Spectroscopic determination of the composition and spatial distribution of active particles in a plasma jet of helium and argon being blown out into atmospheric air

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Abstract. Optical emission spectroscopy was used to determine the composition and spatial distribution of reactive species along a non-thermal plasma jet in a stream of argon and helium, expanding in the ambient air. It was shown that the composition and spatial distribution of reactive species in argon and helium plasma jets differ significantly. The geometric dimensions of the Ar and He plasma jets are also noticeably different. The features of the observed patterns of the composition and spatial distribution of active particles are discussed.

1. Introduction

Non-thermal plasma jets generated in inert gases at atmospheric pressure are widely used for many applications from surface modification to medicine and biotechnology [1-6]. One of the attractive features of plasma jets for practice is their ability to process targets at a distance. When plasma jets flow into the ambient air, many plasma chemical processes occur. As a result, the initial composition and concentration of reactive species formed in the discharge zone change markedly along the length of the plasma jet. In the case when the plasma jet impinging onto liquid or solid targets the evolution processes of the initial reactive species can significantly change compared to the free jet, both due to changes in the structure of the gas stream and the composition of the environment, as well as changes in the electrophysical processes occurring in the plasma jet [7-11]. Knowledge of the reactive species composition in the treatment zone is necessary to achieve the desired treatment effect in the shortest time. In most cases, argon and helium are used as plasma-forming gases in the formation of plasma jets. The physical characteristics of these gases, such as ionization potential, current density in the discharge, energy of metastable states, thermal conductivity, density, etc. are significantly different from each other. For example, the density of helium is about 10 times lower than the density of argon. This means that at the same flow velocity the flow regimes and, accordingly, the exchange rate with the surrounding air in the helium and argon jets will be different. It can be expected that in this case the composition and spatial distribution of reactive species in the helium and argon jets will noticeably differ. In addition to scientific interest, a comparison of the properties of an argon and helium jet is also of great economic importance — argon is much cheaper than helium.

In this paper, the results of experimental optical studies on the composition and spatial distribution of reactive species in excited states and gas temperature in an argon and helium jet are presented. It should be noted that the reactivity of particles in excited states due to the supply of internal energy is
significantly higher than that of particles in the ground state. In this case, the distributions of particles in the ground and excited states along the plasma jet can differ markedly. The effect of a liquid target on the composition and spatial distribution of active excited particles in an argon plasma jet is studied.

2. Experimental setup

Plasma jets were generated by a dielectric barrier discharge (DBD) excited by a sinusoidal voltage with a frequency of 100 kHz in gas flow of high purity argon and helium. The velocity of plasmaforming gases was varied within V = 5-110 m/s. The discharge was ignited in a quartz tube with inner and outer diameters of 2.5 mm and 4 mm, respectively. The DBD electrode system consisted of a metal rod 1 mm in diameter, which was fixed on the axis of the tube, and a strip of copper foil 20 mm long wrapped around the outer surface of the tube. The distance from the edge of the electrode system to the exit of the quartz tube was 8 mm. A saline with a specific conductivity of σ = 16 mS/ cm poured into a glass container was used as a liquid target located at a distance of 22 mm from the tube exit. The plasma jet images were taken by digital camera Canon EOS 550 with the exposure time down to 10^{-4} s. Experimental studies of the composition of reactive excited species, the temperature of a neutral gas, and the evolution of these parameters along a plasma jet were carried out by optical emission spectroscopy. Spectroscopic studies were performed using two fiber optic spectrometers AvaSpec-2048FT-6-RM (range λ = 230-810 nm, spectral resolution Δλ = 0.1 nm) and AvaSpec-2048FT-L (range λ = 200-1110 nm, spectral resolution Δλ = 1 nm). Along with spectral studies, measurements of the electrical characteristics of the discharge were performed: current, voltage, and power consumption. The applied high voltage was measured by HV divider PINTEK HVP-39 (1000:1, 40 kV, 200 MHz). The discharge current was measured by a low-inductive shunt with resistance of 50 Ohm. All electrical signals were recorded by the digital oscilloscopes Tektronix DPO2024 with bandwidth of 200 MHz. The current and voltage waveforms were used to calculate the average discharge power. Figure 1 shows a diagram of experimental setup for DBD plasma jet generation in a gas flow (a), as well as a visual picture of a plasma jet in an argon flow freely being blown out into ambient air (b) and directed into a glass vessel without liquid (c) and with liquid (d).

Figure 1. Diagram of experimental setup for generation of DBD and plasma jet in an argon flow (a). A visual picture of a plasma jet in an argon flow freely being blown out into ambient air (b) and directed into a glass vessel without liquid (c) and with liquid (d). The flow velocity V = 55 m/s (b), V = 40 m/s (c, d). The voltage amplitude is U = 5 kV, the exposure time is 0.02 s.

3. Experimental results and discussion

The overview plasma emission spectrum at the DBD output in the argon flow (a) and, as an example, the spectrum of the hydroxy radical OH in the region λ = 309 nm at different distances from the DBD output (b) is shown in figure2. Here, the plasma jet position x is defined as the distance from the quartz tube outlet (as shown in Fig.1). It is seen that there are spectral lines of atomic oxygen O, molecular nitrogen and OH hydroxyl radical in addition to the lines of argon atoms in the plasma...
emission spectrum at the discharge exit (i.e. inside the quartz tube). According to the passport, high-purity argon contains nitrogen at the level of 10 ppm, oxygen at the level of 2 ppm and water vapor at the level of 3 ppm.

![Emission spectrum at the discharge exit](image)

Figure 2. The emission spectrum of a plasma jet in argon at the exit of discharge (a) and OH radical spectrum at various points of the jet (b). U = 5kV, V = 55 m/s.

The results of measurements of the spatial distribution of the emission of a number of excited species along the length of the plasma jet being blown out into the free ambient air are presented in Figure 3.

![Spatial distribution of emission](image)

Figure 3. Distribution of the intensity of the spectral lines of excited Ar atoms (λ=763.5 nm, 4s–4p) (a), N₂ molecules (λ=337.1 nm, C²Πu, ν=0→ B²Πg, ν=0) (b), OH radicals (λ=309 nm, A²∑⁺, ν=0→ X²Π, ν=0) (c) and O atoms (λ=777.4 nm, 3s -3p) (d) along the plasma jet. Argon, U = 5 kV, V = 55 m/s.

As can be seen, the density of excited argon atoms monotonically decreases with increasing distance from the discharge exit. At the same time, excited nitrogen molecules, OH hydroxyl radical and oxygen atoms show non-monotonic behavior along the plasma jet propagation. The most probable reason for this non-monotonic behavior is the diffusion of molecules of the ambient air (N₂, O₂, H₂O) into the argon stream, which are excited by streamers propagating through the plasma jet.
Figure 4 shows the current and voltage waveforms of the DBD in argon flow (a) and the distribution of the vibrational and rotational (translational) temperatures (b) of nitrogen molecules along the argon plasma jet. The second positive system of $N_2 (C^3Π_u → B^3Π_g (v' - v'' = 0-2)$ transition) was used to determine the rotation and vibration temperature in plasma jet using the SpecAir code [12]. It should be noted that under conditions where the population of the excited state $N_2 (C^3Π_u)$ occurs by direct electron impact from the ground state $N_2 (X)$ and at a high vibrational temperature $N_2 (X) T_{vib} ≥ 3000K$, the vibrational temperature in the excited state $N_2 (C^3Π_u)$ is close to vibrational temperature of the ground state $N_2 (X)$ [13]. As can be seen from the presented results, the translational temperature of the gas is quite high at the discharge outlet, however, at a distance of 7-10 mm from the outlet of the quartz tube it becomes close to room temperature.

![Figure 4](image1.png)

**Figure 4.** The typical current and voltage waveforms of DBD (a) and distribution of the rotation and vibration temperature of excited $N_2(C^3Π_u)$ molecules along the plasma jet (b). Argon, $U = 4.2$ kV, $V = 55$ m/s, discharge power $P = 7$W.

Figure 5 shows the emission spectra of argon plasma jet directed into a glass vessel without liquid (a) and with liquid filled (b). The optical scheme of the measurements in both cases was the same.

![Figure 5](image2.png)

**Figure 5.** The emission spectrum of argon plasma jet directed into a glass vessel without liquid (a) and with liquid (b). The emission was collected from a point located at a distance of 4 mm from the liquid surface. The distance from the tube outlet to the liquid surface is 22 mm. $U = 5$ kV, $V = 40$ m/s

As can be seen from the presented figures, as well as from figure 1 (c, d), the presence of a conducting liquid significantly increased the total (integral) emission intensity of the plasma jet. A detailed comparison of spectra 5 (a) and 5 (b) shows that the greatest increase in the emission intensity is observed for the OH radical (about 5 times), while for argon atoms it increased 2.3 times, and for a nitrogen molecule - 1.4 times.

The visual picture of a plasma jet in a helium flow freely being blown out into ambient air, the typical current and voltage waveforms of DBD in helium and the distribution of the vibrational and rotational (translational) temperatures of nitrogen molecules in the excited state $N_2 (C^3Π_u)$ along the plasma jet are presented in Figure 6. As can be seen from a comparison of Figures 1 (b) and 6 (a) at
the same gas flow velocities, the length of the plasma jet in helium significantly exceeds the length of the plasma jet in argon. It should also be noted that the gas temperature in the helium plasma jet is lower than that in argon. This is due both to the high thermal conductivity of helium and to a noticeably lower electric power of the barrier discharge in helium (about two times) compared to DBD in argon.

![Figure 6](image.jpg)

**Figure 6.** A visual picture of a plasma jet in He flow freely being blown out into ambient air (a), the typical current and voltage waveforms of DBD in helium flow (b) and distribution of the rotation (1) and vibration (2) temperature of excited N₂ (C³Π_u) molecules along the plasma jet (c). The flow velocity \( V = 55 \text{ m/s} \). The voltage amplitude is \( U = 3.2 \text{ kV} \), electric power \( P = 3.5 \text{ W} \), \( f = 100 \text{ kHz} \), the exposure time is 0.05 s.

The overview emission spectrum of a free plasma jet in a helium flow at the exit of the barrier discharge (a) and at a distance of 35 mm from the exit of the DBD (b) is shown in Fig. 7. As follows from the presented figures, there are multiple spectral lines of oxygen atoms O, hydrogen atoms H, molecular nitrogen and OH hydroxyl radical in addition to the lines of helium atoms in the spectrum of the plasma emission at the discharge exit. Comparing Fig. 7a and Fig. 2a, it should be noted the presence of intense emission of the N₂⁺ ion in the spectrum of the helium jet, which is absent in the spectrum of the argon plasma jet. One of the probable reasons for this is the important role of metastable atoms of helium and its ions in the mechanism of generation of the excited state of the N₂⁺. The important role of metastable helium atoms and ions in the mechanism of generation of an excited N₂⁺(B) in a discharge in helium with nitrogen (air) impurities has been noted by many authors [14-17]. The best known are two channels involving helium metastables and ions:

- Penning ionization \( \text{He}^{+} + \text{N}_2 \rightarrow \text{He} + \text{N}_2^+(B) \), \( k = 7.0 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1} \).
- Charge transfer \( \text{He}^{+} / \text{He}^2^+ + \text{N}_2 \rightarrow \text{He} / 2\text{He} + \text{N}_2^+(B) \), \( k = 5.0 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \).

Taking into account that the concentrations of charged and metastable particles in a helium discharge are at the level of \( 10^{13} \text{ - } 10^{14} \text{cm}^3 \) and \( 10^{12} \text{cm}^3 \), respectively, [16], it can be seen that these channels can give a high rate of generation of an excited ion N₂⁺(B). Another possible reason is the higher electron energy in helium compared to argon at the same voltage. It is difficult to estimate this channel without numerical simulation, since in our experiments the operating voltage in argon was noticeably higher than in helium.

It should also indicate the high intensity of the emission of oxygen atoms.
Figure 7. The emission spectrum of a free plasma jet in He flow at the discharge exit (a) and at a distance of 35 mm from the discharge exit. U = 3kV, V = 55 m / s.

The results of measurements of the distribution of the emission of some reactive excited species along the length of the plasma jet in a helium stream blown into the free ambient air are presented in figure 8 (a, b). As can be seen from Fig. 8, the emission of excited nitrogen molecules and oxygen atoms along the plasma jet of helium, as well as in an argon jet (Fig. 3), exhibit non-monotonic behavior. At the same time, the emission of the hydroxyl radical OH in a helium plasma jet monotonically decreases with distance, in contrast to the argon plasma jet. It should be noted the non-monotonic behavior of the N$_2^+$ ion emission in He plasma jet.

Figure 8. Distribution of the emission intensity of the spectral lines from excited OH radicals ($\lambda=309$ nm, $A^3\Sigma^+_u, v=0 \rightarrow X^2\Pi, v=0$) (a), N$_2$ molecules ($\lambda=337.1$ nm, $C^3\Pi_{ua}, v=0 \rightarrow B^3\Pi_{us}, v=0$) (a), N$_2^+$ ($\lambda=391.4$ nm, $B^2\Sigma^+_u, v=0 \rightarrow X^2\Sigma^+_g, v=0$) (b), He atoms ($\lambda=706.5$ nm, 3s -2p) (b) and O atoms ($\lambda=777.4$ nm, 3s - 3p) (b) species along a plasma jet. Helium, U = 3kV, V = 55 m / s.

Figure 9 shows the distribution of ozone concentration along the length of the plasma jet in the flow of a gas mixture of helium + 1% oxygen measured from the IR absorption spectra of the outlet gas. It should be noted that in the flow of pure helium and argon (without adding oxygen), the sensitivity of our equipment was not enough to record the presence of ozone in the plasma jet.
Figure 9. Distribution of ozone concentration along the length of the plasma jet. Mixture He+1% O\(_2\), \(U = 4.8\) kV, \(V = 40\) m / s.

4. Conclusion

We have investigated the composition and spatial distribution of reactive species in excited states, as well as the gas temperature along the length of a plasma jet in argon and helium flow, blown into the ambient air. The electrical characteristics of dielectric barrier discharges of sinusoidal high frequency (\(f = 100\) kHz) in Ar and He flow were also studied. It has been established that in the plasma jets of both gases there are excited atoms, molecules and radicals, which are of considerable interest for various practical applications. It was found that the composition of reactive species in the helium plasma jet is richer than in the argon jet. Excited nitrogen ions and excited hydrogen atoms are present in the helium plasma jet, which are absent in the argon jet. The emission intensity of the excited OH radical, as well as the gas temperature, is higher in argon plasma jet compared with a helium jet. The length of the plasma jet in the helium flow is significantly (several times) longer than the length of the plasma jet in argon at the same flow velocities. Our results will be useful in choosing the type of plasma jet for specific applications.

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