Steady – state and pulsed – periodical regimes for generation of non – thermal plasma jets at atmospheric pressure

N. Trushkin(*), Yu. Akishev, M. Grushin, V. Karalnik and A. Petryakov

SRC RF TRINITI, Troitsk, Moscow region, Russia
(*) e mail: trushkin@triniti.ru

Experimental results and numerical calculations on the detailed search of the properties of non-equilibrium constricted dc glow discharges in N_2 flow and the pulse–periodical spark are presented. These two types of discharge were used for generation of plasma jets. Different current modes of the constricted dc discharge in N_2 were found. It is established that the generation of a long (≈20 cm) luminous afterglow by constricted dc discharge occurs only in a specific current mode. The mechanism of the discharge generation and the plasma parameters are determined in this current mode. The main active agents of the plasma jet generated by a pulse-periodical spark are established. Conjoint action of different agents provides synergy effect in a modification or bio-inactivation of the surface to be treated. Potential applications of generated plasma jets are discussed.

1. Introduction

Atmospheric pressure (AP) non-thermal plasma (NTP) jets are widely used for dry and cold remote treatment of different two- or three-dimensional objects to provide their surface modification, bio-decontamination or sterilization of microorganisms, etc (cold treatment means that average gas temperature in plasma jet at the target is close to room temperature). NTP itself is a gaseous mixture containing a wide spectrum of bio-chemically active agents, specific types of which depend on plasma forming gas mixture. As a rule, plasma active agents are the charged particles (energetic electrons and positive and negative ions), free radicals and atoms like OH and O, excited nitrogen and oxygen molecules, molecular and atomic metastables, ozone, ultra-violet radiation, etc. AP NTP is generated with different kinds of AP electric discharges such as DBD, MW-, RF-, AC-discharges, pulsed and steady-state glow discharges. AP gas discharge generators (GDG) forming NTP jets can be divided into three groups which fundamentally differ from each other by principles used for plasma jet formation.

The fist group includes GDGs forming a steady-state plasma jet. In this case a NTP is created inside the generators, and thereafter the NTP is blown out continuously by flow of the plasma forming gas. In GDGs of the second group a NTP is created outside the generators due to fast ionization waves periodically propagating from the outlet of generator inside a narrow jet of plasma forming gas (as a rule, He). Note that in the literature these ionization waves often are called “plasma bullets” but in reality the plasma itself does not move with high speed – fast movement belongs to the ionization wave creating plasma. The third group comprises the GDGs based on the use of a pulsed-periodical high-current spark excited in a small cylindrical volume. In the case of pulsed-periodical spark generator (PPSG), plasma is periodically produced by spark with little portions of short duration. Active plasma is transported to the target not by a jet of the plasma forming gas but due to the strong expansion of the gas rapidly heated in small volume by spark. Continuous blowing through GDG is required only to recover the gap for the next pulse. So the plasma jet formed by GDG of the third group is not continuous but consists of a sequence of plasma clouds (real “plasma bullets”) rapidly flying out the generator.

In this paper we present the experimental and theoretical results on detailed search of the properties of plasma jets formed by the generators of the first and the third groups.

2. Non-equilibrium constricted DC glow discharge in N_2 flow – a new type of gas discharge for generation a steady – state plasma jet

The interest in nitrogen as a plasma forming gas is the result of many factors, principally its unique ability to accumulate huge energy in vibration, electronic (metastables) and dissociated (atomic) states providing high chemical reactivity of the activated nitrogen. All active particles mentioned above have a long lifetime, and they can therefore be transported a long distance away from the place of their generation.

The DC pin-to-plane discharge was generated inside quartz tube of wide diameter. Flow of high purity nitrogen (purity is 99,999%) was directed along axis from a pin (cathode) to plane (anode). The cathode was fabricated of tungsten 3mm rod sharpened conically. The anode was made of a fine-meshed metallic grid having geometrical transparency of 75%. Inter-electrode gap was 15mm. During the experiments, averaged in time discharge voltage and current were recorded to get a Volt-Ampere Characteristic (VAC). Besides, the waveforms of voltage and current were recorded to trace their real time behavior at different paths of the VAC. These data were complemented with photographs of the discharge at very short exposition time and spectroscopic measurements of translational and vibration gas temperatures at different discharge currents.

The side view of pin-to-plane discharges in turbulent flow of nitrogen changes depending on the average discharge current I. At low current (I<1-2 mA) the discharge is not constricted, and the inter-electrode gap is dimly lighted. At currents 20 > I >1-2 мA the discharge is constricted, unsteady and looks with a naked eye like a yellow-pink thin filament fluctuating quickly transverse to the discharge axis in limits of 1mm. At higher currents (I≥20 mA) the discharge is also constricted but the current filament and glow spot on the cathode are not moving in space and are oriented strictly along the discharge axis. The intensity of yellow-pink emission from filament strongly increases with the average current, and blue halo appears around yellow-pink filament.

Generation of the stationary long-length plasma jet occurs at a discharge current I≥20 mA. Current density and plasma density in high current constricted discharge (HCCD) are equaled approximately to 4-6 A/cm^2 and $(2\text{-}3)x10^{12}$ cm^{-3} respectively. The reduced electric field E/N in this discharge is equal to E/N ≈ 40-65 Td. This value of E/N is not yet enough to provide the charged particle balance between electron impact ionization and electron-ion dissociative recombination. The first positive system 1^+, second positive system 2^+ and first negative system 1^- give the biggest contribution to the total discharge emission. Besides, there are weak bands of the CN radical. The rotation T_r and vibration T_v temperatures strongly depend on the discharge current. With increasing current both temperatures, T_r and T_v, tend to approach each other. This means a gradual transition of the CGD to the state with thermodynamic equilibrium close to that of an arc discharge. However, blowing of the CGD results in an appearance of the NTP which is characterized by a strong deviation from thermodynamic equilibrium at the currents up to 30-40 mA. In this work a numerical modelling of the steady-state regimes of the constricted discharge in N_2 flow at atmospheric pressure was performed. The main goal was to identify the basic elementary processes influencing the dynamic balance of energy and charged particles in the constricted discharge at current I = 40 mA. The 1D model takes into consideration 49 elementary processes that influence the gas heating and cooling, excitation and de-excitation of vibrational and electronic states of N_2, generation and loss of the charged particles due to direct, stepwise and associative ionization, ambipolar diffusion and volume electron–ion recombination. The model also treats the conversion of molecular ions into atomic ones. According to calculations the main ions in the hot constricted discharge are atomic N^+ ions. This circumstance changes drastically the charged particle balance in the discharge because the recombination coefficient of atomic ions is much lower than that of molecular ions. Because of this, the plasma losses in the central hot region of the constricted discharge are determined predominantly by radial ambipolar diffusion. Once atomic ions come to the cold peripheral region, they turn quickly to molecular ions which recombine immediately with electrons. The width of the cold region where conversion and recombination occur is very thin (about 0.5 mm) and situated far (1.5mm of distance) from the wall of the tube. Hence, the places of 'birth' and 'death' for every electron–ion pair are separated in space. In other words, the charged particles dynamic balance in the hot plasma channel is non-local. Due to this, HCCD in the N_2 flow at atmospheric pressure is similar to the low current diffusive glow discharge in the tube at low pressure. However, in the case of the HCCD, the role of the plasma absorbing 'wall' is played not by the real wall of the tube but by a thin cylindrical layer of cold gas surrounding the HCPC where intensive plasma recombination occurs. It is established that two processes of associative ionization

$N_2(A) + N_2(a) \rightarrow N^+{}_4 + e,$

$N_2(a) + N_2(a) \rightarrow N^+{}_4(X) + e$

are dominant in the charged particles generation in the constricted discharge in the N_2 flow.

The composition of active species generated by HCCD plasma-jet source and the distribution of these species along the plasma jet were determined from spectroscopic measurements. It is interesting to note that despite the high purity of nitrogen (99.999%) used as plasma forming gas the light emission in spectral lines does not correlate with the emission from the excited states of nitrogen itself. The very small impurities of radicals CN and NH give the main contribution to the light emission from active N_2 plasma jets at atmospheric pressure. It means that small impurities in pure gas can strongly influence on the efficiency of the plasma treatment. It was established that the light emission at short distances from the nozzle is caused, mainly, by radicals CN and NH while at the longer distances (10 mm or more) the essential contribution to the plasma emission is made by NO (γ-band).

3. Pulsed-periodical spark generator forming non-equilibrium fast-moving plasma clouds

A self-running pulsed-periodical spark discharge was excited in a small cylindrical volume with typical sizes of 5 mm in a diameter and 5 mm in the length. We used a pin-to-ring electrode system with a pin rounded hemisphericaly (but not conically). The pin (anode) was fabricated of W. Ring electrode (cathode) was fabricated of either Al or stainless steel. Our previous investigations on spark development found out that the best parameters of spark plasma can be achieved if the spark gap is stressed under strong overvoltage. In such a case the spark develops very quickly and the release time of energy in gas from the energy storing capacitor is the shortest. The energy loaded in the spark is around of 1 J per pulse. Strong overvoltage was achieved by using both a pin rounded hemisphericaly and an additional spark gap in the external circuit added in series to the main gas gap. It allowed us to increase an overvoltage up to 12-14 kV and decrease the discharging time to 4 μs due to diminishing the capacitance C up to 33 nF Besides, the hemisphericaly rounded pin provides a longer life time for shape of high-voltage electrode and therefore stable discharge parameters compared to the case of acute conically electrodes. Owing to the findings mentioned above our pin-to-ring pulsed-periodical generator is able to operate steadily for a long time in self-running regime at repetition frequency 3 – 30 Hz. The working gases were N_2 (mainly) and air, but in principle it is possible to use any gas mixture (He and Ar as well) at atmospheric pressure.

PPSG is a typical non-linear dissipative system in which the relaxation oscillations are self-sustained by an external energy source. The period of these oscillations is determined predominantly by the RC characteristic time of the charging of energy storing capacitor C up to spark breakdown voltage. The maximum amplitude of the spark current in our experiments was equal to 500 A, minimum resistance of spark channel is equal to 2 Ohm. Taking into account a longitudinal dimension of spark gap (5 mm) and assuming that diameter of hot core of spark plasma column is 3.5 mm, one can estimate that 2 Ohm of resistance corresponds to conductivity of an equilibrium hot plasma $\sigma \approx 1$ $Ohm^{-1}cm^{-1}$. In the case of air and N_2 as plasma forming gases such conductivity can be realized in spark channel at high temperature about of 6000 K. The same temperature is obtained in the calculation of fast gas heating (V=const) due to the deposition of energy of 1 J into the volume pointed above. Note that despite the huge amplitudes of instant current and voltage, the average current and voltage drop across gap the in pulsed-periodical spark generator are low: $\langle I \rangle$=10 mA and $\langle U \rangle$=2.3 kV. A reason is that the duration of spark itself (about of 3.5 μs) is much shorter in comparison with total period (350 ms) of the relaxation oscillations.

Fast spark heating of gas inside the gap acts like an explosion creating high gas pressure. Because spark gap is open at one end, this high gas pressure will force out a stream of hot plasma (plasma cloud). To prove an existence of plasma clouds flying out from the PPSG outlet and their free transportation towards the target, we performed the experiments on recording total light passed through a narrow slit in opaque screen that was parallel with a proposed trajectory of plasma cloud. It was established that for each point of the plasma cloud trajectory there is a clearly defined time delay between the spark current pulse and the appearance of the light emitted from the flying plasma cloud. As the plasma cloud moves away from the PPSG the cloud loses both the velocity and the light emission intensity and increases in size. We have recorded spectra of the light collected from two directions separately: along the plasma cloud trajectory (longitudinally) and transverse (perpendicularly) to this trajectory. It is obtained that there is a weak plasma cloud emission in the atomic lines (N and O) at the PPSG outlet, but the atomic lines and molecular bands of the plasma forming gas are practically absent in the spectrum at a long distance from the outlet. One can conclude that the luminescence (glowing) of the plasma cloud outside the PPSG is sustained owing to light emission in lines of atoms of the cathode material. So that the spark erosion of the cathode material influences the optical properties of the plasma clouds formed by PPSG. Because of the high instant temperature inside the spark gap it is reasonably to expect that the instant temperature in the plasma cloud flying out from the PPSG will be also high. We have determined spectroscopically the instant temperature in the plasma cloud at different distances away from the PPSG outlet. Instant temperature was determined from Boltzmann plot for Fe atomic lines (λ = 404.58, 406.35 and 427.17 nm). It was established that instant temperature decreases with the distance from PPSG, but nevertheless it remains still high (it is more than a thousand Kelvin degrees). Does it mean that hot plasma clouds cannot be applied for treatment of thermal non-resistant materials? It is not so, because of two reasons: the amount of energy contained in a single cloud as well as ratio τ_1/τ_2 are too small (~0.1 J and ~10^{-3} respectively), where τ_1 is typical time for existence in cloud of high temperature (~100μs) and

τ_2 is typical period of the relaxation oscillations (~100ms). Due to these circumstances an average temperature at the place activated by hot clouds will be low. We mean that target activation over each period of the relaxation oscillations can be divided into three stages, each of them characterized by specific active agents. The conjoint action of these agents creates a synergy effect and increases the efficiency of PPSG at processing of different objects. The first stage is short (about of 3 μs) and correlates with the spark breakdown; the target is activated intensively by splash of UV-radiation. The second stage occurs in several tens of μs after the spark and correlates with arrival of plasma cloud onto the target; this stage lasts about several tens of μs; the target is activated by transient high gas temperature and acoustic shock wave. Third stage comes after fast cooling gas in plasma cloud down to room temperature and lasts about several hundreds of μs; the target is activated at this stage by long-lived chemically active species like atoms, metastables, radicals, vibration excited molecules, etc (for instance, the lines of O, N and OH, NO were registered in the emission spectrum of plasma clouds). In the course of third stage of PPSG treatment, cold active plasma species interact with the target already pre-activated by intensive UV radiation at the first stage and transient high gas temperature at the second stage. Besides, there is also small gas-dynamic impact of plasma cloud on the target. Taken together, it provides synergy effect and markedly increases the total efficiency of NTP-treatment by the PPSG compared to NTP processing by steady-state cold plasma jet.

4. Conclusion

Non-equilibrium constricted dc glow discharges in turbulent flows of nitrogen at atmospheric pressure exhibit several different current regimes, which are absent in the glow discharge in gas at rest. The charged particles' dynamic balance in the HCCD is sustained mainly by two processes: associative ionization and ambipolar diffusion of atomic ions from the hot centre to the cold periphery. It is shown that the HCCD in nitrogen flow is a promising NTP source for generation of plasma jets.

Pin-to-ring PPSG works at a repetition frequency of 3 - 30 Hz and activates an object to be treated with intensive flashes of UV-radiation and plasma clouds at high transient temperatures. There are three stages in the activation of a target in each period of the oscillations. The conjoint action of different agents at three stages provides a synergy effect in modification or bio-inactivation of the surface to be treated. The existence of atoms of the cathode material in the plasma cloud can be useful for some applications like selective deposition or implantation at atmospheric pressure of specific atoms onto/into the substrate.

Ackowledgment

This work was performed with partial financial support by RFBR (grant No 12-02-01198a).

References

[1] Yu. Akishev, M. Grushin, V. Karalnik, A. Petryakov and N. Trushkin, *J. Phys. D: Appl. Phys.*43 (2010) 075202 (11pp).

[2] D. Dudek, N. Bibinov, J. Engemann and P. Awakowicz, *J. Phys. D: Appl. Phys.*40 (2007) 7367 -7371.

[3] M. Teschke, J. Kedzierski, E.G. Finantu – Dinu, D. Korzes and J. Engemann, *IEEE Trans. Plasma Sci.*33 (2005) 310-1.

[4] N. Mericam – Bourdet, M. Laroussi, A. Begum and E. Karakas, *J. Phys. D: Appl. Phys.*42 (2009) 055207 (7pp).

[5] Q. Xiong, A.Y. Nikiforov, X. P. Lu and C. Leys, *J. Phys. D: Appl. Phys.*43 (2010) 415201 (10pp).

[6] G.V. Naidis, *J. Phys. D: Appl. Phys.*44 (2011) 215203 (5pp).

[7] B. Z. Cybik, J.T. Wilkerson, K.R. Grossman, *AIAA Meeting* (Portland, USA, 2004) 2004-2131.

[8] Yu. Akishev, M. Grushin, V. Karalnik, A. Petryakov, N. Trushkin, V. Kholodenko, V. Chugunov, I. Irkhina, E. Kobzev, N. Zhirkova and G. Kireev, *Pure and Applied Chemistry,*80 (2008) 1953 -1969.

[9] D. Dobrynin, K. Arjunan, A. Fridman, G. Friedman, A. Morss Clyne, *J. Phys. D: Appl. Phys.*44 (2011) 075201 (10pp).