Effect of oxygen flow rate on the deposition rate of $\alpha$-Al$_2$O$_3$ coatings by anodic evaporation of Al in an arc discharge

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Abstract. Effect of O$_2$ flow rate on the kinetics of growth and properties of $\alpha$-Al$_2$O$_3$ coatings deposited by reactive anodic Al evaporation at 640 °C has been studied. It has been shown that the growth rate of coatings changes non-monotonously with O$_2$ flow, rise of the growth rate is due to the increase in the concentration of atomic oxygen in plasma, and the decrease at large O$_2$ flows is associated with transition from the mode of free transit of Al atoms to the diffusion mode.

1. Introduction
The low-temperature crystallization of Al$_2$O$_3$ coatings and the formation of the high-temperature $\alpha$-phase is accomplished using intense ion assistance [1]. The growth rate of the coating is limited by the low rate of surface diffusion of the adsorbed atoms. The deposition of the oxide coating through reactive evaporation [2] allows regulating the O$_2$ flow and the Al evaporation rate independently, unlike magnetron sputtering; therefore, it is very interesting to study the influence of the ratio of flows of gas and metal particles on the coating surface on the growth rate and characteristics of coatings.

In case of magnetron reactive deposition of oxide coatings, the growing O$_2$ flow increases the oxidation degree of the sputtered target, which reduces its sputtering rate and the growth rate of the coating, and also affects the phase composition of coatings, their degree of crystallinity, texture and mechanical properties. In addition to O$_2$ pressure, the degree of O$_2$ dissociation near the surface plays an important role in magnetron sputtering; its increase helps to reduce oxygen pressure near the target, to stabilize discharge, and to improve the properties of coatings [3].

In the cathodic arc discharge with filtered plasma, an increase in O$_2$ pressure up to 0.01 Pa was used for the energy relaxation of Al$^+$ ions and the reduction of their energy in plasma down to $\sim$ 1.4 eV. This allowed performing the deposition of coatings with the energy of ions (40–200 eV) controlled by the bias voltage change and obtaining single-phase $\alpha$-Al$_2$O$_3$ coatings at 700 °C [4]. However, the influence of O$_2$ pressure on the properties of $\alpha$-Al$_2$O$_3$ coatings obtained through PVD methods at low temperatures is scarcely investigated, since these works emphasized such key factor as ion energy.

The synthesis of $\alpha$-Al$_2$O$_3$ coatings by reactive anode evaporation includes an adjustable discharge with a regulated distribution of current between the anode-crucible and the additional cooled anode [2] that provides both metal evaporation at a given rate and maintaining of the plasma parameters at the required level, in particular, the ion current density. In addition, the use of a hollow electrode with a
small aperture, through which the O₂ is supplied, as a secondary anode, ensures a higher degree of dissociation of O₂ in the discharge. The resulting positive anode potential drop forms a dense flow of electrons with an energy of few tens of eV near the anode, which interacts with the O₂ counter flow. Since the formation of the crystal lattice involves atomic particles, a change in O₂ dissociation can affect the deposition kinetics, phase composition, and microstructure of coatings.

The present work is dedicated to studying the effect of the O₂ flow rate on the deposition rate of α-Al₂O₃ coatings by the reactive anode evaporation of Al in an arc with a self-heating hollow cathode under conditions of intensive ion assistance. The work presents the measurement results for the optical spectrum of plasma emission, volt-ampere discharge characteristics, the deposition rate and parameters of α-Al₂O₃ coatings, as well as the results of probe discharge plasma diagnostics.

2. Experimental technique

The electrode evaporator system is similar to that described in [2]. The discharge burns between the self-heating cathode from TiN, the thermally isolated anode-crucible and the water-cooled hollow anode. The external surface of the latter was either shielded by ceramics (variant A) ensuring burning of the discharge through an aperture with an area of 1 cm² or remained open, with the discharge burning on the external surface with an area of 70 cm² (variant B). O₂ was supplied through the anode cavity (30-200 sccm). The cathode was placed in a magnetic field created by a short coil. A sample holder with forced heating was installed at a distance of 100 mm from the crucible. A bias voltage (50 V, 50 kHz, 10 μs) was supplied to the sample holder. The Ar flow (30 sccm) supplied through the cathodic cavity ensured stable burning of the discharge with the currents up to 40 A. The discharge current was distributed among the anode-crucible (3.5 A) and the hollow anode (8–36 A). Vacuum pumping was done by a turbomolecular pump, the residual pressure was 10⁻³ Pa, the operating pressure of the gas mixture Ar+O₂ was 0.1-0.6 Pa. The coating with a thickness of 1.5–4.5 μm was deposited at 640 °C on the stainless steel substrate with a Cr₂O₃ sublayer used as a crystallographic template for α-Al₂O₃ [5].

The plasma emission spectrum in the wavelength range 190–1100 nm was registered using a fiber-optic spectrometer HR2000 (Ocean Optics). Spectra were registered in a direction perpendicular to the discharge axis at an altitude of ~30 mm from the crucible, as well as in the area nearby the sample holder. The microhardness of the coatings was determined using an ultramicrohardness tester DUH-211/211S (Shimadzu); the thickness of the coatings was measured using a Calotest (CSM Instruments), X-ray analysis was done by diffractometer XRD-7000 (Shimadzu).

3. Results

The deposition rate of Al₂O₃ coatings changes non-monotonously as the O₂ flow function (figure 1). The maximum growth rate (4.5 μm/h) was achieved with smaller O₂ flows in the discharge contracted by the anode aperture (A) than in the discharge with a large anode area (B). The amplitude value of the growth rate is lower in the variant B (3.4 μm/h) and was achieved with large O₂ flows. The dependence of the discharge voltage on the O₂ flow for the discharge with the anode (A) is monotonically decreasing (figure 2). This is due to a change in the positive near-anode voltage drop, while the voltage of the discharge in the system B slightly changes within 64 ± 2 V. The dependencies of ion current density on the sample holder on the O₂ flow shown in figure 2 also have a maximum. The maximum density of ion current in the system A is higher and was achieved with a smaller O₂ flow.

The characteristic spectrum of discharge plasma emission with the anode current 20 A and the ratio of flows Ar/O₂ = 30/60 (sccm) is shown in figure 3. The spectrum is characterized by very intensive lines of atomic oxygen O* (777.4 and 844 nm) and the presence of lines corresponding to the cluster AlO. The dependencies of line intensity for Al* (396.2 nm), Al⁺ (390.1 nm), O* (777.4 nm), O⁺ (656.5 nm), Ar* (811.5 nm), Ar⁺ (487.9 nm) and AlO lines on the O₂ flow are shown in figures 4, 5. The characteristic feature is a monotonous increase in the intensity of O* line throughout the whole range
of O₂ flow changes, with the concentration of O⁺ in the system A being significantly higher than in the system B (figure 4). A decline of the intensity of all remaining lines was also observed at large O₂ flows and the presence of maxima of Ar⁺, Ar*, AlO, O⁺ lines in the area of small O₂ flows (figure 5). Intensity of lines of excited aluminum on discharge axis is similar in both systems. The concentration of Ar⁺ on the axis of the system A at low O₂ flows is four times higher than in the system B and dramatically drops with increasing O₂ flow. This is due to the presence of a dense plasmoid with a high ionizing ability of electrons in the system A near the anode aperture. A higher density of atomic oxygen in the system A leads to higher concentrations of AlO complexes, especially at small O₂ flows.

XRD analysis has shown that the main phase in the coatings throughout the whole range of O₂ flow changes is α-Al₂O₃ (figure 6) with the predominant orientation of the crystal lattice (300). Coatings obtained at low-energy ion assistance (50 eV) are characterized by a low level of micro-strains (0.045–0.2%) and increased average size of CSR (80-115 nm). The hardness of coatings weakly changed with the O₂ flow within 20–24 GPa. Young's modulus amounted to 300–350 GPa, and the elastic recovery of the coating was 60–68%.
Discussion

The main discharge parameters, which define the metal evaporation rate: discharge current, the temperature of plasma electrons and drop of potential near the crucible have changed slightly during the experiment. However, the comparative assessments of the mass of Al evaporated from the crucible and the total mass of Al in the coating obtained by measurement of the specific coating weight and angular integration for the rate of evaporation from the condensed source \( \text{cos} \phi/(R^2) \) [6], where \( \phi \) is the angle between the direction of particle motion and the substrate surface normal, \( R \) is the distance between the evaporator and the substrate, have shown that these values vary by \( \sim 5 \) times. It may be caused by desorption of Al atoms from the coating surface, ion sputtering, a decrease in the density of the flow of evaporated Al atoms due to interactions with plasma particles, etc. The calculation of the Al and O\(_2\) flows has revealed that O\(_2\) flow is \( 2-3 \) order of magnitude larger than the flow of evaporated Al. Obviously, since the formation of the crystal lattice involves only atomic particles, the critical parameter is not the total O\(_2\) flow in volume, but the degree of O\(_2\) dissociation in the plasma, which, depending on the type and parameters of discharge, can be from several units to several tens of percentage points [7].

It is known that the dissociation of O\(_2\) in the Ar-O\(_2\) discharge may be caused by the collision of O\(_2\) with an electron with energy over 4.5 eV [8], or interaction with a metastable Ar atom [9]. Since the intensity of O* lines in the experiments increased slower than the O\(_2\) flow, the degree of O\(_2\) dissociation decreased with increasing O\(_2\) flow; however, the concentration of atomic oxygen in plasma increased. Large values of amplitude of O* lines in the A-discharge caused by the intensive dissociation of O\(_2\) in the anode aperture indicate determining the influence of collision of O\(_2\) with fast electrons on the O\(_2\) dissociation process.

Since mainly Al and O atoms participate in the formation of coating and the Al* line decreases monotonically with increasing O\(_2\) flow, one can conclude that an increase in the concentration of atomic oxygen is the most likely cause of the observed increase in the growth rate of Al\(_2\)O\(_3\) coatings. The ion component of discharge plasma cannot significantly affect the growth rate of the coating, since the ionization degree of aluminum and oxygen in the discharge plasma with a thermally isolated crucible is small [10].

Plasma emission spectra contain lines corresponding to the complex AlO (484.2 and 486.6 nm). Such particles had been previously found in the plasma of magnetron discharge due to sputtering of the oxidized surface of the Al target [11]. However, relatively low concentrations of reactive particles

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in plasma did not provide high-speed generation of AlO through the formation of long-lived intermediate complexes AlO$_3$ [12].

The slowdown in the coating deposition rate at large O$_2$ flows is explained by the fact that with an increasing number of collisions, a transition from the free transit of atoms to the diffusion mode occurs in plasma, which leads to a decrease in the flow of Al atoms on the surface of the growing coating. Since the pressure of saturated Al vapor near the crucible remains constant, and the average mean free path of Al atoms and diffusion coefficient are reduced with increasing pressure, the resulting diffusion of Al atoms in substrate direction and the coating growth rate decrease.

5. Conclusion
Synthesis of coatings by anodic evaporation of Al in an arc discharge in the Ar-O$_2$ medium deposited on the crystallographic template under conditions of a dense ion flow with low (50 eV) energy of ions is characterized by the existence of the maximum of the dependency of the α-Al$_2$O$_3$ deposition rate on the O$_2$ flow rate. Measurements of optical plasma emission spectra show the increase of concentration of atomic oxygen in plasma with increasing O$_2$ flow. A drop in the growth rate of coatings at large O$_2$ flows is caused by a change in motion of Al atoms – a transition from the free transit of atoms to the diffusion mode. The maximum coatings deposition rate can be achieved at the optimal ratio of densities of increasing atomic oxygen flow and decreasing flow of Al atoms on the surface of the α-Al$_2$O$_3$ coating. It has been shown that deposition of Al$_2$O$_3$ coatings under the conditions of a dense ion flow with low (50 eV) energy of ions and low content of aluminum ions in the ion flow ensures the formation of the α-Al$_2$O$_3$ phase with a low level of micro-distortions, an increased nanocrystallite size and low internal stress (up to 2 GPa). α-Al$_2$O$_3$ coatings with thickness up to 9 µm with a rate of 4.5 µm/h have been obtained in this mode at 640 °C. At high-rate deposition of coatings, the growth of density of ion assistance current reduces the content of finely crystalline γ-Al$_2$O$_3$ and ensures the formation of single-phase α-Al$_2$O$_3$ coating.

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