INFLUENCE OF NEGATIVE IONS ON ATOMIC OXYGEN PRODUCTION IN A HOLLOW CATHODE DISCHARGE IN O_2/Ar MIXTURE

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The main mechanisms for atomic oxygen generation in a discharge with a hollow cathode in Ar/O_2 mixture were found. It was shown that for different oxygen concentrations the different reactions are responsible atomic oxygen formation. At higher oxygen concentration in the mixture negative ions play a significant role in the formation of atomic oxygen. This property of the discharge is due to the low electric field in the working volume, and consequently low electron temperature.

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INTRODUCTION

Discharges in oxygen are widely used in plasma technology, such as etching, deposition of protective films, surface modification and others [1-3]. In many industrial gadgets discharges are used not in pure oxygen but in a mixture of oxygen with an inert gas, especially argon, which allows to increase the effectiveness of such devices. One of the most widespread discharges for generation of active particles at low pressure is the discharge with a hollow cathode, which allows obtaining a high yield of such particles at low power cost. A distinctive feature of this discharge is a small electric field in the working volume, and as a consequence, low electron temperature. It was found in experiments [4] that in such discharges the atomic oxygen concentration has substantially nonmonotonic dependence on the composition of the mixture with a minimum at about equal content of argon and oxygen. In the current paper, based on the features of the discharge with the hollow cathode, the main mechanisms responsible for the formation of atomic oxygen at different compositions were founded up, and the influence of other plasma components such as negative oxygen ions was established.

1. THEORETICAL MODEL

For calculations of dependencies of plasma component concentrations on the gas mixture content, averaged model of plasma-chemical processes in hollow cathode discharge was built. The model was mainly analogous to one considered in [1]. We assumed that the component concentrations are uniformly spread over the whole volume of the chamber represented by cylinder with radius R = 19 cm and length L = 40 cm.

In the kinetics calculations we considered 18 components. For oxygen, the following species were considered: molecular oxygen in both ground state $O_2(X^3\Sigma_g)$, and in excited metastable states $O_2(a^1\Delta_g)$, $O_2(b^1\Sigma_g^+)$ and $O_2(A^3\Sigma_u^+$, $A^3\Delta_u$, $c^1\Sigma_u^-)$; atomic oxygen ground state $O(^3P)$ and at metastable level $O(^1D)$; ozone O_3, as well as positive ions O^+ and O_2^+, and negative ions O^-, O_2^- and O_3^-. Argon atoms were considered as the following species: the ground state $Ar(3s^23p^6)$, metastable levels Ar^m (mixture of $1s_5$ and $1s_3$ levels with fixed ratio of 5:1), radiation-bounded levels Ar^r ($1s_2$ and $1s_4$ levels), all levels Ar(4p), as well as Ar^+ ions. Totally, in the calculations 131 elementary processes were taken into consideration. Rate constants for all reactions were taken the same as in [5], excluding reactions of oxygen dissociation and ionization, argon ionization in ground and metastable states, as well as reactions of excitation of electron levels of molecular oxygen and argon.

Mentioned constants were determined from electron energy distribution function (EEDF) which was obtained by solving Boltzmann equation, which was solved together with the system of kinetic equations. The EEDF f(ε) was normalized as follows:

$$\int_0^\infty \sqrt{\varepsilon} f(\varepsilon) d\varepsilon = 1. \quad (1)$$

At solving this equation, electron energy losses to ionization of molecular oxygen and argon, oxygen dissociation, excitation of the first seven electron levels of molecular oxygen, argon levels 1s and 2p (including stepwise excitation 1s → 2p), and oxygen oscillation levels were taken into account. Electron heating was done by electric field, as well as at the expense of "secondary" electrons formed at the gas ionization by electrons accelerated in the near-cathode layer. The dependence of energy distribution of these "secondary" electrons was considered to be proportional to $1/(\varepsilon^2 + \varepsilon_0^2)$, where ε_0 is ionization energy. The density of these "secondary" electrons was determined from specific power density introduced into the discharge, which was supposed to be about 11 mW/cm^3. Cross section values for electron processes used for calculations of rate constants, as well as EEDF calculation, were taken from [6-11].

To show an influence of a low electric field on the discharge the calculations were done for two values. One was produced for E = 20 mV/cm, which is close to the field which observed at an experiments, and other for greater value E = 100 mV/cm. Fig. 1 shows the estimates for the EEDF to these field values, depending on the Ar contribution to the working mixture.

For the reactions with electrons for which cross-section are unknown we used dependences of rate constants on electron temperature. As a temperature we chose 2/3 of the calculated average electron energy. Fig. 2 shows dependence of the temperature on the mixture composition for two values of the electric field.

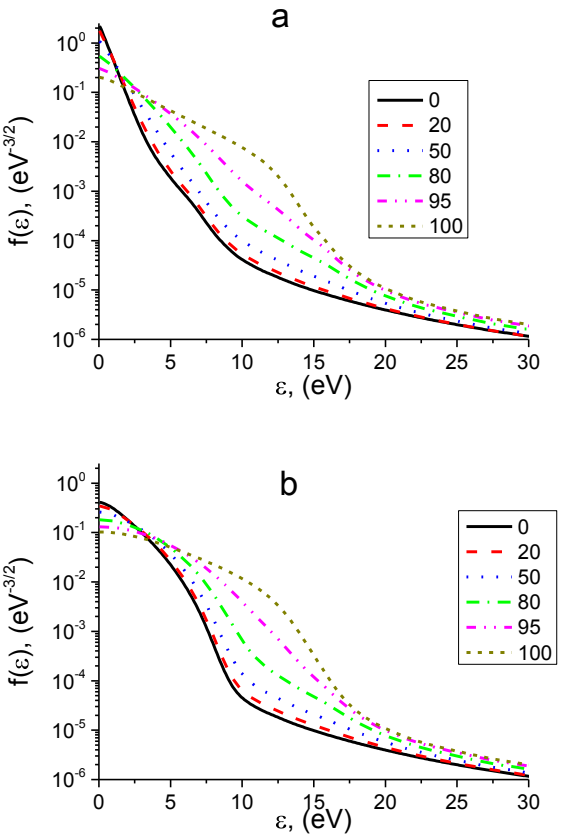

Fig. 1. EEDF for various compositions of the discharge mixture, the numbers indicate the percentage of Ar; a – E = 20 mV/cm; b – E = 100 V/cm

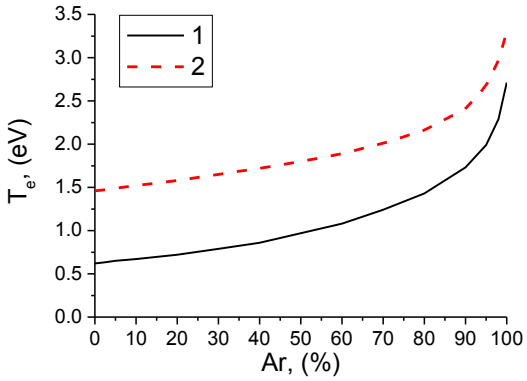

Fig. 2. The dependence of the electron temperature of the Ar content in the discharge mixture: 1 – E = 20 mV/cm; 2 – E = 100 mV/cm

2. RESULTS AND DISCUSSIONS

Fig. 3 shows the dependence of the calculated concentration of atomic oxygen on the composition of the discharge mixture for the two values of the electric field. And Fig. 4 shows the same data obtained by an experiment for discharge with hollow cathode for which the value of the electric field was close to 20 V/cm. One should note the similarity of the shape of experimental and calculated curves for similar values of the electric field – the minimum in the atomic oxygen concentration at about 50 % presence of Ar in the mixture, and increasing in the atomic concentration while portion of oxygen in initial mixture both increases and decreases.

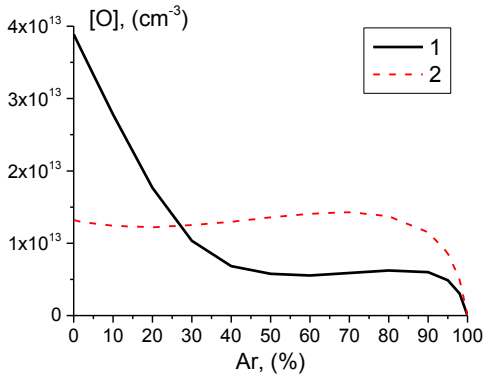

Fig. 3. Calculated dependence of the atomic oxygen concentration on the composition of the mixture: 1 – E = 20 mV/cm; 2 – E = 100 mV/cm

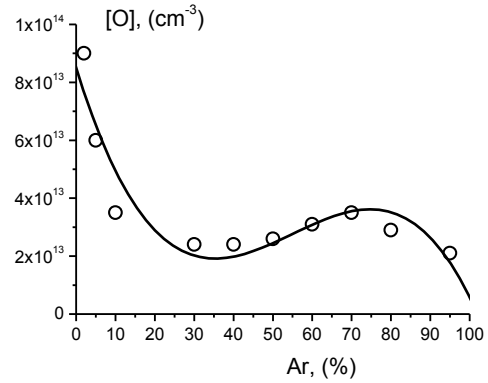

Fig. 4. Experimental dependence of the atomic oxygen concentration on the mixture composition

The most effective oxygen dissociation mechanism is the reaction of direct dissociation by electron impacts:

$$e + O_2 \rightarrow e + O + O. \qquad (2)$$

But due to the fact that the threshold energy of oxygen dissociation (6 eV) is less than the ionization energy of argon (15.8 eV), there is a "stabilization" mechanism for the electron impact dissociation rate in the plasma. This "stabilization" is expressed in the fact that when more oxygen is present in the discharge, the portion of electrons with energy greater than 6 eV becomes smaller, because of effective energy losses in the dissociation and ionization collisions of electrons with oxygen molecules. Consequently, the rate constant of reaction (2) which is defined as

$$k_d = \sqrt{\frac{2q}{m}} \int \varepsilon \sigma_d(\varepsilon) f(\varepsilon) d\varepsilon, \qquad (3)$$

will be inversely proportional to the oxygen concentration (where q and m are charge and mass of an electron, and $\sigma_d(\varepsilon)$ is a cross section of dissociation). And, therefore, the speed of the reaction (2), which is equal to $k_d [O_2] n_e$, will remain nearly constant.

Fig. 5 shows the dependence of the rate constant and the reaction rate itself on the composition of the discharge mixture. And indeed, as expected, when the oxygen concentration changes from 100 to 10 %

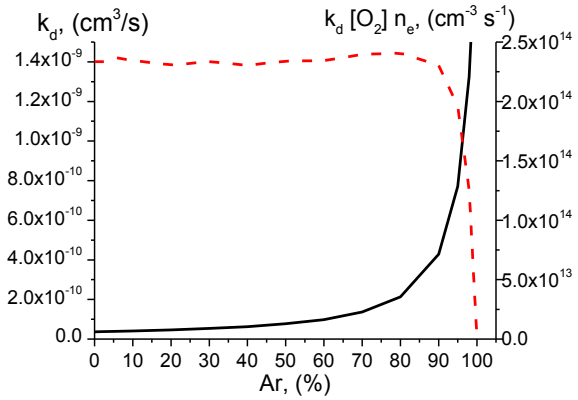

Fig. 5. The rate constant for oxygen dissociation (solid curves, right axis) and the rate of direct dissociation reaction (dashed lines, left axis); electric field E = 100 mV/cm

the rate constant increases ten times, but the reaction rate itself remains substantially constant or, in some other cases decreases no more than 2…3 times.

Therefore, we need additional mechanisms of atomic oxygen formation, different for different mixture compositions. In the case of small oxygen concentrations and, consequently relative high electron temperature, such mechanisms may be the dissociation of metastable levels of oxygen $O_2(\alpha^1\Delta_\gamma)$, $O_2(\beta^1\Sigma_\gamma^+)$, $O_2(A^3\Sigma_\upsilon^+$, $A^3\Sigma_\upsilon$, $c^1\Sigma_u^-)$. The cross sections for the excitation of these states are the order of magnitude smaller than for the reaction of dissociation. Also electron energy loss in such collisions (0.98, 1.64 and 4.5 eV, respectively) are smaller than for dissociation and ionization, so these processes do not have a significant influence on the EEDF. Thus, with decreasing of $[O_2]$ concentration the rate constants of these reactions grow slower than $1/[O_2]$, and the concentrations of metastable oxygen molecules have maximum, the positions of which depend on the electric field in the discharge (Fig. 6). As a result dissociations of metastable molecules are responsible for an increase in the degree of dissociation of oxygen while reducing its portion in the discharge.

As mentioned above, a discharge with a hollow cathode is characterized by low electric field in the main discharge volume and therefore low average electron energy. At high oxygen concentrations, the electron temperature may have a value less than 1 eV (see Fig. 2). These conditions are favorable for the formation and preservation of negative oxygen ions, as the electron affinity of oxygen molecule is 0.87 eV.

Fig. 7 shows the rate of atomic oxygen formation for the mane reactions. Since loss of atomic oxygen is proportional to its concentration, the result of summation of these curves represents, up to a factor, the desired concentration. It can be seen that the contribution of the dissociation of oxygen molecules in the ground state is weakly dependent on the oxygen content in the mixture. Because recombination rate of the positive and negative ions is proportional to their concentrations, which in turn are proportional to the concentration of neutral molecules, as a result, the rate of this reaction has the quadratic dependence. The contribution to the overall atomic oxygen formation from the recombination reaction decreases with increasing of electric field. On the contrary, the value of the metastable atom concentration increases with the electric field, but the maximum production rate of the respective reactions becomes broader and shifts toward higher concentrations of oxygen.

From our point of view, the discrepancy between the results of numerical simulation and experiment can be explained by shortcomings in consideration of processes at walls. First of all, a great variation of a value for recombination coefficient of oxygen at walls exists in the literature [12-14]. These values vary from 0.05 to 0.001 (we have used value 0.05). Moreover, all these values relate to cold walls, but under conditions of a discharge with a hollow cathode when a wall being bombarded by ions, this coefficient may be even less. Since recombination at walls is one of the main mechanisms of atomic oxygen departure, the decrease in this constant may result in a corresponding increase in the atomic concentration in the discharge. Secondly, we do not have confidence in the accuracy of accounting of negative ions departure from the discharge volume. However, these corrections may only affect the specific value, but not the general form of dependency.

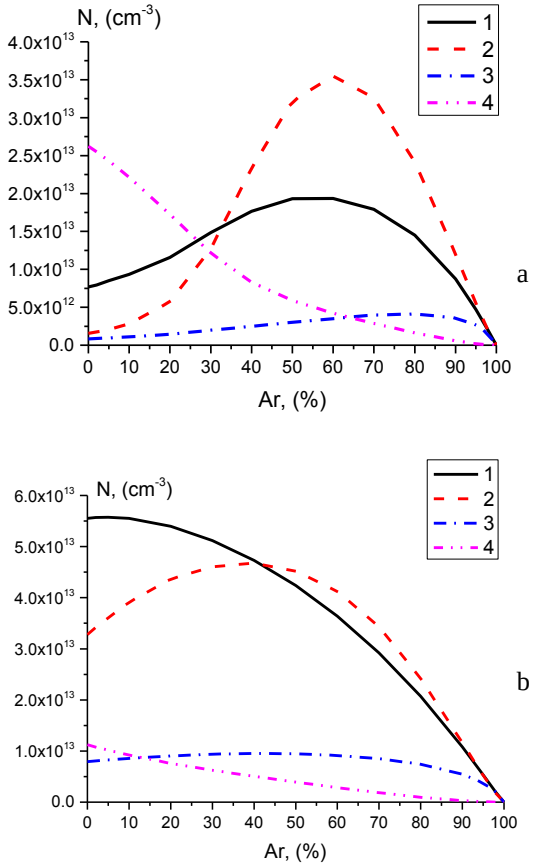

Fig. 6. The dependence of concentration of metastable oxygen molecules and negative ions on the mixture composition: a – electric field E = 20 mV/cm; b – E = 100 mV/cm; 1 – $O_2(a^1\Delta_g)$; 2 – $O_2(b^1\Sigma_g^+)$ multiplied by 10; 3 – $O_2(A^3\Sigma_u^+$, $A^3\Delta_u$, $c^1\Sigma_u^-)$ multiplied by 10; 4 – O_2^- multiplied by 200

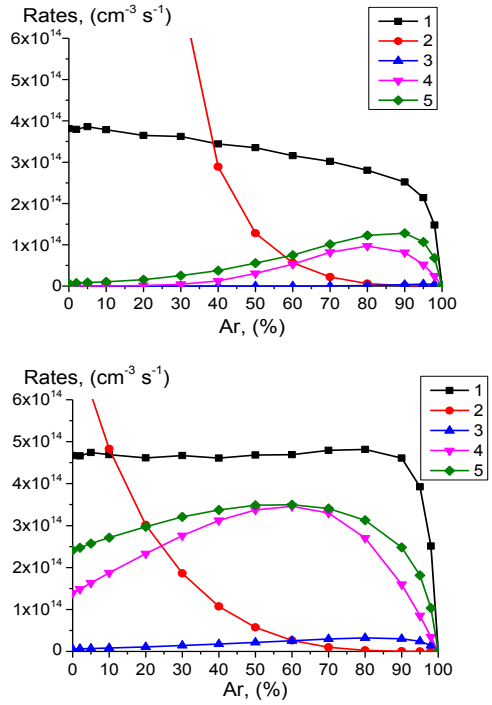

Fig. 7. The rate of formation of atomic oxygen in a variety of reactions: a – E =20 mV/cm; b – E = 100 mV/cm.
1 – dissociation of the ground state; 2 – recombination of positive and negative molecular ions;
3 – dissociation of the metastable level of $O_2(a^1\Delta_g)$;
4 – dissociation of the metastable level of $O_2(b^1\Sigma_g^+)$;
5 – dissociation of metastable levels of $O_2(A^3\Sigma_u^+, A^3\Delta_u, c^1\Sigma_u^-)$

CONCLUSIONS

It was shown that at low argon content in the working mixture of a hollow cathode discharge, the negative oxygen ions play a significant role in the atomic oxygen formation.

It was found that this feature of a hollow cathode discharge is obliged to lower value of the electric field in the volume and hence a low electron temperature.

The calculated dependences are in the good agreement with the experimental data.

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ВЛИЯНИЕ ОТРИЦАТЕЛЬНЫХ ИОНОВ НА ПРОИЗВОДСТВО АТОМАРНОГО КИСЛОРОДА В РАЗРЯДЕ С ПОЛЫМ КАТОДОМ НА СМЕСИ O_2/Ar

Ю. Лаврукевич, А. Рябцев, В. Циолко

Выявлены основные механизмы генерации атомарного кислорода в разряде с полым катодом в смеси O_2/Ar. Было показано, что при различных концентрациях кислорода в разряде за образование атомарного кислорода отвечают различные реакции. При высокой концентрации кислорода в смеси в формировании атомарного кислорода играют значительную роль негативные ионы. Это свойство разряда обусловлено низким значением электрического поля в рабочем объёме, а следовательно, низкой электронной температурой.

ВПЛИВ НЕГАТИВНИХ ІОНІВ НА ВИРОБНИЦТВО АТОМАРНОГО КИСНЮ В РОЗРЯДІ З ПОРОЖНИСТИМ КАТОДОМ НА СУМІШІ O_2/Ar

Ю. Лаврукевич, А. Рябцев, В. Циолко

Виявлено основні механізми генерації атомарного кисню в розряді з порожнистим катодом в суміші O_2/Ar. Було показано, що при різних концентраціях кисню в розряді за утворення атомарного кисню відповідають різні реакції. При високій концентрації кисню в суміші у формуванні атомарного кисню відіграють значну роль негативні іони. Ця властивість розряду зумовлена низьким значенням електричного поля в робочому об'ємі, а отже, низькою електронною температурою.