THE INFLUENCE OF THE PARAMETERS OF AN ATMOSPHERIC PRESSURE BARRIER DISCHARGE IN AIR ON THE PLASMA KINETICS

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The influence of the characteristics of microdischarges representing structural elements of a barrier discharge on the plasma kinetics in the latter is considered. The reasons that affect the behavior of the concentrations of some components are clarified. It is shown that the indeterminacy of the characteristics results in the values of the concentrations that lie within wide limits.

1. Introduction

Nowadays, a barrier discharge (BD) is used for the removal of N_xO_y oxides from industrial gases [1], sterilization of medical instruments [2], modification of surface properties of polymer materials [3], etc. In this connection, it is necessary to study the physical processes and, particularly, the plasma kinetics taking place in discharges.

A BD represents an assembly of short-term microdischarges stochastically distributed over the electrode surface that arise practically simultaneously after the breakdown voltage is reached across the discharge gap. A short lifetime complicates the experimental investigation of the processes taking place in an individual discharge channel. For this purpose, one uses numerical methods. In addition, the plasma kinetics in the bulk of the discharge is influenced by the frequency of the appearance of microdischarges, the radius of a separate structural element, and their number per unit area. In turn, these quantities depend on the surface area of the dielectrics, their properties, and the chemical composition of a gas mixture. But the determination of the characteristics of microdischarges raises certain difficulties: they can not be accurately measured experimentally, whereas the existing numerical models used for the calculation of their values have poor precision. In this connection, the mentioned quantities are considered as free parameters when describing the plasma kinetics. That is why it is important to know in which way their change influences the processes taking place in discharges.

In the given paper, the effect of each of the parameters on the plasma kinetics in an atmosphere pressure BD in air is investigated with the help of numerical calculations. The mechanisms of this influence are determined, by basing on the detailed analysis of chemical reactions.

2. Model of the Discharge

As was noted above, a BD represents an aggregate of thin microdischarges stochastically distributed over the electrode surface, which must be taken into account in studying the kinetics. One should also keep in mind the fact that these structural elements appear in sets (a set is an aggregate of simultaneously appearing microdischarges). The frequency of their initiation is multiple to the double frequency of the supply voltage. In the process of numerical calculations, each set of microdischarges was considered as a rectangular current micropulse with duration τ.

In order to calculate the concentrations of molecules and radicals arising in a microdischarge, the following system of kinetic equations was used:

$$\frac{dN_i}{dt} = S_{ei} + \sum_j k_{ij} N_j + \sum_{m,l} k_{iml} N_m N_l + ..., \qquad (1)$$

where N_i is the concentration of the $i-$th component, k_{ij} and k_{iml} are the rate constants of molecular processes with its participation. The scheme of chemical reactions for the components of the gas mixture was taken from [5]. The rate of generation of the products of electron-molecular reactions S_{ei} was calculated from the equation

$$S_{ei} = \frac{W}{V} \frac{1}{\varepsilon_{ei}} \frac{W_{ei}}{\sum\limits_i W_{ei} + \sum\limits_i W_i}. \qquad (2)$$

The quantity W/V denotes the power introduced into a unit volume of the microdischarge, W_{ei} is the specific power spent for the electron-molecular process

of inelastic interaction with the threshold energy ε_{ei}:

$$W_{ei} = \sqrt{\frac{2q}{m}} n_e N_i \varepsilon_{ei} \int_0^\infty \varepsilon Q_{ei}(\varepsilon) f(\varepsilon) d\varepsilon, \tag{3}$$

where $q = 1.602 \times 10^{-12}$ erg/eV, m is the electron mass, n_e is the electron concentration, Q_{ei} stands for the cross section of the corresponding inelastic process, and $f(\varepsilon)$ denotes the electron energy distribution function. The quantity W_i is the specific power spent for heating the gas:

$$W_i = \frac{2m}{M_i} \sqrt{\frac{2q}{m}} n_e N_i \int_0^\infty \varepsilon^2 Q_i(\varepsilon) f(\varepsilon) d\varepsilon, \tag{4}$$

where M_i are the molecular masses, Q_i denotes the momentum cross section of the electron scattering by molecules of the primary components.

In the calculations concerning the plasma kinetics, the whole time period during which the gas stayed in the discharge chamber was divided into equal intervals. In turn, each of the latter consisted of two stages. In the first stage lasting for τ, the kinetics was calculated in the effective volume of all microdischarges. In the second one, system (1) was solved during the period of one set at $S_{ei} = 0$, i.e. in the absence of the discharge. In addition, the concentrations of all components were averaged over the whole volume of the discharge chamber after the time of the gas diffusion from the channel.

In [5], the concentrations of O_3, HNO_3, HNO_2, and NO_3 were determined experimentally. Their values are compared with the results of our calculations.

The electron energy distribution function (EEDF) was calculated from the Boltzmann kinetic equation in the two-term approximation [4] at the external electric field strength of 20 kV/cm. In the process of its solution, we took into account processes 1–9 listed in the Table of the given work, while equations (1) were solved with regard for the reactions from Tables 1 and 2 given in [5].

Formula (2) includes the quantity W/V that represents the power introduced into a unit volume of the micropulse. It must be expressed in terms of the total power introduced into the discharge volume. For a micropulse with effective volume V_{eff},

$$\frac{W}{V} = \frac{W_0}{M V_{\text{eff}} \tau}, \tag{5}$$

where W_0 is the total power introduced into the discharge (this quantity is considered constant in all calculations), $M = \nu m$ denotes the frequency of micropulses, ν is the electric field frequency, m represents the average number of micropulses per cycle, and V_{eff} is the effective gas volume excited by a set of microdischarges of a single micropulse. Assuming that each of the microdischarges has a cylindrical form, we obtain

$$V_{\text{eff}} = S_{\text{dis}} S h \pi R_0^2, \tag{6}$$

where S_{dis} stands for the electrode area, S is the surface density of microdischarges, $h\pi R_0^2$ denotes the volume of one microdischarge, R_0 is its radius, and h is the interelectrode distance. As the volume of the discharge chamber is equal to $S_{\text{dis}}h$, (6) acquires the form

$$\frac{W}{V} = \frac{W_0}{V} \frac{1}{\pi M \tau S R_0^2}. \tag{7}$$

Thus, the specific power in one micropulse is determined by the following quantities: the frequency of microdischarges M, their duration τ, and the product of the surface density of microdischarges by their squared radius SR_0^2.

In our calculations, the initial relative concentrations of nitrogen and oxygen were equal to 78 and 22%, respectively, while the air humidity amounted to 20%. The alternating voltage frequency was equal to 400 Hz, the specific power introduced into the discharge $W_0/V = 1.5$ W/cm^3, the time during which the gas mixture stayed in the discharge chamber was 0.5 s. These data correspond to the conditions of the experiment described in [5]. The characteristics of microdischarges were varied within the following limits: $M = 5 \times 10^3 \div 4 \times 10^4$ s^{-1}, $\tau = 7 \div 50$ ns, $SR_0^2 = 5 \times 10^{-5} \div 1.5 \times 10^{-3}$. These values correspond to the experimentally determined characteristics of microdischarges [6].

Reactions used for the calculation of the EEDF

N	Reactions	Reference to the scattering cross-section
1	$O_2 + e \rightarrow O + O + e$	[8]
2	$O_2 + e \rightarrow O_2(^1\Delta_g) + e$	[8]
3	$N_2 + e \rightarrow N_2(A^3\Sigma_u^+) + e$	[9]
4	$N_2 + e \rightarrow N_2(a^1\Pi_g) + e$	[10]
5	$O_2 + e \rightarrow O_2(v) + e$	[11]
6	$N_2 + e \rightarrow N_2(v) + e$	[12]
7	$N_2 + e \rightarrow N + N + e$	[13]
8	$O_2 + e \rightarrow O_2^+ + e$	[14]
9	$N_2 + e \rightarrow N_2^+ + e$	[14]

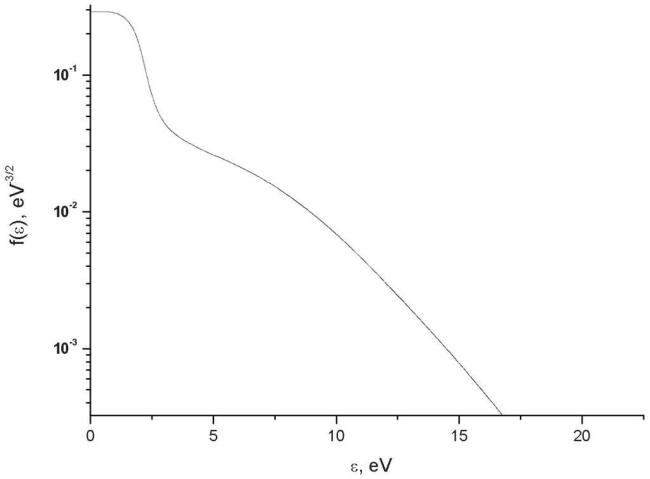

Fig. 1. EEDF in the atmospheric pressure barrier discharge in air at the electric field strength of 20 kV/cm

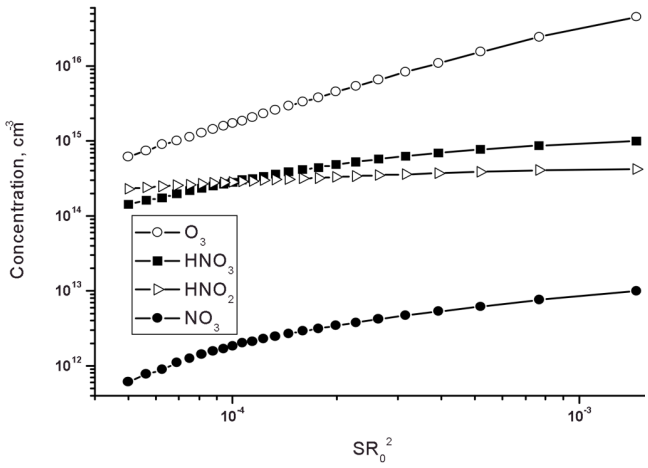

Fig. 2. Dependence of the HNO_3, O_3, HNO_2, and NO_3 concentrations on the quantity SR_0^2

3. Analysis of the Results

Figure 1 demonstrates the EEDF calculated in the atmospheric pressure BD in air. One can see that it significantly differs from the Maxwellian distribution function. The gap at $\varepsilon = 1.5 \div 2.5$ eV is related to the excitation of the vibrational levels of nitrogen molecules.

The concentrations of the investigated components as functions of the parameter SR_0^2 are given in Fig. 2 ($\tau = 15$ ns, $M = 2 \times 10^4 s^{-1}$). One can see that this quantity considerably influences the concentrations of all the components and results in their increase in the whole range of its variation. The experimental value of the O_3 concentration is reached at $SR_0^2 = 9.48 \times 10^{-4}$, those of HNO_3 and NO_3 – at $SR_0^2 = 1.5 \times 10^{-3}$.

The dependences of the concentrations on the micropulse frequency are presented in Fig. 3 ($\tau = 15$ ns, $SR_0^2 = 2 \times 10^{-4}$). The quantities $[O_3]$ and $[NO_3]$ increase in the whole interval of variation of M, whereas $[HNO_3]$ and $[HNO_2]$ decrease. Moreover, the concentration of HNO_3 molecules weakly depends on the indicated parameter. The calculation results coincide with the experimental values for $[O_3]$ and $[NO_3]$ (at $M = 4.8 \times 10^3$ s^{-1} and $M = 8 \times 10^3$ s^{-1}, respectively).

The change of the parameters of microdischarges results in the competition of two factors: that of the specific power that directly influences the plasmochemical processes and the factor related to the characteristics of micropulses: their effective volume, frequency, and duration. Our calculations demonstrate that the raise of the specific power introduced to a microdischarge results in an increase of the concentrations of HNO_2, HNO_3, and NO_3 in the bulk

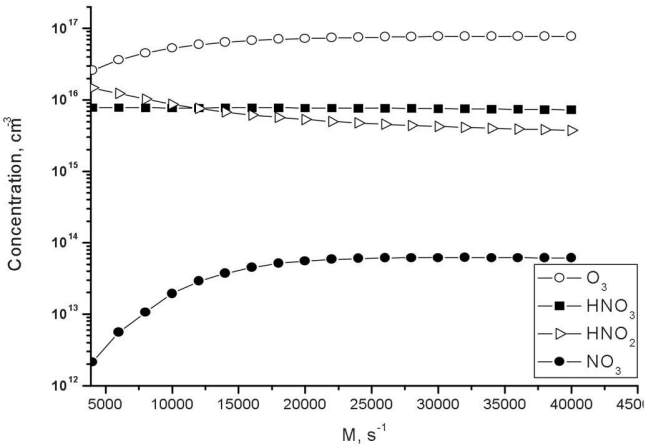

Fig. 3. Dependence of the HNO_3, O_3, HNO_2, and NO_3 concentrations on the micropulse frequency

of the discharge and a decrease of the concentration of ozone.

The behavior of the O_3, HNO_3, and HNO_2 components during a breakdown is determined by the dissociation reactions

$$O_3 + e \rightarrow O + O_2 + e, \tag{8}$$

$$HNO_3 + e \rightarrow OH + NO_2 + e, \tag{9}$$

$$HNO_2 + e \rightarrow NO + OH + e, \tag{10}$$

respectively. According to (2), the rates of these reactions are proportional to the specific power, that is why the concentrations of the indicated components

during microdischarges decrease with increasing W/V. The dominant process that determines the behavior of $[NO_3]$ in a microdischarge is the reaction

$$NO_3 + O \rightarrow NO_2 + O_2. \quad (11)$$

Oxygen atoms are mainly generated in the reaction of electron dissociation of molecular oxygen. As the rate of this reaction is proportional to W/V, rate (11) also rises with increase in this quantity. That is why, the raise of the specific power results in a decrease of $[NO_3]$.

Thus, the concentrations of all the investigated components decrease with increasing W/V during the microdischarges. This fact would result in a decrease of the levels of these components in the bulk of the discharge chamber, which conflicts with the earlier indicated dependences. However, due to a low duration of microdischarges, the processes taking place during this period do not considerably influence the concentrations of the investigated quantities, and their behavior is determined by the processes taking place between two successive microdischarges. Nevertheless, the levels of the atomic components generated during microdischarges later on determine the plasma kinetics in the discharge.

During the time between two successive micropulses, the dominant process of generation of HNO_2 molecules is the reaction

$$NO + OH + M \rightarrow HNO_2 + M, \quad (12)$$

while that of decay is the process

$$HNO_2 + OH \rightarrow NO_2 + H_2O. \quad (13)$$

As OH radicals take part in the both processes, the behavior of $[HNO_2]$ is determined only by the behavior of [NO] mainly generated in the reaction

$$N + O + M \rightarrow NO + M. \quad (14)$$

The rate of the latter process is mainly determined by the concentrations of atomic nitrogen and oxygen established during a microdischarge. On this stage, N and O are mainly generated in the process of dissociation of molecular nitrogen and oxygen, respectively. The rates of these processes are proportional to the specific power, whose increase results in the growth of [N], [O], and [NO], which implies the increase of the HNO_2 concentration.

The behavior of $[HNO_3]$ on the stage between two microdischarges is determined by the reactions

$$NO_2 + OH + M \rightarrow HNO_3 + M, \quad (15)$$

$$HNO_3 + OH \rightarrow NO_3 + H_2O. \quad (16)$$

Taking into account the fact that the rates of both processes are influenced by the concentration of OH radicals, the character of the dependence of $[HNO_3]$ on the specific power is determined by the level of $[NO_2]$ at the end of a microdischarge. During the latter, the dominant process with participation of the indicated component is the reaction

$$NO + O + M \rightarrow NO_2 + M. \quad (17)$$

With increasing W/V, its rate rises due to the growth of the quantities [NO] and [O]. This fact results in an increase of the NO_2 concentration and, consequently, that of HNO_3.

The change of the ozone concentration in the interval between two successive microdischarges is influenced by the following reactions:

$$O_2 + O + M \rightarrow O_3 + M, \quad (18)$$

$$O_3 + O \rightarrow O_2 + O_2, \quad (19)$$

$$O_3 + H \rightarrow O_2 + OH, \quad (20)$$

$$O_3 + NO \rightarrow O_2 + NO_2. \quad (21)$$

One can see that atomic oxygen participates in the generation and the decay of ozone molecules. That is why the behavior of $[O_3]$ is determined by the concentrations of H radicals and NO oxide. During the breakdown, atomic hydrogen is mainly generated in the process of electron impact dissociation of water molecules, which implies the growth of [H] with increasing W/V. Thus, an increase in the specific power results in the growth of the decay rate of ozone and, consequently, a decrease of its concentration.

The basic channels of the generation and the decay of NO_3 molecules are the processes

$$NO_2 + O + M \rightarrow NO_3 + M, \quad (22)$$

$$NO_3 + O \rightarrow NO_2 + O_2, \quad (23)$$

respectively. One can see that the behavior of $[NO_3]$ coincides with that of $[NO_2]$, whose level in a microdischarge takes on a larger value with increase in the specific power.

According to (7), a rise of W/V is related to the decrease of any of the quantities SR_0^2, M, or τ. The

competition of these two factors determines the pattern of variation of each of the investigated concentrations.

Our calculations demonstrate that neither concentration depends on the micropulse duration, i.e. its change completely compensates the variation of the specific power.

A decrease of the quantity SR_0^2 results in a decrease of the effective volume of one micropulse. As was demonstrated above, the plasma kinetics in a BD is determined by the value of the specific power introduced into a micropulse. That is why, at a fixed power, the same number of particles is generated in unit volume. In this case, a decrease of the micropulse effective volume results in a reduction of the number of particles generated in it and, respectively, a decrease of the concentrations of the investigated components in the bulk of the discharge chamber.

A reduction of the micropulse frequency is accompanied by a decrease of the total number of breakdowns taking place in the discharge chamber during the whole time under consideration. At the same time, at a constant value of W/V, there appears a fixed number of particles in each current channel. Due to this fact, a decrease of M results in the lower levels of the concentrations of the components at the end of the whole process.

Thus, on the one hand, an increase in the parameters SR_0^2 and M results in a reduction of the concentrations of the investigated components in the bulk of the discharge chamber due to a decrease of the specific power introduced into a micropulse, while, on the other hand, it causes their increase due to the growth of the effective volume of micropulses and their number. From Fig. 2, one can also see that the dominant factor determining the dependence of the concentrations on SR_0^2 is the increase of the micropulse effective volume. The comparison of the results of the analysis and the curves in Fig. 3 allows us to conclude that the increase of the total number of micropulses is the decisive factor for the quantities $[HNO_3]$, $[HNO_2]$, and $[NO_3]$, whereas the change of W/V is that for $[O_3]$.

4. Conclusions

We have clarified the behavior of the concentrations of some components of a gas mixture in the atmospheric pressure barrier discharge which depend on the characteristics of the structural elements of the discharge – microdischarges. The way, in which each of the parameters influences the kinetics of chemical reactions determining the change of the concentrations, is found out. The reasons for the obtained dependences are determined in the course of the detailed analysis of the plasma kinetics. It is established that the micropulse duration does not influence the concentrations $[HNO_3]$, $[HNO_2]$, $[NO_3]$, and $[O_3]$.

It is obtained that the behavior of the concentrations of all the components is determined by the processes taking place between two successive microdischarges. During the breakdowns, the levels of the concentrations of the atomic components that influence the processes in the bulk of the discharge chamber are established.

1. A.C. Gentile, M.J. Kushner, J. Appl. Phys. **79**, 3877 (1996).
2. V.Yu. Bazhenov, A.I. Kuzmichev, V.I. Kryzhanovsky *et.al.*, in *Proceedings of the 15th International Symposium on Plasma Chemistry, Orleans, France, 2001*, p.3005.
3. St. Kropke, Yu.S. Akishev, and A. Hollander, Surf. Coat. Techn. **141–144**, 512 (2001).
4. P.M. Golovinskii, A.I. Shchedrin, Zh. Techn. Fiz. **59**, 51 (1989).
5. I.A. Soloshenko, V.V. Tsiolko, S.S. Pogulay *et al.*, Plasma Sourc. Sci. Technol. **16**, 56 (2007).
6. V.V. Lunin, M.P. Popovich, S.N. Tkachenko, *Physical Chemistry of Ozone* (MGU, Moscow, 1998) (in Russian).
7. Yu.P. Raizer, *Gas Discharge Physics* (Nauka, Moscow, 1987) (in Russian).
8. R. Higgins, C.J. Noble, and P.G. Burke, J. Phys. At. Mol. Opt. Phys. **27**, 3203 (1994).
9. C.J. Gillant, J.Tennyson, B.M. McLaughlin, and P.G Burke, J. Phys. B: At. Mol. Opt. Phys. **29**, 1531 (1996).
10. J.M. Ajello, J. Chem. Phys. **53**, 1156 (1970).
11. R.D. Hake and A.V. Phelps, Phys. Rev. **152**, 70 (1967).
12. M. Vicic, G. Poparic, and D.S. Belic, J. Phys. B: At. Mol. Opt. Phys. **29**, 1273 (1996).
13. Young Sun Mok, Sung Won Ham, and In-Sik Nam, IEEE Trans. Plasma Sci. **26**, 1566 (1998).
14. H.C. Straub, P. Renault, B.G. Lindsay *et al.*, Phys. Rev. A. **54**, 2146 (1996).

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ВПЛИВ ПАРАМЕТРІВ БАР'ЄРНОГО РОЗРЯДУ АТМОСФЕРНОГО ТИСКУ У ПОВІТРІ НА ПЛАЗМОВУ КІНЕТИКУ

Г.Г. Калюжна, Д.С. Левко, А.І. Щедрін

Р е з ю м е

Розглянуто вплив характеристик мікророзрядів, що є структурними елементами бар'єрного розряду (БР), на плазмову кінетику в ньому. З'ясовано причини, які впливають на поведінку концентрацій досліджуваних речовин. Показано, що невизначеність характеристик дає значення концентрацій, що лежать у широких інтервалах.