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Influence of parameters of the discharge with a self-heating hollow cathode and a sectional anode on the activation degree of a vapor-gas medium

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Abstract. The composition of a discharge plasma with a self-heating hollow cathode and a sectional anode including an evaporated titanium anode has been studied by optical emission spectroscopy. The effect of discharge parameters on the activation degree of a vapor-gas medium including argon, titanium vapor, hexamethyldisilazane vapor, as well as reactive gases nitrogen and acetylene is investigated. It is shown that by changing the discharge parameters it is possible to change the plasma composition within a wide range, in particular, the fraction and degree of ionization of Ti vapors, the dissociation degree of nitrogen and acetylene.
Keywords: TiSiCN, OES, hollow cathode arc, anodic evaporation.

1. Introduction

Nanocomposite TiSiCN coatings are one of the promising protective wear-resistant coatings for various fields of application from medicine to the aerospace field [1–3]. They may have excellent performance characteristics, but the properties of these coatings are determined mainly by the conditions of their synthesis. In [4], a method for obtaining TiSiCN coatings by anodic evaporation of titanium and decomposition of hexamethyldisilazane (HMDS) in hollow cathode arc discharge was described. The advantage of this method is the ability to independently change various deposition conditions over a wide range, in particular the metal vapor flow, discharge current, composition and pressure of the gas mixture. One of the main components of the vapor-gas mixture with this method of deposition is an organosilicon precursor, which contains all the necessary elements and bonds, with the exception of titanium, for the synthesis of TiSiCN. However, the content of chemical elements in it is fixed. Meanwhile, the properties of TiSiCN coatings, in particular their hardness, wear resistance, coefficient of friction, are affected by the content of each of the structural elements. In particular, if the carbon content in TiSiCN is higher than the amount that can react with other elements, excess carbon is deposited in the form of amorphous or diamond-like carbon (DLC) nanoparticles [5], which can significantly reduce its coefficient of friction. To obtain coatings with an optimal C content, acetylene C_2H_2 or methane CH_4 is often added to the gas medium [2], the decomposition of which provides the right amount of carbon atoms in the coating. Since mainly atomic particles participate in the formation of the carbide or carbonitride phase in the coating, a change in the degree of dissociation of C_2H_2 can affect the kinetics of the deposition process. In addition, an important structural component of the active vapor-gas medium is atomic nitrogen, which plays a key role in the formation of nitride coatings. Since the nitrogen content in the initial HMDS molecule is low (8.7%), N_2 must be added to the gas mixture to optimize the elemental composition of the coatings obtained.

The purpose of this work was to study the effect of current on each of the anode sections on the plasma composition, in particular on the degree of activation of titanium vapor and dissociation of auxiliary reactive gases N_2 and C_2H_2, as well as on other plasma parameters.

2. Experimental methods

The studies were carried out on the installation schematically shown in Figure 1. The design of the gas discharge system and the experimental scheme are described in detail in [4]. The gas discharge system is equipped with a hollow cylindrical cathode made of TiN powder by magnetic pulse pressing and a sectional anode. One section, made of stainless steel 12H18N10T, had water

cooling, the second section of the anode was a crucible (graphite MPG-7) with a Ti-hitch (VT1-0) weighing from 0.4 to 0.5 g. Such a power supply scheme allowed to independently change the currents in the circuit of each anode section. The dock in the cooled anode circuit varied in the range of 0-50 A, in the crucible circuit the current was regulated in the range of 0–12 A. A water-cooled cathode assembly equipped with an additional cylindrical ignition electrode was located on the side flange of the chamber. Before the experiment, the vacuum chamber was pumped out to a residual pressure of about $2 \cdot 10^{-5}$ Torr. Plasma–forming gas Ar was injected into the chamber through the cathode cavity, N_2 and C_2H_2 through the cooled anode. The precursor vapor was released through an evaporator heated to a high temperature by a plasma stream and located near the axis of the discharge system between the cathode and the anode. The flow was regulated in the range of 0–10 g/h using the Mini Cori-Flow digital liquid flow controller (Bronkhorst). Hexamethyldisilazane (HMDS) was used as a precursor. The plasma composition in the sample location area was analyzed by optical emission spectroscopy using an OceanOptics HR2000 spectrometer in the wavelength range from 200 to 1100 nm, resolution 0.84 nm. The determination of the electron temperature and plasma potential was carried out by probe diagnostics using a cylindrical Langmuir probe (tungsten wire 0.4 mm thick, 5 mm long). The probe was placed at a distance of 8 cm from each of the anode sections near the axis of the cathode node, in the area of coatings deposition.

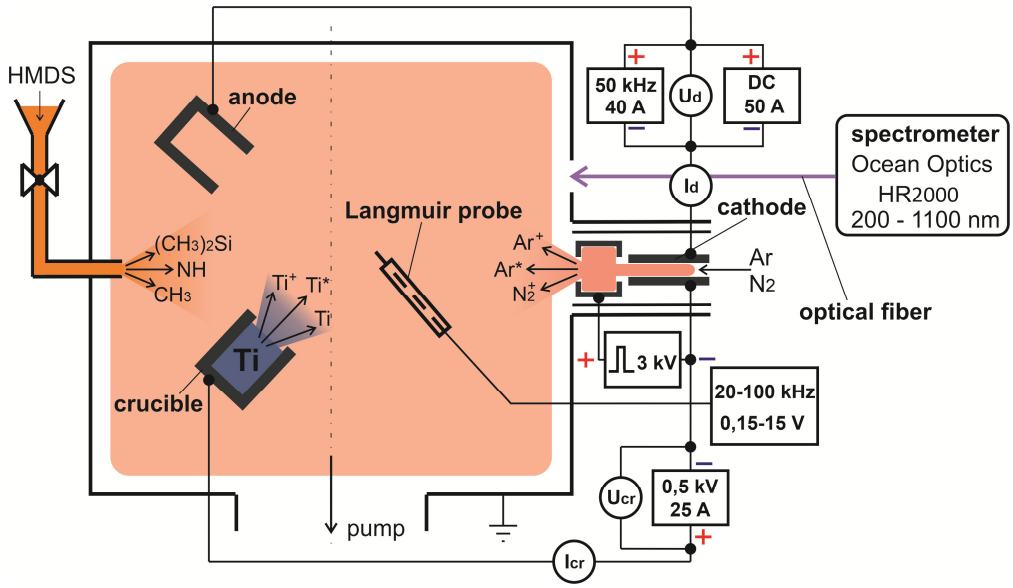

Fig.1. Scheme of the experimental facility.

3. Results and discussion

Figure 2 shows the characteristic emission spectra of discharge plasma in (Ar+N_2+Ti+C_2H_2+HMDS)-vapor-gas medium. In all modes of discharge combustion, the lines of argon (Ar^* – 811.5 nm, Ar^+ – 460.9 nm) nitrogen (N_2^*, N_2^+ – 391.4 nm), titanium (Ti^* – 399.9, 453.3 nm, Ti^+ – 337.3, 364.3 nm) are observed in the spectra. In addition, a strong line of the H^* atom (656.3 nm) belonging to the Balmer series was detected in the plasma spectrum, and its intensity increases with the discharge current, which indicates an increase in the degree of decomposition of HMDS and acetylene. Atomic nitrogen lines N^* (746.8, 868 nm) are detected in the nitrogen-argon plasma, however, in the presence of other components against the background of their intense atomic nitrogen lines, it was not possible to detect. Also in the spectra there were lines of carbon atoms (C^* – 357.8 nm) and hydrogen (H^* – 656.3 nm) appearing in plasma due to the decomposition of acetylene.

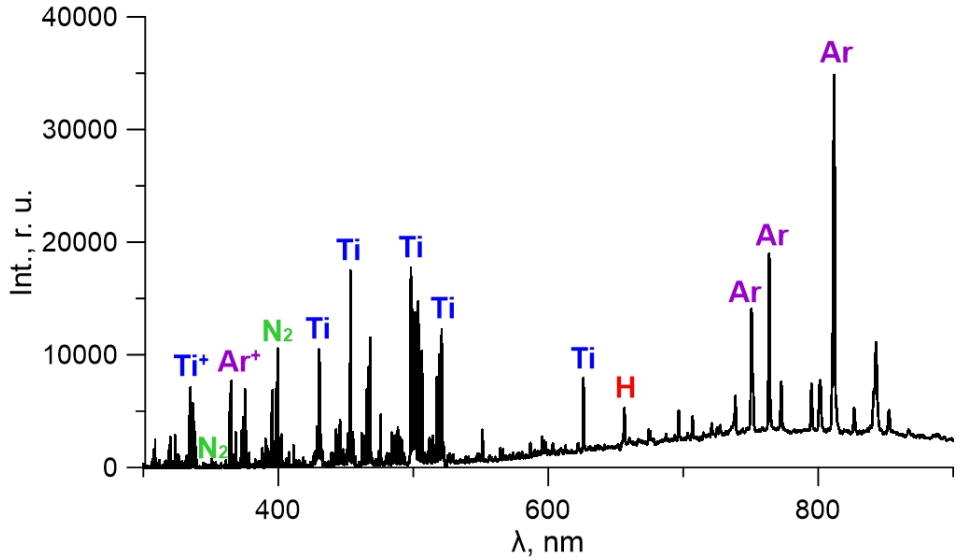

Fig.2. Characteristic spectrum of discharge plasma with SHHC and sectional anode.

In contrast to the work of [6], where the average charge of ions from the low-pressure cathode arc is 2.1, the lines of double-charged Ti^{2+} ions in the plasma of the anode arc could not be isolated. It can be assumed that single-charged Ti^{+} ions mainly arise in the anode region of the plasma by ionization of Ti atoms in a stream of fast electrons with an energy of up to several tens of eV [7], coming from the SHHC to the crucible. The analysis of the plasma composition also showed that the growth of the ion current with an increase in the current in the crucible circuit is due not only to an increase in the number of titanium ions, but also to an increase in the degree of ionization of the gas components of the plasma.

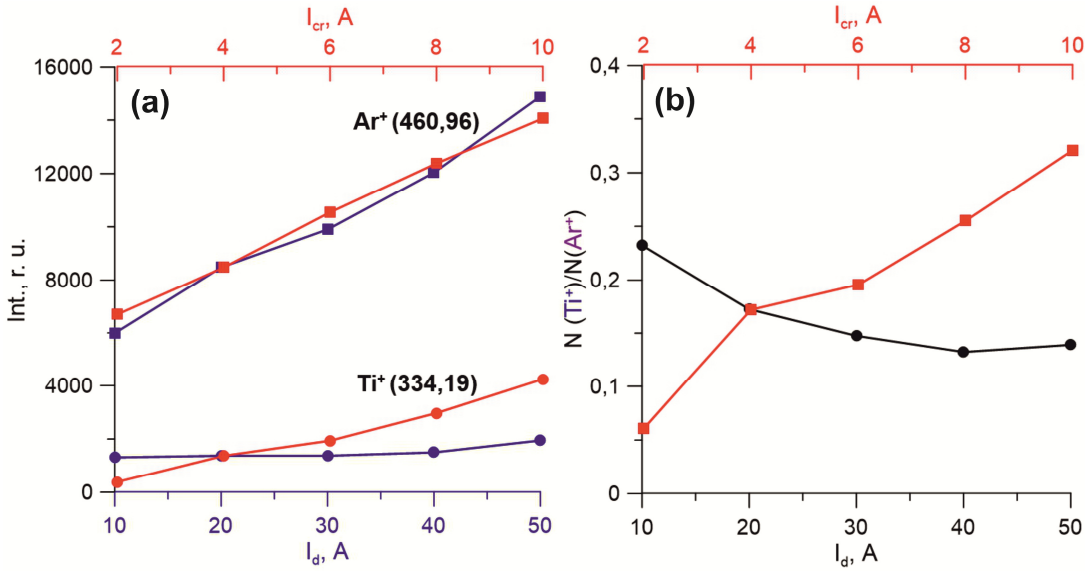

Fig.3. The dependences of the intensities of the Ar^{+} and Ti^{+} ion lines (a) and the relative content of Ti^{+} ions (b) on the current in the cooled anode circuit I_d and in the crucible circuit I_{cr}.

Figure 3a shows the dependences of the intensities of the argon Ar^{+}, titanium Ti^{+} and nitrogen N_2^{+} ion lines on the current to the cooled anode I_d and on the current to the crucible I_{cr}. It can be seen from the results obtained that if the increase in the ion current with an increase in the Id current

is mainly due to an increase in the number of argon ions Ar^+, then the increase in the ion current with an increase in the crucible is due not only to the influx of metal ions. An increase in the current to the crucible and the concentration of titanium vapors also leads to a significant increase in the number of gas ions (Ar^+, N_2^+), which can be explained by the processes of recharging titanium ions on atoms and molecules of plasma-forming gases with increased local pressure of metal vapors in the sample location. At an argon pressure in a 2.2 mTorr, the proportion of Ti^+ ions with an increase of I_{cr} from 2 to 10 A at constant current to the cooled anode section I_d increases from 5 to 30% (Figure 3b), while the increase in the current I_d from 10 to 50 A at constant current I_{cr} leads to a decrease in the proportion of metal ions from 25 to 15%.

The peculiarity of HCA discharge is the presence in the plasma of a stream of fast electrons with an energy close to the discharge voltage [7]. The main mechanism for the generation of neutral nitrogen atoms in plasma in the presence of a stream of fast electrons is the direct ionization of nitrogen molecules by electron impact with the formation of a molecular ion N_2^+ and subsequent dissociative recombination of molecular nitrogen ions with the participation of low-energy plasma electrons [8]. In nitrogen-argon plasma under our conditions, the degree of nitrogen dissociation, estimated using the Einstein ratio with respect to the intensities of the corresponding spectral lines, was 4–6% (Figure 4b).

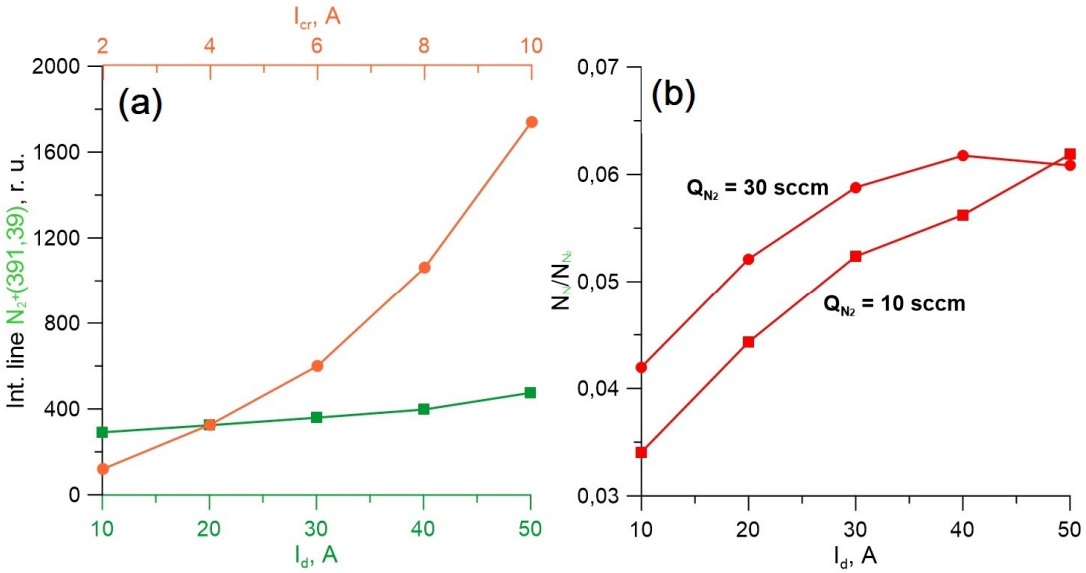

Fig.4. Dependences of the line intensity of N_2^+ ions on the current in the cooled anode circuit I_d and in the crucible circuit I_{cr} (a) and nitrogen dissociation degree on I_d (b).

In the spectra of a vapor-gas mixture with titanium and HMDS, atomic nitrogen lines are not detected against the background of intense lines of other elements, but the number of nitrogen atoms is indirectly indicated by the number of molecular nitrogen ions, according to the basic mechanism of generation of nitrogen atoms described above. It can also be seen from the results obtained that an increase in the current to both anode sections leads to a monotonous increase in the number of molecular nitrogen ions (Figure 4a). However, if an increase in the I_d current in the range of 10–50 A leads to an increase in the intensities of N_2^+ lines by 25–30%, then an increase in the current per crucible and the concentration of titanium vapors leads to a more significant increase in the number of N_2^+ ions, which may be explained by the processes of recharging titanium ions on atoms and molecules of plasma-forming gases at increased local vapor pressure metal.

In the visible part of the spectrum there are lines of argon ions, lines of the H^* characteristic of the Balmer series (656.2 nm), as well as lines of atomic carbon C^* (357.8 nm), which indicates the

intensive decomposition of C_2H_2 molecules in discharge, and the intensity of these lines, and accordingly the intensity of decomposition, increases both with an increase in the current in the crucible circuit and with an increase in the current to the cooled anode. In [9], acetylene-argon plasma of a low-pressure arc discharge was investigated. As a result, typical plasma chemical reactions occurring in this medium were obtained, and on the basis of experimental data, an appropriate model was constructed and the frequency distribution of reactions of decomposition of acetylene molecules was obtained. According to the calculations obtained, argon ions play a key role in the decomposition of C_2H_2 molecules: $Ar^+ + C_2H_2 \rightarrow Ar + C_2H_2^+$, $C_2H_2^{+,*} + e \rightarrow C_2H + H$ (26%), $\rightarrow C_2 + H + H$ (41%), $\rightarrow 2CH$ (7%), $\rightarrow CH_2 + C$ (26%), $\rightarrow C_2 + H_2$ (0%). The plasma spectroscopy results obtained in our work are in satisfactory agreement with these data. A large number of Ar^+ argon ions are also present in the discharge plasma with SHHC and an active anode, the absence of lines of other acetylene decomposition products (in addition to H^* and C^*) is apparently due to the relatively low intensity of the corresponding lines against the background of strong argon lines.

The dependences of the voltage at the crucible U_{cr}, the electron temperature T_e and the plasma potential φ_a on the current in the crucible circuit I_{cr} are shown in Figure 5. It can be seen from the obtained dependences that an increase in the current to crucible in the range of 2–12 A leads to a significant decrease in T_e from 6.3 to 2.2 eV. This behavior of T_e can be explained by an increase in the metallic component of the plasma, which is characterized by a lower value of the electron temperature. Another reason for the decrease in T_e may be a significant increase in the pressure of the vapor-gas mixture caused by an exponential increase in the vapor pressure of the metal with an increase in the heating power and temperature of the crucible. The same factor can also explain the decrease in plasma potential and the discharge voltage with an increase in the current in the crucible circuit. However, when the I_d current changes in the range of 10–50 A, such a significant change in the temperature of the electrons and the plasma potential does not occur, which is apparently explained by the absence of a significant change in the ratio of the gas and metal components of the plasma, as well as their pressure.

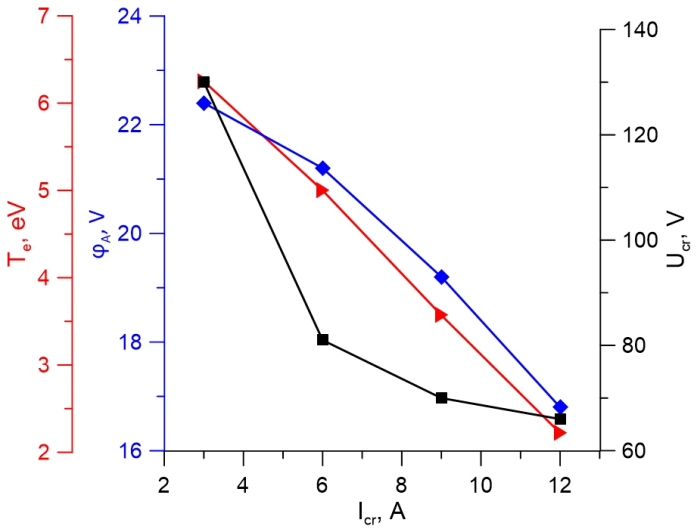

Fig.5. The dependences of the voltage on the crucible U_{cr}, the temperature of the electrons T_e and the plasma potential φ_a on the current in the crucible circuit I_{cr}. Discharge current I_d = 20 A.

4. Conclusion

It is shown that this method of activation of the vapor-gas medium provides, along with the effective decomposition of the organosilicon precursor, a high activation degree of titanium vapor, as well as effective dissociation of nitrogen (the content of atomic nitrogen is 4–6%) and acetylene.

The effect of the operating modes of the sectional anode on the electron temperature and plasma potential is investigated. An increase in the current per crucible in the range of 2–10 A leads to a decrease in the electron temperature from 6 to 2 eV and the plasma potential from 22 to 16 V, while a change in the current in the cooled anode circuit in the range of 10–50 A practically does not affect the electron temperature and plasma potential.

Acknowledgement

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