Deposition of Al$_2$O$_3$ coatings in Ar-O$_2$ low-pressure discharge plasma under a high dissociation degree of O$_2$

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Abstract. The deposition of Al$_2$O$_3$ coating with a corundum structure was done by anodic evaporation in a low-pressure arc with a self-heated hollow cathode. The conditions were created for increasing the energy of plasma electrons and a corresponding increase in the frequency of O$_2$ dissociation by contraction of the discharge in the anode region. The discharge was maintained in a combined mode with a constant current (70 – 100 A), on which current pulses (100 μs, 1 kHz) with adjustable amplitude (up to 220 A) were superimposed. This mode ensured a change in the degree of O$_2$ dissociation in the range of 0.3 – 0.5 at constant average discharge current and Al evaporation rate. It is shown that an increase in the degree of O$_2$ dissociation leads to an increase in the rate of coating deposition by a factor of 1.3 and promotion of the preferred (300) orientation of crystallites. The effect is due to the features of the adsorption of molecular and atomic oxygen on the Al$_2$O$_3$.

1. Introduction
Vacuum-plasma methods allow creating highly non-equilibrium working environment media (conditions) and provide a fundamental change in the properties of the treated surfaces or the synthesis of new materials with unique features. One of the main issues when using such methods for coating deposition is the possibility of adjusting the main parameters of the process. Not only the growth rate of the coatings, the temperature of the substrates, and the working gas pressure (partial pressures of the gas mixture) but also the parameters of the ionic flux on the surface of the deposited coating become extremely important [1]. It is caused by the fact that ion assistance allows changing the microstructure [2], the structural-phase state [3], and the level of intrinsic stresses in the coatings [4].

The efficiency of the ionic flux is estimated using a generalized parameter – the average energy ($E^*$) per coating atom [5, 6]. It is equal to the product of the ion energy ($E$) and the ratio of the ion ($j_i$) and atom ($j_a$) fluxes densities: $E^* = E \cdot j_i / j_a$. At the same time, the deterioration of the coating parameters at an increase in $E$ to values, at which some processes accompanying the formation of the coating are significantly enhanced (initiation of intrinsic stresses [4], changes in the size and predominant orientation of crystallites [3], desorption of particles, etc. [7]), leads to the necessity of separate adjustment of the current density and ion energy.

Limiting the ion energy and independent adjusting the ion current density over a wide range (up to 10 mA/cm$^2$) made it possible to realize the conditions for high-rate (~ 5 μm/h) low-temperature (500-600°C) deposition of α-Al$_2$O$_3$ coatings with a low level of intrinsic stresses [8]. The coatings
were deposited by anodic evaporation of Al in Ar-O$_2$ low-pressure arc plasma. The experiments were carried out in a gas-discharge system, in which a controlled increase in the frequency of gas ionization was achieved by compressing the electron flow by a cylindrical electrode, inside which an additional anode was located and the gas was injected. In subsequent experiments, the effectiveness of this approach was shown to increase the degree of dissociation of the reaction gas [9]. Moreover, it was found that an increase in the concentration of atomic oxygen led to a significant increase in the growth rate of Al$_2$O$_3$ coatings [10]. The influence of the concentration of atomic particles of the reaction gas is also observed in experiments with steels nitriding [11], reactive magnetron deposition of oxide [12], nitride [13] and carbide [14] coatings. The results of theoretical studies suggest a significant difference in the nature of the adsorption of molecular and atomic oxygen on the surface of Al$_2$O$_3$ [15]. Thus, along with the task of controlling the parameters of the ionic flux within a wide range, the issue of monitoring the composition of the reaction medium and the influence of the dissociation degree of molecular gases on the properties of coatings becomes of great importance.

The authors have developed a method for regulating the dissociation degree of the reaction gas in the anode region of the discharge by high-current pulses of the electron current at a constant average value of the ion saturation current density [16]. This work is a development of the subject and includes the results of the study of the influence of the O$_2$ dissociation degree on the growth conditions and properties of Al$_2$O$_3$ coatings.

2. Experimental methods
The studies were carried out in the device for coating deposition, the electrode scheme of which is shown in figure 1. The cathode assembly with a self-heated hollow cathode (SHC) 1 made of TiN was located on the axis of the gas discharge system. The water-cooled anode 2 was located inside a cylindrical screen 3, the length and inner diameter of which were 70 mm and 50 mm, respectively. Ar (90 sccm) flow required for the operation of the SHC with a current of up to 230 A was fed through the cathode cavity using a 4F-201CV flow regulator (Bronkhorst High-tech). O$_2$ was injected through a cavity in the screen 3 at a flow rate of 150 sccm. The deviation from the set values of the gas flows did not exceed 0.8%. The chamber was pumped by a turbomolecular pump; the total pressure of the gas mixture during the experiments was 0.7 Pa.

The forced compression of the electron flow in the screen 3 having a floating potential leads to appearance of a potential difference between the plasma of the discharge column and anode. The value
of the potential difference can reach 35 V [16], which ensures the acceleration of electrons to the energy close to the maximum of the dissociation cross-section by an electron impact [17]. Interaction of high density flows of O₂ and accelerated electrons in the screen cavity increases the frequency of gas dissociation [9]. In the high-current pulsed mode of discharge combustion, the near-anode potential drop increases sharply, which contributes to the increased O₂ dissociation [16]. For low-temperature deposition of α-Al₂O₃ coatings, it is necessary to provide a high average density of the ion current on the coating surface. So a combined DC+pulsed discharge mode was used in the experiments, where the current pulses with an amplitude of 0 – 220 A, frequency of 1 kHz, and duration of 100 μs were superimposed on the direct discharge current. At a low rate of particle loss on the chamber 4 walls, this mode ensures the maintenance of a high degree of oxygen dissociation even with the large pulse duty cycle [16]. The parameters of the combined mode were regulated by a DC source 5 and a pulse-periodic source 6.

A thermally insulated graphite crucible 7 was placed at a distance of 300 mm from the SHC. The temperature of the crucible was regulated by changing the current in the range of 4 – 6 A using the power supply 8.

The change in the plasma composition was determined by the control of optical emission spectra in the wavelength range of 200 – 1100 nm using an HR2000 spectrometer (Ocean Optics). The concentration of atomic oxygen was measured using a nickel catalytic probe 9. Heterogeneous recombination of O with heat release occurs intensively on its surface [18]. The probe temperature was measured by infrared pyrometer Impact IP 140 10. The contribution of the recombination process at high total heating power by particle fluxes and radiation from the plasma was estimated using the technique described in detail in [19]. The degree of O₂ dissociation was determined from the ratio of the concentrations of oxygen molecules and atoms \( n_0 / (2n_{o_2}) \).

Al₂O₃ coatings were deposited on flat substrates made of steel, type AISI430, at a temperature of 600°C. The ion current density per sample was ~ 8 mA/cm². The bias voltage was set in the pulse-periodic mode (50 kHz, 10 ms) with an amplitude of ~200 V. The duration of the coating deposition was 0.5 h. The deposition rate was estimated from the coating thickness (1.5 – 2 μm) measured by the ball abrasion method on Calotest facility (CSM Instrument). The measurement error did not exceed 5%.

X-ray phase analysis of the coatings was carried out using an XPert PRO MPD (Panalytical) diffractometer in CuKα radiation with a high-rate PIXcel solid-state detector. The survey was carried out in the range of diffraction angles 2θ = 15 – 85°, with a scanning step of 0.05° and a time per one step of 150 s. The XRD patterns were decoded using the diffractometer software and PDF-2 databases. The IR spectra of the coatings were recorded using a Vertex 70 IR Fourier spectrometer in the wavenumber range from 400 to 4000 cm⁻¹ with a resolution up to 1 cm⁻¹. The spectrum was captured when the beam tilt angle was 40° to the surface of the sample. The spectra were averaged over 16 measurements.

3. Results and discussion

The results of measuring the degree of O₂ dissociation by a catalytic probe in the discharge plasma were shown in figure 2. Switching to the combined DC+pulse periodic mode and increasing the discharge current amplitude up to 160 A increases the degree of O₂ dissociation from ~ 0.32 to 0.48.

The characteristic spectrum of the plasma optical emission generated in the combined mode is shown in figure 3. The line of atomic oxygen OI (777.2 nm) have the highest intensity. At the increased exposure, the emission of the first negative system of molecular ions O₂II b1Σ⁺→a₃Πₒ (525 and 559 nm) becomes noticeable. The ratio of line intensities O₂II(559)/OI(777.2) is 0.03. The relative intensity of the line of atomic ions OII is an order of magnitude less. The intensity of the OI line increases monotonically as the discharge current amplitude increases (figure 4).

When the crucible is heated by a direct electron current, Al lines with an intensity of an order of magnitude less than that of the gas components are recorded in the optical emission spectra of the plasma. The most intense metal lines correspond to neutral AlI particles (394.4 and 396.1 nm). In
contrast to OI lines, the intensity of AlI lines decreases by 1.5 – 1.7 times when the amplitude of the pulse discharge current increases to 170 A and the current in the crucible circuit remains constant (figure 4).

Figure 2. The O$_2$ dissociation degree as function of discharge current amplitude.

Figure 3. The optical emission spetrum of Ar-O$_2$ plasma generated under anodic evaporation of Al.

Figure 4. The intensity of optical emission as function of the discharge current amplitude. Line wavelength: 1 – 845, 2 – 615 nm.

This effect, caused by an increase in the growth rate of the oxide layer on the melt surface, is discussed in more detail in another paper [20]. Further experiments were carried out at a constant evaporation rate of Al in order to exclude the effect on the growth rate and the structural-phase state of the coatings deposited at different degrees of O$_2$ dissociation. The constant evaporation rate was provided by the control of both the crucible current and the optical emission line AlI. The mean square deviation of AlI line intensities over the entire range of the discharge current amplitude variation during coating application did not exceed 6%. The decrease in the evaporation rate with an increase in
the discharge current amplitude was compensated by an increase in the current in the crucible circuit from 4.5 to 5.5 A.

An increase in the crucible current at a constant value of the flow of vaporized metal (vapor pressure) was accompanied by an increase in the concentration of Al⁺ ions. The intensity of the AlIII optical emission line (390.1 nm) increased by 1.5 times with an increase in the discharge current amplitude to 220 A. For further consideration of the effect of atomic oxygen on the growth rate and the structural-phase state of Al₂O₃ coatings, it is necessary to estimate the proportion of additional components (Al ions and AlO complexes) in the flow of deposited particles.

To estimate the degree of ionization of metal vapor, the basic spectroscopy equation was used, which relates the absolute values of the intensities of the spontaneous transition lines $I_{ij}$ between the levels $i$ and $j$ and the concentration of particles $n_s$ [21]:

$$I_{ij} = A_{ij} h \nu_{ij} n_s g_i / Z_s \exp(-E_i / kT),$$

where $A_{ij}$ is the Einstein coefficient; $\nu_{ij}$ is the transition energy; $g_i$, $E_i$ are the statistical weight and energy of the level, respectively; $T$ is the temperature of the particles. The values of the $Z_s$ partition function were taken from [22], the remaining parameters were determined using the database [23]. The experimentally determined line intensities AlIII(390.1 nm) and AlII(396.1 nm) were used in the calculations. The calculated ratio of concentrations $n(Al^+)/n(Al^1)$ was several orders of magnitude less than 1, which indicates an insignificant proportion of ions in the vaporized particle flow.

The intensity of the AlO peak (484 nm) is increased by 1.2 times with an increase in the amplitude of the discharge current. The growth in the concentration of AlO complexes may be due to an increase in the frequency of reactions of Al with oxygen on the melt surface and in the discharge gap. According to [24], Al atoms are the main component of the particle flow during reactive evaporation, whereas the partial pressure of AlO complexes is $\sim 10^{-5}$ Pa at a temperature of 1200°C and the partial O₂ pressure of 0.1 Pa (the values closest to experimental ones are taken). It can be concluded that the concentration of AlO complexes evaporating from the melt surface is relatively low in the discharge gap.

The homogeneous reaction rate (in the discharge gap) can be expressed as follows

$$Al + O_2 \rightarrow AlO(X^2\Sigma^+) + O .$$

It is determined by the ratio $3 \cdot 10^{-11} \cdot \exp(-18/T) \text{ cm}^3/\text{s}$ in a wide temperature range (300 – 1700 K) [25], which was used to estimate the reaction yield under experimental conditions ($1.4 \cdot 10^{18} \text{ cm}^3/\text{s}$), while the calculated frequency of Al and O₂ collisions per unit volume was $\sim 7 \cdot 10^{10} \text{ cm}^3/\text{s}$, which implies that the probability of formation of complex AlO(X²Σ⁺) does not exceed 0.2. The frequency of occurrence of AlO in the excited (B²Σ⁺) state, the most likely channel of which is a three-particle reaction: $Al + O + O_2 \rightarrow AlO(B^2\Sigma^+) + O_2$ [26], is much lower. Since the estimated time of passage of vaporized Al atoms through the discharge gap is two orders of magnitude less than the characteristic reaction time, equation (2), it can be concluded that the frequency of generation of AlO complexes in the reaction volume is insignificant.

Thus, at a constant average combined discharge current in a wide range of pulse current amplitude, Al reactive evaporation mode is implemented, in which the main component in the flow of metal particles to the surface of the growing coating is Al atoms. Their concentration is maintained constant, and the degree of O₂ dissociation in the volume is regulated in the range from 0.3 to 0.5. The growth rate of Al₂O₃ coatings deposited in this mode increases almost linearly from 3 to $\sim 3.8 \mu \text{m/h}$ with an increase in the discharge current amplitude from 0 to 220 A (figure 5).

The diffractograms of the obtained coatings are shown in figure 6. The main phase of α-Al₂O₃ coatings is represented by the two most intense reflexes (110) $2\theta \sim 37.9^\circ$ and (300) $2\theta \sim 68.5^\circ$. The phase crystallites have a predominant orientation (300) with a texture coefficient ($TK_{300}$) significantly greater than 1. When the discharge current amplitude increases to 220 A, $TK_{300}$ increases to 8.2.
The change in the deposition rate and the phase features of the coating can be explained by the difference in the adsorption conditions of molecular and atomic oxygen on the condensation surface. It was shown by molecular dynamics methods that Al atoms are characterized by a strong adsorption interaction with the surface of Al$_2$O$_3$ crystal structure [15], while there are fundamental differences in the interaction of atomic and molecular oxygen particles with this surface. On the basis of theoretical calculations, it is concluded that the adsorption of O atoms is more stable, and their increased concentration during the growth of the coating leads to an increase in the texture of the crystallites. A similar effect of changing the predominant orientation of TiN crystallites from (111) to (001) is also observed with an increase in the concentration of atomic nitrogen [27].

**Figure 5.** The deposition rate of Al$_2$O$_3$ coating as a function of discharge current amplitude.

**Figure 6.** The XRD patterns of the Al$_2$O$_3$ coatings deposited under different discharge current amplitude.

It should be noted that the formation of the texture (300) in α-Al$_2$O$_3$ coatings may also be related to the state of the condensation surface. The formation of (300) texture in α-Al$_2$O$_3$ coatings was observed as a result of the γ-phase transformation [28]. The nucleation of the α-phase and the further rapid lateral growth of crystallites occurred on the textured surface (440) of γ-Al$_2$O$_3$ [29], whereas on the equilibrium structure, α-Al$_2$O$_3$ crystallites with the texture (300) were not developed. It was concluded that the γ-phase with a predominant orientation (440) stimulated the growth of the α-phase with a texture (300) due to the weak difference in the interplane distances of the crystal lattices (1.5%) [30].

The results of X-ray diffraction of the coatings obtained in this study do not allow reliably identifying the γ-phase. To determine X-ray amorphous phases, IR spectra of the coatings were analyzed (figure 7). By decomposing the spectra into the components described by the normal Gaussian distribution, the peaks with wave numbers ~ 442, 569, 635 cm$^{-1}$ related to the transverse (TO) mode of α-Al$_2$O$_3$ oscillations and the peaks 480, 625, 900 cm$^{-1}$ of the longitudinal (LO) mode were determined. The C-axis of the crystal lattice is directed perpendicular to the electric field vector of the IR beam (C $\perp$ E) [31]. The oscillations occurring at the parallel orientation of the C-axis of α-Al$_2$O$_3$ and the electric field vector of the IR beam (CIIE) correspond to peaks with wave numbers 583 (TO) and 871 cm$^{-1}$ (LO). The spectra contain four peaks of the gamma phase with wave numbers 744, 807 (TO) and 783, 917 cm$^{-1}$ (LO), activated in IR range [32], and peaks 721 and 959 cm$^{-1}$, caused by oscillations of molecules of the Al$_2$O$_3$ amorphous phase [33].
There are no significant changes in peak intensities and wave numbers of X-ray amorphous phases in the entire range of changes in the amplitude of the pulsed discharge current. There is an increase in the oscillation modes of $\alpha$-$\text{Al}_2\text{O}_3$ in the $C\perp E$ direction, which indicates an increase in the proportion of crystallites with the corresponding preferred orientation. It was shown in previous work [34] that $\gamma \rightarrow \alpha$ transformation occurring at the orientation ratio $\gamma(440)/\alpha(300)$ was accompanied by a sharp decrease in the intensity of $\gamma$-peaks and the amorphous phase, and an increase in $TK_{300}$ by an order of magnitude. The results of the experiments carried out in this paper indicate that there are no significant changes in the concentration of the $\gamma$-phase with a simultaneous increase in the predominant orientation of $\alpha$-$\text{Al}_2\text{O}_3$. This allows for the conclusion that in this case, the growth of the texture is mainly due to the increased concentration of atomic oxygen in the plasma of the combined discharge.

![Figure 7. The IR spectra of $\text{Al}_2\text{O}_3$ coating deposited under discharge current amplitude: $I = 0$, 2-220 A.](image)

Thus, it is experimentally shown that an increase in the concentration of atomic oxygen (the degree of $\text{O}_2$ dissociation) at a constant value of Al flux on the substrate contributes to an increase in the growth rate of $\alpha$-$\text{Al}_2\text{O}_3$ coatings and an increase in the preferential orientation (300) of $\alpha$-phase crystallites.

4. Conclusion
Coatings $\alpha$-$\text{Al}_2\text{O}_3$ were obtained at a constant value of Al vapor flux density, the average ion current density on the coating surface, and adjustable $\text{O}_2$ dissociation degree in the range of 0.3 – 0.5 by thermal anodic evaporation of Al in Ar-$\text{O}_2$ low-pressure arc plasma. It is experimentally shown that an increase in the degree of dissociation contributes to an increase in the growth rate of coatings and an increase in the preferential orientation (300) of $\alpha$-phase crystallites. Studies of the structural-phase state of the coatings were carried out. The results showed that the observed effect was due to the more intense adsorption of atomic oxygen compared to the molecules and did not appear from $\gamma \rightarrow \alpha$ transformation with the orientation ratio of $\gamma(440)/\alpha(300)$.

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