OPTICAL AND SPECTROSCOPIC INVESTIGATIONS OF ARC DISCHARGE AT FULLERENE SYNTHESIS

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Abstract. Quasi-periodic time-spatial structure of an arc was found out in a mode of fullerene synthesis. Spatial distributions of the spectral component radiation of arc plasma were studied, and radial profiles of temperature were measured. Mechanism of cathode deposit formation is also discussed.

1. INTRODUCTION

The most perspective approach to study the processes of fullerene formation is an experimental determination of plasma characteristics of the arc between graphite electrodes in inert gases at lowered pressures. Saito and Inagaki (1993) observed only C_2 bands and lines of C and C^+ in emission spectra of such arc. Afanasiev et al. (1994) measured average over discharge gap temperature of plasma by molecular bands of C_2 and CN, and found it to be $T =$ 5000-7000 K, depending on the discharge mode. Similar temperatures were obtained by Huczko et al. (1995) for AC arc. All this results based on assumptions about stability of the arc plasma. However, according to Finkelnburg and Maekker (1961), the DC arc is a non-uniform and non-stationary plasmoid in many operation modes.

The research of pulsation characteristics of carbon arcs at current $I = 60 \div 100$ A and helium pressures $P_0 = 1 \div 500$ Torr was carried out in the present work. The 6 mm rods of pure graphite were used as electrodes, the discharge gap amounted ~5 mm and the arc voltage was $U = 20 \div 40$ V.

2. TIME-SPATIAL STRUCTURE OF THE ARC

The change of shape of electrodes during the discharge is one of possible reasons of the arc plasma instability. Within the first several seconds after arc ignition, relatively uniform layer of carbon deposit is formed on the cathode. At the subsequent discharge stages the deposit is grew on periphery of the cathode end face and its lateral surface. Two areas are distinctly observed in the section of cathode deposit. The internal part of deposit has some millimetres in diameter and represents friable structure, consisting of a mix of nanoparticles, nanotubes and amorphous carbon (see for example Ebbesen and Ajayan (1992)). The hard external metallic-grey shell is formed from needle and sector structures focused mainly in a direction of their growth. For some arc modes there is a hollow crater in the central zone of cathode deposit. The formation of cathode deposit may result in changing the mode of cathode operations and discharge parameters during a work cycle of fullerene synthesis.

The faster processes in the near-electrode regions of discharge result in pulsations of plasma parameters. In the present work, pulsation characteristics were studied with the help of high-speed camera in modes of imaging and continuous scanning with time resolution up to 1 μs. The analysis of obtained data shows, that the considered carbon arc may operate in two modes, distinguished by time-spatial structure. The first mode concerns to the diffuse symmetric stationary arc channel with uniform anode erosion, and other represents non-uniform and non-stationary structure with quasi-periodic pulsations of brightness with frequency 10÷20 kHz. As the high-speed imaging has shown, the diameter of current-conducting channel decreases in this mode, and the channel is bent and continuously displaced in space like moving "spiral" arc, described by Asinovsky et al. (1976).

The transition of arc into non-stationary mode is accompanied by voltage drop of 4÷6 V and by considerable rise of plasmoid brightness. The brightness pulsations correspond to voltage pulsations with amplitude 0.5÷2 V. When increasing the duration of non-stationary stage, the pulsation is increased in frequency and disturbed in periodicity. The mode transition occurs spontaneously every 0.5÷5 ms and does not depend on discharge external parameters. Times of existence of the modes, structure and frequency of pulsations in the non-stationary stage of discharge depend on pressure, kind of gas as well as on arc current. At P_0 = 100 Torr the total duration of non-stationary mode is approximately equal to that of arc in stationary stage. At pressure lower 1 Torr only the non-stationary mode exists.

3. EMISSION SPECTRA OF THE ARC AND PLASMA DIAGNOSTICS

The emission spectra of arc plasma were registered in visible and UV areas by diffraction and prism spectrographs with reverse linear dispersion 6 Å/mm. It was found that spectra do not contain components of radiation of other molecules, except for earlier observable C_2 and CN. In addition to the data of Afanasiev et al. (1994) and Saito and Inagaki (1993), the band near λ = 2320 Å was found out in UV area. This band, according to Landsverk (1939), belongs to molecule C_2 or molecular ion C_2^+. It is necessary to note also registration of the line of carbon double ion at λ = 2296 Å.

The intensities of spectral component have approximately identical distributions over the arc radius. The distinctions are observed in distributions over length of discharge. Molecule CN radiates approximately equally over whole discharge gap. For bands C_2 and lines of carbon atoms and ions, the maxima of radiation are observed in near-electrode regions. The intensity of C_2 near the anode is much higher than that near the cathode, and the radiation of ions is located in cathode region in the main. The molecular band close λ = 2320 Å emitted mainly near the cathode.

In the present work the radial distributions of arc temperature were measured in approximation of stationary equilibrium plasma. The radial distributions of spectral emissivity were calculated by Abel inversion of registered integrated chordal intensities. The measurements were carried out by Fowler-Milne method from band edges of C_2 5165 and 4737 Å for arc cross-section at distance ~1 mm from the anode at initial helium pressure in the chamber P_0 = 1 and 100 Torr. The results of measurements by different molecular bands are well consistent. Instrumental uncertainty of temperature determination does not exceed 10%. Maximal plasma temperature was found to be T = 4100 and 4500 K, for initial helium pressure P_0 = 1 and 100 Torr respectively. Temperature of plasma monotonously falls down to periphery of the discharge. The temperature profile at P_0 = 1 Torr lies below by ~500 K relatively the profile at P_0 = 100 Torr.

4. DISCUSSION

The results of performed optical and spectroscopic investigations of the arc discharge in fullerene synthesis mode may be interpreted in view of properties of plasma with carbon particles as follows.

The plasma parameters are determined by processes at electrodes. The electrons, emitted by the heated up cathode, ionize the gas at collisions. The formed ions under action of an electrical field are directed to the cathode and take part in creation of deposit on its surface. According to Abrahamson (1974) the important role in the cathode deposit formation may belong to carbon crystallites arising from erosion of the anode. When heating in plasma the crystallites get a positive charge due to thermoemission. Thus, the cathode deposit is a result of deposition of the ions and positively charged carbon particles, accelerated by an electrical field, as well as of physical and chemical transformations during high temperature growth and subsequent cooling.

Instability of arc in question is substantially caused by a competition of physical processes under entering of carbon vapour and particles from the anode into the arc and removing them from a zone of the discharge. At small content of carbon atoms and crystallites in plasma, the quasi-periodic fluctuations of plasma arise from development of overheating instability, described by Alexandrov and Ruhadze (1976). This accompanied by contraction of cylindrical arc channel into spiral-like one with an anode spot formation, that lead to rising of input energy density on the anode surface. The increase of erosive flow results in rising the plasma thermal conductivity, therefore the overheating instability is dumped and non-stationary arc passes into the stationary mode. The increase of electron emission due to heated carbon particles reduces the current density near anode and also promotes the suppression of overheating instability. The arc mode transition repeats repeatedly during all time of the arc discharge existence.

The obtained emission spectra of the arc appear to be superposition of spectra of plasma both in stationary and non-stationary modes. The molecules C_2 and CN are the coolest components of plasma of considered discharge. Their radiation may be attributed to the stationary mode with uniform anode erosion. The excitation of ion lines in spectra is apparently due to increase of temperature in the non-stationary arc. Thus, it is possible to assume that measured radial temperature distributions correspond to the stationary mode of arc discharge.

The obtained information on processes in carbon arc at the lowered pressure of helium should be taken into account when measuring the plasma parameters, developing the models of fullerene formation in the arc and designing the reactors for fullerene synthesis.

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