Application of an anti-emission coating of pyrolytic carbon to the grid electrodes of high-power electrovacuum devices by deposition from the gas phase in carbon plasma

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Abstract. A technology for applying an anti-emission pyrocarbon coating by plasma-chemical gas-phase deposition to the grid electrodes of high-power electrovacuum devices has been developed. The plasma of a vacuum-arc discharge from a graphite cathode is simultaneously used for heating the grid electrodes, cleaning the grid electrodes from surface contamination, and for decomposing the reaction gas into active radicals. Experimental studies have shown that the satisfactory structure of the coatings and the adhesion of the coatings to the grid electrodes are provided at the temperature of the grid electrodes in the range from 550 to 1300 °C.

Powerful electrovacuum devices, such as powerful generator lamps, traveling and reverse wave lamps, pulsed and continuous klystrons, magnetrons, and others, have grid electrodes in their design. In the process of operation, the grid nodes located directly in the electron flow zone must provide high thermal dissipation, maintain their geometric characteristics and have a low secondary emission coefficient. The reduction of the thermoelectronic emission of the grids can be achieved by the maximum reduction of their temperature during operation or by achieving the greatest possible work function of the electrons for their surface. The most effective in this case is the use in the manufacture of grid electrodes materials and coatings that have high values of the integral radiation coefficient and work function. One of the most effective materials for this purpose is pyrolytic graphite. The low secondary electron emission of pyrographite is also preserved when evaporation products, including those from the oxide cathode, are deposited on its surface. The «Eimac» company has announced the industrial development of pyrolytic graphite grids for devices operating in the short-wave and ultra-high-frequency ranges. The technology of manufacturing grid electrodes from pyrolytic graphite is complex and requires expensive equipment, large capital expenditures, and high energy consumption. Grid electrodes with a fine-cell structure of some high-power generator lamps can reach a height of several tens of centimeters (figure 1).

Growing blanks for such pyrographite grids by chemical deposition from the gas phase on heated substrates, followed by the creation of a cellular structure by cutting, is a complex task. In connection with the above, it would be more technologically expedient and cost-effective to apply a coating of pyrolytic carbon on the metal grid electrodes currently used in high-power electrovacuum devices. The disadvantage of gas-phase deposition of pyrocarbon is the complexity of the technology, the high...
duration of the process, the high energy costs associated with the need to maintain high temperatures for pyrolysis for a long time, the low content of pyrocarbon in the coating, the low adhesion of pyrocarbon to the surface and the high cost of pyrocarbon coatings. The noted disadvantages can be avoided if the method of plasma-chemical deposition from the gas phase, otherwise called plasma-chemical gas-phase deposition or plasma-stimulated gas-phase deposition, is used for applying the pyrocarbon coating. The use of various methods of plasma excitation in the reaction volume and control of its parameters allows increasing the growth rate of coatings, conducting the film deposition process at significantly lower substrate temperatures, increasing the adhesion of coatings, and making the formation of a required microrelief, structure, and other characteristics of the coating more manageable compared to similar processes in chemical deposition from the gas phase [1]. As a discharge, a glow discharge is usually used, which is initiated by a high-frequency source, but can also be created by AC, DC, or microwave sources.

![Figure 1](image.png)

**Figure 1.** Grid electrodes of high-power generator lamps: (a) – grids of different lamps; (b) – cathode-grid node of the generator lamp in assembly.

In our studies, a vacuum-arc discharge from a graphite cathode was used as the discharge, and acetylene was used as the reaction gas. To carry out the process of forming a pyrocarbon coating on the grids, they were placed in a vacuum chamber and the chamber was pumped out to a pressure no higher than $10^{-3}$ Torr (usually $10^{-3}$–$10^{-6}$ Torr). At this pressure, a vacuum-arc discharge was ignited and the grids were heated to a set temperature in the range of 550–1300 °C using the discharge plasma. Then the reaction gas was injected into the chamber and the pyrolytic carbon was deposited on the grid electrodes. In addition, the plasma of the vacuum-arc discharge itself participates in the formation of a pyrocarbon coating due to the deposition of plasma carbon ions on the surface of the grid electrodes. The noted features of the use of carbon plasma flows of vacuum-arc discharge instead of glow discharge plasma of plasma-forming gas in the formation of pyrocarbon coatings can further reduce the temperature of pyrolysis of hydrocarbons, increase the adhesion of coatings, and increase the deposition rate of pyrocarbon.

The plasma density or the concentration of charge carriers (ions and electrons) in the plasma determines the heating temperature of the grid electrodes, which, in turn, depends on the current of the vacuum-arc discharge, the distance of the grids from the graphite cathode and the angular location of the grid electrodes relative to the plane of the end of the graphite cathode [2]. In addition, the plasma density in the plasma stream can be controlled by the current of the focusing solenoid.

A specific feature of the operation of processing products with a vacuum-arc discharge plasma flow is the increased power output on the product. Let us write down the power balance equation for the treated surface with a unit area, neglecting the specific heat of melting of the applied material:
where \( j_i \) – density of the ion current from the plasma to the treated surface; \( \xi \) – average charge number of an ion in the plasma stream; \( e \) – electron charge; \( U_{bias} \) – negative bias voltage between the surface and the plasma; \( W_i \) – average (taking into account the presence of multicharged ions) ionization energy; \( W_{ev} \) – evaporation energy of the deposited material per atom; \( W_{ik} \) – kinetic energy of the plasma flow (in terms of one ion), due to the acceleration of the plasma in the active zone of the vacuum-arc evaporator and in the cathode spots; \( W_{ek} \) – kinetic energy of a neutral atom; \( \theta \) – accommodation coefficient of neutral atoms on the surface to be treated; \( \sigma \) – Stefan–Boltzmann constant; \( \varepsilon \) – integral emissivity of the surface to be treated together with the coating to be applied; \( T \), \( T_0 \) – surface and ambient temperatures; \( \frac{d^2 N_a}{dSdt} \), \( \frac{d^2 N_{ev}}{dSdt} \) – flux density of neutral atoms on the surface and the flux density of re-evaporated atoms on the surface to be treated, respectively.

If the grid electrodes are not supplied with a voltage relative to the plasma, they will be in the plasma under a floating potential or the potential of an isolated surface in the plasma flow \( U_i \) (this is about \(-3...-10 \) V). The potential of an isolated surface in the plasma flow is calculated based on the equality to zero of the total current of charged particles entering the surface:

\[
U_i = -\frac{kT_e}{e} \ln \left( \sqrt{8kT_e/m} / 4V_{pl} \right),
\]

where \( V_{pl} \) – plasma flow velocity; \( k \) – Boltzmann constant; \( T_e \) – temperature of the electrons in the plasma; \( e \) – electron charge; \( m \) – electron mass.

For an isolated surface, the specific power released on it, taking into account the deposition of ions, can be written as follows:

\[
P^{sp}_{s} \approx j_i (MV_{pl}^2/2\xi e + U_i + W_{ev}/\xi e),
\]

where \( U_i \) – effective value of the ionization potential, taking into account the multicharged ions in the vacuum-arc discharge; \( W_{ev} \) – energy released during the condensation of a single atom \((W_{ev} \sim W_i)\).

If the grid electrodes are connected to the positive voltage source of the vacuum-arc discharge, that is, the grid electrodes will be under the potential of the anode \( U_a \) electrons will be drawn from the plasma by an electric field, and the grid electrodes will be heated to a temperature of \(550–1300\) °C by the electron current.

The power released on the product (grid) located under the potential of the anode is determined by the contribution of the electron and ion components of the plasma, as well as the energy impact from the plasma associated with its radiation and condensation of neutral atoms. For a single surface [2]

\[
P^{sp}_{a} \approx j_a (U_i - \varphi + j_{ca} (\varphi + 2kT/e) + q),
\]

where \( j_a \) – current density of the ions coming from the plasma to the product under the anode potential; \( U_i \) – anode voltage drop; \( \varphi \) – work function of the cathode material of the vacuum-arc evaporator; \( j_{ca} \) – current density of the electrons coming to the product under the anode potential; \( q \) – power density associated with plasma radiation and condensation of the atoms of the cathode material.

The grid electrodes can also be heated by applying a negative bias voltage to them from a power source with a voltage from \(-300\) to \(-1500\) V. In this case, not only the grid electrodes are heated, but also their surface is cleaned by bombarding it with an accelerated flow of ions extracted from the vacuum-arc discharge plasma. At such voltages, the process of spraying the surface of the grid electrodes with the removal of all impurities takes place. This contributes to the creation of conditions for ensuring high adhesion of coatings.

The specific power released on the treated conductive surface, taking into account the deposition of ions, can be written as follows:

\[
P^{sp}_{sp} \approx j_i (U_i + W_{ev}/\xi e),
\]
where \( U_e = \frac{Mv_{ek}^2}{2e} + |U_{bias}| \); \( U_{bias} \) – negative bias voltage on the substrate relative to the plasma. In expression (5), the power released during the condensation of neutral atoms is not taken into account, and it is written under the assumption that the coefficient of condensation of ions is close to one, and \(|U_{bias}| > |U_s|\). The equations presented above can be used to calculate the temperatures to which the grids are heated under various heating methods in carbon plasma flows. Figure 2 shows a photo of a grid in a carbon plasma stream and a grid with a pyrocarbon coating applied.

**Figure 2.** Application of a pyrocarbon coating on the grid electrodes of high-power generator lamps: (a) – grid in a carbon plasma flow; (b) – grid with a pyrocarbon coating.

The structure of the pyrocarbon coating is formed through the so-called growth cone [1], the top of which is located on the substrate, and the axis is directed perpendicular to its surface. Gradually expanding, the bases of the cones fill the entire surface of the substrate, and then the cones turn into cylinders of a columnar structure. As a result, a solid structure of the pyrocarbon coating is formed. In addition, the structure of pyrocarbon depends on the nature of the hydrocarbon and the partial pressure of the gas. This is confirmed, for example, by the kinetic equation of methane decomposition in the presence of a mineral matrix, which is obtained on the basis of experimental data [3]:

\[
W = 0.4 \exp(52200/RT) p^{0.4},
\]

where \( W \) – rate of decomposition of methane; \( p \) – partial pressure of methane, Pa; \( T \) – temperature, K; \( R = 8.31 \) J/(mol·K) – universal gas constant. For acetylene, unlike, for example, methane, the activation energy of embryo formation (143.4 kJ/mol) is slightly higher than the activation energy of crystallite growth (132.6 kJ/mol), which corresponds to a small dependence of the average size of the crystallites on temperature.

Thus, the use of a vacuum-arc discharge from a graphite cathode during the plasma-chemical gas-phase deposition of an anti-emission pyrocarbon coating on the grid electrodes of powerful electrovacuum devices allows simultaneously heating the grid electrodes to a predetermined temperature, activating the reaction gas, and cleaning the surface of the grid electrodes before the deposition of pyrocarbon. This made it possible to reduce the pyrolysis temperature to 550 °C, significantly increase the adhesion of the coating, increase the growth rate of the pyrocarbon coating, reduce the energy consumption of the pyrolysis process and the cost of coatings. The developed technology has been successfully used in the application of a pyrocarbon anti-emission coating on an experimental batch of grids of high-power generator lamps that have passed a full cycle of industrial operation.

**References**

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