Energy efficiency of O_2 dissociation in high pressure electron-beam plasmas

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Abstract: The results of numerical study of the mechanism of O_2 dissociation in oxygen mixtures, excited by pulsed electron beams, are carried out. The energy efficiency of ozone production is obtained as a function of electron beam current density. The analysis of energy efficiency of ozone production in oxygen electron-beam plasmas, and comparison calculation results with available experimental data show that the reactions of O_4^+ ions recombination with electrons and negative ions O_2^- and O_4^- leads to the formation of two oxygen atoms. In this case the energy efficiency of O_3 production can reach $G_{O3} = 12 – 13$.

Keywords: nanosecond high-current electron beams, fast gas heating, energy efficiency of O atoms production

1. Introduction

Recently, considerable interest has been observed in studies of the mechanism of fast gas heating in discharge plasmas in a wide range of reduced electric fields E/N [1-3]. At E/N ≥ 600 Td, a significant part of the discharge energy is spent on the ionization of mixture molecules [1,2]. Therefore, to describe the mechanism of fast gas heating at high E/N values, a detailed analysis of the products of the electron-ion and ion-ion recombination reactions is required [1,2], in particular, the probability of dissociation of O_2 molecules due to recombination of O_4^+ ions with electrons and negative O_2^- and O_4^- ions [2]. However, in the discharges it is rather difficult to spent a significant part of deposited energy in the ionization subsystem. Therefore, to answer the question about the products of electron-ion and ion-ion recombination, numerical studies of the mechanism of O_2 dissociation in pulsed electron beams were carried out in the present work. The energy efficiency of atomic oxygen generation was calculated and compared with the experimental data.

The studies of ozone and $O_2(a^1\Delta_g)$ molecules production in oxygen at P = 1.15 atm under the action of an electron beam with electron energy ε = 100 keV and pulse duration from τ_{imp} = 300 ns up to 100 μs were carried out in [4, 5]. The concentration of ozone molecules was determined by the absorption of diagnostic radiation in Hartley band at a wavelength of λ = 255 nm. In oxygen at P = 1.15 atm and T_0 = 300 K the mole fraction of O_3 molecules was 2.6×10^{-4} at specific deposited energy W = 8.8×10^{-3} J/cm^3·atm [4]. Thus, the energy efficiency of O_3 production in oxygen under the conditions of [4,5] was $G_{O3} \cong 12$ (12 ozone molecules per 100 eV of deposited energy).

The study of ozone production in nanosecond high-current electron beam was investigated in [6,7]: electron energy ε = 1.2 MeV, beam current I_b^{max} = 5 kA, pulse duration 30 ns. The ozone density was measured by the absorption at a wavelength of λ = 256 nm at t = 5 - 10 minutes after the electron beam pulse. The accuracy of determining G_{O3} value was 5%, $G_{O3} = 12.8 \pm 0.6$. In [7], it was first noted that, in order to explain the experimental data on the energy efficiency of ozone production by electron beams with a high current density, it should be assumed that the reactions of electron-ion and ion-ion recombination of positive O_4^+ and negative O_2^-, O_4^- ions results in two oxygen atoms formation.

It should be noted that in a number of articles [8-10], a decrease in G_{O3} value was obtained for the electron beams with relatively low current density. The decrease in G_{O3} also occurred with the introduction of some impurities, for example SF_6 [7], and may be due to the fact that in these cases the atomic oxygen production in reactions involving charged particles is significantly reduced.

To test this assumption, the calculations of ozone production in oxygen excited by electron beams with high and low current densities were carried out for the conditions of experiments [4,5] and [10], respectively.

2. Model description

The action of electron beam on gas mixture leads to the loss of energy of the primary electrons and the formation of secondary electrons [9,11,12]. A number of studies have been devoted to the calculations of the degradation spectrum of secondary electrons in nitrogen-oxygen mixtures (see review [11]). In [12] it was shown that the rates of ionization, dissociation, and excitation of various electronic states of oxygen by an electron beam can be written in the form:

$$Q_k = \frac{dE}{dx}\frac{j_b}{e}\frac{N}{U_k},$$

where *dE/dx* is the energy loss of electrons per unit length (which depend on the electron energy), j_b is the beam current density, *N* is the concentration of mixture mole-

cules, U_k are the energy costs of corresponding processes, which are given, for example, in [9,12]. In the calculations, the temporal evolution of the beam current density $j_b(t)$ was used, which was taken from the experiments.

The kinetic model included the processes describing the evolution of the main charged and neutral components of oxygen mixture. The model set of reactions was based on the set of ion-molecular reactions from [13, 14] and reactions of neutral particles $O_2(X^3\Sigma_g)$, $O_2(a^1\Delta_g)$, $O_2(b^1\Sigma_g)$ $O(^3P)$, $O(^1D)$, $O(^1S)$ [2,13].

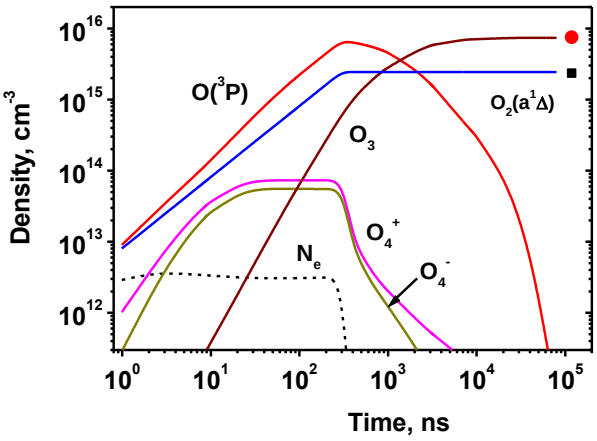

Figure 1. The evolution of oxygen mixture composition (P = 1.15 atm), excited by pulsed electron beam (τ_b = 300 ns, j_b = 10 A/cm^2, ε = 100 keV). Points are the experimental data [4, 5], curves – calculation results.

The main source of ozone production is the reaction

$$O(^3P) + O_2 + O_2 \rightarrow O_3 + O_2,$$

where atomic oxygen are produced both as a result of electron impact dissociation of O_2 molecules, and as a result of electron-ion and ion-ion recombination, so that $G_{O3} = 2\cdot G_{O_2}^{diss} + 2\cdot G_{O_2}^{ion}$. According to the measurement data [7,8], $2\cdot G_{O_2}^{diss} = 6.3 \pm 0.4$. These data were obtained at low beam currents, when O-atoms production due to electron-ion and ion-ion recombination are not important. To explain the values $G_{O3} \approx 13$, obtained in high-current electron beams [5-7], it must be assumed that, for each electron-ion pair produced by electron beam, two oxygen atoms are formed during subsequent reactions of electron-ion and ion-ion recombination, since, according to [7,12], $G_{O_2}^{ion} \approx 3$.

The ozone production in electron beam plasma at P = 83 - 830 Torr was studied in [7]. It was shown that the energy efficiency of O_3 production varies only slightly with gas pressure, amounting to G_{O3} = 12.8 ± 0.6. Increasing of gas pressure in the range of P = 83 - 830 Torr results in substantial change in ion composition [2], in particular, fractions of O_4^+ ions and negative O_2^-, O_4^- ions are increased. The fact that with increasing gas pressure, the value of G_{O3} varies only slightly suggests that in reactions of electron-ion recombination:

$$e + O_2^+ \rightarrow 2\cdot O, \qquad e + O_4^+ \rightarrow 2\cdot O + O_2,$$

and ion-ion recombination:

$$O_2^- + O_2^+ + O_2 \rightarrow 2\cdot O + 2\cdot O_2,$$

$$O_2^- + O_4^+ + O_2 \rightarrow 2\cdot O + 3\cdot O_2 \text{ et al.}$$

the channels resulting in O-atoms production should be dominate.

To verify this assumption, the calculations of ozone production in oxygen, excited by a pulsed high-current electron beam with the parameters of [4,5] were carry out.

3. Simulation results

Figure 1 shows the evolution of oxygen mixture composition under the action of pulsed electron beam with the parameters [5]: ε = 100 keV, j_b = 10 A/cm^2, τ_{imp} = 300 ns. In oxygen at P = 1.15 atm, electrons quickly attached to O_2 molecules, results in negative ions formation. It's clearly seen, that at t > 6 ns the created plasma is already ion-ion plasma, $[O_4^-] >> N_e$. The reactions of ion-ion recombination (R2, R3) are the main channels for charged particles decay under the conditions in question and the dissociation of oxygen molecules in these reactions is an important source of $O(^3P,^1D)$ atoms production.

At t > 8 μs, the oxygen atoms completely convert to ozone molecules. The results of calculations of ozone and $O_2(a^1\Delta_g)$ density are consistent with the measured data [4,5] (points in Figure 1).

As already noted, in a number of papers [8-10], a decrease in G_{O3} value was observed with a decrease in electron beam current density. At low beam currents, the charged particles density is relatively small and their recombination is slower than charge exchange reactions with ozone molecules. At high pressures, electrons quickly attached to the oxygen molecules:

$$e + O_2 + O_2 \rightarrow O_2^- + O_2 \qquad (R1)$$

with negative ions formation. However, at a low density of charged particles, instead of reactions of ion-ion recombination:

$$O_2^- + O_4^+ + M \rightarrow 2\cdot O + 2\cdot O_2 + M, \qquad (R2)$$

$$O_4^- + O_4^+ + M \rightarrow 2\cdot O + 3\cdot O_2 + M, \qquad (R3)$$

leading to atomic oxygen production, the charge exchange of negative ions O_2^- and O_4^- in the reactions with O_3 molecules occurs:

$$O_2^- + O_3 \rightarrow O_2 + O_3^-, \qquad (R4)$$

$$O_4^- + O_3 \rightarrow 2\cdot O_2 + O_3^-. \qquad (R5)$$

Recombination of the produced O_3^- ions

$$O_3^- + O_4^+ + M \rightarrow O + 3\cdot O_2 + M \qquad (R6)$$

leads to the formation of one $O(^3P)$ atom [7,9] instead of one ozone molecule, which is lost in reactions (R4, R5). So, as a result of reactions (R2-R6), the change in the O_3 + O density does not occur. Therefore, when the ratio:

$$[O_3] / [O_2^+ + O_4^+] >> k_2 \cdot M / k_4$$

is satisfied, the energy efficiency of ozone production should decrease to a value of $2 \cdot G_{O_2}^{diss} \approx 6.3$, which corresponds only to the production of oxygen atoms by electron impact.

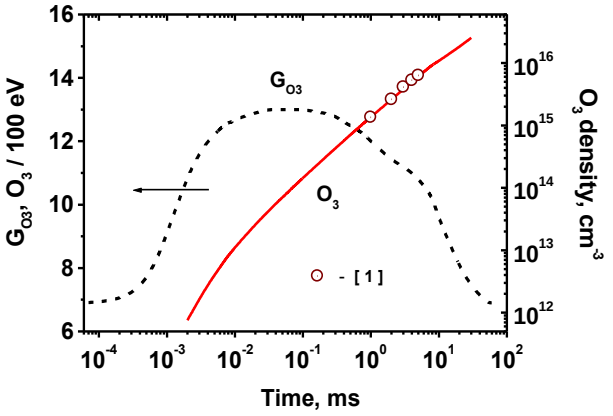

Figure 2. Temporal evolution of ozone density and the energy efficiency of O_3 production in oxygen at P = 760 Torr, excited by electron beam [10]. Points are the experimental data [10], curves – calculation results.

To verify this statement, we calculated the temporal dynamics of the main neutral and charged particles density in atmospheric pressure oxygen excited by a continuous electron beam with the parameters [10]: ε = 100 keV, J_b = 150 μA/cm^2. The ozone density was determined in [10] by the absorption of diagnostic radiation in Hartley band at a wavelength of λ = 253 nm.

The calculation results of the dynamics of ozone density and the energy efficiency of O_3 production are presented in Figure 2. It also presents the experimental data obtained in [10] (points). The calculated density of oxygen atoms during a pulse varies only slightly, amounting to $[O(^3P)] \approx 3 \cdot 10^{12}$ cm^{-3}.

It's clearly seen, that at $t \leq 10^{-3}$ ms G_{O3} value is about 6.8, which corresponds to the predominant electron impact dissociation of oxygen molecules. Reactions of charged particles (R2, R3) do not yet make a significant contribution to O-atoms production, since under the conditions of [10] the characteristic time of these processes exceeds 1 μs. At $t \geq 1$ μs, G_{O3} value increases as a result of the reactions with charged particles participation, reaching a value of $G_{O3} \approx 13$.

At $t \geq 0.6$ ms, due to the increase of O_3 density, the dominant type of negative ion changes and the main ion becomes O_3^-. As a result, generation of "odd" oxygen in reactions with charged particles participation stops and the curve $G_{O3}(t)$ again returns to the value $G_{O3} \approx 6.8$, corresponding to the electron impact production of oxygen atoms.

4. Conclusions

In gas-discharge plasmas at high values of reduced electric fields, E/N ≥ 600 Td, when a significant part of discharge energy is spent on the ionization of mixture molecules, a detailed analysis of the products of electron-ion and ion-ion recombination reactions is required [1,2], in particular, determination of the probability of O-atoms production in reactions of O_4^+ ions with electrons and negative ions. In this work, the mechanism of O_2 dissociation in electron-beam plasmas was studied and the energy efficiency of ozone production as a function of beam current density was determined. It was shown that the recombination of O_4^+ ions with electrons and negative ions O_2^- and O_4^- leads to the formation of two oxygen atoms:

$$O_4^+ + e \rightarrow O(^3P) + O(^3P,^1D) + O_2,$$

$$O_4^+ + O_2^- \rightarrow O(^3P) + O(^3P,^1D) + 2 \cdot O_2.$$

In this case, the energy efficiency of ozone production in oxygen, excited by a pulsed electron beam, is G_{O3} = 12 - 13, which is consistent with experimental data [4–7].

Acknowledgements

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5. References

[1] N. Aleksandrov, S. Kindusheva, M. Nudnova, A. Starikovskii, J. Phys. D: Appl. Phys., **43**, 255201 (2010).
[2] N. Popov, J. Phys. D: Appl. Phys., **44,** 285201 (2011).
[3] E. Mintoussov et al, J. Phys. D., **44,** 285202 (2011).
[4] G. Fournier, J. Bonnet, J. Fort, D. Pigache, 4-th IUPAC Int. Symposium on Plasma Chemistry. (Zürich, 27 August - 1 September), 742 (1979).
[5] G. Fournier, J. Bonnet, J. Fort, D. Pigache, CLEO-82, Phoenix, USA (April 14-16, 1982) Paper WC-28.
[6] J. Ghormley, C. Hochanadel, J. Boyle, J. Chem. Phys. **50**, 419 (1969).
[7] C. Willis, A.W. Boyd, M.J. Young, D.A. Armstrong, Canadian J. Chem**. 48.** 1505 (1970).
[8] J. Sears, J. Sutherland, J. Phys. Chem. **72,** 1166 (1968)
[9] C. Willis, A.W. Boyd, Int. J. Radiat. Phys. Chem. **8**, 71 (1976).
[10] K.S. Klopovsky, A.A. Nechaev, A.I. Osipov, et al. High Energy Chemistry, **19**, 379 (1983).
[11] V.L. Bychkov, A.B. Eletskii, Chemistry of Plasma (Moscow: Energoatomizdat), **12**, 119 (1985).
[12] V.P. Konovalov, E.E. Son, Chemistry of Plasma (Moscow: Energoatomizdat), **14,** 194 (1988).
[13] I. Kossyi, A. Kostinsky, A. Matveev, V. Silakov, Plasma Sources Sci. Technol. **1,** 207 (1992).
[14] N. Popov, Plasma Physics Reports, **36**, 812 (2010).