Spectral analysis of the charge and elemental composition of the vacuum arc discharge plasma flux during deposition of carbon coatings

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Abstract. In the present work spectral analysis of the charge and elemental composition of the plasma flux of a vacuum arc discharge on example of clear dispersion of the graphite cathode and also when adding benzene or argon as a working gas is studied. It is shown that the intensity of the main spectral lines of the atomic and molecular carbon in the emission spectrum of the vacuum arc discharge plasma is almost constant for all considered modes of operation, while the intensity of the spectral lines of ionized carbon changes significantly when adding a working gas.

1. Introduction
Carbon materials and coatings present a great interest in the various fields of science and technology. The unique ability of carbon is an almost infinite number of its condensed forms. One of the most promising technological methods of receiving carbon films and coatings is a vacuum arc discharge that is a high current, self-maintained discharge, growing in a closed volume in the cathode material vapors [1, 2]. The emission center of this discharge is a cathode spot, that is characterized by small dimensions and which is the source of the primary electrons and the base of the arc column [3]. High temperature in the spot causes intensive sputtering of the cathode material and a high concentration of a metal vapor [4–6].

Specificity of a vacuum arc discharge is the fact that the total ion current is only 6…10 % of the value of the discharge current. In the widespread vacuum arc plasma sources of coaxial structure due to the presence of an external axial symmetric magnetic field density distribution of the charged particles in the working volume is not uniform and the maximum of the distribution is located on the axis of the system (figure 1).

2. Features of the vacuum arc discharge affecting the charge composition of the plasma flux
Processes in the arc discharge are divided into:

- generating, occurring in the cathode spot (in the molten layer of a liquid metal) and which have an impact on the cathode surface and the plasma parameters;
- processes in the cathode area, determining the conditions of generation, dynamics of the development and movement of the cathode spots;
• processes in the area of transportation, in other words in the interelectrode space, starting from a region with a strongly nonideal low temperature plasma.

**Figure 1.** Design of a coaxial vacuum arc plasma source: 1 – anode; 2 – cathode; 3 – igniting electrode; 4 – shield; 5, 6 – stabilizing and focusing solenoids; 7 – working volume; 8 – probe or workpiece; 9 – planetary gear mechanism.

Multiple ionization observed in the plasma of a vacuum arc discharge leads to an increase in the average charge of ions and growth of ion beam energy without increase of the accelerating voltage [7–9]. In the cathode area ionization of the plasma stops and there is a stabilization of its parameters. However, it should be noted that in the vacuum arc plasma sources, plasma parameters are changed both in the process of evaporator operation (cathode temperature, discharge current, magnetic field), and when using the working gas which provides the degree of ionization of the plasma flux (argon, helium) and the implementation of the plasmachemical synthesis of compounds (for carbide compounds carbon containing gas is introduced into the plasma flux). Therefore analysis of the charge and elemental composition of the plasma flux in all areas of transportation is a vital task.

Degree of ionization of the erosion products and their charge composition depends not only on the material of the cathode, but also on the mode of operation of the evaporator. The degree of ionization of the vapor of the cathode material is determined by its properties. The proportion of ionized particles in the flux emitted by the surface of the cathode for such materials as carbon, molybdenum and tungsten is 70, 80 and 90 % respectively. With decrease in boiling point of the material this percentage is reduced to 30…50 % for copper and silver, and 15…25 % for cadmium and zinc. Products of the erosion of the cathode contain ions of different degree of charge. Basically there are single, double and triple charged ions. While the more refractory material is (except graphite) the higher the average charge of the ions in the plasma of a vacuum arc discharge.

### 3. Spectral analysis of the charge and elemental composition of the plasma flux

For the determination of the plasma flux composition an emission spectral analyzer on the basis of a modernized one dimensional CCD array Toshiba TCD1304 with 3648 pixels (8×200 μm) was used [10–12]. The investigated range of wavelengths of the plasma was 350…950 nm (optical resolution of the spectrometer is 1 nm). To identify the components that are part of the plasma flux the emission spectra of the arc discharge in the area of the substrate were investigated. Figure 2 shows spectrum of the arc discharge in the visible range obtained in the area of transportation during sputtering of a graphite cathode PGM-6 in vacuum at a pressure of 7.8·10⁻³ Pa and a discharge current of 80 A. Spectral lines show presence of only pure carbon in the plasma flux.

Increase of the discharge current leads to the decrease of the content of charged ions in the flux and growth of the number of singly charged ions. Thus the maximum of the ion energy distribution is shifted towards smaller energies.

For the percentage increase in the carbon component being deposited on the treated surface vapors of benzene (C₆H₆) or another carbon containing gas are introduced into the working volume. In this case to the chemical processes a hydrocarbons decomposition reaction due to the interaction with elements of the plasma flux and by pyrolysis is added. Speed of a chemical reaction is proportional to the current concentration of the reactant products (law of mass action or law of Guldberg and Waage).
Figure 2. Spectrum of the plasma radiation in the process of pure graphite sputtering.

Noticeable decomposition of the aromatic hydrocarbons in the gas phase is observed at the temperatures of about 900 K and more. Under these conditions molecule becomes thermodynamically unstable and decomposes to fragments with a smaller number of atoms or to single atoms. In the gas discharge plasma formation of CH radicals is due to the process of dissociation by a direct electron impact. However the less hydrogen atoms are contained in the molecule the easier is the decomposition of hydrocarbon.

When using benzene vapor splitting of the hydrocarbons with long bonds to molecules of a shorter length with the formation of a whole range of hydrocarbons is as follows:

$$C_6H_6^+ + e \rightarrow C_4H_8^+ + C_3H_6^+ + H_2 \rightarrow C + C_3H_4^+ + H_2^+.$$  

Figure 3 shows spectrum of the plasma radiation during graphite sputtering with the addition of benzene at a pressure of $8.7 \times 10^{-2}$ Pa.

Figure 3. Spectrum of the plasma radiation in the process of graphite sputtering with added benzene.
Introduction of the benzene vapor as a working gas into a plasma flux significantly alters the radiation spectrum. For this spectrum appearance of the Balmer series lines of the atomic hydrogen (Hα and Hβ), line of carbon ion CII and emission spectra of C₂ (Swan band d³Π–a³Π) and CH (Gere band A²Δ–X²Π) molecules is characteristic.

At a temperature of about 2000 K the first radicals of C–H system will be atomic hydrogen and acetylene C₂H₂, concentration of which with further increasing temperature rises dramatically. After 2500 K (temperature of complete decomposition of methane) new radicals CH, C₂H, CH₂ and C₂ emerge, with their quantity increasing with further rise of the temperature. Starting from 3000 K there is a significant amount of monatomic and after 3500 K – diatomic carbon. At temperatures above 3500 K diatomic carbon C₂ and CH reach their maximum concentrations, while the content of C₂ in the system is close to the content of acetylene C₂H₂. Presence of the intense bands of C₂ and CH in the spectrum during pyrolysis (figure 3) shows that the average temperature of a gas according to the equilibrium composition of C–H system is not less than 3000–3500 K.

For maintenance of a stable discharge into the working volume a buffer inert monatomic gas argon (or helium), which do not enter into chemical reactions and form compounds, is often added. The first ionization potential for argon is 15.75 V and for helium – 24.47 V. Due to the chemical reactions the presence of a buffer gas helps to increase the degree of ionization of the plasma flux:

\[ \text{Ar} + e \rightarrow \text{Ar}^+ + e + e; \quad \text{Ar} + e \rightarrow \text{Ar}^+ + e; \quad \text{Ar}^+ + \text{C} \rightarrow \text{Ar} + \text{C}^+ + e + h\nu; \quad \text{Ar}^+ + \text{C} \rightarrow \text{Ar} + \text{C}^+. \]

Figure 4 shows the spectrum of plasma radiation during sputtering graphite with the addition of argon, used as a buffer inert monatomic gas.

![Figure 4. Spectrum of the plasma radiation in the process of graphite sputtering with added argon.](image)

Due to the chemical reactions the presence of a buffer gas helps to increase the degree of ionization of the plasma flux that leads to the appearance on the spectrum of additional lines of carbon (CI, CII, CIII), as well as spectral lines of argon (ArI, ArII).

4. Conclusion

Obtained results show that the intensity of the atomic and molecular lines of carbon is almost constant for all investigated modes of operation, while the intensity of lines of the ionized carbon changes significantly when adding the working gas. Interaction of particles in a dense plasma of a vacuum arc discharge leads to the appearance in the plasma flux of multiply charged ions which would not otherwise emerge due to the lack of energy required for such a degree of ionization.
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