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To cite this article: N V Gavrilov *et al* 2019 *J. Phys.: Conf. Ser.* **1281** 012019

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Effect of oxygen flow rate on the deposition rate of α -Al₂O₃ coatings by anodic evaporation of Al in an arc discharge

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Abstract. Effect of O₂ flow rate on the kinetics of growth and properties of α -Al₂O₃ 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 O₂ flow, rise of the growth rate is due to the increase in the concentration of atomic oxygen in plasma, and the decrease at large O₂ 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 Al₂O₃ coatings and the formation of the high-temperature α -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 O₂ 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 O₂ 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 O₂ pressure, the degree of O₂ 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 O₂ 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 ~ 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 α -Al₂O₃ coatings at 700 °C [4]. However, the influence of O₂ pressure on the properties of α -Al₂O₃ coatings obtained through PVD methods at low temperatures is scarcely investigated, since these works emphasized such key factor as ion energy.

The synthesis of α -Al₂O₃ 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 O_2 is supplied, as a secondary anode, ensures a higher degree of dissociation of O_2 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 O_2 counter flow. Since the formation of the crystal lattice involves atomic particles, a change in O_2 dissociation can affect the deposition kinetics, phase composition, and microstructure of coatings.

The present work is dedicated to studying the effect of the O_2 flow rate on the deposition rate of $\alpha\text{-Al}_2\text{O}_3$ 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 $\alpha\text{-Al}_2\text{O}_3$ 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 cm^2 or remained open, with the discharge burning on the external surface with an area of 70 cm^2 (variant B). O_2 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+ O_2 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 Cr_2O_3 sublayer used as a crystallographic template for $\alpha\text{-Al}_2\text{O}_3$ [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 Al_2O_3 coatings changes non-monotonously as the O_2 flow function (figure 1). The maximum growth rate (4.5 $\mu\text{m}/\text{h}$) was achieved with smaller O_2 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 $\mu\text{m}/\text{h}$) and was achieved with large O_2 flows. The dependence of the discharge voltage on the O_2 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 O_2 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 O_2 flow.

The characteristic spectrum of discharge plasma emission with the anode current 20 A and the ratio of flows Ar/ O_2 = 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 O_2 flow are shown in figures 4, 5. The characteristic feature is a monotonous increase in the intensity of O^* line throughout the whole range

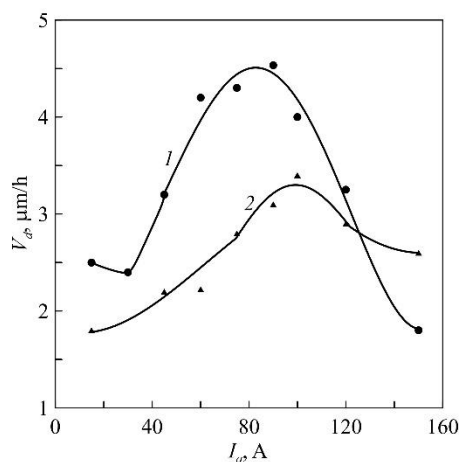


Figure 1. Deposition rate of coatings in the O_2 flow function in the systems A (1) and B (2).

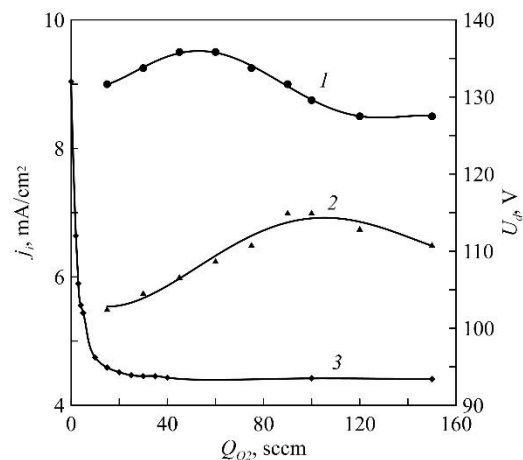


Figure 2. Dependencies of ion current density and discharge burning voltage on the O_2 flow in the systems A (1, 3) and B (2).

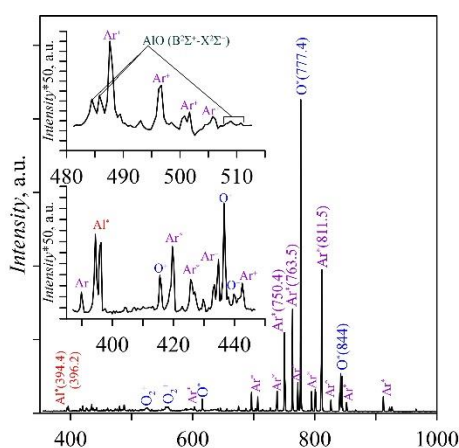


Figure 3. Optical emission spectra of the plasma.

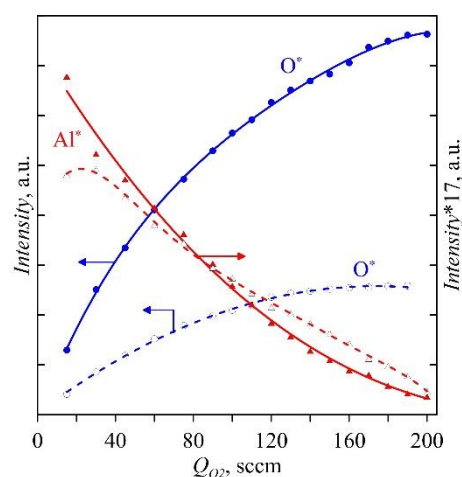


Figure 4. Dependencies of the intensity of the lines of plasma emission on the O_2 flow. Solid lines – system A, dashed lines – B.

of O_2 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 O_2 flows and the presence of maxima of Ar^+ , Ar^* , AlO , O^+ lines in the area of small O_2 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 O_2 flows is four times higher than in the system B and dramatically drops with increasing O_2 flow. This is due to the presence of a dense plasmod 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 O_2 flows.

XRD analysis has shown that the main phase in the coatings throughout the whole range of O_2 flow changes is $\alpha-Al_2O_3$ (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 O_2 flow within 20–24 GPa. Young's modulus amounted to 300–350 GPa, and the elastic recovery of the coating was 60–68%.

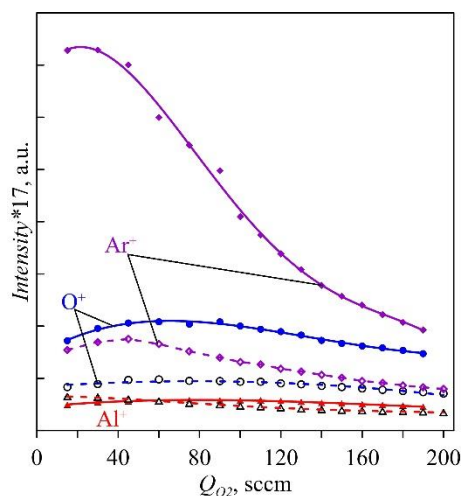


Figure 5. Dependencies of the intensity of the lines of plasma emission on the O_2 flow. Solid lines – system A, dashed lines – B.

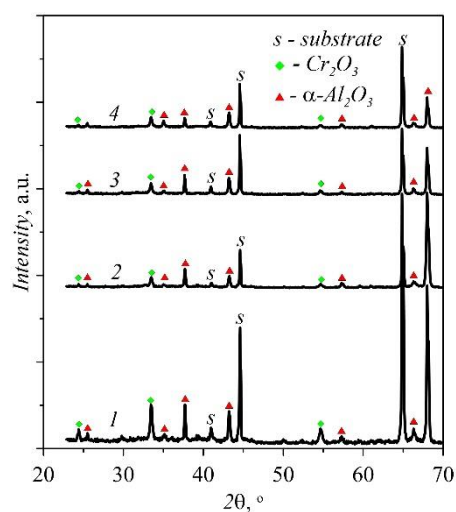


Figure 6. XRD spectra of coatings. Hollow anode current: 1 – 4; 2 – 12; 3 – 20; 4 – 28 A.

4. 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 $\sim \cos\varphi/(R^2)$ [6], where φ 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 ~ 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_2O_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 AIO (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

in plasma did not provide high-speed generation of AlO through the formation of long-lived intermediate complexes AlO₃ [12].

The slowdown in the coating deposition rate at large O₂ 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-O₂ 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 -Al₂O₃ deposition rate on the O₂ flow rate. Measurements of optical plasma emission spectra shown the increase of concentration of atomic oxygen in plasma with increasing O₂ flow. A drop in the growth rate of coatings at large O₂ 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 -Al₂O₃ coating. It has been shown that deposition of Al₂O₃ 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 -Al₂O₃ phase with a low level of micro-distortions, an increased nanocrystallite size and low internal stress (up to 2 GPa). α -Al₂O₃ coatings with thickness up to 9 μ m with a rate of 4.5 μ m/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 -Al₂O₃ and ensures the formation of single-phase α -Al₂O₃ coating.

Acknowledgment

This work was supported by the Russian Science Foundation under grant No. 18-19-00567.

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