KINETICS OF PROCESSES IN AIR PLASMA DISCHARGES AT ATMOSPHERIC PRESSURE IN THE TRANSVERSE FLOW OF GAS

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The paper is devoted to the consideration of some features of the kinetics of the formation of nitrogen oxides and the population of the vibrational levels of the basic electronic states of nitrogen and oxygen molecules in the plasma of dry and humid air of gas discharges in the transverse gas flows to the current channel of the discharge at atmospheric pressure.

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INTRODUCTION

Today, discharges in gas flows transverse to the current channel are of particular interest. Since these discharges can generate wide-aperture high-pressure non-equilibrium plasma streams for hybrid plasma catalysis of high-scale transformation of substances (gliding and rotational gliding discharges), and low-power plasma flows for small electron energies for plasmomedicine (microdischarge plasma injector in vortex flow of gas). The consideration of the kinetics of the population of levels of oxygen and nitrogen molecules and the formation of nitrogen oxides in the plasma of dry and humid air of similar discharges in this work was carried out.

1. METHODOLOGY

The studies were performed using numerical simulation based on software ZDPlaskin [1]. This software integrates Boltzmann's equation for electron energy distribution from a given a set of electronic processes (code Bolsig+) and marches in time balance equations of species concentrations with under typical conditions for the discharge air plasma at atmospheric pressure in the reduced electric field (20…40 Td) [2]. The software ZDPlaskin allows us to solve systems of kinetic equations for r reactions between s components. The reactions can be represented schematically as follows:

$$\sum_{i=1}^{i=n} c_{lij} S_{li} \xrightarrow{kj} \sum_{i=n+1}^{i=n+m} c_{lij} S_{li}, \qquad (1)$$

where S_l is a component with index l = 1,2, ..., s and reaction proceeds at rate k_j with j = 1,2, ..., r. In the zero-dimensional model, the balance equatuins form a system of ordinary first-order differential equations for species concentration

$$\frac{d[S_i]}{dt} = \sum_j \pm c_{ij} k_j \prod_l [S_l] c_{lj}, \qquad (2)$$

where c_{ij} is the stoichiometric coefficient of species i in reaction j and $[S_l]$ denotes the concentration of species with index l.

The dependences of the change in the composition of the gas flow intersecting the region with constant temperature and electric field were obtained from the calculations for the time interval of 10^{-8}…1 s with a time increment of 10^{-8} s. The program complex ZDPalskin for studying the kinetics of formation of nitrogen oxides, and the population of excited levels of oxygen molecules and nitrogen was used. The need for such a study is due to the development of hybrid plasma-catalytic reforming systems for hydrocarbons.

Particular attention should be paid to the process of plasma activation of air prior to submission to the reaction chamber of such systems. Also, the simulation of plasma air kinetics has urgency in the creation of low-temperature plasma generators, which can be used both in medicine and in the chemical industry.

A list of chemical, ionic and electron-molecular reactions for the simulation of chemical and electron-molecular reactions in the region of the plasma channel was created. The mechanism proposed in [3] was the basis of this reactions list. It contains 149 electron-molecular reactions. The cross-sections of the interaction of molecular nitrogen were taken from the Phelps database [4], the cross-section of the interaction of molecular oxygen from Biagi (Magboltz versions 8.9 and higher) [5]. For crossing the interaction with N, O, NO, NO_2, O_3 and oxygen, the Morgan database (Kinemes Research Software) [6] was used. Also, the processes of "removal" of the excited state in the interaction of excited atoms and molecules (VT - processes) and the excitation processes of vibrational and rotational levels of O_2 and N_2 as a result of interaction with plasma electrons were taken into account.

Experimental data indicate the high temperatures existing in the discharge zone. Therefore, mechanism [3] was supplemented by reactions with such particles as N_2O, NO_2, NO_3, N_2O_5, N_2O^+, NO_2^+, N_2O^-, NO_2^-, NO_3^-. Constant rates for chemical and electronic reactions were taken in [7].

The mechanism [3] needed to be supplemented by reactions involving H_2O, H, OH, and the like, since the aim of the simulation was to study the activation process of both dry and humid air. Constant velocities of these chemical reactions were taken from [8]. At the same time, the cross sections for electron-molecular interactions for H_2O were taken from the Hayashi database [9] and the Itikawa database [10]. Also in [9, 10] cross sections of electron-molecular interaction for H, OH radicals were taken.

The database also takes into account the reactions between ions and neutral components and ion-ion reactions. Basically, this is the reaction of the interaction of nitrogen ions and their compounds (since nitrogen is the preferred plasmoforming gas). The number of reactions involving the ions is about 300. Constant rates chemical reactions involving carbon containing particles (CO_2, CO, etc.) were used from works [8] and [11]. The interaction cross sections for electron-molecular reactions with CO_2 and products of its decay were taken from [5]. The simulation was carried out using the chemical reaction database with the addition of chemical reactions and rates of the processes that involved vibrational excited molecules in accordance with the theorem of Macharet-Friedman [12].

The final reaction base is 1436 chemical reactions, 149 electron-molecular reactions, 122 components.

2. RESULTS AND DISCUSSION

The simulation was carried out at a gas temperature in the plasma channel 1000 K and the electric field 1000 $V\cdot cm^{-1}$. Dry air and a mixture of air and water vapor (1 % absolute concentration) were plasma-forming gas. The step at the time in simulation was 10^{-8} s.

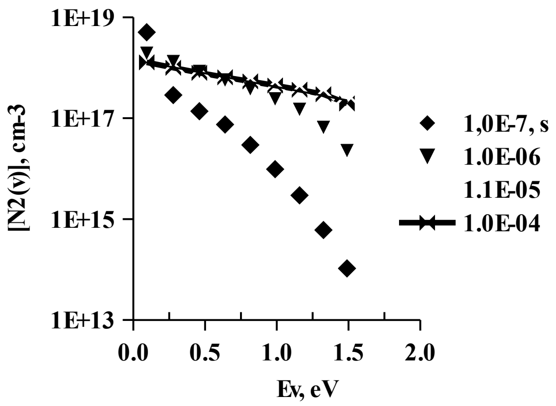
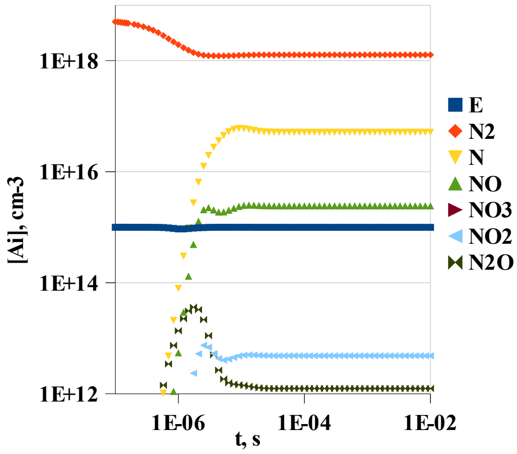


Fig. 1. Dependences of the concentrations of vibrational excited nitrogen molecules on the energy of vibrational excitation at various time exposures of gas in dry air plasma: 10^{-7}, 10^{-6}, 10^{-5}, 10^{-4}s

The dependences of the concentrations of vibrational excited nitrogen molecules on the energy of oscillatory excitation at different time exits of gas in the plasma of dry air are given in Fig. 1.

As can be seen from the dependences see in Fig. 1, the time of establishing of equilibrium distribution of the population of levels τ in a plasma of dry air is ~ 10^{-4} s. The vibrational temperature T_v is 0.8 eV at $\tau \geq 10^{-4}$ s. Accordingly, for a plasma of humid air $\tau \sim 10^{-3}$ s and T_v = 0.36 eV at $\tau \geq 10^{-3}$s. For molecules O_2: $\tau \sim 10^{-5}$ s, T_v = 0.1 eV at $\tau \geq 10^{-5}$ s for both the plasma of dry and humid air.



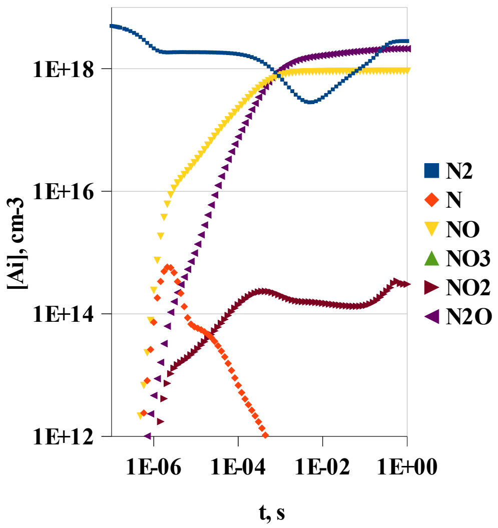


Fig. 2. Dependence of the electron concentration and nitrogen compounds on the time of exposure to dry (a) and wet (b) air in plasma. At E = 1000 $V\cdot cm^{-1}$, T = 1000 K

The dependence of the concentration of electrons E, nitrogen oxide molecules and nitrogen atoms on the time of exposure to dry (a) and humid (b) air in plasma is shown in Fig. 2. At E = 1000 $V\cdot cm^{-1}$, T = 1000 K.

The dependencies in Fig. 2 indicate that the concentration of nitrogen oxides is significantly lower in the plasma of dry air, than in the plasma of humid air. In addition, NO and NO_2 have the highest concentration in the plasma of dry air. NO and N_2O have the highest concentration in the plasma of humid air.

The dependences of the rates of the main reactions that lead to the generation of nitrogen oxide NO from the time of exposure in the plasma of dry (a) and humid (b) air are shown in Fig. 3. The results of kinetics modeling (see Fig. 3) indicate that the fastest reactions that generate NO (all reactions were 89) in the plasma of dry air are the reactions:

$$N+O+O \rightarrow NO+O \ , \qquad (3)$$

$$N+O_2 \rightarrow NO+O \ , \qquad (4)$$

$$N_2(A3)+O \rightarrow NO+N(2D). \qquad (5)$$

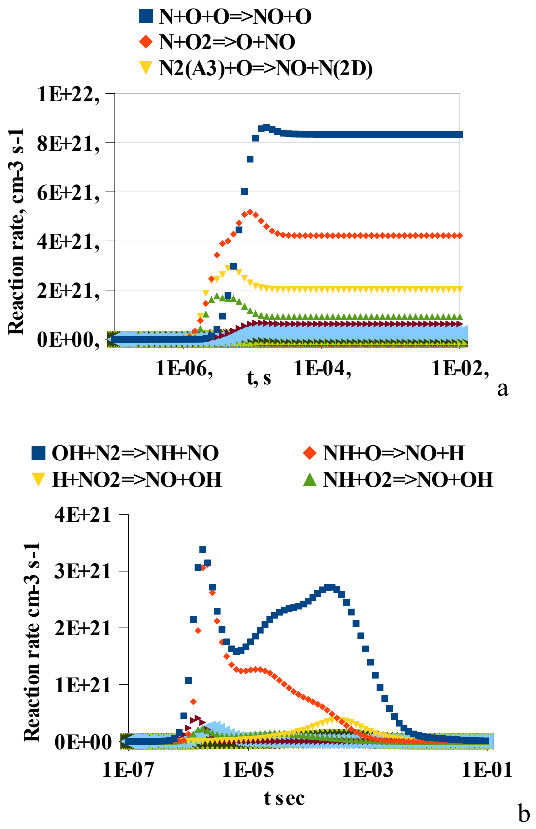


Fig. 3. Dependence of reaction rates which lead to the generation of NO from the exposure time in plasma of dry (a) and humid (b) air. At E = 1000 V cm^{-1}, T = 1000 K

It is worth noting that reactions (1) and (3) actively consume the active radical O, and this may negatively affect the process of oxidative hybrid plasma-catalytic conversion of hydrocarbons.

In the case of plasma of humid air, the main reactions of NO generation (were 119 reactions at all) are reactions involving H, OH or compounds with hydrogen. For example, the fastest reactions are reactions:

$$OH + N_2 \rightarrow NH + NO \tag{6}$$

$$NH + O \rightarrow NO + H, \tag{7}$$

$$H + NO_2 \rightarrow NO + OH. \tag{8}$$

Thus, in contrast to dry air, where reaction with the participation of oxygen radicals and atoms or nitrogen molecules is most intense, the reactions involving H and OH, which are fragments of H_2O, become the main reactions in the humid air.

Consideration of the kinetics of the formation of N_2O in the plasma of dry air, taking into account 45 reactions revealed the dominant contribution of reactions involving plasma components, which are the result of ion-molecular reactions:

$$O^- + N_2 \rightarrow N_2O + e, \tag{9}$$

$$N_2(A3) + O_2 \rightarrow N_2O + O, \tag{10}$$

$$NO^- + N \rightarrow N_2O + e \tag{11}$$

65 reactions were taken into account when considering the kinetics of the formation of N_2O in plasma of humid air. Their time dependencies indicate that there are different mechanisms of generation of N_2O that change each other over time. The dominant reactions for $\tau < 10^{-6}$ s are reactions (9) – (11). But after $10^{-6}\ldots10^{-5}$ s, the reaction becomes dominant (Fig. 4,b):

$$NH + NO \rightarrow N_2O + H. \tag{12}$$

The reaction (12) causes a significant increase in the concentration of N_2O in the plasma of humid air compared with the plasma of dry air. In turn NH is generated mainly by the reaction (6).

Thus, the presence of water in the air leads to an increase in the concentration of nitrogen oxides compared with dry air and significantly changes the kinetics of their generation.

CONCLUSIONS

Numerical simulation of the kinetics of elementary processes in the plasma of dry and humid air revealed that, with the typical values of the reduced electric field for micro-discharge in the vortex gas flow:

• the establish time of the equilibrium distribution of the population of vibrational excited oxygen molecules is significantly less than that of nitrogen molecules. In addition, this time for nitrogen molecules increases with the presence of water vapor;

• the presence of water in the air leads to an increase in the concentration of nitrogen oxides compared with dry air and significantly changes the kinetics of their generation. This leads to significant changes in their composition.

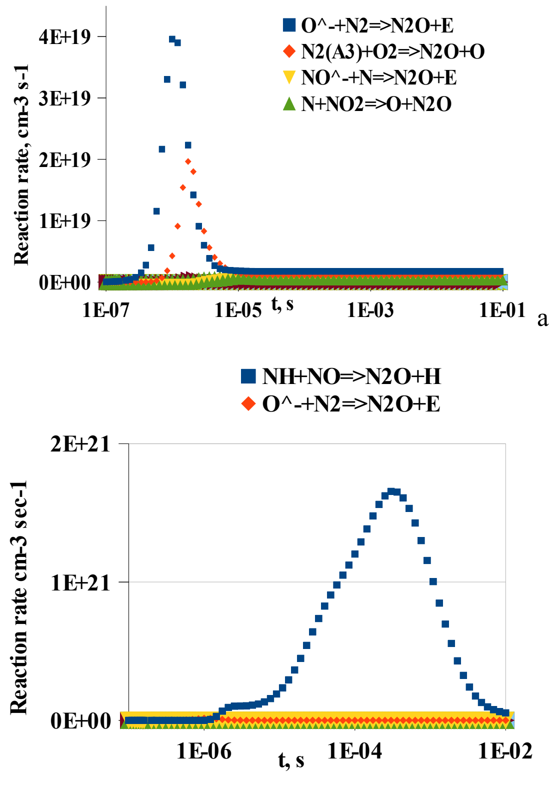


Fig. 4. Dependence of reaction rates which lead to the generation of N_2O from the exposure time of dry (a) and humid (b) air in plasma. At E = 1000 Vcm^{-1}, T = 1000 K

REFERENCES

1. M. Capitelli, C.M. Ferreira, B.F. Gordiets, A.I. Osipov. *Plasma Kinetics in Atmospheric Gases*. Springer. 2000.
2. http://jilawww.colorado.edu/~avp/.
3. www.lxcat.net/Biagi.
4. www.lxcat.net/Morgan.
5. A. Flitti, S Pancheshnyi. Gas heating in fast pulsed discharges in N_2-O_2 mixtures // *Europ. Phys. J. Appl. Phys*. 2009, v. 45, p. 2101.
6. A.E. Rodriguez, W.L. Morgan, et al. An Air Breakdown Kinetic Model // *J. Appl. Phys*. 2015, v. 70, p. 1991.
7. www.lxcat.net/Hayashi
8. www.lxcat.net/Itikawa
9. http://kinema.com/plasma-chemistry-modeling/
10. S. Pancheshnyi, B. Eismann, G.J.M. Hagelaar, L.C. Pitchford. Computer code ZDPlasKin, 2008. http://www.zdplaskin.laplace.univ-tlse.fr
11. Fridman. *Plasma Chemistry.* Cambridge: "Cambridge University Press", 2008.

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КИНЕТИКА ПРОЦЕССОВ В ВОЗДУШНОЙ ПЛАЗМЕ ГАЗОВЫХ РАЗРЯДОВ В ПОПЕРЕЧНЫХ ПОТОКАХ ГАЗА

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Работа посвящена рассмотрению некоторых особенностей кинетики образования оксидов азота и заселения колебательных уровней основных электронных состояний молекул азота и кислорода в плазме сухого и влажного воздуха газовых разрядов в потоках газа, поперечных токовому каналу разряда, при атмосферном давлении. Существенные различия выявлены в кинетике процессов в плазме сухого и влажного воздуха.

КІНЕТИКА ПРОЦЕСІВ У ПОВІТРЯНІЙ ПЛАЗМІ ГАЗОВИХ РОЗРЯДІВ У ПОПЕРЕЧНИХ ПОТОКАХ ГАЗУ

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Робота присвячена розгляду деяких особливостей кінетики утворення оксидів азоту і заселення коливальних рівнів основних електронних станів молекул азоту і кисню в плазмі сухого і вологого повітря газових розрядів у потоках газу, поперечних струмовому каналу розряду, при атмосферному тиску. Істотні відмінності виявлені в кінетиці процесів у плазмі сухого і вологого повітря.