

INVESTIGATION METHODS FOR PHYSICOCHEMICAL SYSTEMS

Synergetics of Formation of Anodic Spark Coatings

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Abstract—Mechanisms of the formation of an anodic coating under the action of electric discharges based on an aluminum alloy in a vanadate phosphate electrolyte are considered. A process model is constructed for the cases of different current densities and studied; its adequacy is estimated in terms of distributions observed in experiments.

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INTRODUCTION

There are three main mechanisms of the anodic oxide structure growth in liquid electrolytes under the action of electric discharges at the electrode-electrolyte interface [1]. According to the first of these mechanisms (I), as a result of numerous isolated electrical breakdowns in the sample, homogeneous growth in the thickness of the coating takes place. In the second case (II), the initial areas of the new phase that contain the electrolyte components (nuclei) are formed on the primary anodic film; with their further growth and fusion, the breakdowns are located along the perimeter of these areas. In the third case (III), we can observe the appearance of electric discharges in the form of luminescent areas and lengthy lines. During the movement of these discharges, they leave behind the film of finite thickness (approximately tens of mkm), which contains the components of the electrolyte. The implementation of the mechanisms is determined by the electrolyte composition and the regime of the anodic spark oxidation. Each of these mechanisms includes a preliminary stage of the formation of the primary prespark anodic film [1, 2].

In this work, we assume that each of the mentioned mechanisms is a kind of single process of the formation of anodic spark coatings. The urgency of this study is caused by the variety of its manifestations in different spheres. For this purpose, it is necessary to make the subject specification of the factor of external action (current and temperature), environment (the composition of electrolyte and its concentration), and the surface and material of the coating and its phases. Apparently, the issues under consideration are of particular interest for medicine and biology, as well as for the localization of forest fires.

These interdisciplinary studies are the subject of synergetics, the purpose of which is to reveal the general mechanisms in the processes of the formation, stability, and destruction of the ordered time and space

structures in complex nonequilibrium structures [3]. Here, propositions of synergetics are used to create and investigate the model of the dynamics of the anodic spark coating area. In particular, it is considered that the multicomponent original system (here electrolyte) is the original resource for the areas of the new phase that forms on the medium surface. The term “phase” is understood to be “the part of the system that is homogeneous in the chemical composition and thermodynamic properties, which is separated from other parts (phases) by the breakdown surfaces” [4]. It means that the new phase areas are consumers of the original resource available for them. In the article, the dynamics of this system is formalized based on the accepted resource–consumer relations [5].

ANALYSIS OF EXPERIMENTAL RESULTS

Works [6, 7] give results of the experiments on galvanostatic formation of coatings on the aluminium alloy in the electrolyte with the vanadophosphorus heteropoly oxoanions. The electrolyte was prepared by sequential dissolution in distilled water 30 g/l $\text{Na}_6\text{P}_6\text{O}_{18}$ of the “ch.” mark and 15 g/l $\text{NaVO}_3 \cdot 2\text{H}_2\text{O}$ of the “ch.d.a.” mark. Conditions of the electrolyte preparation and the anodization cell are described in [2]. Preliminary preparation of the aluminum alloy samples AMcM of the size $40 \times 10 \times 1$ mm consisted in their mechanical grinding and chemical polishing in the mixture of concentrated acids $\text{HNO}_3 : \text{H}_2\text{SO}_4 : \text{H}_3\text{PO}_4 = 1 : 2 : 4$ (according to the volume) at the temperature of 120°C with aging for 0.5 min five to six times with the intermediate washing by water until the formation of a mirror surface. The anodic layers were formed by the galvanostatic method at current densities of $0.01\text{--}0.1$ A/dm². After certain periods of time, beginning with the sparking moment, the process was interrupted; the sample was taken out of the electrolyte, dried by filter paper, scanned; and the anodic spark the processing of the same sample was contin-

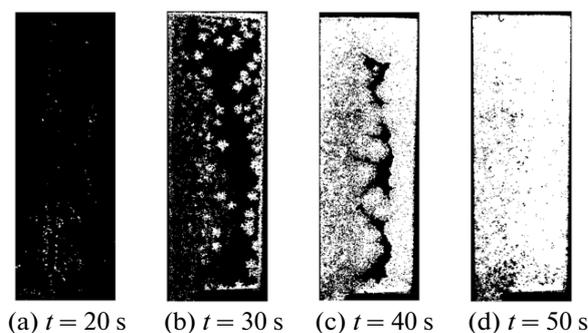


Fig. 1. Photographs of sample surface for current density $q = 0.1 \text{ A/dm}^2$.

ued. The procedure for improving the contrast improvement of the scanned image was realized in the interactive regime by the transformation of the original image pixel values (p) so that the histogram of the pixel brightness of the resultant image would correspond to the certain predefined histogram [8]. Then, the values of the pixels of the resultant binary image were inverted and both isolated pixels (nuclei) and the connected domains of object pixels (clusters) were defined for each scanned image. Then, we should distinguish the concepts of “nucleus” and “cluster.” The term “nucleus” refers to the isolated primary formation of the new phase on the sample surface or what is formed in the case of the electrical breakdown, whereas the “cluster” is the connected domain of the new phase areas. It directly follows from these definitions that the nucleus is the particular case of the cluster.

The experimental results were as follows. First, in the areas adjoining the electrical breakdown channels, the formation of reddish-brown areas (nuclei) of the new phase was observed. Then, the areas of primary nuclei became wider and connected to each other; then, at the moment when spark discharges transition to microarc discharges, they filled the whole surface of the sample. Then, the flat increase in the thickness of the layer that contained electrolyte components was observed (Fig. 1).

Statistical laws of the cluster number dynamics for different current densities show the following. The formation of the nuclei in unit time and the intensity of aggregation between separate clusters are proportional to the current density; the higher the value of q , the higher the corresponding values.

Calculations were carried out based on photo images whose unit of solvability is 1 p. The time of sample coating by the areas of the new phase t_E is in inverse proportion to q . Furthermore, in each experimental series, there is only an evident change in the number of clusters with areas of no more than 100 p. Thus, when $q = 0.1 \text{ A/dm}^2$, the cluster with the area $a = 437 \text{ p}$ ($t = 20 \text{ s}$) occurred only twice; the cluster with $a = 204 \text{ p}$ ($t = 30 \text{ s}$) appeared three times. This situation also takes place for experiments with other cur-

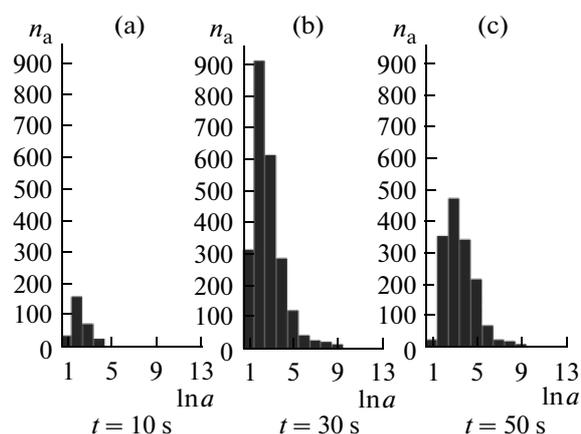


Fig. 2. Histograms of distribution of number of clusters by logarithms of areas for $q = 0.1 \text{ A/dm}^2$ (abscissa axis is logarithm of area of a cluster and ordinate axis is number of clusters found in this area).

rent densities and the accuracy follows directly from the analysis of the cases in Fig. 2. The number of clusters with larger areas does not exceed 5% of their full number. At the same time, they make a dominant contribution to the formation of a new phase layer. Beginning with the definite area for each current density moment of time, the increase in the area of the new phase is only determined by the large-sized clusters. Small clusters were not observed (Fig. 1c); the same situation also takes place for experiments with other q .

Distribution histograms indicate the evident dependence of their form on the sample area free of the anodic coating. Thus, the considered process of the formation of an anodic coating consists of four successive stages. At the first stage, the primary prespark film of aluminium oxide is formed (hereinafter referred to as the primary anodic film). At the second stage, certain electrical breakdowns and the formation of new phase nuclei take place. At the third stage, numerous clusters are formed, grow, and aggregate and the dominant large clusters are formed. At the final stage, there is only one cluster left. Then, numerous spark breakdowns are observed on the surface of the sample along the perimeter of this cluster, method II is transformed into method I.

MATHEMATICAL MODEL

The model is constructed based on the experimentally ascertained facts and ideas of statistical physics. The binary nature of aggregations of certain clusters (new phase areas), as well as the statistical independence of the growth of their area a and thickness h , are accepted. Let $n_{k,i}$ be the number of clusters of the area size k and the thickness size i , and let the pair (k, i) indicate the cluster spatial size (the area size k and the thickness size i). As follows from the experimental results and the chain of simple reasoning, the dynam-

ics of the cluster number is determined by a combination of processes, including the following:

(1) the growth of the number of nuclei as a result of breakdown phenomena;

(2) the sequential transition of the clusters with small area and the thickness to clusters of larger size as a result of their individual growth;

(3) the formation of the clusters of the size of k area and i thickness as a result of the binary aggregation of these clusters (m, j) and sizes (l, r), that $k = m + l$, $a_k = a_m + a_l$ and $h_i = (a_m h_j + a_l h_r) / a_k$;

(4) the transition of the clusters with the (k, i) size to the other size as a result of their aggregation with the clusters of arbitrary area and size.

The suggested scheme on M. Smoluchowski's assumption regarding the character of the aggregation of certain clusters allows for the simple formalization (the term number in the right side corresponds to the scheme item and the particle corresponds to the individual cluster)

$$\begin{aligned} \partial n_{k,i} / \partial t = & f_{k,i} + \varphi_{k,i} + \\ & + \frac{1}{2} \sum_{m+l=k} \sum_{m,l,j,r \in G(k,i)} \beta_{m,l,j,r} n_{m,j} n_{l,r} - \\ & - n_{k,i} \sum_{m=1}^{\infty} \sum_{j=1}^J \beta_{k,m,i,j} n_{m,j}, \end{aligned} \quad (1)$$

where $f_{k,i} \equiv f(t, q, a_k, h_i)$ characterizes the dynamics of the number of primary isolated formations of the new phase areas (nuclei) of the (k, i) size; $\varphi_{k,i} \equiv \varphi(t, q, a_k, h_i)$ is the sequential transition of the clusters from one size to the (k, i) size; $G(k, i)$ is a range of four number sets, so that

$$\begin{aligned} G(k, i) = & \{(m, l, j, r) : m + l = \\ & = k, h_i = (a_m h_j + a_l h_r) / (a_m + a_l)\}; \\ \beta_{m,l,j,r} \equiv & \beta(t, q, a_m, a_l, h_j, h_r) - \end{aligned}$$

correspond to the so-called Smoluchowski equation kernel [9]. This function characterizes the probability of binary aggregation, which is related to the unit of time; it is determined by the approach of the cluster-particles and their contact and fusion. The dimension is opposite of the product of the dimensions $[n_j]$ and $[t]$. The absence of the 1/2 coefficient is caused by recounting the same clusters during their summation. Here, we also assume the absence of a rather large number of types of clusters, which corresponds to the real picture; in the implemented experiments (Fig. 1), the visual area of certain clusters vary from the area $a_1 = 1$ pixel to the general area of the sample $A^* = 1.5 \times 10^6$ pixels. This is why the upper summation limit can be assumed to be equal to ∞ .

Since the area and thickness of the clusters change within a wide range, it is reasonable to transition from their discrete distribution of the fixed area values to the

respective continuous distribution. In this case, the conversion is achieved in a way that is standard for these situations [10]. If $n(t, q, a, h)$ is the density of the distribution of the clusters by area and thickness, the number of clusters with the area from the interval $(a, a + \Delta a)$ and the thickness from the interval $(h, h + \Delta h)$ is equal to $ndadh$. According to these ideas, the dynamics of the cluster number density $n \equiv n(t, q, a, h)$ is determined by the correlation

$$\partial n / \partial t + \partial(\dot{a}n) / \partial a + \partial(\dot{h}n) / \partial h = f + Q, \quad (2)$$

where $\dot{a} \equiv da/dt$, $\dot{h} \equiv dh/dt$ determine the dynamics of the cluster area and thickness, which are caused by the effect of the current; $f \equiv f(t, q, a, h)$ characterizes the rate of primary formation of the new phase area, and $Q \equiv Q(t, q, a, h)$ characterizes the rate of the binary aggregation of the areas. Equation (2) is a particular notation of the continuity equation for the distribution density of the particles with certain dynamic properties [11]. Here, these properties are determined by the cluster area and its thickness.

The second and third terms of the left side of (2) characterize the transition of the clusters from smaller to larger sizes as a result of their individual growth. According to the experiments, the dynamics of the cluster area depends on q and the sample area, which is free from the new phase regions, $A^* -$

$\int_0^H \int_0^{A^*} andadh \equiv A^* - A$, where H is the maximum thickness of the coating, A^* is the sample area (dependence of \dot{a} on the electrolyte composition is evident). The area $A^* - A$ is an available resource for the areas of their consumers, which, here, are the individual clusters. According to the statements accepted for the resource-consumer system [12], the approximation of \dot{a} can be represented by the expression

$B_a(t, q, C)(A^* - A)a$. Here, $C \equiv (C_1, C_2, \dots, C_s)$ characterizes the composition of the electrolyte (each of the elements of the vector C is a certain time function and q , as well as the other elements). Multiplier $B_a(t, q, C)$ characterizes the measure of the electrical current action on the system electrolyte-primary anodic film-new phase (it depends on the composition of electrolyte). Then, $B_a(t, q, C)$ must satisfy the following conditions: (1) the growth of the cluster area is preceded by the certain time interval $[0, t_a(q, C)]$ during which the primary film is formed, and (2) the higher q , the faster the growth of the cluster area. The simple notation $B_a(t, q, C)$ can be represented by the correlation $B_a(t, q, C) \equiv B_{a,1}(q - B_{a,2}/t)$, where $B_{a,1} \equiv B_{a,1}(C)$ and $B_{a,2} \equiv B_{a,2}(C)$ are nonnegative coefficients. Then, $t_a(q, C) = B_{a,2}/q$ and

$$\dot{a} = B_{a,1}(q - B_{a,2}/t)(A^* - A)a. \quad (3)$$

Correlation (3) reflects the experimentally observed peculiarity of the system under consider-

ation: the higher the speed of cluster a , the higher the speed of growth in its area. It also follows from (3) that, when the coating fills the whole area of the sample, further changes in area cease.

In the study of the electrochemical formation of coatings, the thickness of the coating is often determined based on the correlation

$$h = h_0 \exp(kU), \quad (4)$$

where h_0, k are nonnegative coefficients, which should be calculated by the least square method based on experimental data for each composition of electrolyte, and U is the formation voltage [2]. The limitation of practical use is clear (4); in the case of long formation, the thickness of the coating can achieve considerable size, which evidently does not correspond to the facts. Meanwhile, it is obvious that there is an instant in time when the coating thickness reaches a certain value that depends on the current density and the electrolyte composition (this value also depends on these parameters). Furthermore, the coating density does not change. Indeed, the properties of the coating are determined by the composition of the electrolyte and the value of current density. Since the composition is limited, the coating thickness is also limited. In this situation the electrolyte and the coating, as in the previous case, are in resource–consumer relations, and the notion \dot{h} can be implemented based on the same assumptions used to construct the model \dot{a} . Thus, if the thickness of the coating did not achieve its critical value H , it continues to grow. In keeping with (4), the approximation of \dot{h} can be represented in the form

$$\dot{h} = B_{h,1}(q - B_{h,2}/t)(H - h)h, \quad (5)$$

where $B_{h,1} \equiv B_{h,1}(C)$ and $B_{h,2} \equiv B_{h,2}(C)$ are nonnegative coefficients.

When writing f , the following experimental facts were used:

(1) The moment of the appearance of new nuclei is preceded by the time interval $[0, t_0(q, C))$ of the primary film formation.

(2) In the case of film breakdowns, the nuclei are formed in the sample area $A^* - A$, which has no new phase areas.

(3) The density of the probability of the nucleus appearance $p(a, h, C)$ is a rapidly decreasing function of its arguments. Here, the notation $f(t, q, a, h)$ takes the following form similar to (2):

$$f(t, q, a, h, C) \equiv B_{N,1}(q - B_{N,2}/t)(A^* - A)p(a, h, C), \quad (6)$$

where $B_{N,1} \equiv B_{N,1}(C)$, $B_{N,2} \equiv B_{N,2}(C)$ are the nonnegative coefficients. It follows from (6) that $t_0(q, C) = B_{N,2}/q$. Until this moment, the primary anodic film is formed on the surface of the sample.

The parameterization of Q is carried out based on the so-called coagulation term of the Smoluchowski equation [13]. Here,

$$Q = \frac{1}{2} \iint_{\Omega_{ah}} \beta(ah - a'h', a'h')n(a'', h'')n(a', h')da' dh' - n(a, h) \iint_{\Omega} \beta(ah, a'h')n(a', h')da' dh',$$

where $\Omega_{ah} = \{(a', h') : 0 \leq a' < a, 0 \leq h' \leq h\}$; $\beta(z, y)$ is the kernel of the kinetic coagulation equation, which is a symmetrical function, $a'' = a - a'$, $h'' = (ah - a'h')/(a - a')$. [14]. The suggested mechanism consists of the following: the area of the results of aggregation is equal to the sum of the region areas and the thickness is recounted; the sum of the volumes is divided by the total area. In general case, β depends on the parameters of external action (here on q and C) [15]. The real areas of the nuclei are lower than the limit of visual solvability, which is why the lower limit of integration is assumed to be equal to zero.

DYNAMIC MODEL OF COATING AREA

For practical applications, it is interesting to consider the dynamics of the area of the new phase coating $A(t, q)$ and the current number of clusters of different

area $N(t, q, C) = \int_0^H \int_0^{A^*} n(t, q, C, a, h)dadh$. The equation for \dot{A} is obtained when integrating the product (2) and a by a and h taking into account (5) and (6) and, for \dot{N} , it is obtained when integrating it by a and h as follows:

$$\begin{aligned} \dot{A} &= [B_{N,A}(q - C_{N,2}/t) + \\ &+ \Theta(t - t_a)B_{a,1}(q - B_{a,2}/t)A](A^* - A), \quad (7) \\ \dot{N} &= B_{N,1}(q - B_{N,2}/t)(A^* - A) - b_1N^2 - b_2NA - b_3A^2, \end{aligned}$$

where $B_{N,A} = B_{N,1}a_1/(\gamma - 2)$, and $B_{N,1}, B_{N,2}$ are the coefficients from (6) and $\Theta(z)$ is the Heaviside function, which is equal to 1, when the argument is positive and, in other cases, is equal to 0. The starting point for considering (2) should be assumed to be equal to the end point of the primary film formation on the surface of the sample as follows:

$$t_0(q, C) = B_{N,2}/q, \quad N(t_0, q) = 0 \text{ и } A(t_0, q) = 0. \quad (8)$$

When writing \dot{A} , it should be taken into account that the current total area of the coating does not depend on the specificity of the cluster aggregation; during the cluster aggregation, the total area does not

change; i.e., $\int_0^{A^*} aQ(n, a, h)dadh = 0$. When writing \dot{N} , for simplicity, it is assumed that

$$\beta(a'h', a''h'') \equiv 2[b_1 + b_2(a' + a'') + b_3a'a''], \quad (9)$$

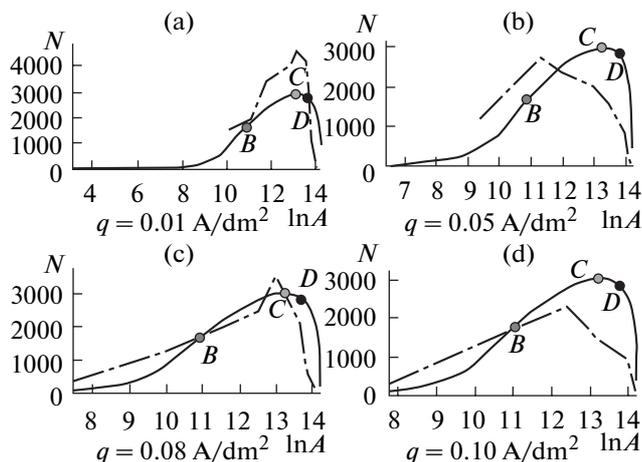


Fig. 3. Graphs of functions $N = N(\ln A(t, q))$, where dash-and-dot lines show experimental observations (B coordinates are determined from condition of function bend, C is determined by bend in its maximum, and D is determined by bend in curve $A(t, q)$).

and b_1, b_2 , and b_3 are nonnegative coefficients of proportionality; in the general case, they can be functions of the parameters of external action.

The notation of β in (9) corresponds to the system, where three different mechanisms of binary aggregation work. For their typification the analysis of the sequence of the right side terms of (9) under the condition of specified values of b_1, b_2 , and b_3 , should be carried out. If the augend is considerably higher than the others, aggregation does not depend on the individual properties of certain clusters, and so it is determined by the average regularity. The addend exceeds the other terms of (9) in the case of the aggregation of the small and large clusters. In the case of high values of a' and a'' , the order of the final summand of (9) is higher than the others. All other conditions being equal, the probability of binary aggregation of large clusters is considerably higher than the aggregation of the clusters of other size. Thus, the first type of kernel characterizes the beginning stage of the process of the formation of the plasma-electrolytic coating (the aggregation of small clusters takes place) and the second and third types of kernel characterize other stages.

Here, the study of the model (7) and its parametric identification was carried out for the type of electrolyte indicated above. For simplicity, vector C is assumed to be fixed and can subsequently be omitted. At the beginning stage $t_0(q) < t \leq t_a(q)$, the area $A_1(t, q)$ of the coating is determined by the area of local breakdowns of the primary film as follows:

$$A_1(t, q) = A^* \{1 - (t/t_0)^{B_{N,A} B_{N,2}} \exp[-B_{N,A} q(t - t_0)]\}.$$

Because we estimate $B_{N,A} = (4.63784 \pm 1.52612) \times 10^{-2}$, $A_1(t_0, q) = 7.96339 \times 10^{-5} A^*$. Therefore, at the initial time of cluster growth, less than 0.008% of the

sample area is occupied by the new phase regions, the total area of which does not depend on the current density q . The mentioned regions are only formed as a result of the local breakdowns of the primary anodic film.

When $t > t_a(q)$, the change in $A(t, q)$ is determined by the behavior of its asymptote $A_M(t, q)$. The equation follows from the first correlation (7), where the terms $B_{N,2}/t$ and $B_{a,2}/t$ are not taken into account (when $t \gg t_a(q)$, the influence of these terms due to their smallness can be neglected). Then,

$$\begin{aligned} A_M(t, q) &= \\ &= A^* B_{N,A} \frac{\exp[(B_{N,A} + B_{a,1} A^*)q(t - t_a)] - 1}{B_{N,A} \exp[(B_{N,A} + B_{a,1} A^*)q(t - t_a)] + B_{a,1} A^*}, \\ A_b &= (B_{a,1} A^* - B_{N,A}) / 2 B_{a,1} t_b = \\ &= B_{N,2} / q + [(B_{N,A} + B_{a,1} A^*)q]^{-1} \ln 2 B_{a,1}, \end{aligned}$$

where $t_b(q)$ is the moment of the curve bend $A_M(t, q)$ and $A_b \equiv A_M(t_b, q)$. It follows from this that the value of the area A_b at the inflection point does not depend on q , and the moment of its achievement t_b is in inverse proportion to q . This fact conforms well to the experimental observations. The joint variation in $N(t, q)$ and $A(t, q)$ is shown in Fig. 3.

One can clearly observe the identity of the changes of $N = N(\ln A(t, q))$ for different values of the current density. The stage of the initial growth of the cluster number is preceded by the stage of primary-film formation. The duration of growth is approximately 10% of the total time of the sample surface filling by the new phase areas. This estimation follows from the expression $100 \times t_0(q)/t_E(q)$, where the denominator is the time of the formation process. In the OB section, in the case of a slight increase in A , we observe a slow increase in N , conditioned by the local breakdowns of the primary film. The initial increase in the areas of certain clusters (point 1 in the scheme accepted during the model construction) and their initial aggregation (points 3 and 4 of the scheme) is also related to the OB section. The much higher value of q corresponds to the lower duration of the stag; when $q = 0.01 \text{ A/dm}^2$, it takes 30% of the coating time and, when $q = 0.1 \text{ A/dm}^2$, it is 17%. In the BC section, there is a fast increase in N up to its maximum $N_{\max}(q)$, whereas the change in A is close to the linear growth. As in the case of the OB area, the higher q corresponds to the lower duration; when $q = 0.01 \text{ A/dm}^2$, it is 29% and, when $q = 0.1 \text{ A/dm}^2$, it is 16%. The expression for $N_{\max}(q)$ can be approximately determined as follows:

$$\begin{aligned} N_{\max}(q) &\approx (2b_1)^{-1} \{-b_2 A(t_{\max}^{(N)}, q) + \\ &+ [(b_2^2 - 4b_1 b_3) A^2(t_{\max}^{(N)}, q) + 4B_{N,1} q b_1 (A^* - A(t_{\max}^{(N)}, q))]^{1/2}\}. \end{aligned} \quad (10)$$

Since the values $B_{N,2}/t_{\max}^{(N)}(q)$ and $B_{a,2}/t_{\max}^{(N)}(q)$ are considerably lower than other terms (10); then, when writing $N_{\max}(q)$, they are not taken into account. In the CD section and below, the term $b_1 N^2$ from (9) can be neglected due to its small value. Moreover, in this section and below, $b_2 NA \sim 10^3$, and $b_3 A^2 \sim 10^{-1}$. This situation corresponds to the fact that the second term of the right side of (9) considerably exceeds its other terms. Therefore, according to model (7), at the final stage of the process under consideration, only one large cluster can exist on the surface of the sample. This fact conforms well with the experiments. The following estimations of the parameters (7) were previously carried out in [9]: $B_{N,A} = (4.63784 \pm 1.52612) \times 10^{-2}$, $B_{N,1} = 1.19067 \pm 0.41623$, $B_{N,2} = 0.32881 \pm 0.10452$, $B_{a,1} = (4.64995 \pm 0.81194) \times 10^{-6}$, $B_{N,1} = (1.78198 \pm 0.725364) \times 10^{-3}$, $b_1 = (6.28497 \pm 1.24913) \times 10^{-7}$, $b_2 = (9.68293 \pm 2.52416) \times 10^{-7}$, and $b_3 = (2.20278 \pm 0.61634) \times 10^{-1}$. According to the confidence interval of the parameters, they differ statistically significantly from zero. This is why there are no processes among those listed above in the dynamics of the coating. The high correlation between the number of samples of clusters and the respective model values (correlation between different current densities does not drop lower than 0.756) indicates the proper adequacy of the suggested model (7). For the area model, the correlation is higher than 0.811.

The computing experiment results shown in Fig. 4 confirm the reliability of the statements given above. While carrying it out the original value of q was assumed to be equal to 10^{-3} A/dm², and the step increment $dq = 6.66 \times 10^{-3}$. The time of consideration of the system was limited to 400 seconds.

Analysis of Fig. 4 indicates the existence of the critical value of the current density q_c (in this case $q_c \approx 0.22$ A/dm²), when the sample surface at the very initial time the plasma-electrolytic coating is formed on the sample surface without the formation of clusters. The existing laws of the evolution of the cluster number are revealed during the analysis of the surface $N = N(t, q)$. Thus, the evolution mechanism is achieved in two different ways. At in the first, so-called divergent, stage [5, 12], growth in different properties of the system occurs, including an increase in the number and different forms of clusters is observed. It is conditioned by the fact that the search of new opportunities of evolution takes place in the system. At the second stage the difference of the properties decreases: the number and the variety of cluster forms decrease. The system and its individual elements evolve so that they could adapt to the effect of external environment to the best advantage. This situation corresponds to the convergent stage of evolution and the processes of adaptation in their classical form [5, 12]. At the same time, the first stage prepares conditions for the second

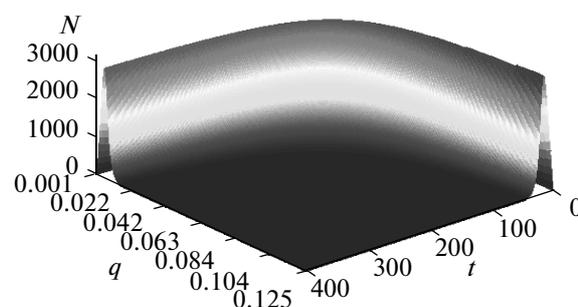


Fig. 4. Dynamics of distribution of total number of clusters $N = N(t, q)$.

stage. However, the cluster aggregation gives rise to a decrease in the time of the first stage. Furthermore, the fulfillment of simple properties of the system, which are observed in the real conditions, indicates the adequacy of the suggested mechanism of coating formation.

CONCLUSIONS

The suggested model of the formation of the plasma-electrolytic coatings is based on the staging of the coating process. At the first stage, the primary film of Al₂O₃ is formed. At the second stage, separate breakdowns of this film appear and, as a result, the nuclei of further clusters are formed. Then, the nuclei are transformed into the clusters, and growth in clusters and their mutual aggregation take place. Then, a large cluster forms that, at the final stage of the process, completely covers the surface of the sample. The sequence of the stages of this process here is represented within the frames of a single model, where the parameterization of each of them is achieved based on the balance correlations for the number of separate breakdowns and the approximation of the cluster aggregation by the formalism of the binary aggregation of the Smoluchowski equation. The considered approach can prove to be an effective instrument for studying similar processes in various spheres, where a new phase forms from the original substance and its further evolution under external action occurs. In the present case, the current density serves as a factor of the external action. It is assumed that, in other systems, it is possible to find a set of these factors, as well as different combinations. For example, the temperature and/or the wind velocity in the atmosphere-ice cover system. In this case, the fundamental side of this approach does not change.

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SPELL: 1. galvanostatic, 2. vanadophosphorus, 3. number