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Effect of the O\textsubscript{2} dissociation degree on the rate of anodic evaporation of Al in a low-pressure arc

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Abstract. The results of probe diagnostics and optical emission spectroscopy of Ar-O\textsubscript{2} plasma of a low-pressure arc generated under anodic evaporation of Al and an increased (0.32 – 0.48) degree of O\textsubscript{2} dissociation are presented. It is shown that an increase in the degree of O\textsubscript{2} dissociation at a constant gas flow into the discharge gap leads to a significant (more than 1.5 times) decrease in the density of the evaporated atoms flux and a corresponding decrease in the coating deposition rate. The observed effect is due to the accelerated growth of the oxide film on the melt surface, which leads to the limitation of the flow of evaporated Al atoms by the rate of diffusion through the alumina.

1. Introduction

One of the main problems of reactive coating deposition by PVD methods is the formation of chemical compounds not only on the surface of the substrates but also on the source surface of deposited particles [1]. The growth rate of such layers and the composition of the particle flow from their surface depend on the partial pressure of the reactive gas. These parameters are determined by the balance of the rates of chemical reactions in the near-surface layers and the rates of processes that inhibit the growth of the layer, for example, the ion bombardment [2]. The influence of reactive processes comes in full force in magnetron sputtering systems due to the relatively low rate of ion sputtering. Numerous studies are focused on it (see, for example, [3]).

An increase in the partial pressure of O\textsubscript{2} when the Al target is sputtered leads to a sharp decrease in the coatings deposition rate and the predominance of AlO complexes in the flow of sputtered particles [4]. The main component of the vaporized particle flow is Al atoms because the rate of thermal evaporation of Al in the O\textsubscript{2} medium is usually much higher than the magnetron sputtering rate in a wide range of changes in the pressure of O\textsubscript{2} (10\textsuperscript{-5} – 10\textsuperscript{-7} Pa) and in the temperature (1200 – 3280\textdegree C), while the proportion of molecules (AlO, Al\textsubscript{2}O, etc.) is several orders of magnitude less [5]. Nevertheless, despite the fundamental differences in the methods, an increase in the partial pressure of the reactive gas leads to a decrease in the deposition rate of coatings, both in the case of magnetron sputtering [4] and thermal evaporation. However, in the latter case, the effect of oxidation of the surface of melt is developed only at a relatively low power density on the target, since the temperature in the melt spot when heated by an electron beam (power density > 10\textsuperscript{6} W/cm\textsuperscript{2}), as a rule, exceeds the melting temperature of the oxide [6].
The surface condition of the evaporated or sputtered target affects the rate and stability of the process of delivering particles of the deposited substance to the volume. The present study is devoted to the investigation of the conditions of Al evaporation in the Ar-O2 plasma of a low-pressure arc. The method of reactive anode evaporation in the arc allows obtaining Al2O3 coatings with a corundum structure at a low temperature (up to 500°C) and a high deposition rate (5 μm/h or more) [7]. The compression of the electron flow in the anode part of the discharge and the use of a pulsed combustion mode make it possible to increase the degree of O2 dissociation and regulate its value [8]. In this paper, the influence of the O2 dissociation degree on the rate of Al evaporation is investigated, the results of studies of the composition of the arc plasma are presented.

2. Experimental methods

Thermal evaporation of Al was carried out in a low-pressure arc maintained in a gas-discharge system with a self-heating hollow cathode and a thermally insulated anode-crucible. A detailed description of the device is given in [8]. An additional anode with a diameter of 45 mm placed inside a cylindrical screen with an internal diameter of 50 mm and a length of 70 mm was used to adjust the concentration and composition of the discharge plasma. The anode and screen were water cooled. Ar was fed through the hollow cathode at a rate of 90 sccm. O2 entered the discharge gap through a cavity in the anode screen at a rate of 150 sccm. The gas flows were set by regulators 4F-201CV (Bronkhorst High-tech) with a deviation from the set values ≤ 0.8%. The chamber was pumped out by a turbomolecular pump with a rate of 500 l/s. The total pressure of the gas mixture was 0.7 Pa. The Al2O3 layer was formed on the chamber walls, which reduced the rate of atomic oxygen recombination and maintained a high concentration of particles in the volume [9].

An increase in the O2 dissociation frequency in the gas-discharge system was achieved by compressing the electron flux in the anode part of the discharge, which resulted in the appearance of potential differences [8], accelerating electrons to energies close to the maximum of cross section of O2 dissociation by an electron impact [10]. The effect was enhanced by imposition of electron and O2 fluxes, which was injected into the anode region. A combined discharge combustion mode was used, in which pulses (1 kHz, 100 μs) with an adjustable current amplitude (0 – 170 A) were superimposed on DC discharge to adjust the degree of O2 dissociation. The average discharge current in all experiments was 100 A. The direct current in the crucible circuit was set by an independent power supply unit.

The plasma composition was determined from optical emission spectra in the wavelength range of 200 – 1100 nm using an HR2000 spectrometer (Ocean Optics). The concentration of atomic oxygen was measured directly in the plasma by a catalytic probe [11] using a technique of evaluating the contribution of the heterogeneous oxygen recombination process at high total heating power by particle fluxes and radiation from the plasma [9]. The degree of O2 dissociation was calculated from the ratio of the concentrations of oxygen molecules and atoms $n_0/(2n_{O2})$.

The plasma probe diagnostics was performed by a Langmuir probe made of tungsten with a length of 5 mm and a diameter of 0.6 mm. The probe potential was set in a pulse-periodic mode; the probe characteristics were recorded by an electronic recorder Hioki 8835. The plasma potential was determined at the maximum point of the first derivative of the probe characteristic averaged by the results of 20 measurements; the electron temperature was determined by the angle of inclination of the semi-logarithmic characteristics of the probe in the linear region of the first derivative.

Al2O3 coatings were obtained under the conditions of reactional evaporation of Al in the discharge plasma. The temperature of the flat substrates made of steel, type AISI430, during the coating process was 600°C. The samples were located at a distance of 10 cm from the surface of the crucible. The average density of the ion current in the experiments was ∼ 8 mA/cm². The amplitude of the bias voltage (50 kHz, 10 ms) was 200 V. The deposition rate of the coatings deposited during 0.5 h was estimated by the thickness of the coatings (1.5 – 2 μm), measured by the method of ball abrasion on Calotest (CSM Instrument). The measurement error did not exceed 5%.
The state of the evaporated material after coating deposition was studied by X-ray diffraction analysis. The studies were carried out on an XPert PRO MPD (Panalytical) diffractometer in CuKa radiation with a high-speed PIXcel solid-state detector. The survey was carried out in the range of diffraction angles 15° – 85° by 2θ, with a scanning step of 0.05° and a time for one step of 150 s. The decoding of diffractograms was performed using the diffractometer software and PDF-2 databases.

3. Results and discussion

The results of measuring the O₂ dissociation degree in a low-pressure arc are shown in figure 1. An increase in the current amplitude to 170 A in the combined mode of discharge combustion increases the degree of O₂ dissociation from ~ 0.32 to 0.48. The typical spectrum of plasma optical emission is shown in figure 2. The most intense OI lines (777.2 and 844.7 nm) correspond to the transitions 3p^3P - 3s^3S^0 and 3p^3P - 3s^3S^0 with upper-level energies of 10.74 and 10.99 eV [12]. The intensity of the lines of molecular and atomic oxygen ions is several orders of magnitude less.

![Figure 1](image1.png)

**Figure 1.** The O₂ dissociation degree as function of discharge current amplitude.

![Figure 2](image2.png)

**Figure 2.** The optical emission spectrum of Ar-O₂ plasma generated under anodic evaporation of Al.

The intensities of OI lines monotonically increase with the growth of amplitude of the discharge current (figure 3). There is an increase in the intensities of lines of transition in the 3S states (777.2 and 844.7 nm), as well as lines with a wavelength of 615.7 nm corresponding to the transition (5p^3S^0-3p^3P) from the high-energy (12.75 eV) upper level [12]. If for the first type of transitions, the intensity of the lines increased by 1.3 times with an increase in the amplitude of the pulse current of the discharge from 0 to 170 A, then for the transition from the high-energy state, an increase in intensity was observed by 1.8 times.

It is known that the main process of formation of atomic oxygen in the plasma of low-pressure discharge is the dissociation of O₂ by an electron impact [13]. The difference in the relative change in the intensities of OI transition lines, which differ in the energy of the upper level, indicates an increase in the proportion of high-energy electrons in the plasma with an increase in the amplitude of the discharge current. Based on the results of probe diagnostics of plasma parameters generated in the combined mode, it was determined that an increase in the current amplitude from 0 to 170 A at a constant average discharge current of 100 A led to an increase in the electron temperature of the plasma in the range of 2.4 – 2.6 eV and an increase in the value of the positive potential drop in the space charge layer at the crucible from ~ 18 to 24 V (figure 4).
The heating of the crucible by electrons with a constant current of 4.5 A was accompanied by the evaporation of Al. In the optical emission spectra of the plasma (figure 2), Al lines (394.4 and 396.1 nm) appeared with an intensity an order of magnitude lower than that of the gas components (argon and oxygen). In contrast to OI lines, the intensity of AlI lines monotonically decreases by 1.5 – 1.7 times when the amplitude of the pulse discharge current increases to 170 A (figure 3).

Al$_2$O$_3$ coatings were obtained by reactional evaporation of Al in Ar-O$_2$ plasma of a combined discharge. The current in the experiment in the crucible circuit was kept constant at 4.5 A, the average discharge current was 100 A. With an increase in the amplitude of the pulse discharge current from 0 to 170 A, the deposition rate of coatings decreased from 3 to 1.9 μm/h (figure 5).

We can conclude that an increase in the amplitude of the pulse discharge current accompanied by an increase in the O$_2$ dissociation degree (figure 1) and leads to a decrease in the flow of Al particles, as indicated by a decrease in the intensity of the optical emission lines AlI (figure 2) and in the coatings deposition rate (figure 5). However, at the same time, the values of the positive anode potential drop and the electron temperature of the plasma increase (figure 4), which at a constant current of the crucible leads to an increase in the power supplied to the crucible.

The observed effect is due to an increase in the intensity of the oxide film growth on the surface of Al melt. The X-ray analysis of the state of the evaporated material after the Al$_2$O$_3$ coating cycle (figure 6) indicate the presence of two crystalline phases: α-Al$_2$O$_3$ and metallic Al. It is known that in the temperature range (T) of 1000 – 1100°C, the α-Al$_2$O$_3$ oxide film on the Al surface grows at a rate of ~ 3.2·10^{-9} g²/cm³s [14]. The evaporation rate of α-Al$_2$O$_3$ is several orders of magnitude less than the evaporation rate of Al [15]. The flux of Al atoms from the film surface is provided by their diffusion from the melt volume, characterized by a coefficient determined by the ratio ~ 1.3·10^{-3}exp(-31,000/RT) [16]. According to calculations, under the conditions of the experiment, the film thickness on the surface of the melt reaches several tens of μm and reduces the density of the Al atoms flux by ~ 20%, compared with the evaporation mode from the open surface of the metal.

It is obvious that the factor causing an increase in the oxide film growth rate on the surface of melt Al is an increase in the concentration of atomic oxygen that occurs in the discharge plasma and interacts with the surface of melt along with molecular particles. It was shown by the method of molecular dynamics that Al atoms and AlO complexes were characterized by a strong adsorption interaction with the α-Al$_2$O$_3$ surface [17], whereas there were fundamental differences in the
interaction of atomic and molecular oxygen particles with the Al$_2$O$_3$ surface. Based on theoretical calculations, it is concluded that the adsorption of O atoms is more stable compared to gas molecules.

![Figure 5](image5.png)  **Figure 5.** The Al$_2$O$_3$ coating deposition rate as function of discharge current amplitude.

![Figure 6](image6.png)  **Figure 6.** XRD pattern of Al piece after evaporation in Ar-$O_2$ plasma and Al$_2$O$_3$ coating deposition.

Under the conditions of the experiment, the resulting rate of reactive evaporation of Al is mainly influenced by two competing factors: 1) an increase in the difference between crucible and plasma column potential and an increase in the input power, which increases the vapor pressure of Al [18]; 2) an increase in the oxygen concentration, which leads to an increase in the thickness of the oxide film on the surface of melt and a decrease in the evaporation rate of Al. In the case of reactive anodic thermal evaporation of Al with an increased degree of $O_2$ dissociation (up to 0.48), the second factor is dominant in the discharge plasma.

Thus, it is experimentally shown that an increase in the degree of $O_2$ dissociation in the range of 0.3 – 0.5 at a pressure of ~ 0.7 Pa leads to a significant (more than 40%) decrease in the rate of reactive anode thermal evaporation of Al as a result of an increase in the growth rate of the oxide film on the surface of melt.

4. Conclusion
Under the conditions of reactive anodic thermal evaporation of Al using a combined low-pressure arc combustion mode, in which high-current pulses (up to 100 A) with a duration of 100 μs are superimposed on a constant discharge current (up to 100 A), the degree of $O_2$ dissociation was regulated in the range of 0.3 – 0.5. Evaporation of Al under such conditions occurs in the diffusion mode through the $\alpha$-Al$_2$O$_3$ film on the melt surface. It is shown that an increase in the degree of $O_2$ dissociation leads to an increase in the rate of Al evaporation and significantly (from 3 to 1.9 μm/h) decrease of Al$_2$O$_3$ coating deposition rate as a result. The effect is caused by an increase in the growth rate of the oxide film on the surface of the evaporated Al target with an increase in the concentration of atomic oxygen in the volume.

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**References**