INVESTIGATION OF THE INFLUENCE OF Ar PRESSURE ON VACUUM-ARC PLASMA WITH Cr-, Cu-, AND Zr-CATHODES

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The work deals with the influence of argon pressure on the ion current of vacuum-arc discharge in the "Bulat-6" setup with Cr-Cu-Zr-cathodes, and also, on the rate of coating deposition on the surfaces being perpendicular and parallel to the plasma stream. It is shown that a substantial decrease in both the ion current density and the rate of coating deposition takes place at Ar pressure above 1 Pa. Consideration is given to the elementary processes occurring during plasma stream-gas target interaction.

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INTRODUCTION

The method of vacuum-arc deposition is widely used in industry for the application of various functional coatings and surface modification of materials (e.g.) [1, 2]. One of the main features of the vacuum-arc discharge that makes it differ from other discharges [3] is the presence of the cathode spot (spots) on the cathode surface. The cathode spot (spots) to generate: the plasma stream consisting of the ionic (including multicharged ions) and electronic components, neutral particles and macroparticles [1, 2]. The generated plasma fills the interelectrode space, where it interacts with the gaseous component of the residual atmosphere or the inlet gas. The most intense interaction of the cathode spot-generated plasma with the gas target takes place with the increasing plasma density (gas neutral particle density). This interaction results in the electron temperature decrease, the ion chargeing exchange, the variation of the ion energy distribution function, the ion scattering [1, 2, 4-12], etc. The best-investigated is the interaction of titanium vacuum-arc plasma with different gases (N_2, Ar, He, etc.) [1, 2, 4-7, 10, 12, 13]. The interest in the studies was caused by the necessity of understanding the influence of discharge-plasma processes on the synthesis of titanium coatings (Ti, TiN, TiO_2), as they are the most commonly encountered in various branches of industry.

At the same time, metal coatings of Cr, Cu, and Zr can be used for metallization of ceramic materials, and as corrosion protection. The inert gas inlet into the deposition chamber can lead to stabilization of the vacuum arc, as well as to the appearance of an additional gaseous ion flux that can be used to intensify the pre-etching process of the substrate material [14]. Besides, the scattering of metal ions by the gas target and the production of inert gas ions may contribute to a more efficient ionic cleaning and metal coating deposition on the parts with intricately shaped surface profiles. However, the data for the influence of inert gas (Ar) pressure in the discharge chamber on Cr, Cu, and Zr vacuum-arc plasma are rather scarce [8, 14].

The aim of this work was to investigate the influence of the argon pressure on the ion current of vacuum-arc discharge with Cr-Cu-Zr-cathodes, and the rate of coating deposition on the sample surfaces perpendicular and parallel to the plasma flow.

1. EXPERIMENTAL DETAILS

The experiments were carried out at the "Bulat-6" installation with camera 50 long and 50 cm in diameter. For better formation of plasma stream a focusing solenoid with inner diameter 18 and 27 cm in length was installed, Fig. 1. A vacuum-arc plasma source with magnetic stabilization of the cathode spot [10], equipped with a Cr (99.9 %), Cu (99.99 %), or Zr (99.9 %) cathode of 60 mm diameter, was used. The arc current for the Cr and Cu cathodes was equal to 100 A, and for Zr – 120 A. The current of the focusing coil ranged between 1 and 3 A. The argon pressure varied in a wide range from 1×10^{-3} to 5.5 Pa. The ion collector was a flat disk (Ø20 cm) placed at the distance 20 cm from the anode, which was supplied with a negative potential -50 V relative to the chamber walls (the collector 6 was installed instead of the sample holder 8).

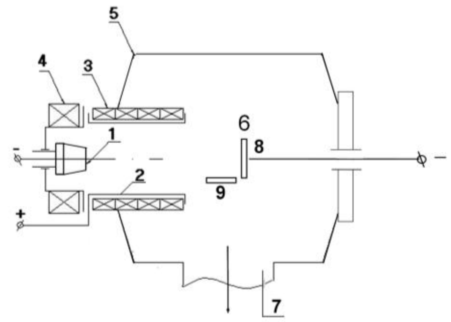

Fig. 1. Schematic diagram of the experimental installation: 1 – cathode; 2 – anode; 3 – focusing coil; 4 – stabilization coil; 5 – vacuum chamber; 6 – ion collector; 7 – to vacuum pump; 8 and 9 – sample holders

The deposition rate of the coatings was measured by the "shadow knife" method on the stainless steel 18Cr10NiTi samples (10×20×1.5 mm) by the use of the microinterferometer MII-4.

2. EXPERIMENTAL RESULTS AND DISCUSSION

The measurement results show that for all the metals studied, a decrease in the ion current density is observed at argon pressure above 0.3 Pa (Fig. 2). For chromium and copper cathodes the current decreased significantly (~30 and ~7 times, correspondingly), and for Zr cathode only about twofold current decrease has occurred at argon pressure >2 Pa.

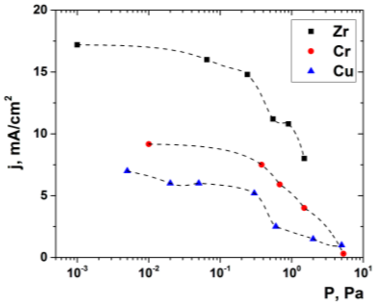

Fig. 2. Ion current density to the probe as function of Ar pressure for different metals

Similarly to behavior of ion current, the rate of coating deposition on the samples oriented at right angles to the plasma stream also decreases with increase of the argon pressure for all the metals under study. By way of example, Fig. 3 shows the Zr coating deposition rate as a function of argon pressure. The deposition rate ranges from ~50 to 100 μm/h at $P_{Ar} < 10^{-1}$ Pa, depending on the focusing coil field value, and at $P_{Ar} \geq 1$ Pa it sharply decreases down to 2…5 μm/h, and is practically independent on the magnetic field. The rate of coating deposition on the samples oriented parallel to the plasma flow increases with the pressure increase from 1…2 ($P_{Ar} < 5 \cdot 10^{-2}$) up to ~10 μm/h at $P_{Ar} \approx 0.4$ Pa. However, further increase of pressure, $P_{Ar} \geq 1$ Pa, leads to reduction of deposition rate down to 0.2…0.5 μm/h, with practically no substantial dependence on the magnetic field of the focusing solenoid (see Fig. 3,b). The ratio of the rates of Zr coating deposition on the sample surfaces parallel and perpendicular to the plasma flow increases within the gas pressure rise and reaches 0.25…0.3 at argon pressure 0.5…1.5 Pa (Fig. 4). Note that the given ratio is practically independent on the magnetic field of the focusing solenoid.

Below we consider the mechanisms of scattering of plasma metal ions on a gas target are considered. Depending on the gas pressure, three regions of interaction of the plasma flow generated by the cathode spot with the gas target can be distinguished. The first region represents the characteristic ion-ion (ν_{ii}) and electron-ion (ν_{ei}) collision frequencies higher than the frequencies of ion-neutral (ν_{in}) and electron-neutral (ν_{en}) collisions. This region corresponds to the low gas-target density (low gas pressure). The second region corresponds to the high gas-target density, and has the characteristic frequencies $\nu_{ii} < \nu_{in}$ and $\nu_{ei} < \nu_{en}$. The third region is an intermediate between the first and the second regions, this corresponding to $\nu_{ii} \approx \nu_{in}$ and $\nu_{ei} \approx \nu_{en}$. At the same time, numerous elementary processes take place as a result of electron-neutral, ion-neutral, electron-ion and ion-ion collisions. We now consider in more detail the elementary processes occurring at collision of plasma particles with neutral atoms of gas and metals.

Among the basic processes that take place at ion-neutral particle collisions we consider elastic scattering and charge exchange [11]. Elastic collisions cause the energy losses by ions and their scattering. In the classical approximation, at polarization interaction of dissimilar ions and atoms, the diffusion cross-section is given by the relation $\sigma_d = 2.21\sigma_c$, where σ_c is the capture cross-section $\sigma_c = (\pi \cdot \alpha \cdot q^2/\varepsilon_0 \cdot \mu \cdot v_0^2)^{1/2}$, α is the atomic polarizability, q is the charge, ε_0 is the dielectric constant, μ is the reduced mass of colliding particles, v_0 is the relative collision velocity. We estimate the diffusion cross-section for the case of metal ion collisions with argon atoms (the polarizability value was taken from ref. [15]). At collision energy of 1 eV (ion energy with high gas pressure [2]) the estimation has given the cross-section values to be $7.2 \cdot 10^{-15}$, $7.7 \cdot 10^{-15}$, $8.7 \cdot 10^{-15}$ cm² for the Cr^+, Cu^+, Zr^+ ions, respectively. It should be noted that at polarization interaction the ion mobility in foreign gases is independent on the ion charge value [11].

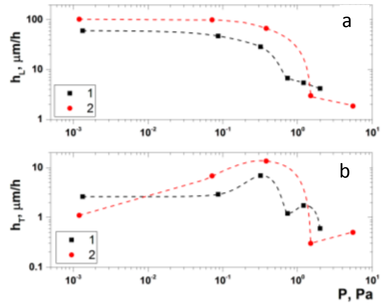

Fig. 3. Rate of Zr deposition longitudinally (a) and transversely (b) to the magnetic field versus Ar pressure. The focusing coil current is 1 A (1) and 3 A (2)

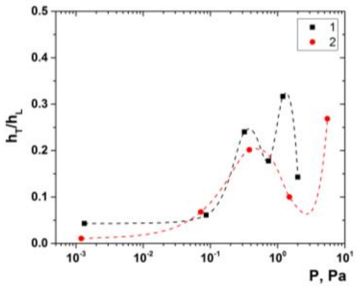

Fig. 4. The ratio of Zr deposition rates versus Ar pressure. The focusing coil current is 1 A (1) and 3 A (2)

In the process of charge exchange, the state of colliding particles changes. In the case of multicharged ions, a distinction is made between the multielectron and the one-electron charge exchange processes [16]: $A_m^{q+} + B_g \rightarrow A_m^{(q-k)+} + B_g^{k+} \pm \Delta E, k \geq 1$, where ΔE is the defect of energy equals to the difference between the binding energies of the target electron and the produced ion (atom), $\Delta E = E_i(A_m) - E_i(B_m)$. At $\Delta E = 0$ and $\Delta E \approx 0$, we have, respectively, the resonant (symmetrical) charge exchange and quasiresonant charge exchange [17]. In the cases of $\Delta E > 0$ and $\Delta E < 0$, the exothermic reaction and endothermic reaction take place, respectively. For the endothermic reaction, the charge exchange cross-section is equal to 0 at $E_{c.m.} < \Delta E$, where $E_{c.m.}$ is the kinetic energy of relative motion in the center-of-mass system [18]. The calculated ΔE values for the case of one-electron charge exchange of metal ions with the argon atom are presented in Table. The ionization potential values are taken from [19]. As is evident from Table, for all single-charged ions and Zr^{2+}, the defect of energy is $\Delta E < 0$, i.e., in this case the process is endothermic. Consequently, in this case the charge exchange is possible only if $E_{c.m.} > \Delta E$. The experimentally measured cross-sections for charge-exchange of Cr^+ and Cu^+ ions with the argon atom at a collision velocity of $2 \cdot 10^7$ cm/s are equal, respectively, to $9 \cdot 10^{-18}$ and $3.8 \cdot 10^{-17}$ cm² [20].

During the vacuum-arc discharge the cathode material is present not only in the form of ions, but as neutral particles as well. The quantity of cathode-material neutral atoms can be rather great [2]. The sources of metal neutral atoms are provided by evaporation from the molten cathode parts and macroparticles, etc. The results of measurements of neutrals concentration in the vacuum-arc discharge [21] have demonstrated that the density of Cu atoms depends on the distance to the cathode (2 to 6 mm), and the maximum concentration ranges from $8\cdot10^{12}$ to $5\cdot10^{13}$ cm^{-3}. The ions of metals also interact (scattering, charge exchange) with eigen neutral atoms. At high vacuum, the charge exchange of metal ions with the eigen vapor play a leading part in reducing the charge of ions emitted from the cathode spot [22]. For single-charged ions, the charge-exchange process with the eigen atom will be resonant, and the scattering angle at the charge-exchange amounts to 180° [23]. In this case, the diffusion scattering cross-section is given by the relation $\sigma_d^* = 2\sigma_{res}$, where σ_{res} is the resonance charge-exchange cross-section. At collision energy 1 eV, the resonance charge-exchange cross-sections are found to be $1.9\cdot10^{-14}$, $1.6\cdot10^{-14}$, $2\cdot10^{-14}$ cm^2 for the colliding particle pairs Cr^+-Cr, Cu^+-Cu, Zr^+-Zr, respectively [23]. As the ion energy increases, the resonance charge-exchange cross-section values decrease, and yet remain rather high, ~ 10^{-15} cm^2 (~1000 eV).

Defect of energy ΔE of single-electron charge-exchange of metal ions on Ar atoms

Metals	Ion charge			
	+1	+2	+3	+4
Cr	-8.99	0.73	15.2	33.4
Cu	-8.033	4.53	21.08	41.62
Zr	-9.13	-2.63	7.41	18.66

The neutral atoms of metallic vapors also experience elastic collisions with gas atoms. To determine the free path versus energy of the metal atom moving in the gas, the atoms of which have the Maxwell velocity distribution, one can use the expression derived in [24]:

$$\lambda = \lambda_0 \left[\left(1 + \frac{1}{2\omega} \right) erf\left(\sqrt{\omega}\right) + \frac{e^{-\omega}}{\sqrt{\pi\omega}} \right]^{-1}, \quad (1)$$

$$\omega = \frac{3}{2} \frac{E_1}{E_g} \frac{M_1}{M_2}, \quad (2)$$

where E_1 is the metal atom energy; E_g is the average energy of the gas atom; M_1 and M_2 are, respectively, the gas atom mass and the metal atom mass; $\lambda_0 = 1/N\sigma$, σ is the effective collision cross-section; N is the particle density. In the elastic sphere model, we have $\sigma = \pi\cdot r^2_{1,2}$, $r_{1,2} = r_1 + r_2/2$, where r_1 and r_2 are the atomic radii of colliding particles (the values for our calculations were taken from [15]). By calculation results, the average mean free path λ of metal atoms (T_0 = 2000 K) in argon (T = 300 K, P = 1 Pa) will be 0.8, 0.83, 0.7 cm for Cr, Cu, Zr, respectively, and 0.66 cm – for Ar. As the atom moves in the gas, its energy relaxation takes place due to collisions. In such a case, the average energy of atoms E_F at some distance from the evaporation surface can be estimated as $E_F = (E_0-E_g)\cdot\exp(-nE_f/E_i)+E_g$, where E_0 is the initial energy of atom; E_g is the energy of gas atom; $/E_i = 2\, M_1M_2/(M_1+M_2)^2$; n is the number of collisions. At identical initial conditions the E_F value is not too different for the given metals.

The free path of the atoms (*at a pressure of ≥ 1 Pa*) is considerably less than the typical dimensions of the vacuum chamber. In this case, one can make use of the kinetic theory of gases and consider the process of vapor atom transport in the gas as metal atom diffusion in a foreign gas. The diffusion coefficient is determined as $D = 1/3\ \lambda v$, where v is the velocity. The increase in the neutral gas particle concentration will lead to the decrease in the free path length of metal vapor atoms, in the velocity of the atoms, and hence, in the decrease of the diffusion coefficient. In turn, at a constant quantity of the evaporant, the decrease in the diffusion coefficient must lead to the increase in the concentration of neutral metal-vapor atoms. This supposition is confirmed by the simulation results obtained in [25]. Eventually, the probability of charge exchange (including the resonant one) of metal ions with metal atoms will increase. The balance of neutral atoms of metals will be determined not only by diffusion and the processes of charge exchange with metal ions, but also by other processes leading to metal atom ionization. These processes include the electron-impact ionization of atoms, the Penning ionization, and the charge exchange with the gas ions. For the sake of completeness, it should be also noted that the ion charge reduction can occur due to the recombination processes.

So, the increase in the neutral particle density of gas will lead to the following: (i) the decrease in the number of multicharged ions due to charge exchange of ions with atoms of gas and metal vapors; (ii) the plasma flow scattering by the target comprising neutral atoms of gas and metal vapors; (iii) the ionization of neutral atoms. All these processes result in that the initial directed plasma flow is scattered by the target (see Fig. 3), and the rate ratio of deposition along and across the flow increases (see Fig. 4).

CONCLUSIONS

Experimental studies into the influence of Ar pressure on the vacuum-arc plasma with Cr-, Cu-, and Zr-cathodes have demonstrated the following: a substantial decrease in the ion current density at a pressure above 1 Pa; deposition rate reduction with increase in the gas pressure; increase in the ratio of deposition rates along and across the flow at pressures above 1 Pa.

The consideration of elementary processes occurring during plasma flow-gas target interaction has shown that in the region of high gas-target density ($\nu_{ii} < \nu_{in}$ and $< \nu_{en}$) the main processes that lead to the multicharged ion density reduction and plasma flow scattering are the charge exchange and ion scattering by neutral atoms of the gas and metallic vapor. Accordingly, this leads to the decrease in the ion collector current density and the deposition rates (h_T and h_L), as well as to the increase in the h_T/h_L ratio.

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ИССЛЕДОВАНИЕ ВЛИЯНИЯ ДАВЛЕНИЯ Ar НА ПЛАЗМУ ВАКУУМНОЙ ДУГИ С Cr-, Cu- И Zr-КАТОДАМИ

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Исследованы влияния давления аргона на ионный ток вакуумно-дугового разряда в установке «Булат-6» с Cr-, Cu-, Zr-катодами, а также на скорость осаждения покрытий на поверхности, перпендикулярные и параллельные плазменному потоку. Показано, что существенные уменьшения плотности ионного тока и скорости осаждения покрытий происходят при давлении Ar выше 1 Pa. Рассмотрены элементарные процессы, происходящие при взаимодействии плазменного потока с газовой мишенью.

ДОСЛІДЖЕННЯ ВПЛИВУ ТИСКУ Ar НА ПЛАЗМУ ВАКУУМНОЇ ДУГИ З Cr-, Cu- ТА Zr-КАТОДАМИ

Ю.В. Ковтун, О.С. Купрін, В.М. Луньов

Досліджено впливи тиску аргону на іонний струм вакуумно-дугового розряду в установці «Булат-6» з Cr-, Cu-, Zr-катодами, а також на швидкість осадження покриттів на поверхні перпендикулярні і паралельні плазмовому потоку. Показано, що істотні зменшення густини іонного струму і швидкості осадження покриттів відбуваються при тиску Ar вище 1 Pa. Розглянуто елементарні процеси, що відбуваються при взаємодії плазмового потоку з газовою мішенню.