The study of the physical processes of low-temperature plasma formation and its effects on metal product surface

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Abstract. The article examines the physical processes associated with the formation and the impact of low-temperature plasma of combined discharge on the surface of metal products. It has been shown theoretically and experimentally that the properties of a gas discharge and the results of its action on the product surface depend significantly on the sign of the bias potential.

1. Introduction

The operating conditions of many products included in the equipment of enterprises of the fuel and energy complex (nozzles of combustion chambers and nozzle blades of 1 stage of gas turbines, burner devices of boiler units, etc.) are extreme. In this connection, the problem of increasing their operational reliability by the criterion of wear resistance is topical. One of the ways to solve this problem is the creation of technologies and equipment for hardening the surface layer of products. These include the technologies and equipment developed by the authors that provide hardening due to the effect of a combined discharge on low-temperature plasma. A low-temperature plasma is a microwave gas discharge that largely has the properties of a high-frequency discharge and is generated directly around the surface of the article when an ultrahigh-frequency electromagnetic field is superimposed at the level of the supplied microwave power of 30 ... 100 W and the electrostatic field when a displacement potential of 50 ... 250 AT. In this case, the properties of the combined gas discharge depend substantially on the sign of the bias potential applied to the product.

2. Combined gas discharge

Let us consider the processes taking place in a plasma cloud formed upon the imposition of an electrostatic field and an ultrahigh-frequency electromagnetic field in a process N2 gas environment with p ≈ 300 Pa pressure immediately around the workpiece (Fig. 1). The visible region of the cloud has a characteristic diameter L ≈ 4 cm. The workpiece size d ≈ 1 cm is small in comparison with the dimensions of the resonator (D = 15 cm).

By its characteristics, the combined gas discharge is a microwave discharge of reduced pressure (usually they are the discharges excited by a rapidly varying electric field in the frequency range ν = 10^9 ÷ 10^11 Hz with wavelengths λ = 0.3 ... 30 cm), with a significant influence on it, as it will be shown below, from the stationary electric field. The discharge is excited by the magnetron and arises in the intracavity space. The excitation source of the resonator (magnetron with operating frequency ν = 2.45 GHz and wavelength λ = 12.5 cm) determines its working mode. When the workpiece is put into the working chamber, the microwave field will be rearranged in some adjacent area, resulting in lines of tension, the beginning and the end of which will be on the workpiece and the section of the working chamber wall located close to it (Figure 1).
A high-frequency electromagnetic field ionizes the gas in the resonator. Slow electrons can not ionize molecules and collide with them elastically. In such collisions, the electron practically does not lose kinetic energy, but the initial direction of its velocity can change substantially and coincide with the direction of the electric field. In this case, the electron does not return energy to the field but receives it again. A certain number of electrons can be greatly accelerated by the microwave field, and their energy becomes sufficient to ionize the gas, after which the process is repeated. In elastic collisions with gas molecules, some electrons in the electric field are accelerated, and new ionization events occur. Ions and electrons accumulate in the gas. As their concentration increases, the role of recombination processes rises. As a result of ionization and recombination, a stationary plasma is established whose concentration and temperature depend on the type of gas, its pressure, and also on the microwave field frequency and amplitude. As the surface area of the workpiece is small compared to the dimensions of the resonator, the lines of strength of the microwave electric field thicken near the workpiece. In this area the microwave energy density is the greatest, and the ionization and recombination processes are particularly intensive.

It will be further shown that under certain conditions, a diode effect similar to that observed with an HF discharge will arise in this case [1, 2]. The diode effect is manifested in the formation of a near-wall layer of a positive space charge with a constant potential difference between the plasma and the wall $U_p \gg k_B T_e$ ($k_B$ is the Boltzmann constant, $T_e$, e is the electron temperature and charge) near the product surface. The value of $U_p$ depends on the intensity amplitude $E_0$ of the operating mode of the microwave electric field, as well as on the potential value of the electrostatic field $\phi_0$ on the workpiece.

When constant $\phi_0 > 0$ is applied to the workpiece, the electrostatic field keeps the electrons arising as a result of ionization by the microwave field near the workpiece surface, which contributes to the plasma cloud formation in this area (Figure 2a). Microwave power level is approximately 100 W. In this case, the gas discharge is accompanied by intense crimson glow and hardens the surface layer.

When $\phi_0 = 0$, the combined discharge is a microwave gas discharge in its pure form. In this case, a weak diode effect and a small constant potential difference $U_p \sim 10\div20$ V occur. The effect of plasma on the surface of the product is negligible.

The application of a small negative potential $\phi_0 < 0$ to the workpiece makes it difficult to create a plasma cloud, since the electrostatic field repels the microwave field-originated electrons from the workpiece surface into the area with a low density of microwave energy, which makes it impossible to achieve energies sufficient for the ionization of $N_2$ molecules. As the experiment shows, when $\phi_0 < 0$, much higher microwave power of the order of 200$\div300$ W is needed for the discharge to occur than in case of $\phi_0 > 0$. There is no intensive crimson plasma glow in this case (Figure 2, b). At values of $\phi_0 < -250$ V,
a powerful bombardment of the workpiece surface with positive ions occurs and, as a consequence, there is an intensive yield of secondary electrons, which can lead to the onset of a high-current $\gamma$ discharge [3-9]. The glow is localized near the electrode surface and consists of several layers.

![Figure 2 (a, b). Plasma discharge with application of a positive (a) and negative (b) bias potential to the product](image)

3. Combined gas discharge parameter estimates

In the range of gas pressures $P = 10^{-2}$ to $10$ mm mercury the surface layer of the workpiece is not collisionless. The ratio of the mean free path of the ions $\lambda_i$ to $d$ at these pressures is $1 \times 10^2$. In [10] an approximate formula was obtained for the microwave analog of the Child-Langmuir law:

$$U_p = \frac{6}{5} \left( \frac{m_i}{2e} \right)^{\frac{1}{2}} \left( \frac{3}{2} \frac{\bar{I}}{e_0} \right) \left( \frac{d + \lambda_i}{2d + \lambda_i} \right) \lambda_i^{\frac{3}{2}} d^{\frac{3}{2}}. \quad (1)$$

Let us give the parameter estimates of the combined gas discharge, based on the relation (1).

3.1. First consider the case when the bias potential is $\phi_0 = 0$. After applying the supply voltage to the magnetron, the frequency of its oscillations is established very rapidly ($\sim 10^{-8}$ to $10^{-7}$ s) and it corresponds to the resonance frequency of the system formed by the magnetron, the volume microwave resonator and the workpiece placed inside the resonator. After this, the energy inside the cavity resonator starts accumulating. The field intensity inside the resonator increases in this case, until it exceeds the breakdown value for the internal air space filling it. Then a discharge is ignited inside the resonator near the workpiece.

To estimate the value of $E_0$, we use the relation

$$W = \frac{e_0 E_0^2}{2} V = \frac{PQ_0}{\omega}, \quad (2)$$

from which

$$E_0 = \left( \frac{2PQ_0}{e_0 V \omega} \right)^{\frac{1}{2}}. \quad (3)$$

Here $W$ is the electromagnetic energy stored in the resonator, $Q_0$ is the resonator $Q$-factor, $V$ is the resonator volume, $P$ is the power given by the magnetron, and $\omega$ is the cyclic frequency. From (3) for the values of the parameters $P = 100$ W, $V = 5$ L = $5 \times 10^{-3}$ m, $Q_0 = 0.5$, $\omega = 1.51 \times 10^{10}$ s$^{-1}$, we find $E_0 = 1.7 \times 10^5$ V/m, which exceeds the threshold of microwave air breakdown which, depending on pressure, frequency and discharge volume, can reach $\sim 10^5$ V/m.
For gas, breakdown means a transition to an ionized state. In this case, current increase leads to an even greater increase in ion concentration and gas conductivity, and, consequently, to the reduction of the voltage required to maintain such a current. After the microwave discharge ignition, the energy stored in the resonator decreases, reducing the electric field strength $E_0$ as well as the value of the microwave potential on the workpiece surface $U_0$ to the values of the order of several hundred volts.

The presence of the microwave electric field in the resonator is responsible not only for maintaining the plasma and microwave discharge in the working chamber, but also for the formation of the wall layer. At the field frequencies of the order of $\nu = 10^9 \div 10^{13}$ Hz, the microwave current in the plasma occurs due to the electron oscillations. Electron displacement in a high-frequency field:

$$x = \frac{e}{m_e \omega^2} E_0 \exp(-i \omega t),$$

(4)

where $m_e$ is the electron mass, $\omega = 2 \pi \nu$.

The displacement of heavy ions, which is $-e m \omega^2$, can be neglected as $m_e < m_i$. Over the period of the field, the ions can be considered stationary. The near-wall plasma layer adjacent to the workpiece has a width of the order of electrons spatial variation amplitude $d \approx eE_0/m_e \omega^2$. For the values of $e = 1.6 \times 10^{-19}$ C, $m_e = 9.1 \times 10^{-31}$ kg, $\omega = 1.51 \times 10^{10}$ Hz, $E_0 = 3.9 \times 10^4$ V/m we find $d = 0.3 \times 10^{-3}$ m.

The concentration of neutral molecules $n = n_0 k_b T$. For $P = 0.00263 \times 10^5$ Pa (2 mm mercury) and $T = 500^\circ$K – the temperature of neutral molecules, find $n \approx 3.8 \times 10^{12}$ m$^{-1}$.

Electron thermal velocity $\langle v_e \rangle = \sqrt{3k_b T_e/m_e}$ at an electron temperature $T_e = (2-10)^9$K reaches the value $\langle v_e \rangle \approx 0.94 \times 10^6$ m/c. Electron thermal energy in the quasi-neutral plasma screen $[1]$ $e = 3k_b T_e/m_e \approx 2.6$ eV.

To estimate the ion saturation current $j_i$, the Bohm semi-empirical formula can be used:

$$j_i = e n_i (d) v_{i0} = e n_{i0} e^{-3/2} v_{i0} = 0.6 e n_{i0} \left( \frac{k_b T_e}{m_i} \right)^{1/2}.$$  

(5)

Here $n_i(d)$ is ion concentration at the boundary surface layer, $n_{i0}$ is ion concentration at distances $x \gg d$ from the article, $v_{i0} = \sqrt{k_b T_e/m_i}$ - the ion velocity at the layer boundary, determined by the Bohm criterion. For $m_i = 2.2325 \times 10^{-26}$ kg is nitrogen ion mass $N^+$ and $T_e = 2 \times 10^5$K, ion velocity $v_{i0} = 3.45 \times 10^5$ m/s.

Processes defined by the parameters some of which are characteristic for electrons (in this case, $T_e$), and the others – for the ions (in the formula (5) – ion mass $m_i$), are commonly called ambipolar.

With the current flowing through the unit $i \approx 8$ mA and the workpiece surface area $S = 6 \times 10^{-4}$ m$^2$, the current density is $j_i = 13.3$ A/m$^2$.

From (5) we find the concentration of ions $n_{i0} = 4 \times 10^{14}$ m$^{-3}$. Plasma frequency for electrons $\omega_p = \sqrt{n_e e^2 / \epsilon_0 m_e} = 1.13 \times 10^{10}$ c$^{-1}$, magnetron frequency $\omega = 2 \pi / \lambda = 1.51 \times 10^{10}$ c$^{-1}$. Thus, the microwave field can penetrate through the plasma, as $\omega > \omega_p$.

The mean free path of an ion $\lambda_i = 1/\sqrt{2n \sigma} = 6.6 \times 10^{-4}$ m, where $\sigma = \pi d_i^2$ is the effective cross-section area of the nitrogen molecule collision, $d_i = 3 \times 10^{-10}$ m is effective diameter of nitrogen molecules.

For $\lambda_i = 6.6 \times 10^{-4}$ m $m_i = 2.325 \times 10^{-26}$ kg, $d \approx 0.3 \times 10^{-3}$ m from (1) we get $U_p \approx 16.82$ V. In this case $\lambda_i / \lambda \approx 0.22$. Note that the obtained value of $U_p$ is relatively small, which is due to small thickness of the near-surface layer $d$, and is substantially smaller than that characteristic of the high-frequency discharge where it reaches hundreds of volts.

3.2. If we apply a constant negative potential $q_0$ to the workpiece, the situation changes significantly (Figure 3). The workpiece potential $\phi(t) = V(t) + q_0$ in this case is the sum of the microwave component $V(t)$, the time average of which is $\langle V \rangle$, and the constant potential $q_0 \langle V \rangle + q_0 = -U_p$. Figure 3 also shows the dependence of the microwave potential $U(t)$, the maximum value of which $U_0$ is determined by the amplitude $E_0$ of the operating mode of the microwave electric field in the resonator and the width of the near-surface layer $d(t)$ [11].
Figure 3. Time dependencies of the near-surface layer thickness $d(t)$, microwave potential of the electric field $U(t)$ and the workpiece potential $\varphi(t)$ when bias potential is applied to a workpiece

Let $\varphi_0 = -300$ V. From (1) for the steady-state potential $U_p = -\langle V \rangle - \varphi_0 = 300 + 16.82 = -316.82$ V, we can find the thickness of the layer $d \approx 1.9 \times 10^{-3}$ m.

The number of ions entering the workpiece surface per unit time, $dN_i/dt = j_i S/e = 8 \times 10^{-3}/1.6 \times 10^{-19} \text{s}^{-1} = 5 \times 10^{16} \text{s}^{-1}$.

The energy of the directed motion, acquired by the ion in the near-surface layer, $\varepsilon_i = e\varphi = 316.82$ V $\approx 5 \times 10^{-17}$ J. The speed of the ion directed motion at the end of acceleration $v_i \approx \sqrt{2e\varphi/m_i} = 6.5 \times 10^4 \text{m/c}$.

Assuming that all the energy $\varepsilon_i$ is transferred from the ion to the workpiece, then per unit time, the surface of the workpiece will get $dW_i/dt = 2.5 \text{Br}$.

Energy supplied to the surface of the workpiece for the typical processing time $\tau = 1000$ s, $W \approx 2500$ J. Thus, during the processing time, the workpiece generates quantity of heat $Q \approx 2500$ J.

The potential barrier near the workpiece undergoes microwave oscillations with respect to its mean value which is equal to $U_p$. At the moment of the barrier disappearance, there is a short-time impulse runoff of electrons to the product surface, which compensates for the constant ion current that is constant in time.

3.3. Let us consider the situation that arises when a positive potential $\varphi_0$ is applied to the workpiece. If $\varphi_0 > \langle V \rangle$, the mean potential of a quasineutral plasma with respect to the workpiece $U_p < 0$. The time dependencies of the potential on the workpiece surface and the thickness of the near-surface layer when a positive potential is applied to the article are shown in Figure 4.

The average electron thermal motion velocity, as shown above, is $\langle v_e \rangle \approx 0.94 \times 10^6 \text{m/c}$. The current flowing through the unit:

$$i = jS = \frac{1}{4} n_e \langle v_e \rangle S,$$

where $S$ is the surface area of the workpiece. For a current $i \approx 8$ mA the value of the electron concentration is: $n_e = 3.54 \times 10^{14} \text{m}^{-3}$.

The number of electrons entering the workpiece surface per unit time $dN_e/dt = 5 \times 10^{16} \text{s}^{-1}$.

Estimates suggest that for the space charge layer formation in the vicinity of the workpiece, the electron should be drawn into this layer with a velocity not less than

$$k_B T_i = m_e v^2_{0\text{e}}.$$
Figure 4. Time dependencies of the near-surface layer thickness \( d(t) \), microwave potential of the electric field \( U(t) \) and the workpiece potential \( \phi(t) \). when bias potential \( \phi_0 > 0 \) is applied to the workpiece.

When this condition is satisfied, the electron concentration exceeds the ion concentration at any point of the layer. Hence, for \( T_i = 500 \, \text{K} \) we find \( v_{oe} = 0.87 \cdot 10^5 \, \text{m/c} \). The area between plasma and the layer in which the electrons are accelerated to energy \( m_e v_{oe}^2 / 2 = k_B T_i / 2 \) is usually called the prelayer. There is a field in the pre-layer that accelerates electrons and inhibits ions, but at the same time the quasineutrality ratio is valid. Thus, the initial drift velocity toward the anode, which the electron has at the boundary between the layer and the prelayer is \( v_0 \approx 0.1 \langle v_e \rangle \).

The energy of directed motion, an electron acquires in an electric field near the surface of the article, with \( U_p = 200 \, \text{V} \) is

\[
\varepsilon_e \approx eU_p = 200 \, \text{vB} = 3,2 \cdot 10^{-17} \, \text{J}.k.
\]

Thus, electrons gain energy and cause an anode glow of a crimson shade (Figure 2, a).

Directed movement velocity acquired after the electron passes the layer is ten times greater than the thermal velocity \( v_e \approx \sqrt{2e \varepsilon_e / m_e} = 0.83 \cdot 10^7 \, \text{m/c} \approx 10 \langle v_e \rangle \). Energy supplied to the surface of the workpiece during time \( \tau = 1000 \, \text{s}, W = 1600 \, \text{J} \). Thus, the quantity of heat the workpiece emits is \( Q = 1600 \, \text{J} \).

The mean free path of an electron is \( \lambda_e = 1/\sqrt{2n \sigma} = 2.64 \cdot 10^{-4} \, \text{m} \) where \( \sigma = \pi d_0^2 / 4 \), \( d_0 = 3 \cdot 10^{-4} \, \text{m} \) is effective diameter of nitrogen molecules.

Using formula (1), we can determine the layer thickness \( d \approx 1 \, \text{cm} \) by the order of magnitude, with the ratio \( \lambda_e / d \approx 0.02 \, \text{cm} \), which corresponds to the domain of applicability (1).

Let us estimate the amount of heat necessary to melt the thin surface layer of the article with a fixed thickness \( l = 0.04 \, \text{mm} \) with the values characteristic of steel: specific heat \( c = 462 \, \text{J/kg} \cdot \degree\text{K} \), specific heat of fusion \( r = 82,000 \, \text{J/kg} \), density \( \rho = 7,700 \, \text{kg/m}^3 \), \( t_f \approx 1500 \degree\text{C} \). The minimum temperature value of 50\degree\text{C} is at the opposite end of the workpiece, the article being fixed in a holder, where the temperature is measured with a thermocouple.

Then \( Q = (c\Delta T + r)pS l \approx 140 \, \text{J} \), which is much less than the amount of heat released in the article during the plasma exposure time, and means the possibility of significant structural and phase changes in its surface layer.

4. Experimental confirmation of estimates

In order to confirm the reliability of the performed evaluations, an experiment was conducted, the methodology of which included:

- plasma processing of steel workpieces in a process unit with the applied bias potential of -200 V to +200 V;
– study of sample surface morphology before and after processing on an analytical complex based on Tescan Mira\LMU scanning electron microscope (SEM);
– measurement of microhardness (Vickers) before and after dynamic method processing [12] using a microdurometer PMT-3;
– statistical data set processing for testing the hypothesis of their mean values coincidence using the Kruskal-Wallis nonparametric variance analysis based on the calculation of $J_v$ Iman and Davenport statistics. The hypothesis is taken at the significance level $\alpha$ if the value of the $J_v$ statistics is less than its $J_v^{\alpha}$ limiting value calculated using the Pearson $\chi^2$-distribution and Fisher's $F$-distribution.

Figure 5, a shows a SEM image of the workpiece surface treated with a negative bias potential of -200 V. We recorded formation of uniformly distributed point structures with average size elements of 12 ... 15 nm reflecting only surface changes which can be defined as an island film. At the same time, the formation of a practically continuous coating containing nanoparticles of 40 ... 90 nm size and an amorphous phase formed from the solidified melt (Figure 5, b), i.e. nanocomposite (or two-phase) structure, was recorded on the sample surface treated with a positive potential. Also note that the processing with a negative potential required 1.6 times more microwave power, as otherwise plasma around the workpiece was not formed.

![SEM images of sample surfaces](image)

**Figure 5 (a,b).** SEM images of sample surfaces, treated with negative (a) and positive (b) bias potential (view field: 1,654 µm)

The results of measuring the surface microhardness and statistical processing of the obtained data made it possible to establish the following.
1. For the samples treated with a negative potential, the microhardness value remained at their initial values (Fig. 6, a).
2. For the samples processed with a positive potential, the microhardness increased up to 2 times. The structure compaction was also noticed, since at the same load the introduction of the indenter occurred to a lesser depth in comparison with the penetration depth when measuring the initial microhardness.
3. The comparison of the calculated and limiting values of Kruskal-Wallis statistics showed that in the case of processing with a negative potential, the changes in microhardness (and, consequently, density) were insignificant, since $J_v < J_v^{\alpha}$ and when processing with a positive potential, they are significant ($J_v > J_v^{\alpha}$). While in operation, this will increase the product wear resistance.
5. Conclusions
1. The study of the properties and evaluation of the main physical parameters of a combined gas discharge in the case of positive, zero and negative bias potentials on the sample show that this type of discharge occurs when microwave gas and stationary electric field jointly influence the technological gas. The properties of the discharge depend substantially on the sign of the bias potential applied to the product.

2. The negative bias potential affects discharge inception and requires a significantly higher power to be supplied to the magnetron. With a sufficiently large negative bias potential, a positive space charge layer is formed near the workpiece where positive ions accelerate to energies of several hundred eV. In this case, the properties of the combined discharge are largely similar to those of the high-frequency discharge.

3. In the case of a positive potential, a plasma cloud with a characteristic crimson shade appears near the workpiece surface. In this event, a powerful surface treatment of the product occurs and a nanocomposite reinforced structure is formed.

4. The nanocomposite structure formation consolidates the workpiece surface layer, and, consequently, enhances its environmental resistance. While in operation, this will help to reduce the product wear intensity.

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