Investigation of composition and parameters of metal-gas plasma at vacuum arc evaporation of molybdenum cathode in the mode of plasma assistance

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Abstract. It is shown that simultaneous functioning of the self-sustained arc discharge with the integral-cold molybdenum cathode and non-self-sustained arc discharge with the thermionic and hollow cathodes allows to generate volume metal-gas plasma with density of $\geq 10^{10}$ cm$^{-3}$, electrons temperature of $\approx 1–1.5$ eV at the gas (argon) pressure of 0.3 Pa and working values of the arc current of evaporator (60–180) A into vacuum volumes of $\geq 0.1$ m$^3$ for effective coating synthesis based on molybdenum by vacuum arc plasma-assisted method. It has been established by the spectrometric method that neutral atoms and single-charged molybdenum ions are present in the area of molybdenum-based coatings condensation along with atoms and ions of the working gas.

1. Introduction
Plasma technologies are increasingly used in up-to-date industry to extend the service life of parts for different mechanisms. The transition metal nitrides have found widespread using. Among the most popular one it is possible to note TiN, ZrN, CrN, MoN coatings, etc. [1–3]. These compounds are characterized by the high hardness and wear resistance [4].

There are many methods for synthesize the noted above coatings. But one of the most effective methods is vacuum arc deposition of functional coatings [5]. This method is characterized by high growth rate of dense coatings. The coatings with high adhesion to the substrate and low porosity can be synthesized by the method. This vacuum arc deposition technique can be improved by complementing the deposition equipment with an original gas-plasma source based non-self-sustained arc discharge with thermionic and hollow cathodes. That leads to increase the stability of the arc evaporator functioning. Also due to work of the additional source of gas plasma it is possible to delicate finish cleaning of materials and products surface by ions of inert gases and their additional preliminary heating [6].

These ion-plasma technologies allow to carry out large-dimensioned and extended details or high-production machining of products with the smaller dimension. However, to optimize the modes of surface products modification and to gain fundamental knowledge of metal-gas plasma generation at first it is necessary to investigate the interactions between parameters of plasma generators of different type (evaporator and gas plasma source) and formation, parameters and composition of metal-gas plasma in vacuum chamber with volumes of $\geq 0.1$ m$^3$. 
The purpose of the present work is the research of parameters and composition of the plasma generated at independent and combined functioning of the arc evaporator with the molybdenum cathode, as well as a gas-plasma source based on non-self-sustained arc discharge with thermionic and hollow cathodes of extended construction in the argon atmosphere.

2. Material and research techniques

The experiments were carried out on the QUINTA vacuum ion-plasma installation (IHCE SB RAS, Tomsk, Russia) [7]. The vacuum chamber of that has the sizes of $750 \times 650 \times 650$ mm$^3$. Installation has personal computer control, that allows to carry out the experiments with high degree of recurrence.

In the present work the operation modes, parameters and composition of the plasma generated at the independent or combined work of the following plasma sources were investigated:

- For the generation of gas plasma the original plasma generator PINK-P (abbreviation in Russian) with extended design based on non-self-sustained arc discharge with thermionic and hollow cathodes was used [8].
- The metal plasma generator was a redesigned DI-100 electric arc evaporator with enhanced cooling of the back side of the cathode. The material of the cathode (Ø 100 mm) was molybdenum ($C_{Mo} \geq 99.96\%$).

Figure 1 shows a simplified scheme of the QUINTA experimental installation. That contains the following main devices: 1 – cylindrical collector; 2 – Langmuir moving cylindrical probe; 3 – DI-100 electric arc evaporator; 4 – vacuum chamber (anode); 5 – hollow cathode of the PINK-P gas-plasma source; 6 – thermionic cathode of the PINK-P gas-plasma source; PSoTC – power supply of thermionic cathode of a PINK-P; PS1 – power supply of discharge of the PINK-P plasma source; APS – arc initiation power supply; PS2 – power supply of DI-100 electric arc evaporator.

![Figure 1. Scheme of the experimental QUINTA installation.](image-url)
The following techniques were selected as the main for measuring of parameters and composition of gas, metal and metal-gas plasma:

- measuring of ion current density on the collector with total square of $S_k = 170 \text{ cm}^2$ located in the center of the working chamber (figure 1);
- research of plasma parameters (temperature of electrons, potential and concentration of plasma, floating potential) by single cylindrical probe of Langmuir and automatic system of probe characteristics measurement [9];
- spectral analysis of a plasma zone with a spectrometer OceanOptics HR4000.

3. Experimental results

To optimize the deposition process the measurement of coating growth rate on the chamber radius were carried out. Molybdenum coatings were deposited in identical experimental conditions: working gas – Ar; working pressure is 0.3 Pa; arc current of the evaporator $I_d = 90$ A. The distance between the neighboring specimens was 5 cm. Coating thickness was measured by the dimensions of a spherical cross-section by Calotest method.

The results of the obtained experiments are presented in the figure 2. The coating growth rate is maximum in the center of the chamber and decreases with increasing distance along the chamber radius. It is not significant at the distance of 10 cm from the center and decreases $\approx 1.5$ times at the distance of 15 cm.

![Figure 2](image.png)

**Figure 2.** The growth rate of molybdenum coating deposited by vacuum arc plasma-assisted method.

Earlier it was revealed that the presence of the additional ionized environment (gas ions) in the discharge gap increases the stability of burning of the arc discharge [10]. But before experiments on plasma research it is necessary to define an optimum operation mode of the gas-plasma source. For this purpose, the voltage-current characteristic (figure 3) of the PINK-P gas-plasma source was measured at the different pressures of working gas. For all range of working pressures the voltage-current characteristic of non-self-sustained arc discharge has linear character in the range of arc currents of 10–150 A.

As shown in figure 3, the gas-plasma source has a high discharge voltage at a minimum gas pressure of 0.1 Pa, especially at high discharge currents. In some cases, due to the specific mechanism of plasma source operation, the high voltage value can lead to its incorrect operation.
Figure 3. Voltage-current characteristic of the PINK-P plasma source at different working gas pressures.

For the measurement of ion current density at the independent work of gas and metal plasma sources the cylindrical collector from stainless steel with rather high square $S_k = 170 \text{ cm}^2$ was used. The experimental scheme is shown in figure 1. The ion current on the collector $I_k$ was fixed by means of the milliammeter, and then ion current density was calculated as $j = I_k/S_k$.

As it was defined in the previous experiments the collector was located in the center of the working chamber at the distance of 300 mm from an output aperture of the PINK-P source and 300 mm from the DI-100 arc evaporator. The dependences of ion current density on discharge current are given in figure 4.

Figure 4. The dependences of ion current density on the arc discharge current for the gas-plasma source with thermionic and hollow cathodes and for the arc evaporator in the center of the chamber (Ar, $p = 0.3 \text{ Pa}$).

According to the results, in this position the conditions of metal-gas plasma formation at the ratio of ion current density of gas $j_p$ and metal $j_d$ plasma component is in the range of $j_p/j_d = 0–2$ were realized.

To research the low-temperature plasma parameters in the dependence on the main characteristics of arc discharges the single cylindrical probe of Langmuir which was installed in the center of the chamber in the position of specimen holder at the distance of 300 mm from the evaporated cathode and at distance of 300 mm from output aperture of the PINK-P gas-plasma source was used. For each required mode the probe characteristic were measured, and the necessary parameters of plasma (plasma potential and
concentration, temperature of electrons, floating potential) were calculated based on the standard technique [11–12].

Figure 5 shows the arc discharge characteristics depending on the arc current. The results were obtained both at independent operation of plasma sources and at their joint operation. All measurements were carried out in argon atmosphere at working pressure of 0.3 Pa.

![Figure 5. The dependences of plasma parameters on the arc discharge current: a) plasma concentration; b) plasma potential.](image)

It was revealed that with increasing the arc discharge current of the PINK-P plasma source from 10 to 150 A the concentration of gas plasma increases linearly from $0.7 \times 10^{10}$ to $7.4 \times 10^{10}$ cm$^{-3}$. At the same time the linear growth of gas plasma potential in the ranges of 4.0–6.0 V was observed. Average temperature of electrons for gas plasma was 1.4 eV; floating potential is in range of 2–10 V.

The metal plasma generated at evaporation of the molybdenum cathode by a vacuum arc ($I_d = 60–180$ A) in the center of the working chamber at the distance of 300 mm from the surface of the cathode has temperature of electrons of $T_e = 1.0–1.2$ eV; plasma potential in the range of $\phi_{pl} = 3.1–5.4$ V and concentration of plasma for argon atmosphere $n_e = (1.7–5.2) \times 10^{10}$ cm$^{-3}$. At the same time with an increase in discharge current of the arc evaporator and metal plasma concentration growth, the increase of ion current density on the collector (substrate) is observed.

There is metal-gas plasma formation in the volume of the working chamber in the field of substrates position at the combined operation of the arc evaporator and PINK-P. That is a source of coating condensation in the mode of plasma assistance. The measurements were carried out at constant discharge current of the arc evaporator of 90 A. The temperature of electrons of metal-gas plasma was in the range from 0.9 to 1.4 eV depending on parameters of the PINK-P gas-plasma source. For metal-gas plasma the plasma potential increases from 4.2 up to 6.9 V at increase of arc current of the PINK-P from 5 to 150 A. The concentration of metal-gas plasma increases at the growth of arc current of PINK-P from $3.2 \times 10^{10}$ to $7.4 \times 10^{10}$ cm$^{-3}$ at constant pressure of argon and constant current of the arc evaporator.

For definition of qualitative composition of the gas, metal and metal-gas plasma generated at independent and combined work of the arc evaporator with the molybdenum cathode and PINK-P gas-plasma source with thermionic and hollow cathodes the spectrometer method was used at different operating parameters. The measurement of optical spectra of plasma emission was carried out by an OceanOptics HR4000 spectrometer. The spectrometer has 3 operating ranges of the measured wavelengths: no. 1 – (200–1100) nm; no. 2 – (350–430) nm; no. 3 – (250–351) nm. The plasma emission from area of substrates position (the center of the chamber) was fixed through a quartz window located on the upper flange of the vacuum chamber. The identification of spectrum lines in the selected range of wavelengths was carried out based on handbook data from the conventional sources [13–15].

Figure 6 shows the emission spectra of plasma generated by the PINK-P gas-plasma source (1), electric arc evaporator with molybdenum cathode (2) and their joint work (3) in the wavelength range
of (330–425) nm argon atmosphere. It is clear that there are argon atoms in the gas plasma, and there are the spectral lines of molybdenum atoms (Mo I) and single-charged ions (Mo II) in the metal plasma. In the range of (414–422) nm there is an overlapping of spectral lines of Mo and Ar (figure 6a), their more detailed decryption is shown in figure 6b.

![Figure 6](image1.png)

**Figure 6.** Optical emission spectra of low-pressure gas (1), metal (2) and metal-gas (3) plasma of arc discharges generated by PINK-P gas-plasma, electric arc evaporator with molybdenum cathode and their joint operation, respectively, in the wavelength range of (330–425) nm (a) and (414–422) nm (b). The parameters: gas – Ar, \( p = 0.3 \) Pa, \( I_d = 90 \) A, \( I_p = 90 \) A. In figure 6a the letters “a–e” indicate the lines decrypted in figure 6b.

At simultaneous operation of plasma sources of different types (spectrum 3), the repetition of spectral lines of spectrum 1 and spectrum 2 is observed. In addition, the intensity of spectral lines of molybdenum atoms and ions is increased; that of spectral lines of argon atoms and ions remains its initial value. The increase of molybdenum spectral lines intensity is connected with more stable arc discharge functioning on molybdenum cathode at additional gas ionization by means of the PINK-P gas-plasma source.

![Figure 7](image2.png)

**Figure 7.** Optical emission spectra of metal (1) and metal-gas (2) plasma of low-pressure arc discharges generated by electric arc evaporator with molybdenum cathode and joint operation of PINK-P plasma source and electric arc evaporator, respectively, in the wavelength range of
(251–349) nm. Parameters: gas – Ar, \( p = 0.3 \) Pa, \( I_d = 90 \) A, \( I_p = 90 \) A. The decryption of spectral lines is presented in table 1.

| №  | Wavelength \( \lambda \) (nm) | Ion    | №  | Wavelength \( \lambda \) (nm) | Atom / Ion |
|----|-------------------------------|--------|----|-------------------------------|------------|
| 1  | 259.371                       | Mo II  | 21 | 294.595                       | Mo II      |
| 2  | 264.028                       | Mo I   | 22 | 295.606                       | Mo II      |
| 3  | 264.579                       | Mo I   | 23 | 296.527                       | Mo II      |
| 4  | 267.327                       | Mo II  | 24 | 297.261                       | Mo II      |
| 5  | 268.558                       | Mo II  | 25 | 307.766                       | Mo II      |
| 6  | 270.261                       | Mo II  | 26 | 308.762                       | Mo II      |
| 7  | 273.696                       | Mo II  | 27 | 311.212                       | Mo I       |
| 8  | 277.540                       | Mo II  | 28 | 312.200                       | Mo II      |
| 9  | 278.004                       | Mo II  | 29 | 313.259                       | Mo I       |
| 10 | 281.615                       | Mo II  | 30 | 315.283                       | Mo II      |
| 11 | 282.655                       | Mo I   | 31 | 315.817                       | Mo I       |
| 12 | 284.823                       | Mo II  | 32 | 317.035                       | Mo I       |
| 13 | 285.323                       | Mo II  | 33 | 319.397                       | Mo I       |
| 14 | 286.381                       | Mo II  | 34 | 320.883                       | Mo I       |
| 15 | 287.151                       | Mo II  | 35 | 322.822                       | Mo I       |
| 16 | 289.445                       | Mo II  | 36 | 329.082                       | Mo I       |
| 17 | 290.307                       | Mo II  | 37 | 332.090                       | Mo II      |
| 18 | 291.192                       | Mo II  | 38 | 335.812                       | Mo I       |
| 19 | 292.339                       | Mo II  | 39 | 336.993                       | Mo II      |
| 20 | 293.048                       | Mo II  | 40 | 337.997                       | Mo I       |

The spectral lines of molybdenum atoms and single-charged ions were identified in the wavelength range of (250–351) nm with high accuracy (figure 7, table 1). In selected ranges in nitrogen-containing atmosphere, all spectral lines of molybdenum atoms and ions fixed in argon are repeated.

It is known from the literature [16] that molybdenum plasma generated by arc discharge with cathode spot contains neutral atoms, single-, two-, three- and fourfold ionized molybdenum atoms with average charge of 2.0. At these operation parameters, Mo I and Mo II were observed at a distance about 300 mm from the erodible cathode in metal and metal-gas plasma. That does not contradict generally accepted conclusions. Molybdenum ion emission lines with higher ionization rate with high intensity are in the short-wave ultraviolet range (< 200 nm). In the range available for recording in these experiments, the spectral emission lines of molybdenum ions with a charge of two or more have a low intensity and, at selected parameters, are indistinguishable across the background.

4. Conclusion

Based on the carried out studies, the growth rate of molybdenum-based coatings was revealed on the radius of vacuum chamber. Parameters of gas, metal and metal-gas plasma are detected in the wide ranges of parameters and their dependence on discharge current of plasma sources of different types. In the field of condensation of molybdenum-based coatings in metal-gas plasma generated by electric arc evaporator with molybdenum cathode and gas-plasma source with thermionic and hollow cathodes, molybdenum neutral atoms and single-charged ions are present along with atoms and ions of working gas.

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