

Dissociation and regeneration kinetics of carbon dioxide in the active medium of sealed-off transverse RF-excited CO₂ lasers

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Abstract. An improved mathematical model describing the dissociation and regenerations kinetics of carbon dioxide in the active medium of sealed-off transverse RF-excited CO₂ lasers is presented. It is shown that the calculation of the active medium composition of such lasers requires the equations of the gas-mixture kinetics to take into account the diffuse flow of oxygen atoms on metal electrodes and on the surface of heterogeneous catalysts used to reduce the degree of the carbon dioxide dissociation. The rate constants of the heterogeneous recombination reaction $\text{CO} + \text{O} \rightarrow \text{CO}_2$ on the surface of alumina ceramics and Al₂O₃ are determined.

Keywords: transverse RF-excited CO₂ laser, degree of carbon dioxide dissociation, gold catalyst.

1. Introduction

The authors of paper [1] developed the mathematical model describing the dissociation and regeneration kinetics of carbon dioxide in sealed-off transverse RF-excited CO₂ lasers. However, although the results of calculations of the CO₂ dissociation degree within the framework of this model are in good accord with the experimental data, the model has a number of disadvantages limiting the field of its application.

First, to calculate the active medium composition it is necessary to know the rate constants of heterogeneous reactions $\text{CO} + \text{O} \rightarrow \text{CO}_2$ and $\text{O} + \text{O} \rightarrow \text{O}_2$ on the surface of the material from which the discharge channel is made. These experimental data are scanty or absent, in particular, for alumina ceramics from which the walls of the discharge gap are often made.

Second, according to [2], because of the high rate of the $\text{O} + \text{O} \rightarrow \text{O}_2$ reaction on the metal surfaces, the near-wall concentration of atomic oxygen $[\text{O}]_w$ is equal to zero. In equations of the gas-mixture kinetics, expressions for the rate of CO_2 $\{(2/d)(k_1[\text{O}]_w[\text{CO}]_w)\}$ and O_2

$\{(2/d)(k_2[\text{O}]_w/[\text{CO}]_w)\}$ production on the electrodes, where d is the interelectrode spacing and k_1 and k_2 are the rate constants of the $\text{CO} + \text{O} \rightarrow \text{CO}_2$ and $\text{O} + \text{O} \rightarrow \text{O}_2$ reactions, also vanish. Physically, it means the absence of production of not only CO₂ but also of O₂ on the metal, which, regarding O₂, contradicts the data of paper [2]. Therefore, it is required to find another expression for the rate of O₂ production in the equations of the gas-mixture kinetics.

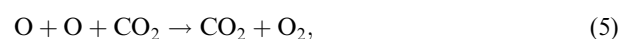
Third, within the framework of the mathematical model proposed in [1] it is impossible to calculate the active medium composition for the CO₂ laser with a heterogeneous catalyst used to reduce the CO₂ dissociation degree.

The aim of this paper is to improve the mathematical model of dissociation and regeneration of CO₂ developed in [1] by eliminating the above-mentioned drawbacks.

2. Mathematic model of dissociation and regeneration of carbon dioxide

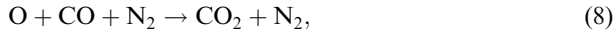
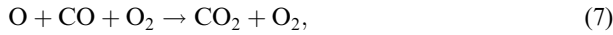
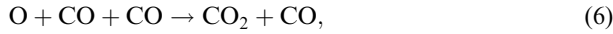
Chemical reactions responsible for CO₂ dissociation and regeneration in the active medium of sealed-off transverse RF-excited carbon-dioxide lasers are discussed in detail in paper [1]. However, in calculating the chemical composition of the active medium, from all the considered reactions of type $\text{O} + \text{O} + \text{M} \rightarrow \text{O}_2 + \text{M}$ it is enough to take into account only the $\text{O} + \text{O} + \text{CO}_2 \rightarrow \text{O}_2 + \text{CO}_2$ reaction, because its rate constant is twice larger than that for other similar reactions [3]. In addition, it is expedient to add the $\text{O} + \text{CO} + \text{M} \rightarrow \text{CO}_2 + \text{M}$ reaction to the reactions $\text{O} + \text{CO} + \text{CO}_2 \rightarrow \text{CO}_2 + \text{CO}_2$ treated in [1], because the rate constant of its formation is comparable with the analogous constants for all other similar reactions [4].

Therefore, the main chemical processes, which should be taken into account in the mathematical model of CO₂ dissociation and regeneration, are as follows:



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Reactions (1) and (2) proceed on the walls of the discharge channel.

According to [1], the equation of continuity for the i th component of the active medium, averaged over the rectangular ($b \times d$) cross section of the discharge channel, with the boundary conditions determining the production and annihilation of particles on the walls of the discharge channel has the form:

$$\frac{2}{b}P_{bi} + \frac{2}{d}P_{di} + \langle Q_i \rangle = 0, \quad (10)$$

where

$$P_{bi} = D_i \frac{\partial N_i}{\partial x} \Big|_{x=b/2} = -D_i \frac{\partial N_i}{\partial x} \Big|_{x=-b/2}; \quad (11)$$

$$P_{di} = D_i \frac{\partial N_i}{\partial y} \Big|_{y=d/2} = -D_i \frac{\partial N_i}{\partial y} \Big|_{y=-d/2};$$

N_i , D_i , $\langle Q_i \rangle$ are, respectively, the concentration, diffusion coefficient and average-over-discharge-channel-section density of the source of the i th type particles produced and annihilated per unit volume in chemical reactions.

Expression $(2/d)P_{dO}$ in equation (10) for atomic oxygen is the rate of ‘annihilation’ of O atoms on the surface of metal electrodes in reaction (2). As was pointed out in Introduction, the rate $d[\text{O}_2]/dt$ of O_2 production on metals cannot be represented in the form $(2/d)(k_2[\text{O}]_w/[\text{CO}]_w)$. Therefore, we will obtain an estimate for $d[\text{O}_2]/dt$ under the following assumptions. Because every two O atoms reaching the metal surface due to diffusion and ‘perishing’ on this surface produce only one O_2 molecule, we have

$$\begin{aligned} \frac{d[\text{O}_2]}{dt} &= \frac{1}{2} \left(\frac{2}{d} P_{dO} \right) = \frac{1}{d} D_O \frac{\partial N_O}{\partial y} \Big|_{y=d/2} \\ &\approx \frac{1}{d} D_O \frac{[\text{O}]}{d/2} = \frac{2}{d^2} D_O [\text{O}]. \end{aligned} \quad (12)$$

Because the [O] concentration is comparatively small, the diffusion coefficient of oxygen atoms in the gas mixture can be calculated with the help of the Blanc formula:

$$D_O^{-1} = \sum_i \Psi_i D_{O_i}^{-1}, \quad (13)$$

where Ψ_i is the fraction of the i th-type particles, and D_{O_i} is the binary diffusion coefficient of the O atom in the i th gas (its values are given, for example, in [5]).

A similar approach can be used to estimate the rate of CO_2 production in reaction (1) on the surface of a heterogeneous catalyst. According to [6], a layer of CO

molecules adsorbed from the gas phase is produced on the catalytic surface. Let each atom falling due to diffusion on the catalytic surface form a bond with a carbon atom of the CO molecule, and the CO_2 molecule produced in this case be desorbed from the catalyst back to the active volume. Then the rate of CO_2 production is equal to the ‘annihilation’ rate of atomic oxygen:

$$\begin{aligned} \frac{d[\text{CO}_2]}{dt} &= \beta \frac{2}{d} P_{dO} = \beta \frac{2}{d} D_O \frac{\partial N_O}{\partial y} \Big|_{x=d/2} \\ &\approx \beta \frac{2}{d} D_O \frac{[\text{O}]}{d/2} = \beta \frac{4}{d^2} D_O [\text{O}], \end{aligned} \quad (14)$$

where the coefficient $\beta = 1, 1/2, 0$ upon depositing the catalytic layer on the surface of both electrodes, only on one of them, or in the absence of the catalyst, respectively.

Equations of continuity (10) for CO_2 and O_2 in which the averaging over the cross section is replaced by the cross-section-averaged values of the component concentrations, take the form

$$\begin{aligned} \frac{4\beta}{d^2} D_O [\text{O}] + \gamma \left(\frac{S}{V} \right) k_1 [\text{O}]_w [\text{CO}]_w \\ + k_6 [\text{O}] [\text{CO}]^2 + k_7 [\text{O}] [\text{CO}] [\text{O}_2] + k_8 [\text{O}] [\text{CO}] [\text{N}_2] \\ + k_9 [\text{O}] [\text{CO}] [\text{CO}_2] - k_3 n_e [\text{CO}_2] = 0, \end{aligned} \quad (15)$$

$$\begin{aligned} \frac{2\delta}{d^2} D_O [\text{O}] + \gamma \left(\frac{S}{V} \right) k_2 \frac{[\text{O}]_w}{[\text{CO}]_w} \\ + k_5 [\text{O}]^2 [\text{CO}_2] - k_4 n_e [\text{O}_2] = 0, \end{aligned} \quad (16)$$

where S is the area of the dielectric surface of the discharge channel; V is the active medium volume; $k_1 - k_9$ are the rate constants of reactions (1)–(9); n_e is the average electron concentration; $\gamma = 1, 1 - (2/d)(V/S)$ and 0 for the discharge channel formed by four identical dielectric walls, two identical dielectric walls or metal electrodes [in this case, $\gamma(S/V) = 2/b$] or in the absence of dielectric walls, respectively; $\delta = 0, 1$ in the presence and absence of the dielectric coating on the electrodes. The main difference of equations (15) and (16) from the equation of continuity for CO_2 and O_2 obtained in [1] consists in the fact that they contain the terms of type $D_O [\text{O}]/d^2$ to take into account the rate of O_2 production on metals and CO_2 regeneration on the surface of heterogeneous catalysts.

To find the concentrations of CO_2 , CO, O_2 and O, as well as the degree of the carbon dioxide dissociation $\alpha = [\text{CO}] / ([\text{CO}] + [\text{CO}_2])$, equations (15) and (16) should be supplemented with relations expressing the maintenance of balance with respect to carbon and oxygen [1]:

$$[\text{CO}_2] + [\text{CO}] = [\text{CO}_2]^*, \quad (17)$$

$$\frac{[\text{CO}_2] + [\text{CO}]}{2[\text{CO}_2] + [\text{CO}] + 2[\text{O}_2] + [\text{O}]} = \frac{1}{2}, \quad (18)$$

where $[\text{CO}_2]^*$ is the initial concentration of CO_2 molecules. Equation (17) is in fact the law of conservation of the number of carbon atoms. Equation (18) reflects the fact

that the ratio of the number of carbon atoms contained in CO and CO₂ to the number of oxygen atoms contained in CO₂, CO, O₂ and O is equal to the ratio (1:2) in CO₂ molecules before dissociation.

The numerical solution of the self-consistent [1] system of equations (15)–(18), the kinetic Boltzmann equation for electrons (KBEE) and the heat conduction equation for the gas mixture (HCEGM) showed that varying the coefficient k_2 in a broad range or the absence of the second term in equation (16) does not lead to a noticeable change in the chemical composition of the active medium and the quantity α . Therefore, the second term can be neglected in equation (16).

Thus, the calculation of the CO₂, CO, O₂, and O content in the active medium requires the solution of a self-consistent system of the following equations: KBEE, HCEGM, equations (15), (17), (18), and equation of continuity for O₂:

$$\frac{2\delta}{d^2}D_O[O] + k_5[O]^2[CO_2] - k_4n_e[O_2] = 0. \quad (19)$$

3. Results of calculations and their discussion

We will present theoretically calculated (α_1 , α_2) and experimentally found (α_{exp}) values of the CO₂ dissociation degree in CO₂ lasers with a slit design of the discharge channel formed by kovar electrodes. For the initial chemical composition of the active medium CO₂:N₂:He:Xe = 1:1:3:0.3, its volume $d \times b \times L = 2.5 \times 30 \times 230$ mm and condition of the discharge maintenance $W_{\text{rf}} = 350$ W, $f = 81.36$ MHz, and $p = 60$ Torr, we have $\alpha_1 = 0.72$, $\alpha_2 = 0.6$ [1] and $\alpha_{\text{exp}} = 0.73$ [1]; for CO₂:N₂:He:Xe = 1:1:3:0.3, its volume $d \times b \times L = 2.5 \times 40 \times 280$ mm, $W_{\text{rf}} = 6050$ W, $f = 81.36$ MHz, and $p = 60$ Torr, we have $\alpha_1 = 0.76$, $\alpha_2 = 0.6$ [1] and $\alpha_{\text{exp}} = 0.81$ [1]. The laser designs are described in paper [1]. The electron concentration n_e in calculations was assumed equal to 1×10^{11} cm⁻³, $\beta = \gamma = 0$ (in the absence of CO₂ regeneration on the metal electrodes). The quantity α_2 , unlike α_1 , was determined by neglecting in equation (19) the first term ($\delta = 0$) describing the rate of O₂ production on the metal electrodes.

It follows from the presented data that the calculations of α with account for the diffuse flow of the oxygen atoms to the metal electrodes [$\delta = 1$ in equation (19)] better agree with the experimental data than the calculation results obtained without this allowance. This is explained by the fact that by neglecting the rapidly proceeding process (2) on the electrodes, the annihilation of the atomic oxygen becomes possible only in volume processes (5)–(9), which lead to an increase in the CO₂ content and thereby to a decrease in the dissociation degree α .

The authors of paper [7] determined experimentally the dissociation degree of CO₂ in the active medium of a slit CO₂ laser ($d \times b \times L = 2.5 \times 40 \times 280$ mm, $p = 70$ Torr, $W_{\text{rf}} = 860$ W, CO₂:N₂:He:Xe:CO = 1:1:6:0.3:0.4) with electrodes coated with a catalytic gold layer. They found α to be equal to 0.18. The presence of the CO molecules on the catalyst surface, which are adsorbed on this surface from the gas phase, leads to the fact that O is annihilated on the metal catalyst as a result of reaction (1) and not of (2) as in the case of the non-catalytic metal surface. Therefore, to calculate α in the laser active medium from paper [7] it is

necessary: (i) to set $\beta = 1$ (both electrodes are coated with a golden layer), $\delta = 0$ [reaction (2) on the metal catalyst is absent], and $\gamma = 0$ [the slit design of the discharge channel lacks dielectric walls on which reaction (1) proceeds]; (ii) to change the balance equations with respect to carbon and oxygen because the active medium initially contains CO:

$$[CO_2] + [CO] = [CO_2]^* + [CO]^*, \quad (20)$$

$$\frac{[CO_2] + [CO]}{2[CO_2] + [CO] + 2[O_2] + [O]} = \frac{7}{12}, \quad (21)$$

where [CO₂]^{*} and [CO]^{*} are the initial concentrations of CO₂ and CO molecules. Equation (2) represents the law of conservation of the number of carbon atoms. It follows from (21) that the ratio of the number of carbon atoms to the number of oxygen atoms is equal to 7:12 because for CO₂:CO = 1:0.4 in the initial gas mixture two CO molecules (two C atoms and two O atoms) produce each five CO₂ molecules (five C atoms and ten O atoms). The numerical solution of the system of equations (15), (19)–(21) together with the KBEE and HCEGM yields $\alpha = 0.22$. If we neglect the diffuse flow of O atoms on the electrodes ($\beta = \delta = 0$) and set $\gamma = 0$, the calculated value of α will be equal to 0.62.

Therefore, the calculation of the active medium composition of the transverse RF-excited CO₂ laser requires an account for the diffuse flow of oxygen atoms on the metal and catalyst-layer electrodes in the equations of the gas-mixture kinetics.

The authors of paper [1] studied theoretically and experimentally the dependence of the CO₂ dissociation degree on the RF pump power in sealed-off waveguide lasers having different designs of the discharge channel. Thus, for example, the square-section discharge channel of laser 1 was formed by two metal (an aluminium alloy) electrodes and two walls made of Al-1 alumina ceramics. Because data on the rate constants of reaction (1) on the surface of the alumina ceramics are absent, the values of k_1 in calculating α in the active medium of laser 1 was chosen in paper [1] equal to that for molybdenum glass. The electron concentration n_e was set equal to 1×10^{11} cm⁻³. However, this n_e is typical of slit discharge structures in which the specific pump power should be reduced approximately twice compared to that for waveguide square-section discharge channels [8]. According to [9], n_e is approximately equal to 2×10^{11} cm⁻³ in waveguide square-section discharge channels. In addition, in paper [1] the first term, $D_O[O]/d^2$, taking into account formation of O₂ on the metal electrodes, was absent in equation (19) when calculating α in the active medium of laser 1. Therefore, if we set, in the system of equations (15), (17)–(19), $\beta = 0$ (catalytic coating is absent on the electrodes), $\delta = 1$ [O₂ is produced on the metal electrodes], $\gamma(S/V) = 2/b$ [reaction (1) proceeds on two alumina-ceramic walls spaced by the distance b], and $n_e = 2 \times 10^{11}$ cm⁻³, by varying k_1 (up to coincidence of calculated and experimental values of α), we can estimate the constant k_1 for the alumina ceramics. The performed calculations showed that with an accuracy sufficient for practical calculations, the coincidence is achieved at $k_1 = (2.1 \pm 0.3) \times 10^{-17}$ cm⁴ s⁻¹. For molybdenum glass, $k_1 = (4.7 \pm 1.2) \times 10^{-17}$ cm⁴ s⁻¹ [2], which exceeds approximately twice the corresponding value for the alumina ceramics.

The square-section discharge channel of laser 2 in paper [1] was formed by four dielectric surfaces: two walls made of Al₂O₃ alumina ceramics and two metal (aluminium alloy) electrodes coated with a $\sim 2\text{-}\mu\text{m}$ -thick Al₂O₃ film. If we set, in the system of equations (15), (17)–(19), $\beta = 0, \gamma = 0$ (metal surfaces on which O₂ is produced are absent), and $n_e = 2 \times 10^{11} \text{ cm}^{-3}$, and write the second term in equation (15) in the form $2[\text{O}]_w[\text{CO}]_w(k_1/b + k_1^*/d)$, where $k_1 = (2.1 \pm 0.3) \times 10^{-17} \text{ cm}^4 \text{ s}^{-1}$, k_1^* is the rate constant of reaction (1) to be determined for Al₂O₃, by varying k_1^* up to coincidence of the calculated and experimental values of α , we can estimate the constant k_1^* for Al₂O₃. The numerical solution of the system of equations (15), (17)–(19) together with the KBEE and HCEGM showed that with an accuracy sufficient for practical calculations, $k_1^* \approx k_1$.

4. Conclusions

We have improved the developed mathematical model describing the dissociation and regeneration kinetics of carbon dioxide in the active medium of sealed-off transverse RF-excited CO₂ lasers, the model being based on the combined solution of the equation of continuity for the active medium components, the kinetic Boltzmann equation for electrons and the heat conduction equation. It has been shown that the calculation of the CO₂, CO, O₂ and O content in the active medium requires the presence of expression of type $D_{\text{O}}[\text{O}]/d^2$ in the equation of continuity for CO₂ and O₂, to take into account the rate of O₂ production on metal electrodes and CO₂ regeneration on electrodes coated with a catalytic layer. We have determined the rate constants of the heterogeneous recombination reaction of $\text{CO} + \text{O} \rightarrow \text{CO}_2$ on the surface of the alumina ceramics and Al₂O₃ during which coincidence of the calculated and experimentally found quantities of the CO₂ dissociation degree is observed.

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