thickness in the final state should be a given constant value. The probability $P(y_0, t)$ of reaching the boundary Q is found by the formula:

$$P(y_0, t) = 1 - \bar{P}(y_0, t) = 1 - \int_{-\infty}^Q \bar{f}(y, y_0, t) dy \quad (18)$$

where $\bar{f}(y_0, y, t)$ satisfies the Equation [43]

$$\frac{\partial \bar{f}}{\partial t} = \alpha \frac{\partial}{\partial y} [y \bar{f}] + \frac{\alpha^2 N_0}{4} \frac{\partial^2 \bar{f}}{\partial y^2} \quad (19)$$

with boundary conditions:

$$f(y_0, Q, t) = f(y_0, a, t) = \bar{f}(y_0, b, t) = 0 \quad (20)$$

The initial condition is as follows:

$$\bar{f}(y_0, y, t_0) = \delta(y - y_0) \quad (21)$$

If $h(t) = Q$, i.e., a layer of the required thickness is deposited to the substrate, then the probability $P(y_0, t)$ has the following form:

$$P(y_0, t) = 2 \left[1 - \Phi \left(\frac{Q - y_0 e^{-\alpha t}}{\sigma(t)} \right) \right] \quad (22)$$

$$\sigma^2(t) = \frac{N_0 \alpha}{4} (1 - e^{-2\alpha t})$$

We considered Φ as the probability integral (standard Gaussian distribution function) [44].

A model of fluctuations in the direction of the deposited particle motion was considered. As a result of such fluctuation, a particle can be deposited not in the intended place, and that can lead to non-uniform density of the coating. In the Oxy plane, the position of a particle is characterized by the values of $x(t)$, $y(t)$. Instead of the parameter t , a parameter s is introduced, defined as follows:

$$s = \int V dt \quad (23)$$

where V is velocity of the particle motion.

At each point, particles deviate from the rectilinear trajectories of the motion along straight lines parallel to the y -axis (Figure 6).

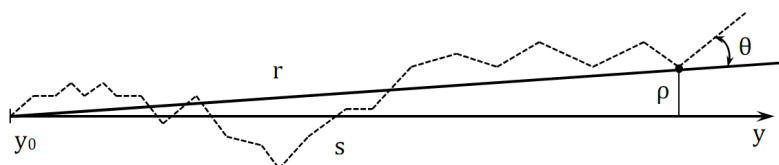


Figure 6. Deviation from the rectilinear trajectories of the motion along straight lines parallel to the y -axis.

The probability density $f(\theta|s, 0)$ satisfies the following equation [45]:

$$\begin{aligned} \sin \theta \frac{\partial f}{\partial \theta} &= \frac{B}{2} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial f}{\partial \theta} \right) \\ B &= \lim_{\Delta t \rightarrow 0} \varepsilon^2 / \Delta t, \quad \varepsilon^2 = r^2 \langle (\Delta \varphi)^2 \rangle, \quad \langle \Delta r \cdot r \Delta \varphi \rangle \\ x &= r \cos \varphi, \quad y = r \sin \varphi \end{aligned} \quad (24)$$

The value of B is related to the correlation function of the particle deposition rate

$$\psi_V(\rho) = \langle V(r)V(r') \rangle - \langle V(\rho) \rangle^2 \quad (25)$$

through the formula as follows:

$$B = - \frac{-2}{\langle V^2 \rangle \int_0^\infty \frac{\partial}{\partial \rho} \left(\rho^2 \frac{\partial \psi_V}{\partial \rho} \right) \frac{d\rho}{\rho}} \quad (26)$$

The solution to the Equation (26) is being sought with the initial condition of:

$$f(\theta|0, 0) = \delta(\theta) / 2\pi \sin \theta \quad (27)$$

and looks as follows:

$$f(\theta|s - s_1, 0) = \frac{1}{4\pi} \sum_{n=0}^{\infty} (2n+1) P_n(\cos \theta) e^{-\frac{n(n+1)}{2} B(s-s_0)} B(s-s_0) \quad (28)$$

where $P_n(\cos \theta)$ are Legendre polynomials [45].

At $s \rightarrow \infty$:

$$\lim_{s \rightarrow \infty} f(\theta|s - s_0, 0) = \omega_1(\theta) = \frac{1}{4\pi} \quad (29)$$

It is convenient to describe the condition for a change in the particle velocity vector through $\cos \theta$, then $\cos \theta = P_1(\theta)$ and the average value of the direction cosine of the velocity vector is calculated by the following formula:

$$\langle \cos \theta \rangle = \int_0^\pi \cos \theta V \sin \theta d\theta \quad (30)$$

The following differential equation $\langle \cos \theta \rangle$ can be derived from (24):

$$\frac{d \langle \cos \theta \rangle}{ds} = -B \langle \cos \theta \rangle \quad (31)$$

The solution of Equation (30) with the boundary condition of $\langle \cos \theta \rangle = 1$ at $s = 0$ is of the form:

$$\langle \cos \theta \rangle = e^{-Bs} \quad (32)$$

At $s \rightarrow \infty$, $\langle \cos \theta \rangle = 0$, and in accordance with (31), that means at a sufficiently large distance from a source to a substrate, all orientations of the particle motion are equally probable. For short distances:

$$\langle \cos \theta \rangle = 1 - \frac{\theta^2}{2} = 1 - Bs \quad (33)$$

which follows that:

$$\theta^2 = 2Bs \quad (34)$$

The mean square of the particle deviation ρ from the initial (rectilinear) direction along the y -axis is calculated by the following formula [46]:

$$\langle \rho \rangle = \frac{4s}{3B} - \frac{2}{B^2}(1 - e^{-Bs}) + \frac{2}{2B^2}(1 - e^{-3Bs}) \quad (35)$$

It follows from (35) that when $Bs \ll 1$, then:

$$\sqrt{\langle \rho^2 \rangle} = \sqrt{\frac{B}{6}} s^{3/2} \quad (36)$$

The mean square distance in a straight line to the particle being deposited is determined as follows:

$$\langle r^2 \rangle = \frac{2s}{B} - \frac{2}{B^2}(1 - e^{-Bs}) \quad (37)$$

The Formula (37) at $Bs \ll 1$ is reduced to the formula for the average square of displacement of a heavy molecule in light gas, obtained by Smoluchowski [47–50]:

$$\langle r^2 \rangle = s^2 \left(1 - \frac{Bs}{3} \right) \quad (38)$$

The fractional degree in the Formula (35) indicates that the deposition of coating particles is described by the fractal dynamics.

An ideal model of coating deposition represents an emission of particles from a certain conventionally planar surface of a cathode with the same velocity (temperature) along a normal to a surface (plane). The particles move along the parallel trajectories and are being layer-by-layer deposited on the surface due to the complex planetary motion of the substrate surface (Figure 7a). The process is described by the convection equation.

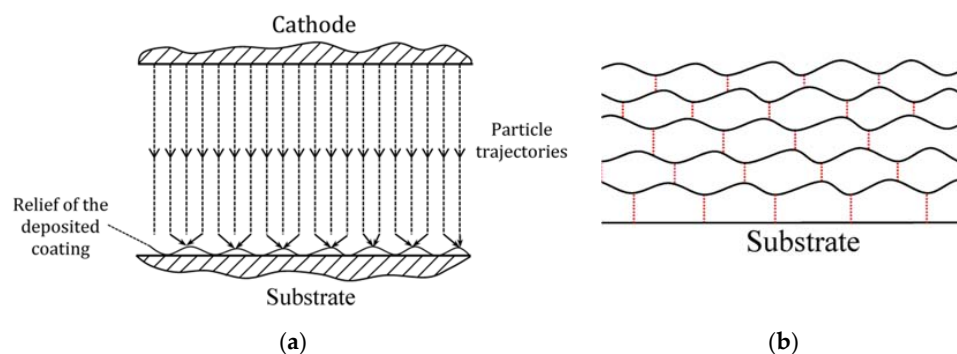


Figure 7. Diagram for (a) the formation of the relief of the coating being deposited; (b) the predicted cracking for the multilayer coating.

Under the real conditions, while emitted, particles demonstrate velocity fluctuations in value and direction, and during the particle motion, the process becomes even more irregular. The cloud has density fluctuations, and diffusion of particles occurs, as a result of which the density and hence the stiffness and strength of the layer being deposited fluctuate over the surface area. Furthermore, the very surface of the substrate is in the process of the complex planetary motion (rotation). As a result, at the initial stages of the coating destruction, damages and then cracks arise in the places of the deposited coating, in which the density is lower [28–30,49]. In terms of mathematics, this is described by a model of Brownian motion of a particle (Equation (3)), and the probability density satisfies the Equation (4).

The analysis of the resulting model indicates that the very coating deposition process implies the formation of a fractal structure, which further contributes to the formation of stress concentration areas, which, in turn, stimulate the process of cracking. At the initial stages of the coating destruction,

damages and then cracks arise in the places of the deposited coating, in which the density is lower. During the formation of the multilayer coating structure, mismatched fractal structures of the layers overlap each other, and thus the clustering effect is largely leveled out. In turn, the above reduces the likelihood of cracking in the coating structure and makes it possible to predict an increase in the performance properties of the coating [27–31,51–53] (see Figure 7b).

3.2. Influence of the Nanolayer Period λ on the Cluster and Hierarchical Coating Structure

The study was focused on the influence of such an important coating parameter as the nanolayer period λ on a cluster and hierarchical structure using an example of the Ti–TiN–(Ti,Cr,Al)N coating with a nanostructured wear-resistant layer (Figure 8). For a coating with $\lambda = 10$ nm (Figure 8a), there is a formation of hierarchical feather-like structures, modeled and described, in particular, in [19,20,24–26] for various techniques of the coating deposition. While a coating is being deposited, there is an obvious increase in the cluster size. The studies conducted earlier [52,54,55] also detected an increase in grain size. With an increase in the nanolayer period up to $\lambda = 38$ nm (Figure 8b), the feather-like structure becomes less pronounced, and at $\lambda = 160$ nm (Figure 8c), no grain growth is detected with an increase in the coating thickness, while the deposition of a coating begins “from scratch” within each nanolayer period. No feather-like structure was also detected for a coating with an extremely long nanolayer period ($\lambda = 1100$ nm, Figure 8d). A column structure, without any noticeable increase in crystal size, is formed inside a nanolayer.

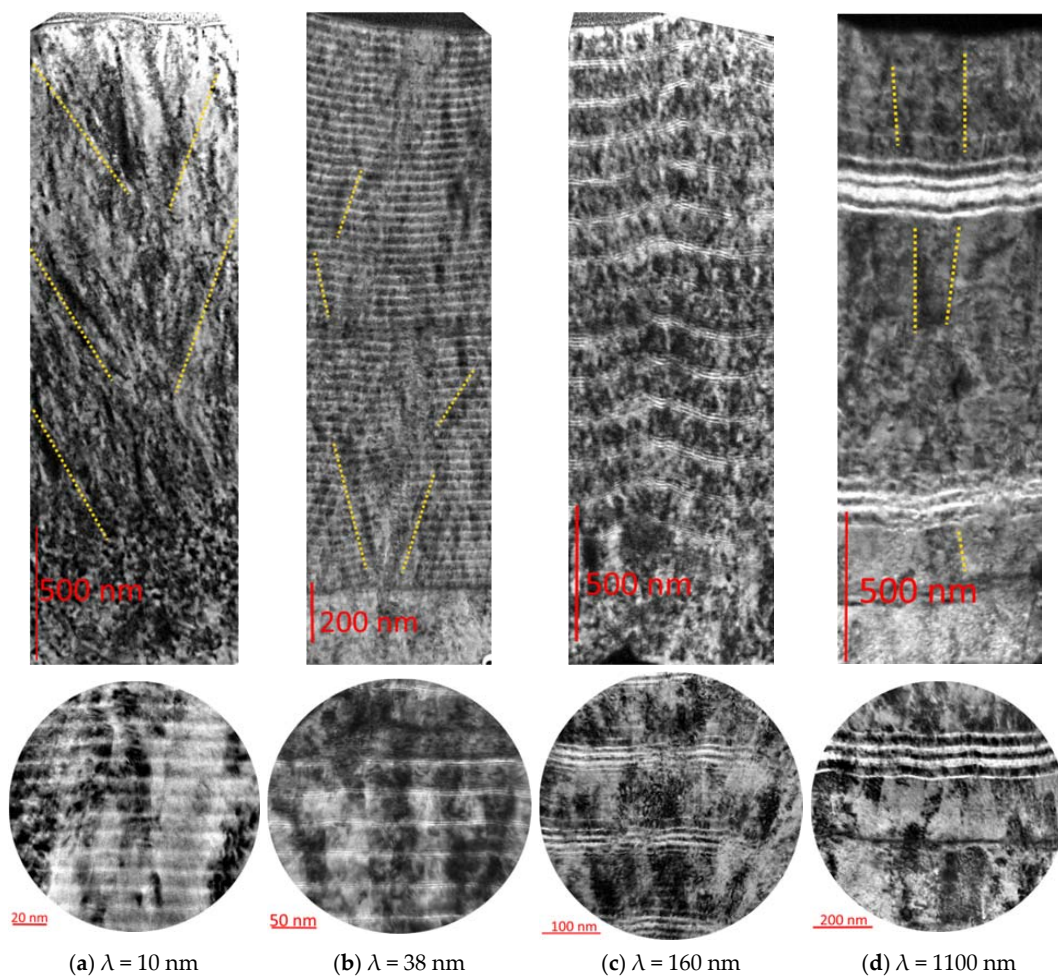


Figure 8. Formation of the cluster structure of the Ti–TiN–(Ti,Cr,Al)N coatings depending on the nanolayer period λ . (a) $\lambda = 10$ nm; (b) $\lambda = 38$ nm; (c) $\lambda = 160$ nm; (d) $\lambda = 1100$ nm.

4. Conclusions

- The obtained formulas prove that due to diffusion, particles can participate in collisions with other particles during the motion, and as a result, the velocity decreases and a particle enters a substrate at an angle, which may lead to a coating inhomogeneity over the area and the appearance of the surface microrelief, which also worsens the resistance and reliability of the coating. The Equation (16) is stochastic for various deposition trajectories.
- The Formula (32) indicates that if the distance from a cathode to a substrate is large enough, then there are a lot of particle in front of the substrate, and those particles move perpendicular to the initial direction of the motion (parallel to the substrate). The Formula (34) suggests that the dispersion of the motion direction in front of the substrate increases, which indicates an increase in randomness in the trajectories of the particles being deposited. The Formula (36) proves the fractal nature of the process of particle deposition on a substrate.
- During the formation of the multilayer coating structure, mismatched fractal structures of the layers overlap each other and thus the clustering effect is largely leveled out (averaged). In turn, the above reduces the likelihood of cracking in the coating structure and makes it possible to predict an increase in the performance properties of the products with such coatings.
- The nanolayer period λ has a significant influence on the fractal structure of the coating. When λ is low (less than 38 nm), with an increase in the coating structure, a pronounced feather-like structure is formed, and grains grow. With an increase in λ up to 160 nm and higher, no feather-like structure is formed, and no grain growth is detected during the coating deposition.

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