Technical Physics, 2022, Vol. 67, No. 9

13

Methods for the study and control of microplasma processes in the synthesis of coatings

© A.I. Mamaev, V.A. Mamaeva, Yu.N. Bespalova

Tomsk State University,
634050 Tomsk, Russia
e-mail: aim1953@yandex.ru

Received April 8, 2022
Revised May 24, 2022
Accepted May 28, 2022

The physical bases for determining the ignition and quenching potentials of microplasma discharges in solutions have been developed. Chronopotentiometric, chronoamperometric dependences on the conditions for obtaining coatings and the dependence of the time constant of the transient process on the voltage and duration of the process, as well as current-voltage dependences at the rates of rise and fall of the potential voltage from 10^6 to 10^8 V/s, are obtained. The developed method is applicable to control the process of deposition of microplasma non-metallic inorganic coatings and is the basis of the technique for *in situ* control of coating deposition. Key words: pulsed microplasma oxidation, current-voltage dependences, controlled synthesis of oxide coatings.

Keywords: pulsed microplasma oxidation, current-voltage dependences, controlled synthesis of oxide coatings.

DOI: 10.21883/TP.2022.09.54690.90-22

Introduction

The passage of a high voltage electric current through the interface in an aqueous electrolyte solution is accompanied by physical, chemical and plasma-chemical processes, including the transfer of electrons through the phase boundary, collective microplasma discharges, the transformation of substances, the recharging of double electric layers, heat transfer, mass transfer of reagents and products into boundary hydrodynamic layer, etc. [1,2]. There are two types of impact on the interface: the creation of a voltage jump and the impact of an electric current of controlled density. In the first case, the value of the applied energy is controlled (for equilibrium processes, this is equivalent to a change in the Gibbs energy, at that the rate of physical and chemical processes on the surface changes). In the second case, it is possible to control the rate of processes on the surface, while the magnitude of the energy impact on the interface changes [2]. In both cases, this provides unique opportunities for studying processes at the interface by one or another method (using current or voltage) and simultaneously recording the rate of physical and chemical processes by the current or voltage response. The complexity and diversity of the processes implemented at the interface when electric current passes through it is reflected in the current-voltage, chronopotentiometric, chronoamperometric dependences [3–6].

Recently, methods of high-energy action on the interface in electrolyte solutions were developed, which leads to the appearance of a relatively new phenomenon, i.e. microplasma processes on the surface. This type of plasma refers to low-temperature plasma under pressure. This process was used to obtain non-metallic inorganic coatings, which are very much in demand in industry [6–10]. Other teams of scientists are also developing the conditions for microplasma production of coatings, for example, P.S. Gordienko and V.S. Rudnev (Institute of Chemistry FEB RAS, Vladivostok), V.I. Vershinin (Omsk State University, Omsk), I.V. Suminov (MAI, Moscow) [11,12] etc., but at sinusoidal, alternating or direct current. Such types of current are not suitable for developing methods for studying and control the microplasma processes in the synthesis of coatings, since the methods are based on the idea of eliminating the effect of the power source, and at a sinusoidal voltage there is no disconnection of the current source from the microplasma system, but the voltage is controlled by the power source, and this does not allow the characteristics estimation of microplasma discharges. Sturdy methods based on the electrical characteristics of microplasma processes occurring during the current passage in the electrolyte solution are not enough. Therefore, the authors [6–10] propose to use high-voltage (100−400 V) trapezoidal pulses of polarizing voltage as the most effective type of current from the point of view of versatile control of microplasma processes. Depending on the parameters of action, the process of producing the coatings and films can be electrochemical or plasma. The nature of the process determines the properties of the coatings (structure, thickness, composition, etc.).

For pulse processes with sinusoidal current, you need to make special power supplies. Most researchers select asymmetric current, since this process requires relatively simple equipment. To study microplasma processes using trapezoidal pulses of polarizing voltage, it is necessary to develop more complex special voltage sources, which was done by the authors of this paper. Previous theoretical and experimental studies [6–10] resulted to the conclusion that the trapezoidal shape of voltage pulses is by ten times more efficient in terms of energy consumption compared to other types of current, which is very important from a technological point of view. The trapezoidal shape of the voltage was also chosen from the considerations of the most constant conditions for the coating formation from the energy impact point of view. On the horizontal porch of the trapezoidal voltage pulse, both the current and the amount of electricity are maximum, respectively, physical and chemical processes proceed at a constant maximum speed. This ensures the predictable and stable quality of the coating. Since the speed of most physical and chemical processes at the initial moment is maximum, a pause between impulses plays an important role, during it the system returns to its initial state (relaxes). During the pause, no energy is consumed. Besides, the adjustable pulse width allows you to control the size of the oxide grain [10], which is formed as a result of a single microdischarge.

The purpose of the work is to determine the regularities of the effect of physical and chemical processes on the form of current-voltage, chronopotentiometric, chronoamperometric dependencies, the time constant of the transient process (RC) on the voltage and duration of the process, the rate of electrode potential decreasing on time and on the system potential in the process of coating growth in the microplasma mode.

1. Materials and equipment for coating application in microplasma mode

The process is implemented in a microplasma system consisting of two electrodes: aluminum (anode; AMg6 alloy) and steel (cathode; stainless alloy 12Ch18N10T) placed in a container with a salts solution, between which a high voltage electric current passes.

Particular attention was paid to the stabilization of the electrolyte temperature — 25−28°C.

Electrolyte composition: H_3BO_3 — 35 g/l, NaOH — 15 g/l, NaF — 10 g/l, H_3PO_4 — 11 g/l, H_2O. Qualification of materials used — ACS.

1.1. Polarization system

The voltage measurement error on the aluminum electrode, which is possible due to the polarization of the auxiliary electrode, is eliminated by creating high salt concentrations in the electrolyte and a large surface area of the stainless steel counter electrode, which by 100 times exceeds the surface area of the working electrode. In the present paper we study the processes occurring at high-energy pulsed potentiostatic action on the interface. A trapezoidal voltage pulse of 0 to 600 V was chosen as a polarizing signal. The power source was created according to the diagram of energy storage in capacitors and transistor discharge of the accumulated energy to the microplasma system. This provides high voltage rise and fall rates (10^6-10^8 V/s). Power supply Korund M1, developed by Sibspark LLC, provides these characteristics and allows adjustment of the feed frequency (1−300 Hz) and width (5−200 μs) of impulses.

1.2. Registration system

The registration is based on the use of high-speed digital oscilloscopes, which allow recording current and voltage values simultaneously. The error of the measurements of currents and voltages did not exceed 3.76%. To remove current surges from random processes, the recorded instantaneous values of current and voltage were averaged over 32 successive measurements of current and voltage. The duration of each such measurement was 0.64 s.

2. Physical and chemical bases of measurement processes

The trapezoidal polarization voltage pulse has great potential in the study and control of coatings application in the microplasma mode. Such voltage pulse is characterized by the largest amount of electricity that passed through the system (as opposed to sinusoidal, triangular) during the pulse time. The voltage pulse width (τ) makes it possible to control the duration of electrochemical and microplasma processes, which affects the quality and nature of the coating. The magnitude of the voltage (U) relates to the magnitude of the energy localized at the interface [1,2]. Impulse processes at the initial moment have a high speed. The pause between pulses allows the system to restore equilibrium and return to its initial state without energy consumption [6–10]. The trapezoidal pulse with steep rising and falling fronts of the potential voltage has sections with alternating and constant voltages, which makes it possible to evaluate the ongoing processes and the state of the coating by various methods during a short period of time when the system is unequilibrium, in an excited state, and when equilibrium is restored. Chronopotentiometric and chronoamperometric studies at the pulse fronts make it possible to study the microplasma process and, accordingly, the surface when the system is taken out of equilibrium, and when equilibrium is restored.

The microplasma process is a collective process of discharging a multiple of spark processes occurring simultaneously (Fig. 1).

During the synthesis of microplasma coatings a current pulse is recorded as a response, the pulse is determined by the mode, electrolyte composition, and the state of the interface. Fig. 2 shows typical pulses of the driving voltage and the current density detected on aluminum (AMg6 alloy) electrode; electrolyte composition: H_3BO_3 — 35 g/l, NaOH — 15 g/l, NaF — 10 g/l, H_3PO_4 — 11 g/l, H_2O; electrolyte temperature — 25−28°C; coating application time — 10 min, voltage — 300 V, pulse width — 100 μs, current frequency — 1−100 Hz. The 30×10 mm flat electrode is placed parallel to the stainless steel counter electrode. The distance between the electrodes and the

Figure 1. Photography of sample during coating application.

surface to be treated is 5 cm on both sides. Under these conditions, microplasma processes take place on the electrode.

The dependences obtained (Fig. 2) are very informative. Of these, by measuring the total current density after $25-100\,\mu$s from the beginning of the pulse, one can determine the active current density. At this time, the driving voltage is constant ($U = \text{const}$) and, accordingly, the voltage derivative, as well as the capacitive current density ($I_c = C(dU/dt)$), becomes zero:

$$I_o = I_a + I_c = U/R + C(dU/dt), \qquad (1)$$

where I_o is total current density, I_a is active current density, I_c is capacitive current density, U is reference voltage, C is capacitance, R is resistance, t is time [6].

Measurements of the current value after $25\,\mu$s from the beginning of the voltage pulse make it possible to register the total density (I_o) of active (I_a) and capacitive (I_c) currents corresponding to this voltage. By acting on the system with voltage pulses with different parameters, it is possible to obtain the dependence of the active current density on voltage. The difference in the value of the total current makes it possible to estimate the value of the pseudocapacitive current. If the total current significantly exceeds the active current, then the pseudocapacitive current is equal to the capacitive charging current of dual electric layers, which allows us to estimate the charging current of dual layers formed at the interface [2–4].

A special moment is associated with rising and falling fronts of voltage and current, when the processes associated with the system unbalancing and with the system return to the equilibrium state are realized. At this moment, the processes listed above are started or stopped. The combination of stationary and transient processes makes it possible to carry out *in situ* the parameters measurements of the microplasma system. The potential voltage rise rate on the rising branch is determined, on the one hand, by the internal resistance and capacitance of the power source, and, on the other hand, by the resistance and capacitance of the microplasma system at variable voltage. The use of high-speed systems to form the voltage pulse, for example, IJBT matrices, leads to the fact that it is possible to ignore the internal characteristics of the power source after the matrix is switched on/off for a time of up to 200 ns. Such switch on time does not introduce significant distortions into the system for recording chronopotentiometric and chronoamperometric dependences on the rising and falling parts of the trapezoidal voltage pulse.

There is no effect of power supply parameters on the falling branch. In this case, the system can be modeled as a capacitor and resistance, the parameters are determined by the composition of the electrolyte, the structure of the interface, the structure of the coating, and the physical processes on the surface when equilibrium is restored, which is favorable for revealing the relationship between the structure of coatings and the physics and chemistry of plasma processes in a microplasma system. In our understanding, this part is more suitable for physical and chemical studies of both the microplasma process itself and the process of coating formation.

When a high-voltage pulse is applied to the treated surface, all possible electrochemical reactions are started, which lead to the concentration changes of ions in the surface interface. The process of formation of an oxide layer starts, which, together with concentration changes in the boundary layer, creates a barrier layer [4,5]. A further voltage increasing leads to a breakdown of the barrier layer and the microplasma discharges occurrence. Thus, in the process of applying voltage, physical, chemical, electrochemical, plasma-chemical processes are realized, which replace and complement each other depending on time and voltage in the microplasma system. The process nature change, including the ignition and quenching of microplasma discharges, should be accompanied by a sharp change in the capacitance and resistance of the microplasma system. The change in capacitance and resistance due to the process nature change should affect the form of current-voltage, chronopotentiometric and chronoamperometric dependences.

The rising and falling branches of these dependencies are of great interest. On the rising branch of the chronoamperometric dependence the start of ignition of microplasma discharges is recorded at the time $3\,\mu$s from the beginning of the pulse (section *1* in Fig. 2, *b*), and on the falling branch — the beginning of their quenching at the time $107\,\mu$s from the beginning of the pulse (section *2* in Fig. 2, *b*).

According to the second switching law, when the voltage pulse is disconnected, the surface keeps voltage, which was formed before the start of the discharge. The system turns into a capacitor with a capacitance C, the parameters of which are determined by the structure and capacitance of the dual electrical layers of the interface in the coating, connected in series with a resistor R, the value of which corresponds to the rate of electrode and plasma reactions

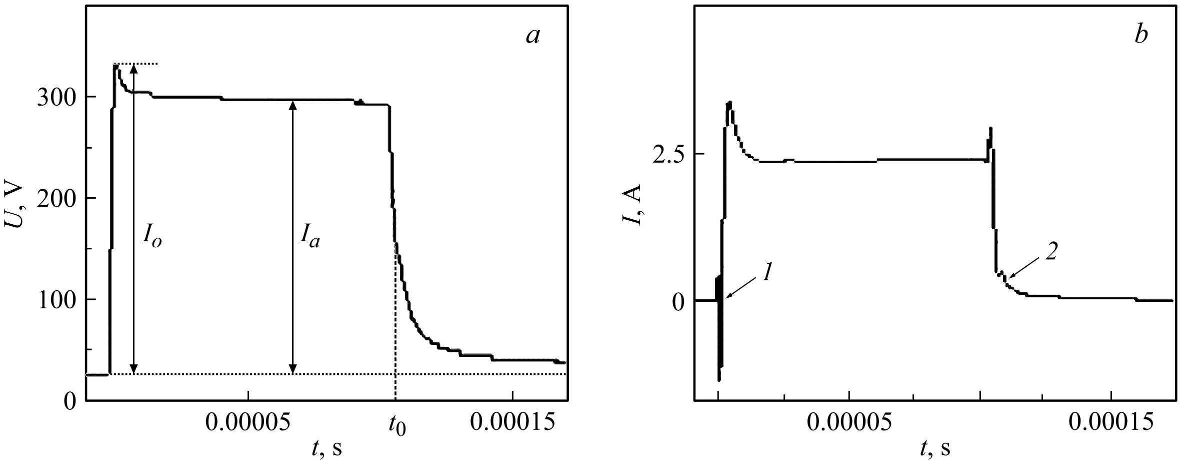

Figure 2. Chronopotentiometric (a) and chronoamperometric (b) dependences obtained during the synthesis of microplasma coating on an aluminum electrode.

occurring after the pulse disconnection, and is determined by the concentration changes of ions in the interface layer. For such a system, at constant values of resistance and capacitance, the expression for the voltage and current drop is [6]:

$$U(t) = U_0 \exp(t/RC), \tag{2}$$

where $U(t)$ is voltage at time t, U_0 is voltage at initial time ($t = 0$). For short periods of time, when the value of resistance and capacitance changes slightly, the following expression is valid:

$$U_i(t) = U_{oi} \exp\big(t/(R(t)C(t))\big). \tag{3}$$

The voltage rise at the moment of switching on is determined by the expression [13]:

$$U_i(t) = U_{oi}\Big(1 - \exp\big(t/(R(t)C(t))\big)\Big). \tag{4}$$

In accordance with equation (2) the expressions (5) are obtained for the transient time constant (RC) on the falling branch:

$$\begin{aligned} R(t)C(t) &= -\Big(d\big(\ln(U_i(t)/U_{io})\big)/dt\Big)^{-1} \\ &= \big(dU_o/U_o dt - dU_i(t)/U_i(t)dt\big)^{-1} \end{aligned} \tag{5}$$

and (6) for the transient time constant (RC) on the rising branch of the trapezoidal voltage pulse:

$$R(t)C(t) = -\Big(d\big(\ln(1 - (U_i(t)/U_{io}))\big)/dt\Big)^{-1}. \tag{6}$$

The experimentally obtained chronopotentiometric dependences (Fig. 2, a) make it possible to plot the graph of instantaneous values of the transient time constant (RC) in accordance with the above equations. Sections of chronopotentiometric dependences (Fig. 2, a) after the voltage disconnection point (t_0) are used to study the ignition and quenching of the arc process. Ignition and quenching are accompanied by a change in the transient time constant (RC); therefore, on the dependences of the instantaneous value of the transient time constant (RC) of the falling branch of the trapezoidal pulse on voltage and on the duration of the process (Fig. 3), calculated from Fig. 2, abrupt changes in (RC) should be observed. When quenching arc processes, the resistance increases and the reverse of the transient time constant ($-1/RC$) decreases (Fig. 3).

As can be seen from Fig. 3, a sharp decrease in the reverse of the transient time constant ($-1/RC$) is observed at voltages from 200 V, which is associated with the quenching of arc processes, which reaches its minimum values at voltages of 90 to 140 V depending on the duration of coating application and, accordingly, on the thickness of the coating (Fig. 4). The process of quenching the arc processes, designated in Fig. 3 as ($-1/RC$), corresponds to the time 118 μs from the beginning of the process. The microplasma process is a collective process, therefore, one should not expect instantaneous quenching of microplasma discharges both with time, and when the potential changes, and this process must be considered in time. To study the causes of oscillations of the reverse of the transient time constant ($-1/RC$) at voltages from 100 V, and below its changes in this interval for coating application processes in the absence of microplasma discharges are given (Fig. 3, c). The reverse of the transient time constant ($-1/RC$) for the anode part has insignificant fluctuations and tends to zero, which indicates a high resistance of the anode process (Fig. 3, c). This is confirmed by the dependences of the oscillatory process (Fig. 3, a) at low voltages in the presence of microplasma discharges caused by transient processes that occur after the microdischarges are quenched.

We studied the rate of potential change (dU/dt) on the falling branch of the trapezoidal voltage pulse depending on the duration of the microplasma process and on the thickness of the coating at different times of treatment of

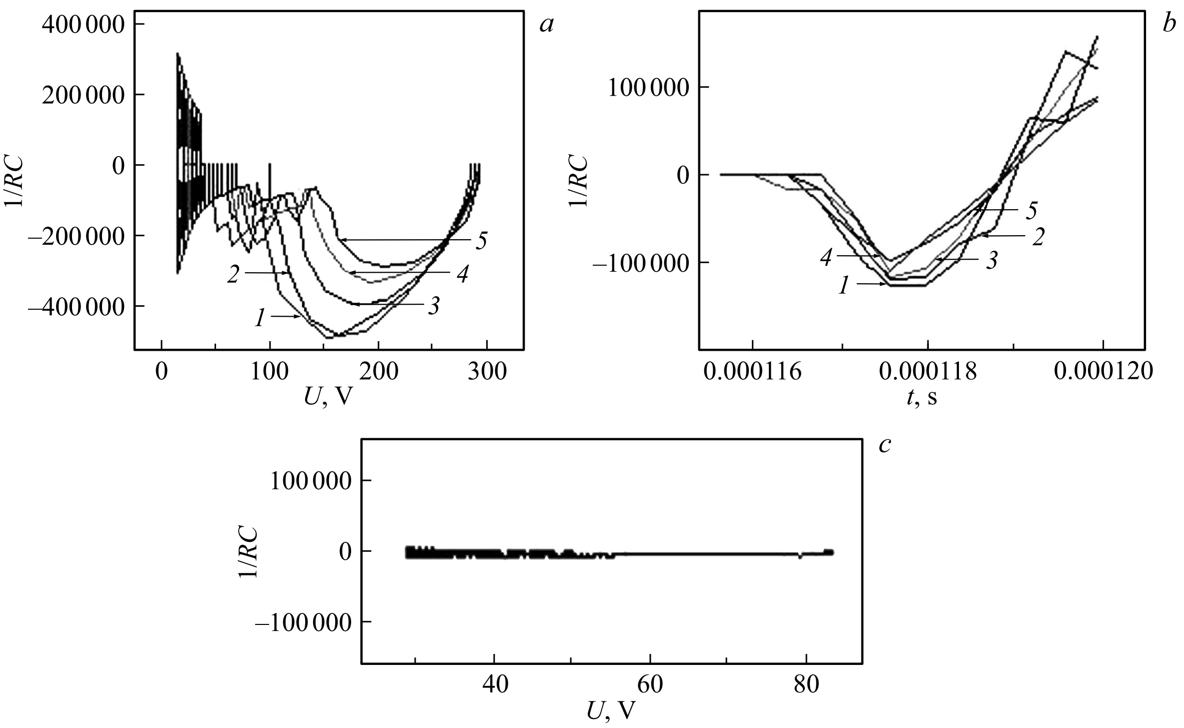

Figure 3. Inverse of transient time constant $(-1/RC)$ of falling branch of trapezoidal voltage pulse vs. voltage (a) and vs. duration of the process (b): *1* — 120, *2* — 240, *3* — 360, *4* — 480, *5* — 600 s during the microplasma process and in the absence of microplasma discharges (c).

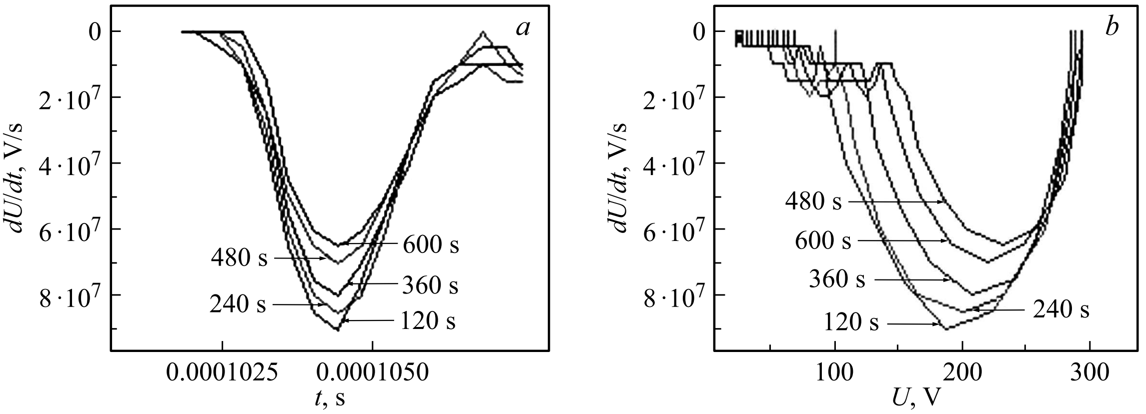

Figure 4. Rate of potential change (dU/dt) on falling branch of the trapezoidal pulse after voltage disconnection vs. time (a) and vs. voltage (b).

the surface of AMg6 aluminum alloy in an electrolyte of composition: H_3BO_3 — 35 g/l, NaOH — 15 g/l, NaF — 10 g/l, H_3PO_4 — 11 g/l, H_2O (Fig. 4).

In the absence of microplasma discharges there is no transient processes; this indicates that the transient oscillatory process is initiated by microplasma discharges (Fig. 4). With the increasing of duration of application, and, accordingly, of the coating thickness the maximum rate of potential change decreases at a rate of 10^7 V/s with the coating thickness increasing by 1 μm. With the coating thickness increasing, the maximum rate of voltage change shifts towards higher voltages.

Since the microplasma process is a collective process, including many microplasma (corona) discharges on the surface (Fig. 1), one can observe the beginning of the quenching of microplasma discharges in time, which is associated with decreasing of the reverse of the transient time constant $(-1/RC)$ in the voltage range 200–140 V, which corresponds to voltage jumps on the falling and rising branches of the current pulse (Fig. 2, b). The quenching potential of microplasma processes corresponds to the potentials 90–140 V. In this case, a minimum of the transient time constant (RC) is observed, which depends on the thickness of the coating, which increases with the increasing

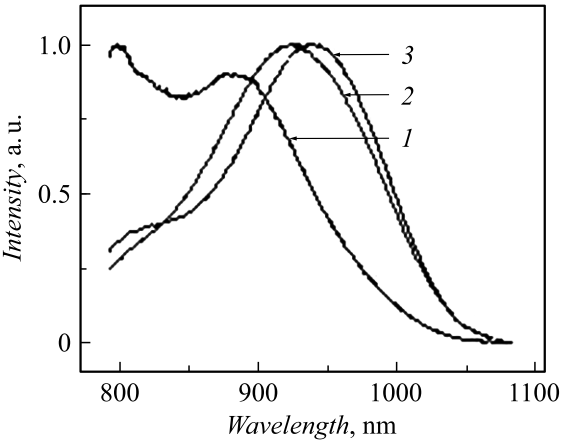

Figure 5. Reflection spectra ($\lambda_{ex} = 785$ nm) of coatings obtained in electrolyte: H_3BO_3 — 35 g/l, NaOH — 15 g/l, NaF — 10 g/l, H_3PO_4 — 11 g/l, H_2O; $t = 600$ s. For the curve *1* — $U = 100$ V, $\tau = 100\,\mu$s; for the curve *2* — $U = 400$ V, $\tau = 100\,\mu$s; for the curve *3* — $U = 400$ V, $\tau = 200\,\mu$s.

of the duration of the coating application. This affects the value of resistance and capacitance and, accordingly, the value of the transient time constant (RC), and the rate of potential change (dU/dt). The revealed dependence makes it possible to determine the ratio of the coating thickness and through porosity, since the thickness and porosity of the coating affect the resistance and capacitance at the interface. At the moment of arc quenching the current passes through the minimum value, which can correspond to the current of the electrochemical reaction, and the nature of the process changes: the high-temperature chemical reaction of material formation, proceeding under the action of microplasma discharges, becomes an electrochemical one, and the composition, design and structure of the coating change accordingly. Fig. 5 shows the reflection spectra of coatings obtained by anodization (curve *1*) and in the microplasma oxidation mode (curves *2, 3*).

As can be seen from Fig. 5, the reflection spectra of microplasma coatings differ from the spectrum of the coating obtained in the anodizing mode. Consequently, the structure and design of such coatings are different, which indicates the importance of determining the quenching voltage of microplasma processes.

The increasing of the coating thickness is accompanied by change in the resistance of the oxide film. Besides, in the process of the arc quenching, the resistance increases, since the arc process turns into the electrochemical one. The reverse of the transient time constant ($-1/RC$) tends to zero at potentials below 150 V, and with the coating thickness increasing (treatment duration) on the dependence of the transient process time constant (RC) on the potential and on the duration of the process there is a shift of the potential of the minimum of the reverse of the transient time constant (RC) towards the potential increasing from 100 to 140 V, which is associated with the coating thickness. This makes it possible to determine the moment of microplasma arc quenching depending on the duration of the microplasma process, on the voltage and on the coating thickness. Knowing the quenching potential of microplasma discharges makes it possible to control the structure of the received coatings by changing the nature of obtaining oxide materials on the metal surface in electrolyte solutions [6].

The process of the microplasma discharges quenching is accompanied by transient processes (current fluctuations), which are observed at low potentials. One of the main characteristics of microplasma and electrochemical systems is the current-voltage dependence that relates the process rate (current density) and the magnitude of the energy impact (for equilibrium processes $\nabla G = -zFU$ is valid, where ∇G — change of the Gibbs energy, z — number of moles of transferred electrons, F — Faraday number, U — voltage), in the process of the equilibrium restoration in the system. It is energy that affects the structure and nature of chemical bonds. The measurements carried out make it possible to obtain the current-voltage dependences of the microplasma and electrochemical systems when they are taken out of equilibrium, and when it is restored.

The current-voltage dependence reflects the properties of microplasma and electrochemical systems, characterizes the electrolyte, the base material, synthesis modes, and the state of the product. Fig. 6 shows typical falling branches of current-voltage dependences for the trapezoidal voltage pulse, obtained for different durations of formation and for different thicknesses of nanostructured non-metallic inorganic coatings under conditions when microplasma processes are realized (Fig. 6, *a*) and are not realized (Fig. 6, *b*).

On the falling branch of the trapezoidal voltage pulse the current maxima are observed at the voltage of 200 V and current minima at 90–140 V (Fig. 6, *a*). When the thickness increases of the formed porous non-metallic inorganic coating, the value of the maximum current density (I_m) decreases, the potential of the minimum shifts to the region of higher voltages at a rate of 4 V/μm, and the current value decreases at a rate of 1.2 A/μm. This is due to the fact that thicker coatings are characterized by a larger voltage drop, so there the current minimum shifts towards higher voltage. The current maximum decreasing is also associated with the coating thickness increasing: the thicker the coating is, the lower the current density is. The value of the current maximum is affected by the porosity of the nanostructured non-metallic inorganic coating.

The moment of the microplasma discharges quenching is associated with the kink of the current-voltage dependence at voltages of 90–140 V. With the coating thickness increasing, the shift of the quenching voltage of microplasma processes towards voltage increasing is observed, which is associated with the coating thickness increasing.

The through porosity of the formed coatings should be taken into account.

The current-voltage dependences in the absence of microplasma processes (Fig. 6, *b*) are characterized by a low

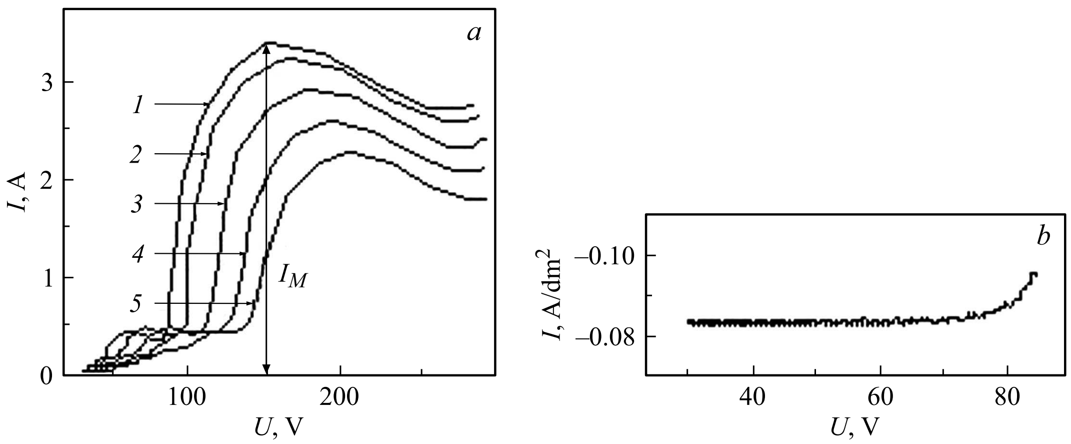

Figure 6. Falling branches of the current-voltage dependences for trapezoidal voltage pulse during the implementation of microplasma processes (*a*) with the coating application duration: *1* — 120, *2* — 240, *3* — 360, *4* — 480, *5* — 600 s and without microplasma processes (*b*).

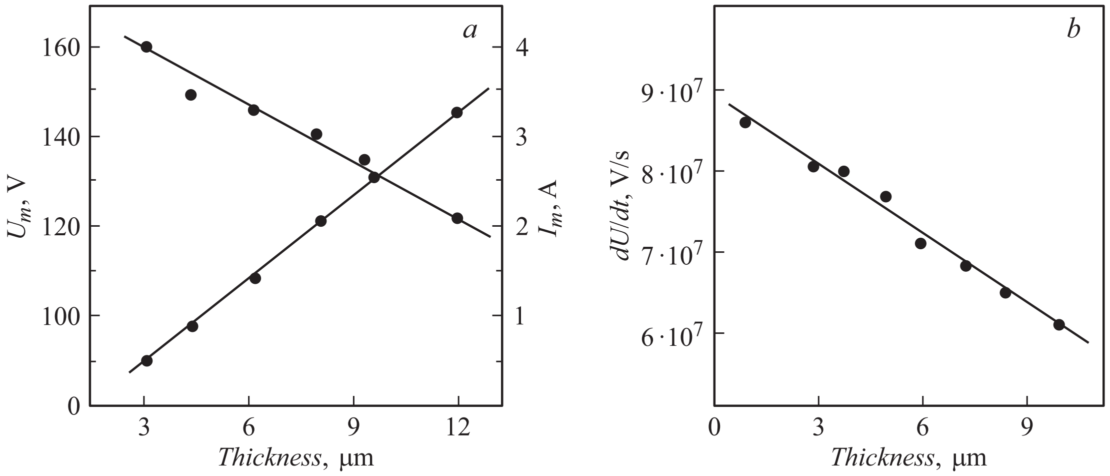

Figure 7. Shift of the voltage maximum (U_m) and the current maximum (I_m) vs. coating thickness (*a*) and potential change rate (dU/dt) vs. coating thickness (*b*).

current density, which is up to 15% of the total current at low voltages (up to 100 V). This allows us to consider the rate of anodic processes to be insignificant at high voltages. So, the contribution to the structure of the formed materials and coatings is determined by the intensity of high-temperature chemical reactions and microplasma processes.

The dependence of the shift of the voltage maximum and the current maximum, as well as the dependence of the potential change rate on the coating thickness are shown in Fig. 7.

As can be seen from Fig. 7, the quenching potential of microplasma processes U_m, determined from the current-voltage dependences (Fig. 6) and the time of the transient process (Fig. 4), varies linearly depending on time and coating thickness. This makes it possible to control the structure of the coating if the process is maintained at one voltage value exceeding the value of microplasma discharges quenching. The quenching potential of microplasma discharges, determined from the quenching potential, the current maximum, and the maximum value of the voltage drop rate, makes it possible to control the thickness and nature (electrochemical or plasma) of the coating application directly in the process of its production.

The results of the studies performed make it possible to predict and to control the dynamics of the coating thickness change even at the stage of development of the electrochemical system and directly in the process of coating application.

3. Conclusions

1. The physical and chemical bases for determining the ignition and quenching potentials of microplasma discharges are developed, based on the analysis of the transient time constant (RC) dependence on voltage and on the pulse duration when trapezoidal high-voltage pulse acts on the interface, leading to microplasma processes in electrolyte

solutions, based on measurements of currents and voltages on the porch, on the falling and rising branches of the trapezoidal voltage pulse. Knowledge of the ignition and quenching potentials of microplasma discharges makes it possible to determine the nature of the process in which the coating is formed. The high-temperature chemical reaction of material formation, proceeding under the action of microplasma discharges, at the moment of arc processes quenching, changes to the electrochemical one.

2. Chronopotentiometric and chronoamperometric measurements at the fronts of the trapezoidal pulse make it possible to eliminate the effect of the power source and allow us to study physical and chemical processes when the system is taken out of equilibrium, and when equilibrium is restored.

3. The nature of the coating formation process (electrochemical or plasma) determines the properties of the resulting coatings (structure, thickness, composition, etc.).

4. Regularities of changes in current-voltage, chronopotentiometric, chronoamperometric dependences on synthesis conditions, the dependence of the transient time constant (RC) on the voltage and duration of the process, the dependence of the electrode potential drop rate after disconnection on time and on the potential of the microplasma system in the process of coating growth under high-energy pulsed action on interface were identified.

5. It is shown that the revealed regularities are systemic and valid for microplasma systems, the processes in which are associated with the synthesis of non-metallic inorganic coatings. The growth rate and porosity of the coatings can be estimated based on the current maxima of the current-voltage dependences, the shift of the minimum of the current-voltage dependence, the rate of potential change, the reverse of the transient time constant $(-1/RC)$ at the quenching voltage of microplasma discharges directly in coating synthesis.

6. Current-voltage dependences are obtained for the rates of rise and fall of the potential voltage from 10^6 to 10^8 V/s.

7. The results of the study will help in the development and *in situ* control of the coatings synthesis.

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] V.I. Roldugin. *Fizikokhimiya poverkhnosti* (Intellekt, Dolgoprundy, 2011) (in Russian)

[2] B.B. Damaskin, O.A. Petry. *Vvedenie v elektrokhimicheskuyu kinetiku* (Vysshaya shkola, Moscow, 1983) (in Russian)

[3] K. Fetter. *Electrokhimicheskaya kinetika* (Khimiya, M., 1967) (in Russian)

[4] B.B. Damaskin, O.A. Petriy, G.A. Tsirlina. *Electrokhimiya* (Khimiya, KolosS, M., 2006) (in Russian)

[5] R.G. Compton, C. Batchelor, ed J.F. Dickinson. *Understanding Voltammetry: Problems and Solutions* (Imperial College Press, 2012)

[6] A.I. Mamaev, V.A. Mamaeva, V.N. Borikov, T.I. Dorofeeva. *Formirovanie nanostrukturnykh nemetallicheskikh neorganicheskikh pokrytiy putem lokalizatsii vysoenergeticheskikh potokov yf granitse razdela faz* (Izd-vo Tomsk University, Tomsk, 2010) (in Russian)

[7] A.I. Mamaev, V.A. Mamaeva, Yu.N. Dolgova, A.E. Ryabikov. Izvestiya Vuzov. Fizika, **65** (1), 119 (2022) (in Russian) DOI: 10.17223/00213411/65/1/119

[8] A.I. Mamaev, V.A. Mamaeva, E.Yu. Beletskaya, A.K. Chubenko, T.A. Konstantinova. Russian physics journal, **56** (8), 959 (2013). DOI: 10.1007/s11182-013-0124-3

[9] A.I. Mamaev, Yu.N. Dolgova, A.A. Yeltsov, G.V. Plekhanov, A.E. Ryabikov, T.A. Baranova, V.A. Mamaeva. Russ. Phys. J., **63** (7), 1265 (2020). DOI: 10.1007/s11182-020-02149-6

[10] A.I. Mamaev, Yu.N. Dolgova, E.Yu. Beletskaya, V.A. Mamaeva, T.A. Baranova. Russ. Phys. J., **63** (9), 1605 (2021). DOI: 10.1007/s11182-021-02212-w

[11] I.V. Suminov. *Plazmenno-elektroliticheskoe modifitsirovanie poverkhnosty metallov i splavov* (Tekhnosfera, M., 2011) (in Russian)

[12] A.V. Suminov. *Mikrodugovoe oksidirovanie* (*teoriya, tekhnologiya, oborudovaniye*) (EKOMET, M., 2005) (in Russian)

[13] G.V. Zeveke, P.A. Ionkin, A.V. Netushil, S.V. Strakhov. *Osnovy teorii tsepey* (Energoatomizdat, Moscow, 2007) (in Russian)