Generation of atmospheric pressure plasma in molecular gas flows

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Abstract. We have investigated an atmospheric pressure discharge, similar to a plasma jet, in the N₂ and CO₂ gas flows. We have also carried out an experimental modeling with the argon Ar flow. It has been shown that the use of a tantalum cathode and a copper anode provides a stable discharge in the nitrogen and carbon dioxide flows. We have studied the dependence of the discharge voltage on the discharge current (VAC). Optical emission spectra of discharge glow was investigated also. Using a single probe and a thermocouple, we have studied the axial distribution of the floating potential in the plasma jet and the gas temperature at the anode nozzle exit of the plasma generator. In applying to polymer surface modification, we have determined the optimal operation conditions: gas flow rate up to 5 l min⁻¹; continuous or pulsed working regime; discharge current about 80 mA; pulse duration up to 10 µs; pulse repetition rate 50 kHz.

1. Introduction
Investigation of electrical discharges in the nitrogen and argon gas flows are of interest in studying plasma generation for the purpose of creating a dense active media to treat polymer surfaces [1], as well as for supporting conversion of carbon dioxide contained in active gas mixtures [2]. To this end, the barrier discharge is the most widely applied technique [3]. There are known works that have researched discharges that use the classical point-plane type electrode system [4]. The discharge plasma-jet based systems are less commonly engaged for this purpose. The reason for that may lie in small size of plasma volume: these type of sources can generate a several centimeter long plasma formation with a diameter up to 1 cm [5]. Stability of the plasma jet and perseverance of the discharge regarding transition to the arc regime strongly depend on the type of plasma-forming gas [6]. Coaxial high-current plasma generators are distinguished for their stability and efficiency [7]. However, such devices generate a thermodynamically equilibrium plasma, whereby the gas temperature of several thousand Kelvins makes it almost impossible to treat low-temperature resistant materials. All indicated plasma generators share the same principles of ionization, excitation and heating of the gas molecules flowing through electrodes of their discharge systems. In the present work, we have researched a plasma generator that
is based on a low-current (at the level of 100 mA) and sufficiently high-voltage (burning voltage being at the level of hundreds volts) discharge at atmospheric pressure in the carbon dioxide, nitrogen, and argon gas flows. With the selected discharge parameters, the plasma generator supports a stable temperature regime and a long run time.

2. Experimental setup
The skim of plasma generator is shown on figure 1. Insulator 3 is the core assembly part of the generator. Inside it there are installed contact base 4 of current input 6, anode 7, and anode insert 9. To study the effect of the cathode material on the discharge parameters, we used cylindrical electrodes 8 and inserts 9 made of copper, aluminum, stainless steel and tantalum. The diameter of cathodes 8 was 6.5 mm. Their surface had a conical shape on the side facing the output window. The curvature radius at the vertex was 0.2 mm. The output window in electrode 8 had a diameter 2.5 mm. The shortest distance between the point of electrode 8 and the aperture edge in electrode 9 was no greater than 1.5 mm. The discharge was stable at the gas flow rate $Q$ 1–5 min$^{-1}$. For a wide range the discharge current and regardless of the flow rate, the plasma formation seen by the naked eye had an elongated loop shape stretching for no more than 8 mm from the aperture edge to the inflection point. So the plasma generation processes were studied beyond the output aperture in the anode insert, where the working gas flow was mixing with ordinary air at normal atmospheric pressure. The discharge was electrically fed by a source of DC or pulsed voltage with an amplitude up to 2000 V. The current was limited by a 10 kΩ ballast resistor. The voltage was measured using a 1:1000 high-voltage probe Tektronix P6015A, the current was measured using a low inductance shunt resistor 50 Ω. The signals from the voltage probe and the shunt were input to a Tektronix MDO3024 oscilloscope. The gas discharge plasma glow was analyzed using an optical spectrometer USB2000 Ocean Optics.

3. Experimental results and discussion
3.1. Discharge parameters
In the continuous regime of voltage pulse repetitions, the voltage applied to the discharge system electrodes initiated discharge at the beginning of each pulse at 1000 V, 850 V и 300 V for respectively CO$_2$, N$_2$ and Ar (figure 2). It should be noted that the delay of the leading edge of the discharge current pulse relative to the ignition voltage depends on the type of working gas. The maximum delay time
about 2 µs was observed in the experiment with carbon dioxide. The delay for the nitrogen flow was somewhat greater than 0.1 µs. During the discharge in argon, the current increase occurred practically simultaneously with the voltage. This may be a consequence of simultaneous excitation of both molecular vibrations and ionization. Since atomic argon does not have vibrational degrees of freedom, the energy supplied to the discharge by the power source is more effectively spent on ionization. As a result, the discharge current grows faster at the pulse leading edge for argon than for nitrogen or carbon dioxide. When maintaining the discharge current at a constant level, the burning voltage $U_d$ also depended on the type of working gas. For example, at the discharge current $I_d = 80$ mA, during the steady mode, 4 µs after the discharge initiation, $U_d$ was about 680 V, 530 V, and 230 V for respectively CO₂, N₂, and Ar flows.

Figure 2. Oscillograms of the discharge current and voltage in the flows of argon, nitrogen, and carbon dioxide. Flow rate $Q$ up to 5 min⁻¹, $f = 50$ kHz, $\tau = 8$ µs.

Figure 3. Dependence of the discharge burning voltage on the discharge current for the flows of argon, nitrogen, and carbon dioxide. Flow rate $Q$ up to 5 min⁻¹, $f = 50$ kHz, $\tau = 8$ µs.
The experimental dependences of the discharge burning voltage on the discharge current are shown in figure 3. Curves plotted in the current range 60 to 100 mA behave differently. For the discharge in the argon flow, the burning voltage is about 230 V and practically does not depend on the current. For nitrogen, the voltage $U_d$ grows almost linearly from 560 to 670 V. The dependence of $U_d$ in the CO$_2$ flow decreases from 740 V to 630 V in the current range 55 mA to 70 mA, has a weakly expressed minimum at the discharge current about 80 mA and slightly increases to 700 V with current increasing to 95 mA.

Basing on the classical volt-ampere curve of the gas discharge [8], the dependence of $U_d$ on the current in the argon flow corresponds to an ordinary glow discharge when the burning voltage is mainly determined by the drop of potential in the cathode layer and remains constant for a wide range of the discharge current at a constant current density on the cathode. The discharge VAC in the nitrogen flow probably corresponds to the section of the classical curve that describes transition to the anomalous burning regime when for supporting the self-maintained discharge current the cathode voltage drop increases with increasing cathode current density. Since the dependence of $U_d$ on the current in the carbon dioxide flow has a minimum, it probably includes the sections corresponding to subnormal, normal, and anomalous working regimes of the glow discharge.

3.2. Influence of electrode materials
Stability of discharge characteristics and its lifetime in the nitrogen and carbon dioxide flows are determined by the type of electrode material used in the plasma generator. The discharge running time before extinction for a copper cathode, as well as for an anode made of aluminum, brass, or stainless steel, was no more than several seconds since triggering. It was caused by high chemical activity of the selected gases, which in combination with high temperature was conducive to formation of dielectric films on active surfaces of the electrodes.

The use of a tantalum cathode and a copper anode insert press-fit into a bulky aluminum holder produced a positive effect. High thermal conductivity of copper and the holder, serving as a radiator, provided an effective cooling of the anode. Interaction of tantalum with carbon dioxide at elevated temperature, while preserving the electrical conductivity of its surface, is apparently driven by the balance between the growth processes and the erosion of inert oxide film [9]. Tantalum interacting with nitrogen at high temperature forms titanium nitride, which is electrically highly conductive [10].

3.3. Optical emission spectra
To provide a quality analysis of the processes occurring in atmospheric pressure discharge plasma, we have studied optical spectra of the optical emission of the positive discharge column and the plasma-jet afterglow. It should be noted that the measurements were integral with the averaging over 300 ms. The input aperture of a flexible optical fiber was located at a distance 1.5 cm off the discharge system axis at the edge of the anode nozzle at an angle of about 75° relative to this axis (figure 1). So the cathode active surface was located in the geometric shadow of the shielding plate. When operating under the discharge conditions in the nitrogen and carbon dioxide flows, the hot surface of the cathode emitted highly intensive continuum from 450 nm to 800 nm, and the use of the plate prevented this radiation to interfere with measurements.

The optical radiation spectrum for the discharge in the argon flow at the discharge current from 40 to 150 mA is shown in figure 4a. The spectrum contains lines of exited argon atoms [11]. The presence of a line band with a 20 % intensity of maximum, corresponding to the second positive nitrogen group, is due to excitation of molecular vibrations by the electron impact occurring in the discharge plasma at the edge of the output aperture.

Figure 4b shows optical radiation spectrum for the discharge in the nitrogen flow. The spectral lines for the case of nitrogen are mostly the lines belonging to the N$_2$ system of the second positive transition ($C^3\Pi_u ^+ - B^3\Pi_g ^+$). There are also observed less intensive peaks of the N$_2^+$ first negative system ($B^3\Sigma_u ^+ - X^3\Sigma_g ^+$) [12]. The line band in the range from 540 nm to 760 nm indicates the presence of NO$_2$ molecules formed as a result of nitrogen oxidation.
The optical spectrum observed for carbon dioxide used a plasma-forming media is shown in figure 4c. There are observed in this spectrum the lines corresponding to the CO2 dissociation products, such as atomic oxygen, triatomic oxygen, atomic carbon, CO molecules and C2 radicals [13].

3.4. Temperature distribution

We have studied the distributions of the gas temperature (figure 5) along the axis of the discharge system. The local temperature was measured using a thermocouple. The thermal EMF was measure by a digital voltmeter. The thermocouple and the voltmeter were under applied floating potential relative to the discharge system electrodes. Thus the presence of a metal object in the immediate plasma vicinity did not perturb the discharge. In the experiment, we made sure to supply approximately the same average discharge power at the level of 50 W to burn the discharge for all of the three gas flows.

Since the discharge voltage greatly differ for the flows, the power was set by changing the discharge current. In the steady state mode, the values of $U_d$ and $I_d$ were about 700 V and 70 mA for the discharge in CO2; 520 V and 95 mA for the discharge in N2; and 245 V and 192 mA for the discharge in Ar. The dependences in figure 5a show that gas temperature in the discharge decreases as moving away from the inflexion point of the positive column, which was set to be the reference point and where the maximal temperature was observed. Figure 5b shows dependence of the reduced temperature $T/T_0$ on the distance, where $T$ is the local point temperature and $T_0$ is the maximal temperature. Hereby it is possible to estimate the temperature gradients characteristic for discharges in the flows of the selected gases. In the present experiment, the maximal temperature was observed for nitrogen. For each of the gases, the temperature dropped to 0.38 of the maximum at a distance 10 mm. The experimentally established significant difference between the temperatures of the gasses heated by passing through the discharge ($T_0 = 977, 746, \text{ and } 342$ degrees of Celsius for N2, CO2, and Ar) arises from the fact that when using

Figure 4. Optical radiation spectrum for the plasma generator operating: a – in the argon flow at $U_d = 230 \text{ V}, I_d = 40–150 \text{ mA} \ (Q = \text{up to } 5 \text{ min}^{-1}, f = 50 \text{ kHz}, \tau = 8 \text{ µs});$ b – in the nitrogen flow. $U_d = 530 \text{ V}, I_d = 40–100 \text{ mA} \ (Q = \text{up to } 5 \text{ min}^{-1}, f = 50 \text{ kHz}, \tau = 8 \text{ µs});$ c – in the carbon dioxide flow. $U_d = 680 \text{ V}, I_d = 45–95 \text{ mA} \ (Q = \text{up to } 5 \text{ min}^{-1}, f = 50 \text{ kHz}, \tau = 8 \text{ µs}).$
molecular gases, the neutral gas molecules acquire energy not only in the electron collisions but also through the energy stored in the vibrational states of polyatomic molecules [8].

Figure 5. Dependence of the gas temperature on the distance along the plasma generator axis: a – absolute values; b – reduced valued. $Q = \text{up to } 5 \text{ min}^{-1}, f = 50 \text{ kHz}, \tau = 8 \mu\text{s}$.

3.5. Floating potential distribution
In order to determine the geometric size of the generated plasma formation, we have studied the distributions the floating potential (figure 6) along the axis of the discharge system. The dependence of the floating potential on the distance was studied using a cylindrical probe made of tungsten wire with a diameter 0.7 mm inserted in a ceramic tube. The length of the wire section that collected the charged particles was about 1 mm.

A floating potential relative to the discharge system electrodes was applied to the probe. The probe potential relative to the reference electrode (the grounded anode) was measured reading the probe signal attenuated by 10 times and delivered through the oscilloscope probe to its input. The oscilloscope internal resistance was 100 MΩ. Being placed near plasma, the probe was charging to the potential determinable by the flow of charged particles from plasma. It should be noted that measurements of the floating potential were carried out under a continuous discharge regime because the electromagnetic interference induced by the time-variable voltage significantly distorted the useful signal.

Figure 6a shows absolute values of the floating potential measured during the discharge burning with the selected gas flows. Figure 6b shows the dependence of the floating potential relative value $\phi/\phi_0$, where $\phi$ is a local point potential, $\phi_0$ is the maximal potential measured at the reference point. The inflexion point of the discharge positive column was taken as a reference point (figure 1, 11).

Thus the potential distribution can be used to estimate the length of the plasma jet. It follows that under conditions of the present experiment, the plasma formation generated in the CO$_2$ flow was the shortest, less than 8 mm. The longest length, up to 14 mm, was observed for the nitrogen flow. It also follows from figure 6b that for argon and nitrogen the floating potential distribution is more uniform as compared to the case of carbon dioxide. The studied set of distributions can be used to make estimates required for the plasma treatment of plane surfaces. Namely, at what distance the samples surface must be placed so that it would come into contact with the plasma and to what temperature the surface will heat up.

3.6. Surface treatment
This plasma generator was used for modification of the nitrile butadiene rubber (NBR) surface modification. A few testing samples were treated at the discharge in Ar and CO$_2$ flows. The conditions of treatment for each gas were the next: gas flow rate up to 5 min$^{-1}$; pulsed discharge working mode;
discharge current about 80 mA; pulse duration 8 µs; pulse repetition rate 50 kHz. The experimental samples were exposure in the immediate contact with plasma at the inflexion point of the discharge positive column. Exposition time was 10 min. For homogeneous treatment samples were axially rotated and stepwise displaced in the direction perpendicular to the axis of rotation.

![Figure 6](image_url)

**Figure 6.** Dependence of the floating potential on the distance along the plasma generator axis: a – absolute values; b – reduced values. \( Q = \) up to 5 min\(^{-1}\), DC mode.

After plasma treatment, the friction coefficient of NBR samples surfaces were studied by using dry friction on a “TRIBOtechnic” ball-on-disk tribometer with a hard WC–Co ball of diameter 6 mm. The conditions were the following: room temperature, relative humidity 50 %, normal indenter load 1 N, sliding velocity 0.5 cm\( \cdot \)s\(^{-1}\), track diameter 2 mm, sliding distance 10 m.

The friction coefficient of initial NBR was about 0.6 and the specific wear rate \( 3.48 \times 10^{-3} \) mm\(^3\)(N\( \cdot \)m\(^{-1}\)). After argon plasma treatment these parameters reminded almost the same: 0.63 and \( 2.43 \times 10^{-3} \) mm\(^3\)(N\( \cdot \)m\(^{-1}\)). But after treatment in CO\(_2\) plasma, friction coefficient and specific wear rate becomes 0.13 and \( 1.58 \times 10^{-3} \) mm\(^3\)(N\( \cdot \)m\(^{-1}\)).

In comparison with argon plasma, this difference consists in the presence of active radicals in the plasma discharge in carbon dioxide, which modify the molecular composition of the polymer surface. The effects of heated gas should also not be excluded. When NBR sample was treated by argon plasma, the local temperature in contact point was about 400 °C. In case of CO\(_2\) the temperature was near 600 °C.

4. Conclusion

We have experimentally investigated the working specifics of the atmospheric discharge plasma generator with a tantalum cathode and a copper anode in the nitrogen, carbon dioxide, and argon flows. In has been shown that in the current range 40 to 100 mA, the generator works in the glow discharge mode.

Analysis of optical spectra has revealed the traces of the working gas molecules (N\(_2\) and CO\(_2\)) and their derivatives (NO\(_2\), CO, C, C\(_2\), O, O\(_3\)) formed as a result of reactions occurring in the discharge plasma. The absence of spectral traces of metals, constituting cathode and anode materials, indirectly testifies to the glowing character of the discharge under study and the absence of transition to the spark discharge [14].

Based on the spatial distributions of the gas temperature and the floating potential, we have determined the jet lengths of the decaying plasma generated in the selected range of the discharge current using N\(_2\), CO\(_2\), and Ar.

The obtained results can be useful for studying the effects of atmospheric pressure plasma on surfaces of polymeric materials, applied to wear reducing.
Acknowledgments
The reported study was under project No 19-48-700019-r_a. Investigation on treatment of NBR surface by atmospheric pressure plasma was funded by RFBR and NSFC according to the research project No 19-58-53001.
Authors are thankful to Dr. Elizaveta Petrikova, Institute of High Current Electronics SB RAS for help in tribology investigations of experimental samples.

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