On the reasons of spatial heterogeneity of the plasma chemical composition in ablation controlled discharges

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Abstract. The reasons of spatial heterogeneity of the plasma chemical composition in ablation controlled discharges are analyzed. The “locking” of atoms of chemical elements with a low ionization potential in the vicinity of a negatively charged wall due to the backflow of a significant fraction of ionized atoms onto the wall is considered as one of the effective mechanisms of plasma demixing and change of its chemical composition in comparison with the initial stoichiometry of the ablating substance. The proposed approach is consistent with the results of spectroscopic studies of a capillary discharge with an ablating wall (polymethylmethacrylate), during which a significant decrease in the carbon mole fraction with a simultaneous increase in the hydrogen mole fraction in the discharge core was revealed. According to the obtained results, the physical processes leading to the spatial separation of chemical elements occur exactly in the capillary spatial domain. The observed demixing of the plasma jet is mainly a consequence of the processes that take place inside the capillary.

1. Introduction
In most cases of scientific and practical applications of gas discharge physics, it is necessary to deal with plasma of complex chemical composition. The behavior of atoms and ions can vary greatly for different chemical elements, their concentrations can depend on coordinates and time in different manner. As a result, the stoichiometric composition of the plasma may differ from the initial composition of the plasma-forming substance. The main reasons for the change in plasma stoichiometry of stationary discharges are the processes of concentration, thermo-, baro- and ambipolar diffusion [1,2]. These processes, however, can hardly noticeably influence the discharge stoichiometry in high-speed flows, when the diffusion times significantly exceed the gas exchange time. Such conditions can arise in discharges where the plasma is created on the surface, such as: vacuum arcs, ablation controlled discharges (capillary discharges with an evaporating wall and/or electrodes [3,4], magnetoplasma ablation accelerators [5,6], laser ablation discharges [7]), etc. The ablation process and plasma parameters are interconnected in these discharges and substantially determined by the plasma-wall interaction.

The modern approaches to describing ablation [8–12] are based on the kinetic model, first formulated in [13], according to which a part of the vaporized atoms returns back to the wall due to collisions at the interface between the Knudsen and hydrodynamic layers. As a result, a layer of particles is deposited on the surface, which subsequently reevaporates. The ablation rate, eventually, is determined by the balance between evaporation and condensation, and is much lower than the values determined by the saturated vapor pressure [14].
The kinetic model is widely used to describe the ablation of substances both of simple and complex chemical composition, providing good qualitative and quantitative agreement with the experiment [10]. Its latest modifications take into account the temperature dependences of the ablating substance component composition and its effective molar mass, including the thermal and ionization non-equilibrium conditions, which can significantly improve quantitative agreement with experiment [12]. However, none of the kinetic model modifications takes into account the dynamics of partial flows, which can vary significantly for different sorts of particles. The importance of the partial flows dynamics account is especially relevant when considering the ablation of chemically complex substances. Such, in particular, are carbon-containing polymers (polyethylene, polymethylmethacrylate, fluoroplast, etc.), which serve as a source of the working fluid in ablation controlled discharges. The spatial separation of various chemicals is observed in these discharges, that results, in particular, in the carbon deposition on the ablating surface [5,6,9]. In [9], this circumstance is taken into account by introducing the artificial assumption according to which only the carbon atoms and ions are deposited on the surface, while the volatile components (hydrogen atoms and ions) are desorbed and enter the discharge volume. This assumption, however, does not clarify the physics of the processes responsible for the chemical elements separation, which in general case differ in mass and ionization potential.

2. The role of partial flows of charged particles in the separation of chemical elements with different ionization potentials

The possible approach to solving the problem of separation of chemical elements in multicomponent plasma, in our opinion, is to take into account the flows of charged particles that inevitably arise when plasma becomes into contact with a surface. In a capillary discharge, such a surface is the capillary wall, which acquires an excess negative charge upon contact with the plasma. The potential of an isolated wall relative to the plasma is about $\varphi = -\frac{kT_e}{e} \ln \frac{m_i}{m_e} \sim -10 \, V$. A layer of positive space charge adjacent to the wall retards the electrons and accelerates ions, which moves from the plasma onto the wall against the flow of vaporized atoms. Therefore, if the ablation substance is ionized near the wall, where the ion-accelerating electric field is strong enough, then not all evaporated atoms can enter the bulk plasma. Some of them being ionized return back to the wall, where they recombines, reevaporates, ionizes again, return to the wall, etc. (Figure 1).

To estimate the fraction of atoms returning to the wall, one can use the expressions for the density of ion backflow onto the wall in the Bohm approximation

$$J_i = \frac{j_i}{e} = n_i \sqrt{kT_e/m_i} \quad (1)$$

and for the density of the flow of vaporized atoms, in accordance with the Hertz-Knudsen equation [14]

$$J_a = n_a v_a = \frac{p_{sat}}{\sqrt{2\pi m_a k T_e}}, \quad (2)$$

where $p_{sat}$ – saturated vapor pressure of the ablating wall substance, $T_i$ – temperature of the wall surface, $T_e$ – electron temperature, $m_i$, $m_a$ – masses of ion and atom ($m_i=m_a$), $k$ – the Boltzmann constant, $n_i$ and $v_a$ – concentration and velocity of the flow of evaporated atoms, $j_i$ – ion flux density from plasma onto the wall, $e$ – electron charge. Taking into account the fact that the saturated vapor pressure of the wall substance does not much different from the plasma pressure inside the capillary, $p_{sat} \approx p_{cap}$, and considering the simplest case of a single-ionized plasma $\alpha=n_e/(n_i+n_a)=1$, for which the approximate equality $p_{cap} \approx 2n_e kT_e$ is fulfilled, using equations (1) and (2) we obtain the relation for estimating the fraction of evaporated atoms returning to the wall

$$\frac{j_i}{j_a} \approx \frac{\sqrt{2T_e}}{\sqrt{2T_i}} \quad (3)$$
It can be seen that in the range of electron temperatures on the capillary axis, $T_e = 1.5-3 \, eV$ [4,15], and wall temperatures $T_s = 600-700 \, K$ corresponding to saturated vapor pressure $p = 1-10 \, bar$ of commonly used polymeric materials (polyethylene [16], polymethylmethacrylate), the fraction of vaporized atoms that, being ionized, return back to the wall, is significant $J_i/J_a = 0.2-0.3$. 

![Diagram](image.png)

**Figure 1.** Scheme explaining the separation of chemical elements during the ablation of the polymeric wall. The ion backflow from the plasma onto the wall consists mainly of carbon ions, whose ionization boundary is located closer to the wall than the ionization boundary of hydrogen and oxygen atoms.

A similar scenario was considered in [17] for a plasma whose chemical composition is determined by a single chemical element. If the ablating substance includes more than one chemical element, the different sorts of atoms will ionized at different distances from the wall, depending on the ionization potential and local electron temperature. For definiteness, the position of the layer corresponding to the onset of intense ionization of atoms of a given chemical element will be called "the ionization boundary". In this case, the ion backflow of easily ionizable chemical element will be prevail, whose ionization boundary is located closer to the wall in the region of relatively high electric field intensity. The carbon atoms act as easily ionizable component in carbon-containing polymers, whose ionization potential is lower than for hydrogen and oxygen. If the electron temperature near the wall does not fall below $1 \, eV$ [16], which corresponds to the onset of intense carbon ionization, then most of the ionized carbon atoms will return back to the wall. The contribution of the remaining components (hydrogen and oxygen) to the ion backflow will be the lower, the farther from the wall their ionization boundaries are located (Figure 1). It seems that the described scenario plays an important role in the separation of chemical elements and, as a consequence, a change in the stoichiometric composition of erosive plasma compared with the initial chemical composition of the ablating substance.
3. Plasma chemical composition in the axial zone of capillary discharge

The deviation of the chemical composition of the plasma of a pulsed capillary discharge from the initial stoichiometry of the ablating wall substance we noted in [4]. This, in particular, is manifested in the preferential localization of hydrogen in the paraxial zone, and of carbon and its derivatives (C₂, CN, etc.) at the discharge periphery. The capillary arrester with following parameters used in these experiments [4]: the capillary diameter – 1 mm, the capillary depth – 5 mm, the energy storage in capacitor – Q=80 J, the discharge pulse duration – τ=9 ms, the algorithm of discharge current – sine half-wave, the discharge current amplitude – Iₓₘₓ=60-80 A. The mass loss of the capillary wall substance is ∆m≈0.4-0.5 mg per discharge pulse that is approximately 100 times greater than the initial mass of air inside the capillary at atmospheric pressure (~4 μg). Therefore, the chemical composition of the plasma inside the capillary and in the initial jet section is completely determined by the decomposition products of the polymer C₃H₅O₂, more than half of which (~53%) is the hydrogen.

The plasma chemical composition can be determined by using the spectral diagnostics. We used an AvaSpec UL-2048 fiber-optic spectrometer to record the plasma emission spectra of the discharge core inside and outside the capillary with different time delays relative to the discharge beginning. To do this, a sharp enlarged image of the discharge was projected onto the screen, wherein the entrance of the spectrometer fiber-optic cable was placed (Figure 2). The size of the discharge spatial domain projected onto the fiber optic cable entrance, taking into account the selected projection scale, does not exceed 0.5 mm.

![Figure 2. General view of the projection of an enlarged image of a capillary discharge on a screen: (1) the anode, (2) the capillary boundary, (3) the plasma jet, (4) positions of the AvaSpec UL-2048 spectrometer fiber-optic cable entrance.](image)

A typical emission spectrum of a discharge core is shown in Figure 3. The main portion of the plasma emission belongs to the line and molecular spectra including the well-resolved lines of the hydrogen Balmer series – Hα, Hβ, Hγ, the atomic carbon lines and the Swan band system of the C₂ radical (the capillary wall material), the lines of the excited atoms of copper (the internal electrode material) and aluminum (the external electrode material), the lines of the excited atoms of oxygen, and the violet system of the CN radical bands - the result of the interaction of polymer decomposition products with atoms and molecules of ambient air.

Although the absolute values of the intensities of the observed spectral lines and molecular bands are absent, the measurements of their relative intensities make it possible to estimate ratios of total local concentrations of plasma components in the studied spatial domain – [H]/[C], [H]/[O]. For this purpose, we used the lines of the hydrogen Balmer series - Hα and Hβ, the carbon line CI (477 nm, 493.2 nm, 505.2 nm) and the oxygen line OI (777.4 nm). The spatial positions and the length of their glow region were also taken into account, because these intensities are integrated along the line of sight (along the “chord”), whose length for the discharge core (atomic particles) and for the shell is about 1 mm. The spectral intensities of these emitters, measured in relative units, are used as initial data for calculating the equilibrium plasma composition [18]. Based on the results of this calculation, the ratio of the measured concentration of a given chemical element [X] to the concentration corresponding to the initial stoichiometry of the ablating substance [X]₀ – δ(X)=|X|/|X|₀ (we will call this parameter as “demixing factor”) is determined. The basis for this calculation is the fulfillment of the conditions of thermal (Tᵣ=Tᵣ₀) and Saha-Boltzmann equilibrium for the plasma in the discharge core [4].
Figure 3. Typical emission spectrum of a discharge core obtained by means of the AvaSpec-UL2048 spectrometer; exposure time is 2 ms.

The performed estimates show that the chemical composition of the plasma in the discharge core differs significantly from the initial stoichiometric composition of the ablating wall substance both inside and outside the capillary (in the initial jet section). The concentrations of carbon and hydrogen change most strongly: the mole fraction of carbon decreases by 3-4 times, and the mole fraction of hydrogen increases by 1.2-1.5 times relative to the initial stoichiometry corresponding to formula C₅H₈O₂ (Figure 4). Inside the capillary, the mole fraction of oxygen is not much different from the original stoichiometry (Figure 4 (a)). A slight increase in the mole fraction of oxygen in the jet section (Figure 4 (b)) is apparently due to its influx into the discharge region from the surrounding atmosphere (air).

Figure 4. Temporal dynamics of the plasma constituents in the paraxial zone of discharge (a) inside and (b) outside the capillary. δ(X)=[X]/[X₀] - demixing factors for hydrogen, carbon, and oxygen, [X], [X₀] – concentrations (or mole fractions) of the X-th element estimations based on spectral data, and corresponding to the original stoichiometry of the ablating substance C₅H₈O₂, respectively.
As for the temporal dynamics of the plasma chemical composition, it turns out to be somewhat different inside and outside the capillary. In the region inside the capillary, the plasma composition in the discharge core, which differs from the original stoichiometry, is established almost immediately after discharge ignition and remains almost unchanged during the main discharge stage (Figure 4 (a)). A different trend is observed in the initial section of the jet (Figure 4 (b)). Here, in the first moments after the discharge ignition, the plasma chemical composition is close to the original stoichiometry of the ablating substance, and then changes approximately in accordance with the discharge power algorithm (the sine half-wave). In both cases, at the final discharge stage, the plasma chemical composition becomes close to the original stoichiometry of the ablating substance. Note, that the strongest deviation from the original stoichiometry always takes place in the region inside the capillary.

The discovered features indicate that the physical processes leading to the spatial separation of chemical elements occur exactly in the capillary spatial domain. The observed non-stoichiometricity of the plasma jet is only a consequence of these processes. The possible reason for the change in the plasma chemical composition, in our opinion, is the "locking" of a significant fraction of the atoms of chemical elements with a low ionization potential in the vicinity of a negatively charged wall. In our case, these are the carbon atoms \( I_C = 11.26 \text{ eV} \). The oxygen and hydrogen atoms with close ionization potentials \( I_O \approx 13.6 \text{ eV} \), as follows from the experimental results, are much less prone to "locking", because their ionization boundary is located much further from the wall than that for the carbon atoms.

4. Conclusions
The reasons of spatial heterogeneity of the chemical composition of the plasma in ablation controlled discharges are analyzed. The "locking" of atoms of chemical elements with a low ionization potential in the vicinity of a negatively charged wall due to the backflow of a significant fraction of ionized atoms onto the wall is considered as one of the effective mechanisms of plasma demixing and change of its chemical composition in comparison with the initial stoichiometry of the ablating substance. Atoms with a higher ionization potential are less prone to "locking", since they begin to ionize farther from the wall, where the conditions for the ion backflow onto the wall are less favorable. The proposed approach is consistent with the experimental results of the authors who observed plasma demixing in ablation controlled discharges, as well as with the results of spectroscopic studies of capillary discharge plasma, during which a significant decrease in the carbon fraction with a simultaneous increase in the hydrogen fraction in the discharge core was found. According to the obtained results, the spatial separation of chemical elements occurs exactly inside the capillary. The observed demixing of the plasma jet is mainly a consequence of the processes that take place inside the capillary.

The obtained results indicate the important role of the ionization processes of the ablating substance in the formation of the plasma chemical composition and the necessity of accounting the partial flows of particles with different ionization potentials when modeling the dynamics of multicomponent plasma of the ablation controlled discharges.

We do not exclude the influence of diffusion processes (concentration, thermo-, baro- and ambipolar) on plasma demixing. These processes can be quite significant at low flow velocities, what is the case for the boundary layer adjacent to the capillary wall. The role of diffusion processes in plasma demixing will be the subject of future research.

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