Ion composition of nitrogen plasma jet with carbon admixture

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Abstract. With the aim of studying nitrogen plasma flow impacting graphite surfaces, we investigated the evolution of a plasma jet moving from the nozzle of the plasma torch to the target. The motion is accompanied by a decrease in temperature from 10 to 7 kK with a loss of ≈ 60% of the deposited energy and an increase in the density of carbon-containing impurities with partial preservation of the local thermodynamic equilibrium. The main reactions are thermal processes of the formation and decomposition of molecules, dissociative recombination and recharging of nitrogen ions. In the presence of carbon impurities, this set is supplemented with the substitution reaction $\text{C} + \text{N}_2 \leftrightarrow \text{CN} + \text{N}$, electron-collision processes of stepwise ionization and recombination, and a whole ion-molecular cascades of reloads and substitutions. It has been established that a small admixture of carbon ($\sim 0.1\%$) manifests itself only in ion-molecular kinetics, increasing the electron concentration, determining the ionic composition of the plasma, and thereby violating the equilibrium between its neutral and charged components. This leads, in particular, to the recombination nonequilibrium distribution of carbon atoms over electronic states. Other carbon-containing impurities (CN and $\text{C}_2$) are not significant.

1. Introduction

Studying the service life and the nature of destruction of heat-resistant materials is an urgent task. The most effective research method is to expose the sample to conditions similar to atmospheric entry using a direct current plasma torch [1–4]. This leads to the need of studying inhomogeneous plasma with time-varying composition due to ablation of the sample material [1,3,5,6]. The features of isotropic and anisotropic graphite sample destruction by exposure to an atmospheric pressure nitrogen plasma jet were experimentally studied in [6–8]. This work studies interaction between a nitrogen plasma jet with the surface of fine-grained dense graphite sample [7,8] under atmospheric conditions. In particular, spatial and temporal changes in the composition and parameters of the plasma will be shown, which receives carbon-containing impurities throughout the experiment. Figure 1 shows the experiment setup.

In order to register optical emission spectra of the plasma with near-surface region spatial resolution of 20–50 µm we utilize two recording systems:

- MS5204i high-resolution spectrometer with “Andor” charge-coupled device (CCD) matrix attached to its output performs registration of two-dimensional images of plasma emission spectra of a given spectral region with $X$ being the location in space, $Y$ being the wavelength with 0.2 nm resolution and pixel intensity corresponding to emission spectra intensity at...
Figure 1. Experimental setup schema: 1—sample; 2—plasma jet; 3, 4—high-speed cameras; 5, 6—interference filters; 7—ultra-high-speed camera; 8—control system; 9, 10, 16—condensers; 11, 12—optical fibers; 13—AvaSpec 2048 spectrometer; 14—AvaSpec 3648 spectrometer; 15—MS5204i spectrometer with “Andor” camera matrix.

A single-channel optical fiber spectrometer AvaSpec 3648 monitors optical emission spectra of the plasma in the wavelength of 240–1100 nm and stability of its parameters in the non-disturbed region of the incident stream 5–10 mm above the sample.

Plasma is generated by a dc electric arc plasmatron with vortex stabilization, self-adjusting arc length and expanding anode channel which provides high flow, efficient working gas heating and low heat losses onto the water-cooled anode surface. The plasmatron generates a nitrogen plasma jet with low divergence (\(2\alpha = 120^\circ\)), diameter \(D = 10–12\) mm, enthalpy \(20–50\) kJ/g at arc current from 100 to 500 A, full electric power of the discharge \(20–50\) kW, plasma gas flow \(1.0–2.0\) g/cm and mean mass temperature at the exit \(7000–12\,000\) K. The expanding anode channel of the plasmatron is pointed at the heat-resistant material sample so that the plasma exiting the plasmatron creates specific heat flux on its surface \(q_0 = 0.25–2.5\) kW/cm\(^2\). This work is a continuation of works [6–8] in which we have provided detailed descriptions of the experimental setup, measurement equipment and methods for processing experimental data. In this work we shall concentrate on analysis and interpretation of the experimental data obtained earlier.
Figure 2. Optical emission spectra of argon plasma jet at various distances from the sample surface on the 60-th second of heating at arc current 150 A.

The jet has the velocity $v$ approximately from $3 \times 10^3$ to $10 \times 10^3$ cm/s on the path from the output nozzle of the plasma torch ($T_0 \approx 10000$ K [7,8]) to the surface of the carbon sample ($T_w \approx 3000$ K [6, 7]) which is about 15 mm long. This path can be conventionally divided into two characteristic sections. In the first section the plasma jet can be considered pure nitrogen being cooled by heat transfer. In the second section (last 1/3 of path) carbon ablation from the sample surface can be observed in the optical emission spectrum in the form of atomic carbon (spectral line C I 247.8 nm) and cyanide (product of carbon-nitrogen chemical interaction, CN violet bands of transition $B^2 \Sigma_u^+ - X^2 \Sigma_g^+$ which are shown in figure 3). These sections can be considered separately, without and with taking carbon and features of near-surface plasma into account.

2. Region far from the sample
At a distance exceeding 6 mm from the sample surface, plasma jet can be considered consisting of pure nitrogen. In order to provide strong thermal impact on graphite surface, we used a plasma generator with flow temperature at the nozzle exit of about 10 kK according to experimental data in [6–8]. The parameters of such plasma had been calculated in a number of works including [9,10]. The most important result for the present study was spectral data on spatial distribution of carbon-containing particles concentrations: carbon atoms C and cyanide molecules CN, shown in figure 3. There are no external causes for the violation of local thermodynamic equilibrium (LTE) before the interaction with the products of sample surface destruction.

At the point where the presence of the sample begins to affect the plasma flow, its temperature $T$ drops to $\approx 8$ kK [6–8]. Further decrease of $T$ to $\approx 7$ kK and lower in the subsequent section of the jet is shown in figure 4. Thus, at the first stage, only an undesirable drop in the temperature
Figure 3. Section 2, spatial variations of C and CN concentrations obtained from radiation intensities of C I spectral line 247.9 nm and CN band 388.3 nm on 40-th (a) and 140-th (b) second of the experiment. Sample is graphite mark MPG-6 cylinder with 2 cm diameter and 3 cm length, heat flux 1.0 kW/cm$^2$. The vertical shaded lines show sample surface location—the points beyond them are obtained from the plasma flowing past the sample.

from 10 to 8 kK of nitrogen plasma moving in the atmosphere under LTE conditions occurs. In such plasma, the concentration of atomic components is higher than that of molecular ones at
Figure 4. Distribution of electron temperature $T_e$ over section 2 of plasma flow. The vertical shaded lines show sample surface location at given time.

At $T = 10$ kK, concentration of nitrogen atoms $[N]$ exceeds that of its molecules $[N_2]$ by 90 times, and concentration of ions $[N^+]$ exceeds that of molecular ions $[N^+_2]$ by 180 times, at $T = 6530$ K concentrations of atomic and molecular components are equal [10].

3. Region close to the sample
Nitrogen plasma under atmospheric pressure and LTE conditions has simple composition: atoms N, molecules $N_2$, ions $N^+$ and $N^+_2$ and electrons. For plasma temperature $T = 7$ kK the total density of heavy components $[N] + [N_2] = [M]$ has the value of $10.50 \times 10^{17}$ and electron concentration $n_e$ is $1.5 \times 10^{14}$ cm$^{-3}$. For $T = 10$ kK $[N] + [N_2] = [M]$ falls to $7.34 \times 10^{17}$ cm$^{-3}$ and $n_e$ rises to $6.5 \times 10^{15}$ cm$^{-3}$. As plasma temperature falls from 10 kK at nozzle exit to 7.5 kK near the sample surface, energy balance in plasma changes significantly. In this region, the plasma flow begins to interact with carbon particles entering it, and the role of molecules in the plasma kinetics and energy exchange processes also increases. The degree of ionization and electron density are also significantly reduced. Plasma is cooled by heat conduction and radiation processes that consume the energy invested in dissociation and ionization. This energy is mainly released to the translational degrees of freedom of plasma particles during association of atoms and recombination of electrons, association of ions with atoms, pre-dissociation, and other processes. Even at such short transportation distance most of the energy invested in the plasma is dissipated into the environment.

A simple estimate of energy loss can be made from the following considerations. When plasma is generated, most of energy (90%) is spent on creation of hot atoms [10]. Let us compare their ratio in the plasma at the beginning and end of the path. Plasma composition is mostly atomic at $T = 10$ kK and it becomes half-molecular $[N] \approx [N_2]$ at $T = 7$ kK, that is, the ratio of free atoms $[N]/([N] + 2[N_2])$ decreases by 3 times. Therefore, 2/3 of the invested energy leaves
the plasma jet into the environment. This estimate is only 6% higher than the more accurate estimate, which takes into account kinetic, vibrational, and rotational energies of molecules, excitation energy of atoms and molecules, and the energy of ion production, which gives the energy loss value of 60%. The ratio of the enthalpies of nitrogen plasma under equilibrium conditions at 10 kK (55 080 kJ/kg) and 7 kK (25 590 kJ/kg) gives a close value of 54% [11].

According to experiments [6–8], plasma temperature decreases at the second section of the plasma flow where it interacts with the products of the graphite surface destruction (carbon atoms and molecules). At temperature of ≈7 kK due to nitrogen degree of ionization decreasing by 2 or more orders the role of electrons in the kinetics of plasma decreases and although the plasma state remains mostly equilibrium, kinetics of the processes occurring in it becomes significantly more complicated, including over 50 primarily ion-molecular reactions. Let us consider these reactions for carbon-containing neutral (C, C₂, CN) and charged (C⁺, C⁺₂, CN⁺) particles at a temperature of 7 kK in the light of the available experimental data [6–8].

3.1. Neutral particles
The maximum concentration of atomic carbon near the surface of the sample according to the experimental data is ~10¹⁵ cm⁻³ (shown in figure 3). By comparing intensities of the CN and N₂⁺ bands, we can assume that the concentration of CN radicals does not exceed 10¹⁴ cm⁻³. The same follows from the data shown in figure 3. Neutral particles participate in the following reactions:

\[ C + N₂(ν > 1) \leftrightarrow CN + N \quad (≥-2.01 \text{ eV}), \]  
\[ C₂ + N₂ \leftrightarrow 2CN \quad (-0.46 \text{ eV}), \]  
\[ C₂ + N \leftrightarrow CN + C \quad (+1.55 \text{ eV}), \]  
\[ C + N + M \leftrightarrow CN + M \quad (+7.75 \text{ eV}). \] (4)

Reaction rate constants of (1)–(4) at \(T = 7 \text{ kK}\) are large enough [12–14] for these interactions to get finished during the plasma flow time. The main process governing the ratio between [C] and [CN] is reaction (1) since it contains main plasma components N₂ and N on both sides. Although the reaction threshold is 2.01 eV (because N₂ has higher than CN dissociation energy—9.8 eV and 7.8 eV), the concentration of CN is large enough (~10¹⁸ cm⁻³) to facilitate high population of vibrational energy levels with energy of 2 eV (~10¹⁶ cm⁻³), which are probably main contributors to the direct reaction (1).

Figure 3 shows the second section of the flow where C and CN particles are present in the plasma as far as in 5–10 mm from the sample surface. The reasons for carbon particles appearing at such distance from the sample have not yet been studied enough. This could be its radial diffusion from the surrounding space since axial diffusion from the near-surface plasma does not occur upstream. Carbon diffusion speed does not exceed 10³ cm/s according to our estimates while nitrogen jet velocity is 10³–10⁴ cm/s. Reaction (1) is by several orders of magnitude faster than any transport process and other reactions with C and CN.

Let us estimate the ratio of C and CN particle concentrations. At \(T = 7 \text{ kK}\) the equilibrium constant of reaction (1) is \(K₁ = 8.2\) [12–14]. From the equilibrium condition we obtain

\[ [C]/[CN] = K₁[N]/[N₂] ≈ 17, \] (5)

where \([N]/[N₂] ≈ 2\). As \(T\) decreases, the ratio \([C]/[CN]\) decreases as well: at \(T = 4360 \text{ K}\) it is 1, and at \(T = 3710 \text{ K}\) CN concentration would be 10 times higher than that of carbon.

At \([C] ≈ 10¹⁵ \text{ cm}^{-³}\) it follows from (5) that \([CN] ≈ 6 \times 10¹³ \text{ cm}^{-³}\). These are approximately concentrations values that are observed near the sample surface in figure 3.

The plasma jet is stable far from the sample. A weak emission of C atoms is observed in this region, while CN molecules are practically absent in accordance with (5), and they prevail in the
cold boundary regions of the jet. This is confirmed by parallelism of [C] and [CN] dependencies far from the sample in figure 3.

It is important to note that reaction (1) is taking place in all cases and it is possible to find [C]/[CN] ratio from (5) if the temperature of the region is known. For C this temperature is given in figure 4 and for CN this temperature is the low peripheral temperature for all regions except the near-surface region.

For neutral particle reactions (2) and (3) governing C₂ concentration we note that they are rather high-speed as well [12–14]. They give concentration values of [C₂] that are by two orders of magnitude lower than that of [CN], and C₂ molecular bands are indeed almost not observed in the optical emission spectra.

3.2. Ion-molecular composition
Recharge reactions usually have the rate constants with high values from 10⁻¹² to 10⁻⁹ cm³/s [15,16] and are therefore mostly defining ion composition of the plasma. Their combined effect leads to predominance of an ion with the lowest ionization energy, which can no longer recharge with anything and becomes the main ion of the plasma. In this case, it is C⁺ ion, which participates only in a relatively slow triple recombination reaction and in an even slower three-particle recombination reaction. Thus it interrupts the cascade of recharges in the plasma.

Among other reactions, we should note reactions involving the main plasma components N₂ and N which are much faster than other reactions involving carbon-containing molecules with concentration 3 orders of magnitude lower than nitrogen atoms and molecules, with the exception of substitution reaction of one of CN⁺ and C⁺ ions constituents by N atom. Substitution reactions have large rate constants as well as charge exchange reactions [15]. As a result, the concentration of these ions should become even lower than in the charge exchange chain. By identifying the main processes of appearance and disappearance of ions present in the plasma, for [C] ≈ 1 × 10¹⁵ cm⁻³ and T ≈ 7 kK, the following hierarchy of ionic concentrations can be obtained:

\[ [C^+] \approx n_e \gg [N^+] \approx [N_2^+] \gg [CN^+] \approx [C_2^+]. \] (6)

The difference between [C⁺] and [N₂⁺] is about one order of magnitude, and between [N⁺] and [CN⁺] it is about four orders thus allowing us to conclude that the plasma has only atomic ion composition. One of the main reasons for the extremely low concentration of molecular ions along with the above is dissociative recombination, which is not balanced for carbon-containing ions by the reverse process of associative ionization of carbon atoms due to their low concentration.

3.3. Concentration of electrons and ions
The presence of relatively easily ionized C atoms in the plasma (ionization potential 11.26 eV), despite the predominance of N atoms (ionization potential 14.53 eV), causes an increase in the plasma ionization flux: the rate constant of stepwise ionization of C atoms at T = 0.6 eV is 2000 times greater than for N atoms. This means that electron concentration nₑ can become considerably higher than in a purely nitrogen plasma under LTE. In our case, its values are in the range from 2.8 × 10¹⁴ to 4.4 × 10¹⁴ cm⁻³, which is 2–3 times larger than the values for pure nitrogen plasma under LTE. The concentration of nitrogen ions [M⁺] becomes as many times lower with values from 5.4 × 10¹³ to 8.5 × 10¹³ cm⁻³, and carbon ions expectedly become the main plasma ions with their concentration value [C⁺] being in the range from 1.9 × 10¹⁴ to 3.8 × 10¹⁴ cm⁻³.

Assuming the average value of the average rate constant of the ion-molecular processes of C⁺ formation, which are mostly charge exchange during the interaction of nitrogen ions and carbon-containing particles, to be \( k_e = 10–11 \text{ cm}^3/\text{s} [15,16] \), we can find concentrations of charged particles at T = 7 kK and [C] ≈ 1 × 10¹⁵ cm⁻³: \( n_e = 3.3 \times 10^{14} \text{ cm}^{-3} \), [C⁺] = 2.6 × 10¹⁴ cm⁻³,
Figure 5. Composition of the plasma in section 2 and near the sample surface on 40-th (a) and 140-th (b) second of the experiment. The vertical shaded lines show sample surface location at given time. $n_e^0$ denotes electron concentration under equilibrium conditions.
[N+] = 4.6 × 10^{13} \text{ cm}^{-3}, [N_2^+] = 2.6 × 10^{13} \text{ cm}^{-3}. Concentration of C^+ accounts for almost 80% of total ion concentration. In nitrogen plasma under LTE and same conditions we have \( n_e^0 = [\text{M}^+] = 1.5 × 10^{14} \text{ cm}^{-3}, [\text{N}^+] = 9.8 × 10^{13} \text{ cm}^{-3}, [\text{N}_2^+] = 5.5 × 10^{13} \text{ cm}^{-3}. \) Preservation of LTE for the nitrogen component means that \( n_e [\text{M}^+] = \text{const}, \) thus electron concentration remains constant and the contribution from the carbon admixture is compensated by nitrogen ion contribution decrease by 2.1 times. Setup time for the density of carbon ions C^+ at \( T = 7–10 \text{ kK} \) and for the value of electron concentration we found, \( n_e = 3.3 × 10^{14} \text{ cm}^{-3}, \) meets the quasi-stationarity criterion: \( \tau \approx 170 \mu \text{s} < \tau_0 \approx 200–600 \mu \text{s}. \)

Figure 5 shows calculated results for ion composition of nitrogen–carbon plasma from the obtained experimental distributions [C] (see figure 3) and \( T \) (see figure 4) on the jet axis. Concentrations of carbon atoms and ions are generally close to each other and exceed the concentration of nitrogen ions near the sample surface, and the region of their predominance decreases with time. The same is true for electron concentration, which becomes higher than neo after 11 mm on the 40-th second, and only after 16 mm on the 140-th second. Their ratio also decreases from \( \approx 2 \) to \( \approx 1.5 \) at its maximum. This weakening of carbon influence is associated with \( T \) increase and [C] decrease during prolonged exposure of the sample to the plasma jet, its causes should be sought in the thickening of the surface plasma region and in decrease of ablation rate of the sample surface which requires a separate consideration.

4. Conclusion
Plasma loses about 60% of supplied energy on its movement from the nozzle to the sample while retaining the LTE state. Kinetics of processes in it is determined by reactions of recharging and substitution.

Small admixture of carbon atoms (\( \approx 0.1\% \)) entering the nitrogen plasma on its path to the sample in LTE state manifests itself only in the ion-molecular kinetics, determining the ion composition of the plasma and doubling the electron concentration relative to the pure nitrogen plasma. The role of other carbon-containing admixtures (CN and C_2) is insignificant.

The processes responsible for the propagation of carbon particles upstream in plasma jet at distances up to \( \approx 1 \) cm from the sample are not completely understood. This matter requires studying near-surface plasma, which will be undertaken in a subsequent paper.

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References
[1] Luo L, Wang Y, Liu L, Duan L, Wang G and Lu Y 2016 Carbon 103 73–83
[2] Suzuki T, Fujita K, Ando K and Sakai T 2008 J. Thermophys. Heat Transfer 22 382–9
[3] Helber B, Turchi A, Scoggins J, Hubin A and Maquin T 2016 Int. J. Heat Mass Transfer 100 810–24
[4] Mikhutulina D S, Polezhaev Yu V and Reviznikov D I 2011 Heat Transfer, Thermochemical and Thermo-Erosive Destruction of Thermal Protection (Moscow: Jamus-K)
[5] Bykova N G 2014 Physical-Chemical Kinetics in Gas Dynamics 15 76
[6] Chinnov V F, Tyufyayev A S, Kavyrshin D I, Ageev A G, Sargsyan M A and Gadzhiev M Kh 2018 High Temp. 56 25–32
[7] Belevtsev A A, Kavyrshin D I, Sargsyan M A, Chinnov V F, Efimov A V and Shecherbakov V V 2019 J. Phys. D: Appl. Phys. 51 484002
[8] Kavyrshin D I, Korshunov O V, Sargsyan M A, Chinnov V F and Shecherbakov V V 2019 J. Phys.: Conf. Ser. 1394 012016
[9] Surzhikov S T 2009 Computational Models of Subsonic Dynamics of Low-Temperature Plasma Based on Navier-Stokes Equations (Encyclopedia of Low-Temperature Plasma vol VII) (Moscow: JIHT RAS)
[10] Meher K, Tiwari N and Ghorui S 2015 Plasma Chem. Plasma Process. 35 605–37
[11] Engel’shta V S 1990 *Theory of the Column of the Electrical Arc (Low-Temperature Plasma)* vol 1) (Novosibirsk: Nauka)

[12] Standard Reference Database 17, Version 7.0 (Web Version), Release 1.6.8, Data Version 2015.09, Available: http://kinetics.nist.gov/kinetics

[13] Shavelkina M, Filimonova E, Amirov R and Isakaev E 2018 *J. Phys. D: Appl. Phys.* 51 294005

[14] Brun R (ed) 2012 *High Temperature Phenomena in Shock Waves* (Springer-Verlag Berlin Heidelberg)

[15] Anicich V G 1993 *J. Phys. Chem. Ref. Data* 22 1469–569

[16] Bates D 1964 *Atomic and Molecular Processes* (Academic Press)