Temperature distribution in the zone of graphite destruction by a nitrogen plasma jet

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Abstract. Using the automated system of high-speed visualization and spatial-temporal spectral diagnostics, the destructive effect of an atmospheric pressured nitrogen plasma jet with a temperature of 0.7 - 1.0 eV on samples of isotropic and anisotropic graphite was studied. Measurements of the electron, vibrational, and rotational temperatures of the plasma in the zone of destructive interaction were performed, and the pattern of the spatial-temporal distribution of the products of graphite destruction (carbon atoms and cyanogen molecules) was revealed. The efficiency of local spectral analysis of near-surface plasma is shown using a combination of longitudinal and transverse periodic scanning of the emission spectra and recording of instantaneous 2D spectra of the selected spectral region containing the CN and N2 + bands. The spectral estimate of the concentration of the graphite destruction main product (carbon atoms) is in quantitative agreement with the results of measuring the mass loss rate of the sample material, made by two-positioned visualization of its surface. In the zone of realizable heat loads of 0.5-1.5 kW/cm², heating of the graphite surface to temperatures of 2800 ÷ 3600 K was achieved and the rate of loss of its material was 3-15 mg/cm²s, which is consistent with the literature data.

1. Introduction.

Presently, modelling of spacecraft atmospheric re-entry conditions is performed in Russia and in the world on large-scale and mock-up installations in close cooperation with developers of new heat-resistant coating materials with required properties [1, 2]. Work [3] studies interaction between high-velocity nitrogen plasma jet with samples of composite carbide-silicon material with heat-resistant coating. Studies of carbon material ablation in chemically active environments shows the principal role of graphite oxidation processes in border layers and on the surface of the heat-resistant material [1, 3, 4] as well as that of carbon nitriding process [5]. The works of particular interest are experimental works dedicated to the roles of nitrogen plasma chemistry processes in decomposition of heat-resistant materials which have been published in recent years [2, 3, 5].

This paper presents the results on spatial and temporal optical emission spectra diagnostics of interaction region of air pressure nitrogen plasma jet impacting graphite surface. The plasma is generated by a DC electric arc plasmatron with nozzle exit temperature $T_{in} = 10000 \div 12000 K$ interacts with a graphite surface heated by the jet to $T_w \leq 3600 K$. 

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2. Measuring system.
A slightly divergent ($2 \alpha = 12^{\circ}$) plasma jet with a diameter of 5 to 10 mm with an enthalpy of 10–100 kJ/g is formed at the output section of the plasma torch with a plasma-forming gas flow rate of 1–3 g/s and an average mass plasma temperature at the outlet of 10000–20000 K. From the expanding anode channel of the plasma torch a high-enthalpy plasma jet flows into the free space of air at atmospheric pressure. Samples of graphite are mounted on supporting tungsten rods and are located at the front of the jet at a distance of 15-25 mm from the outlet of the plasma torch.

Automated measuring complex includes (see Fig.1) the following measuring systems. Synchronized video recording system for the interaction of incident plasma flow with sublimating heat-resistant sample, consists of high-speed cameras Motion Pro X3 (USA) and VS-FAST (Russia) and ultra-high-speed (with a frame rate of up to 100000 s-1) camera Phantom (USA). In combination with long-focus lenses with a system of camera extension rings, the image of the “jet-sample” interaction zone is recorded at a selected scale during the entire observation period (usually 60–200 s).

![Figure 1. Schematics of the diagnostics set-up. Designations: 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 3648 spectrometer, 14 - AvaSpec 2048 spectrometer, 15 - MS-257 spectrometer with Andor camera.](image)

To use these cameras as a high-speed micro-micrometer, in front of the lens, interference filters with a bandwidth $\delta \lambda_{1/2} = 10–12$ nm are introduced before a lens.

Simultaneous video recording of the interaction region by two high-speed cameras provide the means to determine in real time the loss rate of the sample material and the temperature of its surface [6].

Spectral measurements are performed using a three-channel and a single-channel fiber-optic spectrometers AvaSpec2048 and AvaSpec 3648. A single-channel fiber-optic spectrometer AvaSpec 3648 with a spectral range of 220–1100 nm and spectral resolution of about 1 nm monitors the radial distribution of plasma jet radiation from the near-surface plasma, during the continuous transverse optical fiber guide displacement. Measurements provide control over the temporal change (with a frequency of 2 spectrum/s) of the plasma chemical composition and plasma parameters in the interaction zone ($Z \approx 1–5$ mm above the sample surface). AvaSpec 2048 three-channel fiber optic spectrometer (spectral range 220–1000 nm) with a spectral resolution of 0.2–0.5 nm records plasma emission along the longitudinal coordinate of the plasma flow incident on the sample. Spatial-temporal changes in plasma emission spectra are monitored by scanning the plane of the intermediate sharp image of a plasma jet formed by condensers 9, 10 (Fig. 1) with spectrometers optical fiber guides.
3. Differences in plasma jet flow patterns around isotropic and pyrographite samples

The investigated samples of isotropic graphite MPG-6 had a cylindrical shape, a diameter of 20 mm and a length of 15–30 mm and were turned to a free-flowing jet with a diameter of 6-10 mm either with its front or side surface. Samples of pyrographite (Scientific Research Institute Grafit) - the parallelepiped 20x12x4 mm³ are facing the jet with a plane 20x12 mm². The systems of longitudinal and transverse scanning of the emission spectra of a near-surface plasma record the radiation from extended plasma regions that have a complex movement pattern in the stagnation zone. As shown by the measurements, the possibilities of recording spatial and temporal changes in the radiation intensity of the main products directly in the zone of destruction are different for these types of graphite.

In isotropic samples, the formation of a crater in the stagnation zone and an increase in its depth leads to the appearance of a “stagnant” flow region with a large residence time of plasma particles and degradation products in the crater, which increases the efficiency of plasma processes involving C and CN. In this case, the registration of the spectral composition of the near-surface plasma itself is possible only in the initial period of exposure, while the crater depth is small h ≤ 1 mm. After that, the near-surface plasma region is blocked by the crater edge, and the observed spectrum characterizes the state of the plasma above the edge, relative to which the bottom of the crater is diminishing with time. For this reason, the registered 2D spectra can be attributed to the near-surface plasma only during the first 10–15 seconds of plasma exposure to an isotropic sample.

In experiments with pyrographite, the screening effect of the edge is practically not manifested. Plasma deceleration occurs on a flat surface of 20x12 mm², the role of a shallow crater is small, and the recorded spectra carry information about the near-surface plasma. And although this spectral intensity is integrated along the line of sight of the optical recording system, a simultaneous longitudinal scanning of the spectra across the plasma jet allows us to correlate the longitudinal scanning spectra with the parameters of the axial plasma region in the corresponding z coordinate.

4. Spatial-temporal scanning of the emission spectra of the plasma and the destroyed sample

Spatial-temporal changes in the intensity of the radiation of the main radiating components of the incident plasma flow (NI, N₂, N₂⁺) and the products of its effect on the samples (CI, CN*) were obtained (Fig. 2). The plasma emission spectra in the interaction zone in the local thermodynamic

![Figure 2. 3D - spectra of the nitrogen plasma jet radiation at different distances from the sample surface (mm) in the quasi-stationary period of its heating. Arc current 300 A.](image)
The equilibrium approximation (which is valid under the experimental conditions) established the pattern of spatial-temporal temperature variations of the nitrogen plasma electrons, as well as the nature of changes in the vibrational and rotational temperatures of the CN, N₂ molecules and the N₂⁻ ion during heating and destruction of the samples. Fig. 3 (isotropic graphite) and Fig. 4 (pyrographite) show the dynamics of changes in the radiation intensity of the most important radiating components of plasma: spectral lines of atomic nitrogen NI (measurement of electron plasma temperature), atomic line of carbon Cl 247.8 nm (indicator of “blowing” of the samples destruction material into the stream), the molecular spectrum of the radical CN (the main product of interaction of C with nitrogen plasma), as well as continuous thermal radiation of the sample (with a temperature at its surface T_w ~3000 K) in the region with a wavelength of 775 nm free of the spectrum lines.

![Graph showing cyclic changes in plasma radiation intensity](image)

**Figure 3.** Cyclograms of changes in the intensity of the atomic nitrogen line, the thermal continuum (above), and the intensity of the atomic carbon line, the molecular bands of CN and N₂⁻ (below) in the interaction zone. The sample is MPG-6 graphite, with a diameter of 20 mm and a height of 30 mm. Arc current 300A. A sawtooth insert between cyclograms establishes a connection between the longitudinal coordinate z and the moment of impact.

Analysis of the cyclic change in the intensity of plasma radiation acting on an isotropic sample (Fig. 3) shows that the atomic line NI reaches its maximum values near the plasma nozzle, at the greatest distance from the target, at z = 10 mm, and minimum - at z = 20 mm. At the same time, the intensity of the samples surface emission reaches its maximum at its upper edge with the initial coordinate z ≈ 15 mm. As the sample warms up and its mass decreases, this maximum (corresponding to the coordinate of the most heated sample surface at the stagnation point) slowly shifts down from cycle to cycle along the z axis, up to z ≈ 17-18 mm.
The spectral lines of atomic carbon served as an indicator of the main primary product of the destruction of graphite in our study. Other carbon-containing particles in the gas phase (C$_2$, C$_3$ ... C$_8$) were not detected in the spectra. The cyclograms show the change in the region of the interaction of the intensity of the CI line at 247.8 nm with the excitation energy $E^* = 7.68$ eV and the transition probability $3.4 \cdot 10^7$ s$^{-1}$ [7]. The maximum of its radiation, which monotonously decreases with exposure time due to the gradual lowering of the crater bottom surface (where the actual concentration of atomic carbon is maximum) from the upper edge of the sample, is near this edge. The secondary product graphite destruction is the radical CN, the change in the radiation intensity of which is also shown in the cyclograms.

![Figure 4](image)

**Figure 4.** Cyclograms of changes in the intensity of the atomic nitrogen line, the thermal continuum (top), and the intensity of the atomic carbon line and the molecular bands of CN and N$_2^+$ (bottom) in the interaction zone. The sample is pyrographite. Arc current 150A.

It is noteworthy that a quasi-stationary mode of samples heating is established after 20-30 s of continuous plasma effect on samples, during which the temperature of the sample surface facing the jet for a long time (up to 150 s) remains unchanged.

5. **Results of 2D diagnostics of the boundary layer.**

The best possibilities of recording the intensity of radiation with high spatial resolution are provided by system 15 (Fig. 1), consisting of an MS-257 spectrometer and Andor matrix camera. To record the 2D spectra of the near-surface interaction region, a sharp image of the stagnation region with a vertical length of about 6 mm is projected onto the entrance slit of the spectrometer, capturing a plasma jet (~4 mm) and 1-2 mm of the samples side surface. When using a diffraction grating of 1600 lines/mm a matrix with a length of 25 mm (1200 pixels), accommodates a portion of the spectrum 40–45 nm in length, which is recorded with a resolution of better than 0.1 nm (see Fig. 5).

New possibilities for analyzing the state of the plasma in the interaction zone are provided by the electron-vibrational-rotational structure of the CN spectrum, whose simulation allows us to estimate both the vibrational $T_v$ and the rotational $T_r$ temperatures of the CN molecules. This is even more important because in the near-surface region, where a plasma jet with $T_e \approx 7000$ K runs onto the surface with $T_w \approx 3000$ K, $T_v$ and $T_r$ may not coincide.

As a result of processing of numerous spectra, an averaged pattern of changes in the vibrational $T_v$ and rotational $T_r$ temperatures in the near-surface region of pyrographite interacting with a nitrogen plasma jet was obtained, as shown in Fig.6.
Figure 5. The matrix spectrum of the nitrogen plasma incident on the graphite sample, and the result of its comparison with the model spectrum in order to determine $T_v$ and $T_r$. The 0 coordinate in the left figure corresponds to the sample surface.

Figure 6. Vibrational and rotational temperatures of the CN radical according to the results of molecular diagnostics of the near-surface layer. $\Delta z$ - distance from the surface.

The spectrum bands of the $1^-$ system of the $N_2^+$ ion (transition $B^2\Sigma_u^+ - X^2\Sigma_g^+$, isoelectronic with the transition CN) are close in their spectral position to the corresponding bands of the CN radical and can be used to estimate the concentration [CN]. At the same time, the almost identical excitation energies of the $B^2\Sigma^+$ system of the $N_2^+$ and CN molecules, as well as an important feature of the composition of the equilibrium nitrogen plasma in the temperature range 5-10kK, consisting in the presence of a maximum concentration of $[N_2^+] \approx 10^{14}$ cm$^{-3}$ at $T\approx 7000$K [8], make this estimate of the concentration of [CN] fairly accurate.

An important analysis tool is the comparison of the observed molecular spectra of $N_2$ ($2^+$ system), $N_2^+$ ($1^-$ system) and CN (violet system) in the 300-430 nm wavelength range, containing several sequences of these molecules, with their model representation by varying $T_v$ and $T_r$ values for these molecules, which provide the best agreement between the experimental plasma radiation intensities and the sum of their model values. In fig. 7 such a comparison was made for the plasma region at the distance of 3 mm from the pyrographite surface. Within the error range of 15–20%, all considered molecular components of the plasma in the interaction region are characterized by a single temperature $T = T_v = T_r = 7000 \pm 1000$ K.
6. The rate of loss of material.
Experimental estimation of the mass loss rate of the sample material in real time is performed by the method of two-positioned synchronous visualization of the “jet-sample” system. The results of measuring the rate of destruction of isotropic and pyrolytic graphite under the influence of a nitrogen plasma jet are shown in Fig.8.

Two estimates of the flux of atomic carbon particles with thermal velocity $u_C$ ($T_W$) leaving the graphite surface

$$ f_C = u_C \cdot [C] \approx \mu_C \cdot (N_0/M_C) = 10^{20} \text{ particles/cm}^2 \text{s}, $$

in which data is used on the spectral estimate of the maximum carbon concentration $[C] \approx (1\div2) \cdot 10^{15} \text{ cm}^{-3}$ (second term of equality) and the results of measuring the mass loss rate of the material $m$ (third member of equality), they give the same results.

7. Conclusion.
We have measured spatial and temporal variations of the following plasma parameters in the region of graphite sample decomposition by the high enthalpy nitrogen plasma jet: electron temperature,
vibrational and rotational temperature of the CN molecule. In the area of real heat loads of 0.5-1.5 kW/cm², heating of the graphite surface to temperatures of 2800-3600 K was achieved. At the same time, the mass loss rate of the material was 3-15 mg/cm² s, which is in good agreement with the previously performed measurements [1].

In the zone of graphite destruction, the main process regulating the relationship between [C] and [CN], apparently, is the substitution reaction [9]

\[
C + N_2 (\nu > 1) \leftrightarrow CN + N (\geq -2.01 \text{ eV}),
\]

since the main components of plasma N₂ and N are involved in it on both sides. In more distant (from the samples surface) regions of the plasma jet, where \([N] \geq [N_2]\) and \(n_e \geq 10^{15} \text{ cm}^{-3}\), the recharge process can become significant

\[
N^+ + C \rightarrow N + C^+.
\]

Analysis of the cyclic change in the intensity of the nitrogen atomic lines and nitrogen ions molecular bands during the quasi-stationary heating of an isotropic sample (see Fig. 4) indicates that when there is a crater and a “stagnant” near-surface zone monotonous heating is observed, eventually leading to a small “ablative” cooling of the sample.

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