Analysis of optical spectra of microplasma discharges initiated by plasma flow on the surface of the grade 45 carbon steel sample

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Abstract. The results are presented from studies of the optical emission spectra of the microplasma discharge. The discharge is initiated by the pulsed plasma flow on the sample surface made from the grade 45 carbon structural steel. The discharge was initiated at a voltage of 400 V applied to the sample and maintained by a pulsed current with an amplitude of ~600 A and duration of 20 ms. The discharge plasma electron temperature was calculated using data on the relative intensities of the iron atom lines. Based on the recorded continuous spectra in the optical spectral range, the melt temperature and the state of aggregation of matter were estimated at the points of microplasma discharge localization on the sample surface. It was found that the melt temperature on the steel surface determined using data on the continuous spectrum is approximately 5000 K, while the electron temperature calculated using data on the line spectra of atoms is approximately ~7400 K.

1. Introduction

It is known that, in vacuum at a residual air pressure of \( p < 0.001 \) Pa, under the effect of the pulsed plasma flow (with a density of \( n_e > 10^{15} \text{ cm}^{-3} \), a temperature of approximately 10 eV, and pulse duration of ~1 \( \mu \)s), the electric discharges can be initiated between two sufficiently pure metal electrodes, when there is a potential difference of ~100 kV between them [1]. A new phenomenon was experimentally discovered in [2], namely, the initiation of low-threshold microplasma discharges on the metal surface exposed to the plasma flow. It is important that the metal surface should be partially covered with a thin dielectric film (its thickness should be \( d \approx 1 \mu m \)). Under these conditions, both the threshold negative potential applied to the metal sample (~100 V) and the threshold plasma density (\( n_e \sim 10^{11} \text{ cm}^{-3} \)) considerably decreased (by a factor of 1000).

In [3], a new mechanism was proposed for the initiation of microplasma discharges on the metal surfaces partially covered with a dielectric film. This mechanism is based on the fact that, being exposed to the plasma flow, the surface of the dielectric film becomes electrically charged and its floating potential becomes zero \( U_f \approx 0 \). As the metal potential is negative (\( U_M \sim 100...400 \) V), the strong electric field of \( E = \frac{U_M - U_f}{d} \approx 1...4 \text{ MV/cm} \) forms across the film cut. At such high electric field intensities, the electric breakdown occurs along the dielectric film cut accompanied by the dense plasma formation, which initiates the electron field emission and the explosive electron emission from the metal surface. These processes result in the metal local melting and the formation of
craters at the points of microplasma discharge localization.

The proposed mechanism was experimentally confirmed and the role of dielectric films in the initiation of microplasma discharges under the effect of the external low-density plasma flows was cleared up. For example, under the effect of the plasma flow with an electron density of \(n_e \approx 10^{12} \text{ cm}^{-3}\) and an electron temperature of 10 eV, microplasma discharges (MPDs) were stably initiated on the surfaces of titanium samples with the 0.1–1-\(\mu\)m-thick rutile dielectric films deposited on them and an electric potential of 400 V applied to the metal. The MPDs are initiated at the points of rupture of the dielectric film or at the boundary between the film and the open metal surface [2, 3].

Computer simulations of the electric field occurrence at the dielectric film edge exposed to the plasma flow predict the field strength of approximately 2 MV/cm, which is quite sufficient field for the production of dense plasma as a result of the electric breakdown on the film surface or the explosive emission from micropoints on the metal surface [4, 5]. Both these processes initiate the microplasma discharge, which causes metal melting in local regions accompanied by the formation of high-pressure region in the discharge above the melt [6]. The MPD localization regions can move over the metal surface at a speed of up to 500 m/s [7]. In this case, the solidification of the molten local metal regions proceeds very quickly (with a temperature drop rate of more than 10^6 K/s) due to the heat removal deep into the metal. At such cooling rates, the shape of the crater formed under the effect of high plasma pressure above the crater becomes fixed or “frozen” on the metal melt. During one MPD pulse with duration of 20 ms, many microcraters are formed with characteristic sizes from 0.3 to 30 \(\mu\)m [8–10]; as a result of the surface treatment by ten pulses, the entire surface of the steel sample with an area of approximately 2 cm^2 becomes covered with the craters, and, at high currents, also with the continuous melt regions with sizes of approximately ~100 \(\mu\)m (see Fig. 1).

![Figure 1](image.png)

Figure 1. Image of a fragment of the sample surface made from the grade 45 carbon structural steel, which was treated with ten microplasma discharge pulses with a current of 600 A.

Thus, a continuous microrelief is formed on the sample surface, which is characterized by the increased microhardness and wear resistance [11].

The low threshold values of the applied potential difference, as well as the density and temperature of plasma initiating the discharge, provide opportunities for widespread technological applications of the method of microplasma discharge treatment of various metal surfaces in order to form hard microrelief on them. So, the detailed studies are required of the microplasma discharge properties and the state of agerration of metals in the regions near the melt surface. Optical emission spectroscopy is a convenient technique for diagnosing the state of agerration of metal surfaces by means of studying the line spectra of atoms and ions, the molecular spectra of the discharge emission and the continuous spectra of the melt surface directly under the discharge.
These studies contribute to understanding the processes that determine the microrelief formation and the phenomenon of hardening the metal surface layer. Based on the analysis of these spectral data, the important data on the parameters of metal and plasma near the metal melt surface can be obtained. As a result of fast cooling, the craters are formed in the metal melt, and the fast thermal hardening of metal occurs accompanied by the formation of a hardened surface layer on the metal sample surface. The grade 45 carbon steel was chosen as a material to be studied because it is widely used in various industries and has good prospects in terms of developing the methods for hardening the surfaces of steel products.

2. Experimental conditions and main results

The experiments were performed at the Sfera facility (Fig. 2). The diameter of the vacuum chamber is 50 cm. The built-in plasma injector produced the pulsed plasma flow with duration of 25 µs and the electron density ranging from the threshold value of $10^{11}$ cm$^{-3}$ (required for initiation of microplasma discharge) to the maximum value of $10^{14}$ cm$^{-3}$, the electron temperature being 10 eV. The grade 45 carbon steel samples with dimensions of $4 \times 4 \times 12$ mm$^3$ were preliminary annealed in air at a temperature of 400°С in order to form the 1-µm-thick oxide films on their surfaces. After that, the samples were placed inside the chamber, which was pumped out to a residual air pressure of not more than 5 Pa. Under the effect of the pulsed plasma flow with a density of $10^{13}$ cm$^{-3}$, which is considerably higher than the threshold density, the microplasma discharges were initiated on the steel sample surface coated with the dielectric oxide film. In these discharges, the rectangular pulsed current with duration of 20 ms and an amplitude of 600 A was maintained with the help of the current stabilizer. In similar experiments, when the microplasma discharges were initiated near the graphite sample surface, plasma was formed near the points of discharge localization with a charged particle density amounting to $10^{18}$–$10^{19}$ cm$^{-3}$ and a temperature of approximately 1 eV [13–15].

The optical emission from microplasma discharges was recorded using the AvaSpec-3648 spectrometer with a spectral resolution of 0.3 nm. The discharge emission at the sample surface was focused by the lens onto the end of the fiber-optic cable connected to the spectrometer. The spectra were recorded with an exposure of 1–7 ms several times during the microplasma discharge with duration of up to 20 ms.

Typical microplasma discharge spectrum is shown in Fig. 3. It was recorded in 7 ms after the beginning of the discharge with an exposure of 7 ms that made it possible to record all three components of the spectrum. The first component consists of rather narrow lines of iron atoms and ions and other elements present in the chamber (the impurities present in the sample material,
contaminants of the vacuum chamber occurring due to the initiator operation and processing of the previous samples, and residual gas). The second component consists of the vibrational-rotational bands of molecular nitrogen, which is the main component of the residual gas. And the third component is the continuous spectrum, which serves as a mildly sloping “pedestal” for the two first components of the spectrum.

Figure 3. Original spectrum of microplasma discharge initiated at the surface of the grade 45 carbon steel sample. Readings up to 15000 correspond to the zone of linearity.

The atomic line spectra were processed first. The lines of both atoms and singly charged Fe ions were recorded. No lines of iron ions with higher degrees of ionization were discovered. The recorded spectral lines of atoms and ions, which were not saturated and do not overlap, turned out to be quite narrow, and their half-widths were determined by the spectrometer instrumental function. This makes it possible to relatively easy isolate them without considerable distortion of their amplitudes. Table 1 presents the reliably identified lines of iron atoms present in the spectra of microplasma discharges initiated at the surface of the grade 45 carbon steel sample.

Table 1. Transition wavelengths (\( \lambda \), nm) and energies of the of the upper levels levels (\( E_k \), eV) for the iron atom lines reliably identified in the microplasma discharge spectra.

| # | 1    | 2    | 3    | 4    | 5    | 6    | 7    | 8    | 9    |
|---|------|------|------|------|------|------|------|------|------|
| \( \lambda \), nm | 410.7 | 411.9 | 423.6 | 441.5 | 473.7 | 486.0 | 490.3 | 507.5 | 530.2 |
| \( E_k \), eV | 5.849 | 6.583 | 5.352 | 4.415 | 5.828 | 5.426 | 5.410 | 6.663 | 5.621 |
| # | 10   | 11   | 12   | 13   | 14   | 15   | 16   | 17   | 18   |
| \( \lambda \), nm | 538.3 | 541.5 | 542.4 | 543.0 | 557.3 | 558.7 | 640.0 | 641.2 | 649.5 |
| \( E_k \), eV | 6.615 | 6.675 | 6.605 | 3.241 | 5.621 | 5.587 | 5.539 | 5.587 | 4.312 |

When processing the spectra, we take into account the dependences of the spectrometer sensitivity and the absorption of the optical elements on the radiation wavelength. In calculations,
the spectral line intensities were counted in units of the number of photons. Further analysis of the line spectra was based on the model of local thermodynamic equilibrium [16]. Eighteen reliably identified spectral lines of iron atoms (FeI) were used. The intensities of reliably identified lines (FeI), normalized to the product of the corresponding transition probability and the degree of degeneracy of the upper level, as functions of energy of this excited state upper level are shown in Fig. 4 on a semilogarithmic scale.

![Boltzmann plot](image)

**Figure 4.** The Boltzmann plot for the reliably identified iron atom lines. The vertical coordinate axis represents the natural logarithm of the population ratio of the upper excited and ground states for different transitions. The horizontal coordinate axis represents energy of the corresponding upper level level in electronvolts.

The cotangent of the slope angle of the straight line, approximating the obtained points using the least square procedure, determines the electron temperature. The accuracy of its determination can be calculated in a standard way [17]. An arbitrary numerical factor for the line intensities was chosen so that the resulting straight line passes through the coordinate origin. In this case, the plotted intensities can be interpreted as logarithms of the relative populations \( n_k \) of the upper levels of atoms with respect to the ground level population \( n_0 \). The electron temperature of plasma determined in this way using data on the spectral lines of Fe atoms turned out to be 7400 ± 800 K.

The iron spectrum recorded in the visible spectral range is overfilled with lines that, at the available spectral resolution, many lines merge and some lines cannot be reliably identified. As a result, the number of the reliably identified lines of iron ion turned out to be insufficient for obtaining one more estimate of the electron temperature.

In the previous measurements of the spectra of the microplasma discharges initiated on the titanium sample surfaces [12], the discharge current ranged up to 200 A, and only line spectra were clearly observed, while the continuum amplitude was at a level close to the measurement error. In the present experiments with steel samples at a pulsed current amplitude of ~600 A, the continuous component of the emission spectra can be recorded, which we identify as the emission of melt forming under the discharge at a temperature of several thousand degrees.
In the spectral range of 560–770 nm, with exception for the spectral regions near the atomic sodium (Na) resonance doublet and Hα line of the Balmer series of atomic hydrogen, which are oversaturated with lines, the shape of the spectrum (after subtracting all atom and ion lines) is noticeably similar to the spectrum of the first positive system of the N2 molecule. This spectrum occurs as a result of the transition $B^3\Pi_g \rightarrow A^3\Sigma_u^+$, see [18, 19]. Figure 5 shows the microplasma discharge spectrum after subtracting the lines (curve 1) and, for comparison, the spectrum of the extended glow discharge in nitrogen (curve 2) obtained using the same AvaSpec-3648 spectrometer.

![Figure 5](image-url)

**Figure 5.** Comparison of the microplasma discharge spectrum after subtracting all atom and ion lines (1) with the molecular spectrum of the glow discharge in N2 (2). In the first spectrum, the data in the spectral ranges near the Hα line and the Na resonance doublet were removed. The glow discharge spectrum is sized and shifted up to 14 units to provide the convenient comparison. The molecular nitrogen spectrum in a glow discharge (2) was measured independently in a separate experiment.

Thermal radiation and the molecular bands can be distinguished in curve (1). Due to a rather rough procedure for eliminating the line spectrum, some traces of the subtracted spectrum can be seen, and also the molecular spectrum is somewhat smoothed out. In the spectral range presented in Fig. 5, there are no traces of any other molecular bands, except for the already indicated first positive system of the nitrogen molecule N2. The dips on curve (1) near 565 and 690 nm correspond in wavelength to almost-to-zero dips in the glow discharge spectrum (2), as well as the similar dips on the molecular nitrogen spectra presented in [19]. Finer spectral details are also noticeably similar. The intensity of this molecular component of the spectrum correlates with the residual gas pressure in the chamber, the bulk of which is molecular nitrogen.

Assuming that, in the spectral range shown in Fig. 5, only the first positive nitrogen system and the thermal radiation of the melt formed under the discharge are present in the recorded MPD spectrum, we can believe (with a sufficient accuracy) that the intensities of the approximating spectrum (2) in the wavelength ranges in the vicinities of 565 and 690 nm are determined only by the Planck thermal continuum.
Then we can represent the radiation spectrum in the Wien coordinates (Fig. 6), and, using the Wien approximation, which, in this spectral range, is almost indistinguishable from the Planck spectrum, estimate the temperature of the molten iron surface from the slope of the straight line drawn through these points [20, 21].

![Figure 6](image.png)

**Figure 6.** (1) Fragment of the microplasma discharge spectrum in the wavelength range of 554–720 nm presented in the Wien coordinates. The vertical coordinate axis represents the values of \( \log(I/\lambda^4) \), where \( I \) is the relative spectrum intensity, and the horizontal coordinate axis represents the values of \( C_2/\lambda \), where \( C_2 = 1.44 \times 10^7 \) nm·K is the Wien second radiation constant. (2) The straight line corresponding to the Wien approximation.

Thus, the estimated temperature is 5000 ± 500 K. It is obtained using the continuous spectrum radiation intensities in the vicinities of 565 and 690 nm, where the molecular spectrum intensities are negligible. This estimated temperature is lower than the lower range limit of the electron temperature obtained by analyzing the iron atom spectrum. At the same time, this temperature is much higher than the boiling point of iron at atmospheric pressure (~3000 K), but considerably lower than the critical temperature of iron [22]. The validity of assumption underlying the calculations is confirmed by the fact that the spectrum dip in the vicinity of 615 nm (Fig. 5) turns out to be very close to the Wien approximation straight line drawn in Fig. 6.

In [19], the rotational temperature was determined using data on the molecular nitrogen spectrum in the glow discharge, which turned to be approximately 700 K (see [19], Fig. 7). The molecular nitrogen spectrum in a glow discharge was measured independently by the same spectrometer in a separate experiment (spectrum 2 in Fig. 5). This spectrum is similar to this spectrum presented in [19]. At the same time, in the short-wavelength range, molecular nitrogen spectrum measured in the microplasma discharge (spectrum 1 in Fig. 5) is much more intense than that measured in the glow discharge (spectrum 2 in Fig. 5) and, in the long-wavelength range, it decreases faster, as compared to
spectrum 2. This indicates that the temperature in the microplasma discharge region, where the nitrogen molecular spectrum forms, is considerably higher than 700 K. Thus, we see that, basically, it is possible to use molecular spectrum for diagnostic purposes. But in order to do this, the higher spectral resolution is required. The higher resolution will enable to better isolate the molecular spectrum from the lines of atoms and ions. Apparently, the more accurate temperature estimate will contribute to determining the localization of the microplasma discharge region, where the N$_2$ molecular spectrum forms.

The pressure corresponding to a molten iron temperature of 5000 K was estimated in accordance with [22] using the equilibrium curve (binodal). The estimated pressure of vapor iron is in the range of 200–700 atmospheres. Such pressures are consistent with the iron surface morphology, the microrelief of which is formed as a result of initiation of microplasma discharges (see Fig. 1). Local pressures of the same order (100–300 atmospheres) were previously observed in similar experiments on initiation of microplasma discharges on the graphite surface by the plasma flow [6].

3. Conclusions
The optical emission spectra of the microplasma discharge initiated on the surface of the grade 45 carbon steel sample were studied experimentally. It was found out that the discharge radiation spectrum contains the line spectra of both iron atoms and singly charged iron ions. The spectrum of molecular nitrogen was also detected, since molecular nitrogen is a background gas, which is present in the vacuum chamber at a residual pressure of 5 Pa. The continuous radiation spectrum was also detected, which occurs due to the emission of the local molten metal region on the steel surface.

In the framework of the local thermodynamic equilibrium model, the plasma electron temperature was determined using data on the relative intensities of the iron atom lines. The temperature turned out to be $7400 \pm 800$ K.

For the first time, based on the experimental data, the continuum was distinguished in the spectrum of microplasma discharge initiated on the metal surface partially covered with a thin dielectric film, which was interpreted as the continuous spectrum of thermal emission of the local molten metal region, which occurs on the sample surface as a result of metal melting due to the effect of microplasma discharges. Analysing this continuous spectrum, we managed to estimate the temperature of iron melt on the sample surface: it turns out to be approximately 5000 K.

Comparison between the temperatures of the melt formed under the discharge determined using the data on the continuous emission spectrum and the data on the line emission spectrum of iron atoms in microplasma discharge shows that these temperatures are considerably different. In this case, the temperature of the molten metal surface determined using data on the continuous spectrum is lower.

Thus, the electron temperature of the discharge plasma, which causes the metal melting, is considerably higher than the melt temperature. And, on the liquid-vapor equilibrium curve, the melt temperature corresponds to the range of rather high pressures that are required for the formation of microrelief, consisting from craters and continuous melt regions.

Since the characteristic microrelief consisting of craters also forms during the microplasma treatment of surfaces at lower currents, it is likely that the similar melt temperatures and vapor pressures affecting the melt can be observed also in those treatment modes. However, in those treatment modes, the simultaneously observed melt area is insufficient for the reliable detection of the melt thermal radiation. This problem, as well as the problem of estimating the gas temperature using data on the molecular spectrum component, can be solved by means of increasing the sensitivity, dynamic range and spectral resolution of the used measurement technique.

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