Modeling of the protective coatings formation mechanism by micro-arc oxidation

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Abstract. An electrophysical model of the micro-arc oxidation process, which allows, on the basis of the equivalent electrical circuit and fundamental laws of physics and chemistry, to describe the formation mechanism of protective coatings by the micro-arc oxidation method taking into account the large number of physical effects inherent in this process is proposed. The proposed model can be used to increase the controllability of micro-arc oxidation technology.

1. Introduction

At present, the technology of micro-arc oxidation (MAO) is actively developing: oxide films that protect against wear and corrosion, antibacterial coatings for titanium implants and even layers sensitive to radiation have been obtained [1, 2]. The main interest of scientists is directed to the modification of MAO coatings with nanoparticles in order to further increase their functional properties and expand the scope [3-5]. However, this does not take into account the main problem of the MAO process - the complexity of the technological parameters selection, the solution of which is of great importance for industrial production [6].

For the effective MAO process control, knowledge of the physical phenomena occurring during the coating formation is necessary, which makes it possible to purposefully act on them in order to obtain oxide layers with desired properties. There is a large number of works aimed at studying the MAO coatings formation mechanism, but there is still no comprehensive mathematical description that takes into account all the physical effects inherent in the MAO process, in particular, the microdischarges burning [7].

The electrophysical model based on the equivalent electrical circuit “metal-oxide-electrolyte” system and known physicochemical regularities, proposed in this work, allows to mathematically describe the MAO coatings formation to determine the properties of the oxide layer (thickness, porosity, corundum content) during the MAO process.

2. Development of an electrophysical model of the MAO process

As it is known, the MAO process includes several stages: the stage of anodization and the stages of microdischarges (spark, micro-arc, arc). In this case, at the anodization stage during electrochemical reactions, a dense oxide film (barrier layer) is formed on the anode, and then a porous layer, which allows to divide the anodization stage into two stages corresponding to the formation of these layers. At the stages of micro-arc discharges, plasma-chemical processes associated with the transition of amorphous alumina to corundum occur; the appearance of powerful arc discharges is undesirable, because they destroy the coating. The stage of spark discharges is intermediate: the first breakdowns
of the anode oxide film occur in it and the energy is redistributed between the electrochemical and plasma chemical processes. In view of the foregoing, the “metal-oxide-electrolyte” (MOE) system can be represented in the form of an equivalent electrical circuit (figure 1), the parameters of which depend on the stage of the MAO process.

**Figure 1.** Equivalent circuit of the MAO process: $U(t)$ – source of alternating voltage; $I(t)$ – technological current, including electronic $I_e$ and ionic $I_i$ currents; $R_{el}$ – electrolyte resistance; $R_{coat}, R_{bl}, R_{pl}$ – resistances of the coating, barrier and porous layers respectively; $C_{coat}$ – coating capacity; $R_{dis}$ is the microdischarges resistance.

Since at the stage of the barrier layer formation at the anodization stage, the porous layer is not yet formed and there are no microdischarges, $R_{pl} = R_{dis} = 0$, $R_{coat} = R_{bl}$; the coating capacity is the barrier layer capacity: $C_{coat} = C_{bl}$. In this case, the impedance of the obtained equivalent circuit can be written as follows:

$$Z_{bl}(t) = \frac{U_{Fibl}(t)}{I(t)} = \sqrt{R_{bl}(t)^2 + X_{Cb}(t)^2}$$

$$R_{bl}(t) = R_{bl}(t) + R_{el} = \frac{r_{ox} h_{bl}(t)}{S_{tot}} + R_{el}$$

$$X_{Cb}(t) = \frac{1}{\omega C_{bl}(t)} = \frac{h_{bl}(t)}{\omega e_{ox} e_0 S_{tot}}$$

where $U_{Fibl}(t)$ is the voltage drop across the sample with a barrier layer, $I(t) = I_i$ is the technological current, $R_{bl}(t)$ and $R_{el}$ are the resistance of the barrier layer and electrolyte between the anode and cathode of the galvanic cell, respectively, $h_{bl}(t)$ is the thickness of the barrier layer, $r_{ox}$ and $e_{ox}$ are the resistivity and permittivity of the oxide, $S_{tot}$ is the total area of the sample, $e_0$ is the dielectric constant, $\omega = 2\pi f$ is the cyclic frequency.

At the stage of the porous layer formation, $R_{dis} = 0$, and the impedance is calculated by the formula:

$$Z_{pl}(t) = \frac{U_{Fipl}(t)}{I(t)} = \sqrt{(R_{p}(t) + R_{el})^2 + X_{Cp}(t)^2}$$

where $U_{Fipl}(t)$ is the voltage drop across the sample with a porous layer, $R_{p}(t)$ and $X_{Cp}(t)$ are the equivalent active and reactive resistance of the coating, respectively. Since the porous layer can be represented as a parallel connection of many columns of electrolyte with resistance $R_{ep}(t)$ filling the pores and the resistance of the oxide matrix $R_{ox}(t)$, the resistance $R_{p}(t)$ can be calculated as follows:

$$R_{p}(t) = R_{bl}(t) + \frac{R_{ep}(t) \cdot R_{m}(t)}{R_{ep}(t) + R_{m}(t)}$$
\[ R_c(t) = \frac{r_{el} h_{pl}(t)}{S_p(t)}, \]  
\[ R_m(t) = \frac{r_{ox} h_{pl}(t)}{S_{wp}(t)}, \]  
where \( h_{pl}(t) \) is the thickness of the porous layer, \( S_p \) and \( S_{wp} \) are the total pore area and the area of the sample free from pores. These areas can be calculated according to the Keller model:

\[ S_p(t) = \frac{S_{tot} \pi d_p^2(t)}{4D_{int}^2(t)}, \]  
\[ S_{wp}(t) = S_{tot} - S_p(t) = S \left( 1 - \frac{\pi d_p^2(t)}{4D_{int}^2(t)} \right), \]  
where \( d_p(t) \) is the pore diameter, \( D_{int}(t) \) is the distance between the centers of neighboring pores.

The equivalent reactance of the coating is calculated by the formula:

\[ X_{Cp}(t) = \frac{1}{\omega C_{eq}(t)}, \]

where the coating capacity \( C_{eq}(t) \) is calculated for the series connection of the barrier layer capacitances \( C_{bl}(t) \) and the dielectric matrix \( C_{bl}(t) \):

\[ C_{eq}(t) = \frac{C_{m}(t) C_{bl}(t)}{C_{m}(t) + C_{bl}(t)} = \frac{\varepsilon_{ox} \varepsilon_0 S_{wp}(t) S_{tot}}{S_{wp}(t) h_{pl}(t) + S_{tot} h_{bl}(t)}. \]

The thickness of the barrier and porous layers can either be expressed from formulas (1) - (3) and (4) - (7), or calculated according to the Faraday law as follows:

\[ h_{bl}(t) = \frac{M_{ox} I t \eta}{z F P_{ox} S_{tot}}, \]
\[ h_{pl}(t) = \frac{M_{ox} I t \eta}{z F P_{ox} S_{wp}}, \]
where \( M_{ox} \) is the molar mass of the oxide, \( I \) is the ionic current, \( t \) is the processing time, \( z \) is the number of electrons participating in the reaction, \( \rho_{ox} \) is the oxide density, \( F \) is the Faraday constant, \( \eta \) is a coefficient showing the fraction of the ionic current gone into oxidation. The surface \( P_s(t) \) and bulk \( P_v(t) \) porosity of the coating at the anodization stage is determined from geometric considerations using expression (8):

\[ P_s(t) = \frac{S_p(t)}{S_{tot}} = \frac{\pi d_p^2(t)}{4D_{int}^2(t)}, \]
\[ P_v(t) = \frac{V_p}{V} = \frac{2\pi}{\sqrt{3}} \left( \frac{d_p(t)}{2D_{int}(t)} \right)^2, \]
where \( V \) is the total volume of the coating, \( V_p \) is the pore volume.

At the stages of microdischarges (spark, micro-arc, arc), electrolyte boiling in the pores due to the release of Joule heat; formation and breakdown of a gas-vapor bubble, ignition and quenching of a microdischarge occur. In this case, the coating thickness can be calculated according to known empirical formulas using the forming curve (figure 2). In figure 2, point A corresponds to a fully formed barrier layer, point B - to the end of the porous layer formation and the appearance of the first
spark discharges; point C - transition to the stage of micro-arc discharges; at point B1, energy is redistributed between electrochemical and plasma processes. The calculation of the coating thickness is as follows.

The initial value of the thickness \( h_{cr}(0) \) is calculated by the formula:

\[
U_{cr}(0) = k_1 h_{cr}(0) + k_2 ,
\]

where \( k_1 \) and \( k_2 \) are empirical coefficients. In this case, the initial value of the critical voltage (breakdown voltage) is found as the ordinate of the transition point of the MAO process to the spark stage (point B on the forming curve). Next, the found values of the critical thickness \( h_{cr(i)} = h_{cr(0)} \) and the breakdown voltage \( U_{cr(i)} = U_{cr(0)} \), where \( i = 1 \), are substituted into the expression

\[
h_{cr(i+1)} = h_{cr(i)} \exp \left( k(U_{f}(t) - U_{cr(i)}) \right),
\]

where \( U_f(t) \) is the measured forming voltage, \( k \) is the coefficient. Further calculation of the coating thickness is carried out according to this formula, and when the next “bend” of the forming curve is reached (point B1), the values of the coefficients \( h_{cr(i)} = h_{cr(i-1)} \), \( U_{cr(i)} = U_{cr(i-1)} \) calculated at point B1 and so on. Thus, formulas (9) and (10) for calculating the coatings thickness are recursive relationships.

As it is known, electrochemical processes are associated with ionic current, and dielectric breakdown and plasma processes are associated with electronic one. Then the total current density \( j(t) \) in the “metal-oxide-electrolyte” system will be equal to the sum of the ion and electron currents densities \( j_i(t) \) and \( j_e(t) \), respectively:

\[
j(t) = \frac{I(t)}{S_{tot}} = j_i(t) + j_e(t) = \frac{I_i(t)}{S_i} + \frac{I_e(t)}{S_e} ,
\]

where \( S_i \) and \( S_e \) are the area over which electrochemical and plasma processes occur, respectively. Introducing the assumption that breakdown occurs simultaneously in all pores, and taking into account the fact that the current in the pore is determined by the resistance of the electrolyte and the barrier layer at the bottom of the pore, and the area \( S_e \) is equal to the pore area \( S_p \), we determine what part of the electron current density is from the total:

\[
\frac{j_e(t)}{j(t)} = \frac{1}{P_s} \cdot \frac{I_e(t)}{I(t)} = \frac{Z_{pl}(t)}{R_{b1}(t) + R_{l}(t)} , \tag{11}
\]
where \( R_l(t) \) is the resistance of the electrolyte layer with thickness \( h_{pl}(t) \) and area \( S_{tot} \):

\[
R_l(t) = \frac{r_{el} h_{pl}(t)}{S_{tot}}.
\]

From the expression (11) we obtain the minimum electron current at the beginning of the sparking stage:

\[
I_e(t) = \frac{P_\xi I(t) Z_{pl}(t)}{R_{bl}(t) + R_l(t)}.
\]

We obtain the minimum current in a single pore, divide \( I_e(t) \) by the number of pores \( N_p \):

\[
I_p(t) = \frac{I_e(t)}{N_p} = \frac{I_e(t) \pi d_p^2}{4 S_p}.
\] (12)

The length of the discharge gap at the beginning of the sparking stage is determined by the formula:

\[
l_d = \frac{4 V_b}{\pi d_p^2},
\]

where \( V_b \) is the volume of the vapor-gas bubble formed in the pore due to boiling of the electrolyte:

\[
V_b = \frac{L \rho_{el}}{Q_p}.
\] (13)

In the formula (13), \( L \) is the specific heat of vaporization (for water as the main component of the electrolyte, \( L = 2260 \text{ kJ/kg} \)), \( \rho_{el} \) is the electrolyte density. In order for the electrolyte to boil in the pore to begin, it is necessary that the amount of heat \( Q_p \) released during one current pulse of duration \( t_p \) exceed the heat of the electrolyte vaporization:

\[
Q_p \geq L m,
\]

\[
Q_p = I_{pol}(t)^2 R_{ep} t_p = I_p U_{ci}^2 R_{ep}^{-2},
\]

where \( m \) is the electrolyte mass in the pore.

As the thickness of the oxide layer increases, the energy transmitted to the coating increases, which is expressed through the total power \( P_{tot} \):

\[
P_{tot} = U_f(t) I(t),
\]

where the forming voltage \( U_f(t) \) is the voltage drop across the coating. A part of this energy is spent on boiling the electrolyte, and another part goes on the breakdown of the vapor-gas bubble and maintaining the combustion of the microdischarge. The latter value can be found as excess energy:

\[
P_{dis} = P_{tot} - Q_p = U_{bd}(t) \cdot I_{dis}(t),
\]

where \( U_{bd}(t) \) is the breakdown voltage of the vapor-gas bubble, \( I_{dis} \) is the discharge current, the minimum value of which is described by the expression (12). If this energy exceeds the work of electron transfer from the cathode to gas, conditions are created for the occurrence of microdischarge. In [8], on the basis of the Stefan-Boltzmann law, an expression for an approximate calculation of the temperature \( T \) in the channel of a spark discharge was obtained:

\[
T = \sqrt[4]{\pi \sigma^{-1} q_{nk}},
\]
where $\sigma$ is the Stefan-Boltzmann constant, $q_{mk}$ is the heat flux density from the side of the microdischarge. In fact, this value is equal to the specific power of the microdischarge:

$$q_{mk} = \frac{4 \cdot U_{ba}(t) \cdot I_{dis}(t)}{\pi d_p^2} = \frac{P_{dis}}{S_{sp}},$$

where $S_{sp}$ is the base area of a single pore.

With increasing microdischarge power as the coating thickness increases, the temperature in the discharge channel also increases, and at the stage of micro-arc discharges the phase transition “amorphous alumina – corundum” becomes possible. The content of crystalline alumina modifications in the coating depends on the temperature of the walls and bottom of the pore during microdischarge and obeys the Kolmogorov-Johnson-Mehl-Avrami equation:

$$C_\alpha = 1 - \exp(-k t_p^n),$$

where $C_\alpha$ is the fraction of the formed corundum, $k$ is the rate constant (at a temperature of 1050 °C $k = 8.5 \cdot 10^{-5} \text{s}^{-1}$), $n$ is the Avrami exponent.

3. Conclusion

The developed electrophysical model allows to obtain expressions for the MAO coatings properties (thickness for all stages of the MAO process and porosity at the anodization stage; corundum content in the coating) based on the parameters of the equivalent electrical circuit and the fundamental laws of physics and chemistry. These formulas take into account the relationship between electrochemical and plasma phenomena, which makes it possible to obtain a systematic analytical description of the MAO process.

The proposed model has some limitations associated with insufficient knowledge of the MAO coatings formation mechanism at the spark and micro-arc stages. Nevertheless, this model can be used to develop more general mathematical models, as well as to create an intelligent automated system for the controlled synthesis of oxide coatings in order to increase the controllability of the MAO process [9, 10].

Acknowledgments

The reported study was funded by RFBR according to the research project № 19-08-00425.

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