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Diagnostics of a low-pressure arc plasma (N_2, 0.1–1 Pa) in the mode of aluminum anodic evaporation

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Abstract. The use of an arc with a thermionic cathode burning in vapors of the anode material for the coating deposition provides high deposition rates, a controlled level of ion assistance, and the absence of microdroplets characteristic of a cathode arc. The use for this purpose of a low-pressure arc with a self-heating hollow cathode makes it possible to use an active gaseous medium for the synthesis of binary coatings, for example, nitride or oxide coatings. The rate of deposition of such coatings, their structure, and properties depend on such parameters of the discharge plasma as the plasma density and its electron temperature, the anode potential drop, the mass composition of the plasma, the degree of vapor ionization, and the degree of reactive gas dissociation. In this work, to diagnose the discharge plasma, probe diagnostics and optical emission spectroscopy were used. The results of measurements obtained in wide ranges of discharge current (5–30 A), reactive gas pressure (N_2, 0.1–1 Pa), and evaporation rate of Al ($(1.4–18)\cdot 10^{-5}$ g/cm$^2\cdot$s) are presented.

Keywords: low-pressure arc, self-heated hollow cathode, anodic evaporation, vapor-gas plasma.

1. Introduction

The high rate of anodic evaporation of metals in a low-pressure arc and the absence of microdroplets in the vapor flow determine the interest in this deposition method. Thermionic cathodes are used in deposition devices of this type as an electron emitter, usually, which quickly degrade in chemically active gases; therefore, thermionic vacuum arc (TVA) method is mainly used for deposition of metal coatings [1]. To obtain binary coatings by reactive evaporation, arcs with a self-heating hollow cathode (SHC) are used, which are able to function stably for a long time under conditions of pumping an inert gas (or N_2) through the cathode cavity and supplying the reaction gas to the discharge gap [2], both in continuous and pulse-periodic (10–1000 Hz, 10–100 ms) modes [3]. Oxide [4], nitride [5], and composite [6] coatings are obtained by reaction anode evaporation in a discharge with SHC at a rate of more than 1 μm/h.

To solve the problems of high-rate deposition of coatings with the required structural-phase state and functional characteristics, it is necessary to provide independent control of the main operating parameters: the deposition rate, the current density and energy of ions on the coating surface, the pressure and composition of the gas, and the temperature of the substrates. For this purpose, additional means are used to control the current density of gas ions [4], as well as the degree of gas dissociation [7], increase the degree of vapor ionization [8] or, conversely, reduce the degree of their dissociation [5]. Data on the parameters and composition of the arc plasma in the anode vapor are important to determine the optimal conditions for the formation of coatings.

The first systematic studies of arc plasma with an evaporating anode were carried out in [9]. Spectroscopic measurements showed that the discharge burns stably in vapors of the anode material (Cr, Ti, Al), the degree of ionization of which reaches ~10%. The plasma concentration was ~10^{16} m^{-3} at discharge currents up to 40 A, and the electron temperature was ~1 eV. Under such conditions, the deposition rate of metal coatings reached 50 nm/s. The study of the characteristics of a discharge with a thermal cathode and a diffusely evaporating anode, the working medium of which is a vapor-gas mixture, or metal vapor (Ti) or gas (N_2) separately, is the subject of work [10]. Distinctive features of this type of discharge are a positive feedback between the discharge power and the pressure of the working medium (metal vapor), as well as a significant pressure gradient in the discharge gap. The results of studies [10] indicate that the gas can have a decisive effect on the combustion of a discharge in metal vapor at pressures that are several percent of the vapor pressure.

The present work is aimed on study of a low-pressure arc with an SHC maintained in an Al-N_2 vapor-gas mixture at comparable partial pressures (0.1–1 Pa). The main attention is paid to the determination of the parameters and composition of the plasma and the features of anodic evaporation under conditions of increased pressure of the reaction gas and the concentration of gas ions.

2. Methods of the experiment

The studies were carried out in a gas-discharge system, the scheme of which is shown in Fig.1.

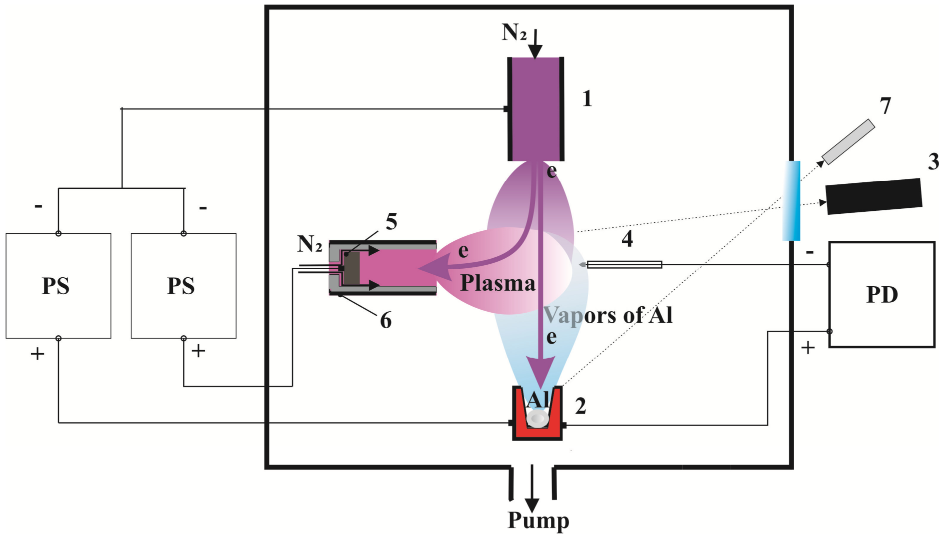

Fig.1. The scheme of a gas discharge system: *1* – tubular SHC; *2* – crucible; *3* – spectrometer; *4* – Langmuir probe; *5* – anode; *6* – cylindrical screen, *7* – pyrometer.

Tubular SHC made of titanium nitride *1* had a diameter of 8 mm and a length of 70 mm. Crucible *2* made of graphite was placed coaxially at a distance of 200 mm from the cathode. The crucible had an outer diameter of 19 mm. The cavity of the crucible with a volume of 1.9 cm^3 was filled with granular Al (analytical grade). The discharge current maintained between the SHC and the crucible was regulated in the range of 6–14 A. The temperature of the crucible heated by the electron flow exceeded 1000°C, which provided an Al vapor pressure of ~10^{-3} Torr. The pressure of the working gas (N_2) was regulated in the range (4–16)·10^{-3} Torr.

The plasma of the gas-vapor mixture was studied by the method of optical emission spectroscopy. The emission spectra of the plasma were recorded using an HR2000 spectrometer (OceanOptics Inc.) *3* in the wavelength range from 190 to 1100 nm. The intensity of plasma optical emission lines was determined as the average of 15 measurements carried out in the automatic mode for a time of no more than 100 ms. Probe diagnostics of plasma was carried out with a Langmuir probe *4* with a diameter of 0.5 and a length of 5 mm. The probe was located at a distance of 5 cm from the crucible. The probe characteristic was recorded with a Hioki 8835 digital recorder at a frequency of 20 Hz. The characteristic averaged over the results of 50 measurements was used when determining the plasma parameters

An additional anode *5* was used, installed inside the cylindrical screen *6*, for control the degree of dissociation and ionization of N_2. The electrodes were water-cooled. The electron current to the additional anode was controlled independently of the crucible current in the range of 0–30 A. The geometric contraction of the arc column in the anode region leads to potential jumps, which provide an increase in the electron energy and efficient dissociation and ionization of N_2 [11].

3. Results and discussion

The lines (391.4 and 427.8 nm) of the first negative system of molecular N_2^+ ions ($B^2\Sigma_u^+$–$X^2\Sigma_g^+$) is dominated in optical emission spectrum of plasma (Fig.2) as well as the 661 nm line of N^+ ($3d^1F_3^0$–$3p^1D_2$).

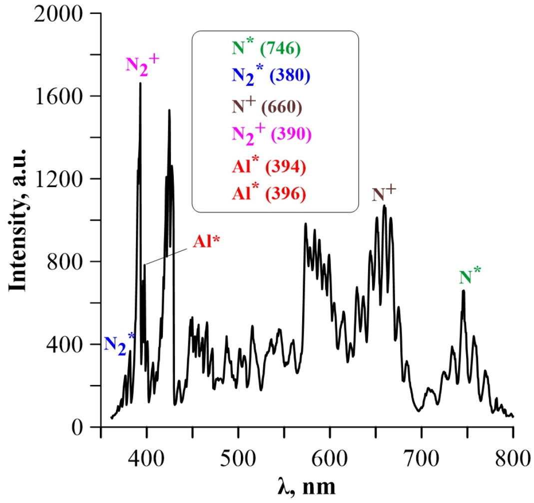

Fig.2. Characteristic spectrum of optical plasma emission.

The lines of neutral particles, including the first ($B^3\Pi_g$–$A^3\Sigma_u^+$, spectral range 550–700 nm) and the second ($C^3\Pi_u$–$B^3\Pi_g$) positive N_2 systems, and the line of N (746 nm, $3p^4S_{3/2}^0$–$3p^4P_{5/2}^0$), have a lower intensity. We determined the intensity of the 380.5 nm line of the second positive N_2 system in the experiments, the main contribution to the formation of excited particles of which is made by electrons, while metastable atoms and molecules do not have a significant effect [12]. With an increase in the discharge current, the intensities of the nitrogen lines increase linearly (Fig.3), which indicates the dominant effect of the electron concentration and a weak change in the electron temperature of the plasma [13].

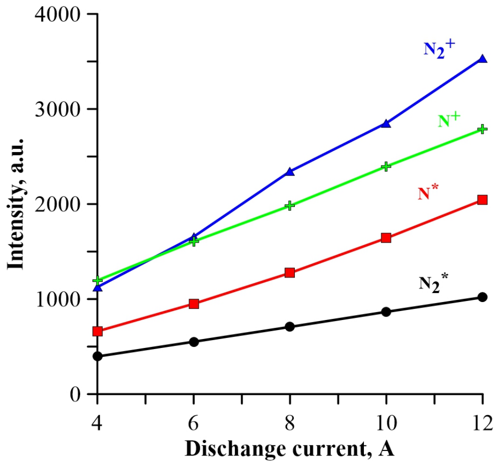

Fig.3. Dependences of the intensities of optical emission lines on the discharge current in the mode without evaporation of Al.

Al evaporation was monitored using the 396.2 nm line ($3s^2S_{1/2}$–$3s^2P_{3/2}0$) (Fig. 2). With an increase in the discharge current from 6 to 14 A, the temperature of the crucible (T) increases from ~1070 to ~1220°C, while the intensity of the Al lines increases by a factor of 9 (Fig.4).

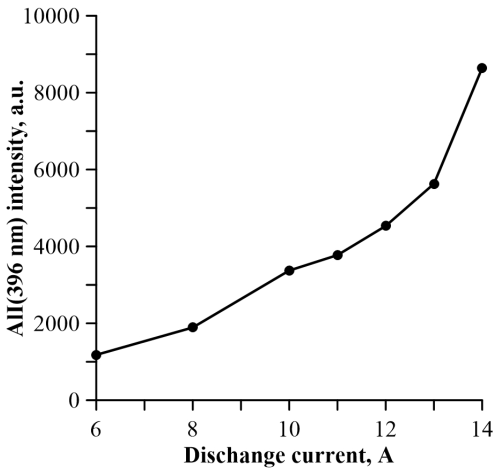

Fig.4. Dependence of the intensity of the Al line in the vapor-gas mixture.

The change in the intensity of the Al line is well described by the equation for the vapor pressure $\lg(p) = 9.2776 - 16540/T$ [14]. The evaporation rate of Al (V_e) determined from the Hertz-Knudsend equation ($V_e \sim (M/T)^{1/2}\cdot p$, where M is the molar mass of the evaporated material) [15] was $(1.4–18)\cdot10^{-5}$ g/(cm$^2\cdot$s) in the range of discharge current variation 4–12 A.

A change in the Al vapor pressure has a significant effect on the anodic potential drop and has weak effect on the electron temperature of plasma (T_e), which was ~3.4 eV. The dependences of the positive anode potential drop (AD) on the discharge current are shown in Fig.5. In the gas regime without evaporation of Al, the AD value increases from 9.4 to 12 V with an increase in the discharge current from 6 to 12 A. In the vapor-gas regime, with an increase in the discharge current to 11 A and an increase in vapor pressure, a decrease in the AD is observed down to 0.

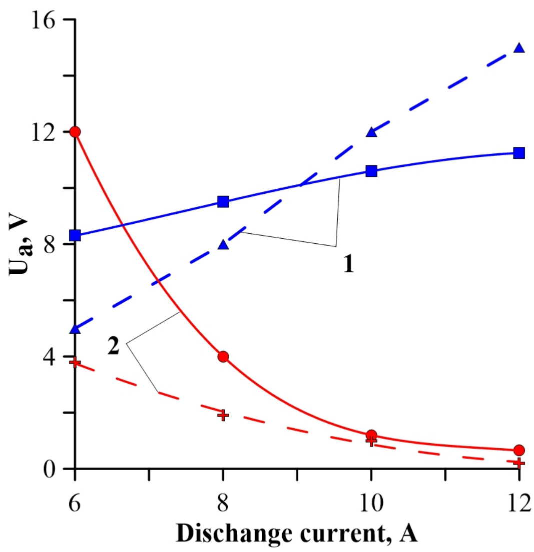

Fig.5. Dependences of the positive anode potential drop on the discharge current: *1* – in the mode without evaporation of Al; *2* – for a vapor-gas mixture. Solid line – experimental data, dashed line – calculated data.

It follows from an analysis of the phenomena in the anode region of a low-pressure gas discharge [16] that the sign and magnitude of the AD are determined by the conditions for the generation and losses of positive ions in the space in front of the anode. The formation of a negative AD is ensured the conditions under which the concentration of ions in the layer before the anode is sufficient to neutralize the space charge of the electron flow. The deficiency of ions causes the formation of a positive AD, the value of which, as a rule, reaches ~ (U_i - kT_e), where U_i is the ionization potential of the plasma-forming gas [16]. The conditions for the applicability of the Engel theory [17] are satisfied, namely: ambipolar diffusion prevails over volume recombination, there is no discharge contraction, there is no significant increase in the temperature of the plasma gas ionization ~1, in the range of current densities j and p, characteristic of our experiment. Under such conditions, the relationship between the positive AD value U_a, j, p and the parameters characterizing the gas can be described by the relation:

$$\frac{j}{p^2} = \frac{1.17}{16\pi}\frac{M}{m}\sqrt{\frac{2e}{m}}C_1^2 U_a^{1/2}(U_a + \langle U_e \rangle - U_i)^3, \quad (1)$$

where $\langle U_e \rangle$ is the average energy of electrons, which enter the AD from the positive column of the discharge. It follows from the theory [17] that U_a decreases with increasing gas pressure and slowly increases with increasing current density. The qualitative dependences of U_a on the discharge current, obtained using relation (1), are shown in Fig.5. It was assumed in the calculations that the p value corresponds to the Al vapor pressure directly at the anode surface, $\langle U_e \rangle$ were determined from the electron energy distribution function obtained by double differentiation of the probe characteristics. The correspondence of the dependences indicates that the decrease in the AD value with an increase in the Al vapor pressure is due to an increase in the electron ionization frequency in the anode part of the discharge.

The features of anode evaporation caused by changes in the pressure of the reaction gas and the degree of its ionization were studied in the experiments along with the effects caused by the influence of the vapor flow on the parameters and composition of the plasma. Fig.6 shows the dependences of the Al optical emission line intensity, as well as the T_e and U_a, on the N_2 pressure.

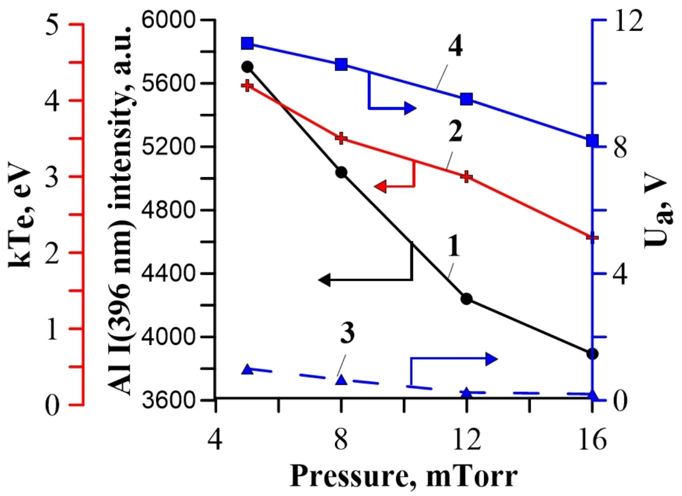

Fig.6. Dependences of the intensity of the optical emission line of Al, the positive anode potential drop and the electron temperature of the plasma on the pressure N_2. *1* – Al I intensity; *2* – electron temperature; *3*, *4* – positive anode potential drop (solid line – mode of without Al, dashed line – mode with Al).

An increase in the N_2 pressure leads to a decrease in the intensity of the Al line by a factor of 1.5. The reason for the decrease in the evaporation rate is a decrease in T_e and, accordingly, a decrease in the heating power of the crucible, the value of which is defined as: $W = I (U_a + kT_e + \varepsilon)$, where I is the electron current to the anode, ε is the work function of the evaporated material.

Thus, the main reason for the decrease in the flux of evaporated particles with an increase in the pressure of the reaction gas is a decrease in the electron temperature of the plasma. It should be noted that this is the fundamental difference between anode evaporation and widely used magnetron sputtering where the decrease in the flux density of sputtered particles with an increase in the pressure of the reactive gas is caused by the growth of compounds with a low ion sputtering coefficient on the metal surface [18]. The relatively small effect of such compounds on the rate of anodic evaporation is due to the high rate of diffusion of metal atoms through the growing nitride layer at high temperatures [19] and the discontinuity of this layer during evaporation (due to the significant difference between the thermal expansion coefficients of liquid metal and solid oxide) [20, 21].

In a study of the influence of the parameters of the gas medium on the rate of anode evaporation, an additional anode (hollow anode) was used. The fluxes of N_2 and electrons were combined in the region of hollow anode. The crucible current was 10 A in the experiments. The electron current to the hollow anode was controlled independently of the current to the crucible. The intensity of the optical emission lines of gas ions (N_2^+, N^+) increased linearly with an increase in the hollow anode current up to 30 A. On the contrary, the intensity of the Al lines decreased (Fig.7), which indicates a decrease in the concentration of Al in the plasma.

It follows from probe measurements that the AD at the surface of the crucible anode decreases from ~12 V with increasing the hollow anode current and changes sign at a current of ~25 A (Fig.8).

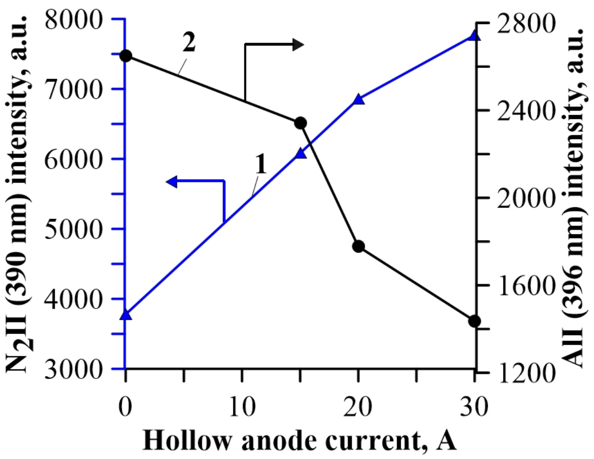

Fig.7. Dependences of the intensity of the optical emission line of Al and N_2^+ on the hollow anode current. *1* – N_2 II intensity, *2* – Al I intensity.

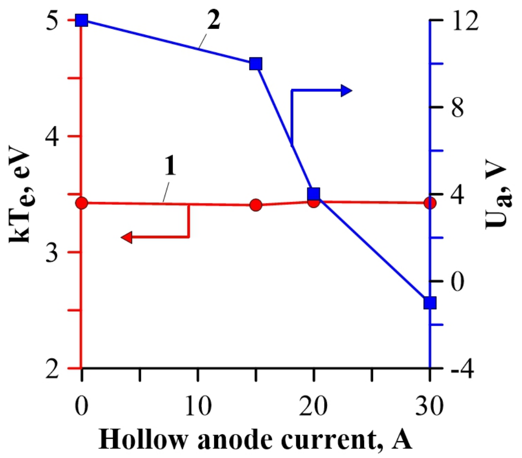

Fig.8. Dependences of the positive anode potential drop and electron temperature on the hollow anode current. *1* – electron temperature, *2* – positive anode potential drop.

The value of T_e does not change significantly in this case and amounts to 2.5 eV.

Thus, the effect of the gas component (N_2) manifests as a decrease in plasma T_e with an increase in gas pressure and a decrease in AD with an increase in the degree of gas ionization. The result is a drop in the power supplied by the electron flow to the anode-crucible and the rate of Al evaporation.

4. Conclusion

A plasma discharge with a self-heating hollow cathode and an evaporating anode in a vapor-gas mixture (Al-N_2) has been studied. It is shown that an increase in the Al vapor pressure is accompanied by a decrease in the positive anodic potential drop down to 0 as a result of an increase in the electron ionization frequency in the anode region. The influence of the gas component of the gas-vapor mixture on the conditions of anodic evaporation of Al manifests as a decrease in the electron temperature of the plasma with an increase in gas pressure and in the magnitude of the anodic potential drop with an increase in the concentration of gas ions. As a result, the energy of electrons entering the anode decreases, and, as a result, the rate of metal evaporation decreases.

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5. References

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