A study of conditions of Al₂O₃ coatings deposition by the anodic reactive evaporation of aluminum

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Abstract
The conditions of the stable burning of high-current discharge with a self-heating hollow cathode and a hollow anode were studied. The parameters of the ion flow and the double electric layer arising in the vicinity of the hollow anode aperture were determined. It was shown that the use of a hollow anode allows for increasing the ion current density ~2-fold compared to the mode of discharge burning with a flat anode and provides for an increase in the molecular gas dissociation degree. Single-phase nanocrystalline α-Al₂O₃ coatings were obtained at a temperature of 600°C using the reactive anode Al evaporation technique.

1. Introduction
Alumina has high working characteristics in a crystalline state, whereas the amorphous phase is characterized by low thermal stability, chemical stability and hardness [1]. Among the plurality of polymorph modifications of Al₂O₃, the only thermally stable α phase is of the most interest; transition to it from the low temperature phases using annealing in air occurs at temperatures of higher than 1100°C [2]. α-Al₂O₃ is obtained using the chemical vapor deposition at a temperature of 1000°C [3]. For the low-temperature deposition of nanocrystalline Al₂O₃ coatings, vacuum and plasma methods are used such as plasma enhanced chemical deposition (560°C) [4], electron beam evaporation (700°C) [5], arc evaporation (780°C) [6], double glow plasma technique (580°C) [7], pulse magnetron sputtering (500°C) [8]. Due to the fact that the formation of crystalline phases occurs in a certain range of current density and ion energy values on the growing coating surface [9], for the high-rate deposition (~10 nm/h) a significant intensity of ion assistance is required. For example, in the [5], in order to deposit the nanocrystalline Al₂O₃ coating at a rate of 1.5-3 μm/min using the electron beam evaporation technique, the ion current density was increased using an additional high-current (250 A) discharge to 75 mA/cm². At the temperature of 700 °C and bias voltage of 75-150 V, γ-Al₂O₃ coatings were obtained but no α-phase was formed.

Higher values of the ionization degree of the particle flow on the sample surface and deposition rates of the Al₂O₃ (as a rule, ~1 nm/s) are achievable when using cathode evaporation in an arc discharge. As it is shown in the [10], the coatings obtained using such method at the temperatures of 600-700°C and bias voltages of 50-300 V are a mixture of phases, the γ-Al₂O₃ being dominant. Providing conditions for decreasing the charge of aluminum ions and formation of a mono-energetic
ion flow allowed for setting optimal values of ion energy for the growth of α-Al₂O₃ and for depositing single phase coatings [11].

The alternative method used in the present work is based on using a high-current discharge with a self-heating hollow cathode, a crucible anode and an additional hollow anode, providing for an increase in the ionization degree and oxygen dissociation. Such a type of discharge stably burns in a wide range of discharge current (1-10² A) and gas pressure (0.01-0.1 Pa) in the Ar flow with feeding of O₂ into the anode part, allows for heating the crucible to high temperatures and thus providing a high rate of Al₂O₃ coating deposition.

The aim of the study was to measure the parameters of the ion flow generated in a high-current discharge with a self-heating hollow cathode and an additional hollow anode, to obtain Al₂O₃ coatings using the reactive anode evaporation of aluminum with intensive ion assistance and to determine the range of current density and ion energy, within the limits of which the α-Al₂O₃ coatings are formed.

2. Experiment technique

The experiments were carried out using the device, a scheme of which is depicted by figure 1. A self-heating hollow cathode 1 with internal diameter of 12 mm was made out of titanium nitride using the magnetic pulse pressing method [12]. A hollow cylindrical electrode 2 16 mm in diameter (its external surface was enclosed with a ceramic screen) or a disc 3 40 mm in diameter was used as an anode. Ar and O₂ were fed into the discharge gap separately via the cathode and anode correspondingly. In the experiments with the flat anode, O₂ was fed to the region adjacent to the anode. The partial pressure of Ar was 0.13 Pa; the pressure of O₂ was controlled in the range of 0–0.5 Pa by altering the gas flow (0-40 sccm). The discharge current was set using the current stabilizer 4 in the range from 2 to 30 A.

In the gas discharge system with a hollow anode, the experiments on deposition of Al₂O₃ coatings were carried out using the method of anodic arc evaporation. A detailed description of the method is outlined in [13]. A thermally insulated crucible 5 with an inner diameter of 8 mm, made out of the graphite (MG-1) was used in the experiments. The crucible was charged with reagent grade Al. The maximum electron current to the crucible set by the power supply unit 6 was 4 A, the crucible temperature reaching 1050°C. The coatings were deposited on the samples made of the AISI430 steel, the surface of which was preliminarily coated with the Cr₂O₃ layer 100 nm thick, isostructural to α-Al₂O₃, using the reactive magnetron sputtering. The samples were placed in the holder 7, the backside of which was equipped with the resistance heater 8. During the deposition, the samples were heated with heat radiation to 600°C. The coating deposition rate was 4 μm/h.

The potential drop on the double electric layer formed in the aperture of the hollow anode was measured using the double probe method. The measurements were carried out using the Tektronix TPS 2034 oscilloscope with 200 MHz bandwidth. The ion current density was measured using the flat collector with surface area of 40×40 mm², having the – 100 V potential with respect to the grounded vacuum chamber. The collector was located at the position of the sample holder 7.
The X-ray phase analysis of the coatings was carried out using the XRD-7000 X-ray diffractometer (Shimadzu) in Cu-Kα radiation with a graphite monochromator on a secondary beam. The size of crystallites and the value of the micro stresses were determined using the Rietveld full-profile refinement technique.

3. Experimental results and discussion
The current-voltage characteristic of the discharge with a self-heated hollow cathode in the burning mode with hollow and flat anodes are depicted in figure 2. After cathode heating in a plasma discharge with a current of up to 2 A, a transition to thermal electron emission occurs that is accompanied by a decrease in the discharge combustion voltage by several hundred volts. In the flat anode mode, at an increase in discharge current from 2 to 30 A, the discharge voltage monotonously decreases to 48 V. The volt-ampere characteristic of the discharge in the hollow anode mode is also falling; however, the discharge voltage value appears to be higher by ~70 V.

Plots of the discharge voltage vs. gas flow in the region adjacent to the anode for these modes have significant differences (figure 3). As the gas flow to the hollow anode increases to 10 sccm, the discharge voltage drastically drops from 130 to 90 V and insignificantly changes at further flow increase. In the flat anode mode, the gas flow does not significantly affect the discharge voltage and its value is 62-66 V.

In the gas discharge system with a hollow anode, the discharge current is closed on the anode via the small diameter channel. The anode current density exceeds the chaotic electron current density which, as it is known, leads to the emergence of a negative anode potential drop [14]. In this case, an increase in the discharge gap voltage occurs and its value under the experiment conditions reaches 70 V and exceeds the working gas ionization potential by several times. Gas ionization in the anode cavity leads to the emergence of reverse ionic current and formation of a double electric layer in the anode aperture [15].

![Figure 2](image1.png)  
**Figure 2.** Volt-ampere characteristic of the discharge in burning mode with a flat anode 1 and a hollow anode 2.

![Figure 3](image2.png)  
**Figure 3.** Discharge voltage plots in the mode with a flat cathode 1 and a hollow cathode 2 vs. O₂ flow to the region adjacent to the anode. Discharge current is 10 A.

Figure 4 demonstrates plots of the ionic current on a flat collector located against the aperture of the hollow anode vs. discharge current. As the discharge current increases, the ionic current density linearly increases and at the 20 A discharge current it reaches 6 mA/cm², which is about 2 times higher than the density of the ionic saturation current obtained in the flat anode mode. The results of calculation of the ionic current density carried out using the Langmuir equation [16]: \( j/j_e \approx (m_e/M)^{1/2} \) (where \( j \) and \( j_e \) are the densities of ion current and electron current through the double layer, \( m_e \) and \( M \) are mass of electron and ion correspondingly) correspond to the experimental data.
Figure 5 demonstrates the results of probe measurements of a double layer voltage. The measurements were carried out using the constant discharge current of 10 A and Ar pressure, controlled by the value of the gas flow through the hollow anode in the range of 0.25 to 0.5 Pa. As the gas pressure increases, the layer voltage monotonously decreases from 68 to 35 V.

The compliance with the Langmuir condition at the preset electron current density over the hollow anode aperture is provided by the achievement of the required conditions for gas ionization frequency \( n_0 \sigma_i(E) V_e(E) \) (where \( n_0 \) is gas concentration, \( \sigma_i(E) \) – cross-section of the electron impact ionization in the electron energy function \( E \), \( V_e(E) \) is velocity of electrons). As \( n_0 \) increases in the anode cavity, such values of \( \nu_i \) would be achievable at lower values of \( \sigma_i(E) \) and \( V_e(E) \), as a result of which the voltage on the double layer and, correspondingly, the energy of electrons supplied in the anode cavity decrease. Figure 5 demonstrates a calculated plot of the \( \nu_i \) in the gas flow rate function obtained under condition that the energy of electrons corresponds to the experimentally measured voltage on the double layer. The values of the ionization cross-section were taken from [17]. It is seen that the alteration of voltage on the double layer correlates with the dependence of \( \nu_i \) on gas pressure.

Therefore, in the hollow anode mode, a stream of accelerated ions is formed, the density of which is proportional to the discharge current, and its energy is determined by voltage on the double layer and is mainly controlled by the value of gas flow rate through the anode cavity.

Studies have been carried out of the content of Ar-O\(_2\) plasma, generated under the conditions of feeding O\(_2\) to the anode discharge region. Figure 6 demonstrates a typical optical emission spectrum of the plasma in the wavelength range of 300-900 nm. The obtained spectra, apart from intensive argon lines (Ar I and Ar II), also contain atomic oxygen lines (O I). The most intensive lines are 777.4 (3p\(^3\)P\(\rightarrow\)3s\(^5\)S) and 844.6 nm (3p\(^3\)P\(\rightarrow\)3s\(^3\)S) of the atomic oxygen O\(^+\) emission, and the most probable process of its formation is dissociation with direct electron impact \( e+O_2\rightarrow e+O^++O \) [18]. The relative intensities of the lines of atomic ions O II (374.5 nm)/O I (844.6 nm) are \( \sim 10^{-2} \) and they monotonously decrease as the discharge current grows. The emission bands (525.9, 559.8, 597.4 and 635.1 nm) of the first negative system of O\(_2^+\) \( b^4\Sigma^+\rightarrow a^4\Pi_u \) are observed on the spectra taken with increased exposure (figure 6). The intensity of these lines varies with O\(_2\) flow rate and discharge current proportionally.

The obtained results correspond with the results of the paper [19], which has shown that the dissociation of O\(_2\) by direct electron impact is the main mechanism of formation of O I both in pure O\(_2\) and in the Ar-O\(_2\) plasma. The dissociation rate constant is \( \sim 10^{-9} \) cm\(^3\)/s, which is by two orders of magnitude higher than the constant of dissociation for the molecules O\(_2^+\) \( +e\rightarrow O^++e \) and it is by several orders of magnitude higher than the constant of the reaction O \( +e\rightarrow O^+ + e \) [20]. The absence of lines corresponding to molecular oxygen in the spectra is determined by the fact that the molecule
dissociation time is significantly lower (~0.05 ns) than the transition time from the excitation state (~500 ns) [17].

The relative content of atomic oxygen in the discharge plasma was assessed according to the alteration of the ratio of intensity of the O I line (844.6 nm) and Ar I line (750.4 nm), emerging as a result of the excitation of Ar with electron impact from the main state [21]. At constant Ar pressure, the concentration of O I monotonously increases, as the discharge current and O$_2$ flow increase (Figure 7). In the plasma of the discharge with a hollow anode the concentration of O I is 1.3–1.7 times higher than in the discharge with a flat anode, the most significant difference in concentrations being observed at elevated gas flows. Such dependence behavior nature is determined by a decrease in voltage on the double layer in the hollow anode aperture at an increase in the O$_2$ pressure (figure 4), accompanied by a decrease in the energy of electrons and the cross-section of the O$_2$ dissociation with electron impact. According to [17], the energy of electrons corresponding to the dissociation cross-section maximum is ~20 eV.

Figure 7. Dependencies of the ratios of the intensities of the O I line (844.6 nm) and Ar I line (750.4 nm) vs. discharge current (a) and the flow of O$_2$ (b) in the discharge burning mode with a flat (I) and hollow (2) anode.

Therefore, in the discharge with a hollow anode together with the formation of an ion flow with energy of 20-70 eV, an increase in the concentration of oxygen atomic particles occurs in the discharge gap.

Al$_2$O$_3$ coatings were obtained at changing the discharge current (2-28 A) and the sample bias voltage (25–250 V). The X-ray diffraction patterns for coatings obtained in the discharge with a hollow anode are depicted in figure 8. In all samples, the $\alpha$-Al$_2$O$_3$ phase has formed. The $\gamma$-Al$_2$O$_3$ crystalline phase is found in coatings formed at discharge currents of up to 4 A.
Figure 8. X-ray diffraction patterns of the Al₂O₃ coatings, obtained at various discharge currents (a) and bias voltages (b).

The intensity of γ-Al₂O₃ reflexes (2θ~37.5°; 45.5° and 66°) decreases as the discharge current increases, which indicates the suppression of phase formation. The formation of α-Al₂O₃ occurs at relatively low bias voltages of -25 V already. The α-Al₂O₃ crystallites have the average CSR size of 60 nm, which decreases to 12 nm at an increase in the bias voltage to 200 V. A further growth in the bias voltage is accompanied by an increase in the γ-Al₂O₃ percentage and full suppression of the α-Al₂O₃ phase formation. Transition from the dominant α-Al₂O₃ phase in the coatings to γ-Al₂O₃ with an increase in the bias voltage is determined by a decrease in the crystallite size to critical sizes, not providing for stabilization of the α-Al₂O₃ phase. It was shown in the paper [22] that the formation of α-Al₂O₃, having a higher surface energy than γ-Al₂O₃, becomes energetically unfavorable at a decrease in the crystallite size to the values of ~12 nm.

4. Conclusion
The use of the hollow anode in a high-current discharge provides for an increase in the ion current density on a remote collector and the degree of O₂ dissociation 2-fold compared to the values achievable in the discharge with a flat anode.

Using the Al reactive anode evaporation method in the discharge with a self-heating hollow cathode and a hollow anode, Al₂O₃ coatings were obtained on metallic substrates with nanostructural Cr₂O₃ sublayer at the temperature of 600°C at a rate of 4 μm/h. It was shown that conditions for the formation of single-phase α-Al₂O₃ coatings are provided in the discharge current alteration range of 4-28 A and negative bias voltage of 25-200 V.

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References
[1] Kumar R, Prabhakar V and Saini J 2013 Inter. J. Current Engin. Technol. 3 1679
[2] Eklund P, Sridharan M, Singh G and Bottiger J 2009 Plasma Process. Polym. 6 S907
[3] Lux B, Columbier C, Altenna H and Stjernberg K G 1986 Thin Solid Films 138 49
[4] Jiang K, Sarakinos K, Konstantinidis S and Schneider J M 2010 J. Phys. D: Appl. Phys. 43 325202
[5] Zywitzki O, Goedicke K and Morgner H 2002 Surf. Coat. Technol. 151-152 14
[6] Yamada-Takamura Y, Koch F, Maier H and Bolt H 2001 Surf. Coat. Technol. 142-144 260
[7] Lin Y, Wang C and Tao J 2013 Surf. Coat. Technol. 235 544
[8] Andersson J M, Wallin E, Helmersson U, Kreissig U and Munger E P 2006 Thin Solid Films \textbf{513} 57
[9] Prenzel M, Kortmann A, Stein A, Keudell A, Nahif F and Schneider J M 2013 \textit{J. Appl. Phys.} \textbf{114} 113301
[10] Rosen J, Mraz S, Kreissig U, Music D and Schneider J M 2005 \textit{Plasma Chem. Plasma Proces.} \textbf{25} 303
[11] Sarakinos K, Music D, Nahif F, Jiang K, Braun A, Zilkenes C and Schneider J M 2010 \textit{Phys. Status Solidi RRL} \textbf{4} 154
[12] Gavrilov N V, Kamenetskikh A S, Paranin S N, Spirin A V and Chukin A V 2017 \textit{Instrum. Exper. Tech.} \textbf{60(5)} 742
[13] Gavrilov N V, Kamenetskikh A S, Tretnikov P V and Chukin A V 2018 \textit{Surf. Coat. Technol.} \textbf{337} 453
[14] Klyarfeld B N and Neretina N A 1958 \textit{JTF} \textbf{18} 297
[15] Block L P 1978 \textit{Astrophysics and space science} \textbf{55} 59
[16] Langmuir I \textit{Physical review} 1929 \textbf{33} 954
[17] Lock E H and Fernsler R F and Walton S G 2011 Memorandum Report \texttt{NRL/MR/6750-11-9333}
[18] Hrachova V and Kanka A 1997 \textit{Vacuum} \textbf{48} 689
[19] Smirnov S A, Rybkin V V, Ivanov A N and Titov V A 2007 \textit{High Temperature} \textbf{45} 291
[20] Vlasov V I, Zalogin G N and Prut'ko K A 2014 \textit{Physicochemical kinetics in gas dynamics} \textbf{15} 1
[21] Pavlik J and Hrach R 1999 \textit{Superficies y Vacio} \textbf{9} 131
[22] McHale J M, Auroux A, Perrotta A J and Navrotsky A 1997 \textit{Science} \textbf{277} 788