Romanian Reports in Physics, Vol. 66, No. 4, P. 1147–1154, 2014

OPTICAL AND MASS SPECTROMETRY DIAGNOSIS OF A CO_2 MICROWAVE PLASMA DISCHARGE*

S. DOBREA, I. MIHAILA, V. TIRON, G. POPA

"Alexandru Ioan Cuza" University, Faculty of Physics, Carol I Boulevard, nr.11, Iasi, 700506, Romania, E-mail:dobrica_sorin@yahoo.com; ilarion.mihaila@gmail.com; ghpopa@uaic.ro

Received July 15, 2013

Abstract. The experimental results on parameters of carbon dioxide (CO_2) and CO_2 and hydrogen (H_2) gas mixture microwave plasma discharge measured by means of the emission and absorption spectroscopies as well as end products of the CO_2 plasma dissociation by means of mass spectrometry are presented. The plasma parameters were determined for different flow rates and their corresponding pressures. The optical emission spectroscopy (OES) realized with high resolution spectrophotometer gives information about species existed inside the plasma volume, while the Tunable Diode Laser Atomic Spectrometry (TDLAS) performed by Toptica DL-100 system allows the oxygen metastables density and temperature to be measured.

Key words: CO_2 dissociation, microwave plasma, mass spectrometry, optical emission spectroscopy, TDLAS.

1. INTRODUCTION

Increasing of the green house effect in the last years and especially of the CO_2 quantity, which has a major contribution to global warming process [1], asks for developing of the new methods for environmental decontamination. In this respect the non-thermal plasmas method attracted a great interest over the years due to the ionization (positive and negative ions) and molecule dissociation in the discharge plasma due to high energetic electron collisions [2, 3]. In this paper preliminary results are presented regarding plasma parameters measurement of a carbon dioxide (CO_2) microwave plasma discharge. The microwave plasma discharge is used to dissociate carbon dioxide and the optical and mass spectrometry diagnoses were performed to investigate the dissociation mechanism and its correlation with the end product obtained by the carbon dioxide dissociation.

* Paper presented at the 16th International Conference on Plasma Physics and Applications, June 20–25, 2013, Magurele, Bucharest, Romania.

2. EXPERIMENTAL SET-UP

The microwave discharge is presented in Fig. 1. It consists of SAIREM 2.45 Ghz/2 kW microwave generator coupled by a wave guide, as an applicator, surrounding the cylindrical quartz tube (50 cm in length and 5 cm in diameter). The CO_2 gas was injected in the discharge tube at flow rates in the range of 25 ml/min to 150 ml/min and the total gas pressure in the discharge tube in the range $3.2x10^{-1}$ Torr to 2.1 Torr. The microwave power was in the range of 200 W to 600 W (with the reflected power less than 10 W). The OES spectra were acquired by a high resolution spectrophotometer (Jobin-Yvon TRIAX 550) equipped with a CCD detector and an optical fibre mounted through a hole placed in the waveguide applicator. To perform investigation on the evolution of oxygen metastables (777,194 nm) density and temperature we used a Toptica DL 100 system placed in the same position of the OES system. The mass spectra of the end stable gas components were acquired and investigated by downstream plasma connected Hiden Analytical Mass Spectrometer (HPR60) set as Residual Gas Analyse (RGA) mode and using a 30 μm diameter skimmer.

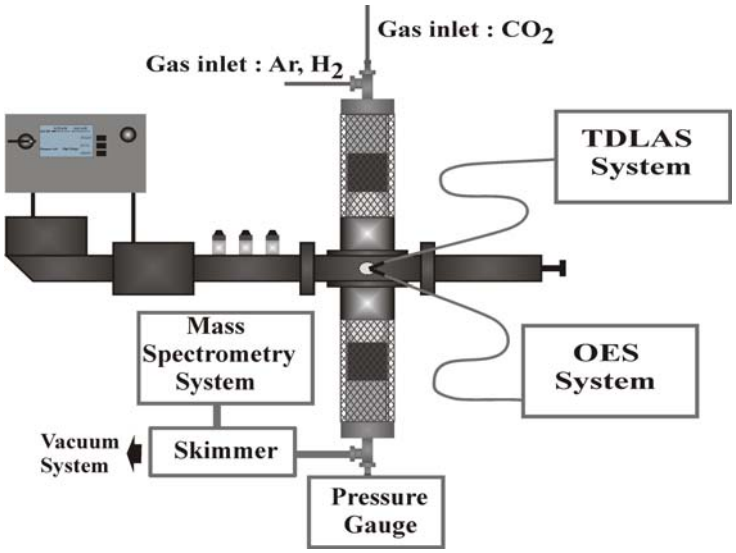

Fig. 1 – The experimental device.

3. RESULTS AND DISCUSSIONS

The optical methods are used to collect information from the plasma volume while the mass spectrometry method is used to investigate CO_2 dissociation and the plasma final products. Many reactions can occur inside the plasma volume related to carbon dioxide dissociation but only part of these reactions were selected and

presented in Table 1. These are specific for low pressure plasma and the criterion for selecting them was to find which one has the highest probability to appear inside the plasma volume, in order to be able to describe the CO_2 dissociation process. The reactions from this table describe different process that occurs in plasma volume such as: dissociation, recombination or charge transfer. Examination and comparing these reaction constants it appear that the following two are the most important in a CO_2 microwave discharge:

$$CO_2 + e^- \rightarrow CO + O \quad (1)$$

$$CO_2 + O \rightarrow CO + O_2. \quad (2)$$

Due to electron collisions the carbon dioxide molecules are dissociating into carbon monoxides and atomic oxigen which, at its turn, being very reactive, recombine and produce molecular oxigen.

Table 1

The reactions that may occur within carbon dioxide microwave plasma volume

No.	***Reactions***	***Reaction constant*** cm^3s^{-1} cm^6s^{-1}(*)	***Reference***
1	$CO_2+e^- \rightarrow CO+O$	$k=1.2\times10^{-9}$ $k=4\times10^{-7}$ $k=4\times10^{-7}$	[4] [5] [6]
2	$CO+O_2 \rightarrow CO_2+O$	$k=10^{-12}$	[7]
3	$CO_2+O \rightarrow CO+O_2$	$k=10^{-12}$	[7]
4	$CO+O \rightarrow CO_2$	$k=8\times10^{-11}$	[4]
5	$2e+CO_2^+ \rightarrow CO_2+e$	$k=10^{-19}$ (*)	[5]
6	$CO_2^+ + O_2 \rightarrow O_2^+ + CO_2$	$k=6.5\times10^{-9}$	[6]
7	$O^+ + CO_2 \rightarrow O_2^+ + CO$	$k=1\times10^{-9}$	[6]
8	$CO^+ + O_2 \rightarrow O_2^+ + CO$	$k=1\times10^{-10}$	[6]
9	$CO^+ + CO_2 \rightarrow CO_2^+ + CO$	$k=8.5\times10^{-10}$	[6]
10	$e^- + O_2 + M \rightarrow O_2^- + M$	$k=10^{-30}$ (*)	[8]
11	$CO_2^+ + O_2^- \rightarrow CO_2 + O_2$	$k=4\times10^{-7}$	[6]
12	$CO^+ + O_2^- \rightarrow CO_2 + O$	$k=4\times10^{-7}$	[6]

These reactions are well observed from the emission spectra as in Fig. 2 where it shows clearly the main plasma components are: atomic oxygen with 777 nm and 844 nm atomic spectral lines, CO with many spectral bands $B^1\Sigma^+ \rightarrow A^1\Pi$ in two specific domains of wavelength 290–325 nm and 400–650 nm [9] and even CO_2 as a continuum spectra due to superposition of various spectral bands in the range 400–750 nm [10].

The oxygen metastables were investigated with the absorption technique in order to find their density modification with respect to increasing of the carbon dioxide flow rate and corresponding pressure. The oxygen metastables temperature around 420 K was also determined which, in many cases, can be used as good approximation of the gas temperature. The experimental results presented in Fig. 3 show a monotonic increasing of oxygen metastables density ($[O^*]$) with microwave power transferred to plasma volume for all gas pressure used, but, with increasing of initial carbon dioxide pressure from 0.55 Torr to 2.1 Torr, the $[O^*]$ oxygen metastables density decreases from about 10^{16} m^{-3} to 10^{15} m^{-3}. The $[O^*]$ density increase with microwave power can be easily explained by plasma density increase and so the number of elementary processes by which the CO_2 dissociation increase and consequently increase of the both atomic oxygen and oxygen metastables densities Moreover, the $[O^*]$ density decrease with increasing gas pressure can also be explained by increasing of reverse reaction (reaction 11 from Table 1) in which CO_2 is generated by CO_2^+ recombination and lowering the both atomic oxygen and metastables. The oxygen atoms are formed mainly in the CO_2 dissociation reaction so, according to reaction (1), decreasing of the atomic oxygen density indicated by both emission and absorption spectra can be interpreted as a main reason of the CO_2 total equivalent dissociation coefficient decrease with increasing of the carbon dioxide pressure as mass spectrometry results is also showing.

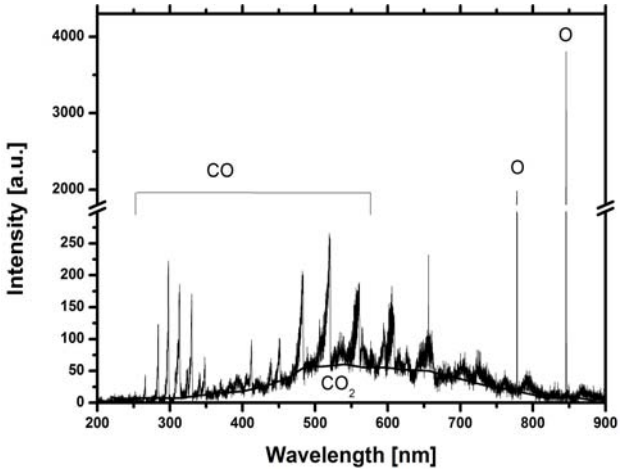

Fig. 2 – Optical emission spectrum of a CO_2 microwave plasma discharge for initial pressure of 0.55 Torr and 500 W microwave radiation power.

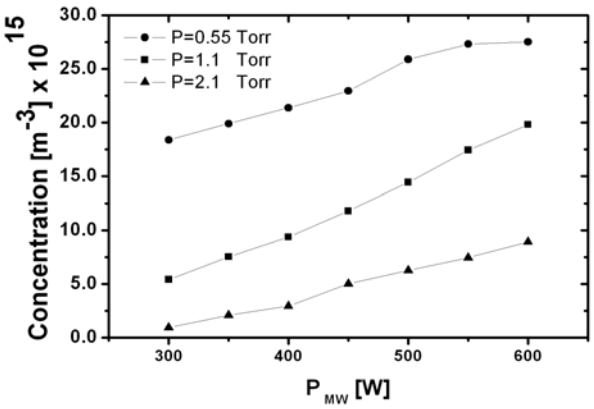

Fig. 3 – The evolution of oxygen metastables density with microwave discharge power and with increasing of the carbon dioxide pressure.

This result is also verified by mass spectrometry technique and measuring the partial pressure of the final components result from microwave discharge plasma produced in CO_2. The carbon dioxide dissociation was expressed using the η dissociation coefficient. The η was calculated using the counts C_i and C_f measured by mass spectrometer in flowing gas before and after plasma breakdown, respectively, with relation:

$$\eta = \frac{C_i - C_f}{C_i} \cdot 100 \,. \tag{3}$$

The percentage of CO_2 dissociation in microwave discharge plasma produced in pure CO_2 *versus* gas flow rate and inlet pressure are presented in Fig. 4. It can be observed that for 7 ml/min flow rate and its corresponding pressure of 0.6 Torr the dissociation coefficient is up to 90 %.

The η coefficient increases with the increasing of the microwave power for almost all initial CO_2 initial gas pressure but is decreasing with the increasing of the initial CO_2 pressure. This result is confirming the results previously obtained by the absorption spectral method and presented in Fig. 3. For low pressure the dissociation coefficient is very high, up to 90%, and even saturation can be observed in which CO_2 dissociation degree almost does not change with increase of the microwave power. For higher initial CO_2 pressure the dissociation coefficient is lower but this coefficient increases with increasing the microwave power transferred to CO_2 plasma.

It is well known that carbon dioxide is the main gas that produces the green house effect. Unfortunately, the carbon monoxide CO, which is the CO_2 dissociation product of the method investigated in present paper, is more toxic because it may, even in rather low percentage in the environmental air, produce death because of carboxyhemoglobin formation as a stable blood compound which may block oxygen transport mechanism by haemoglobin. Consequently, it would

be compulsory that after CO_2 dissociation and carbon monoxide generation within microwave plasma discharge to find a method for CO transformation in a less poisoned component. One possibility recommended and used in some experiments is to use additional hydrogen which at high temperature may produce Syngas.

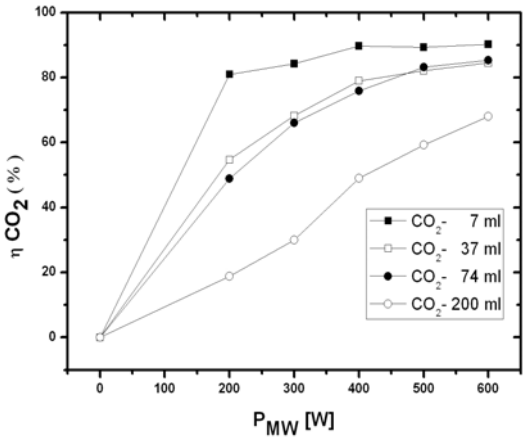

Fig. 4 – The percentage of CO_2 dissociation in microwave discharge plasma produced in pure CO_2 *versus* gas flow rate.

The experiment requires special precautions and so we limited ourselves to calculate the dissociation effect of carbon dioxide by adding hydrogen gas to initial CO_2. In Fig. 5 it is shown the optical emission spectrum obtained for this case where it can be seen the presence of the first three spectral lines of Balmer hydrogen series (H_α-656.26 nm, H_β-486.13 nm and H_γ-434.04 nm) and the OH spectral bands.

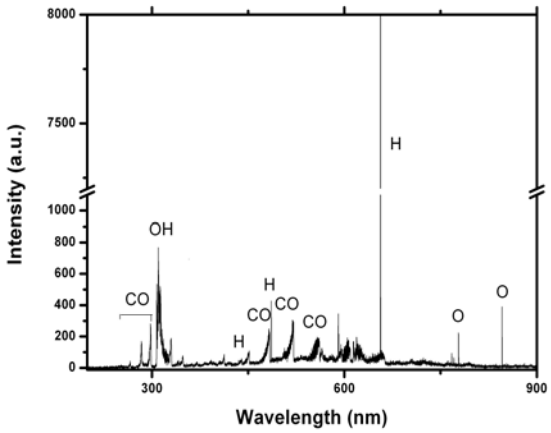

Fig. 5 – Optical emission spectrum of a $CO_2 + H_2$ microwave plasma discharge for initial pressure of 0.55 Torr and 500 W microwave radiation power.

Figure 6 shows the percentage of CO_2 dissociation in microwave discharge plasma produced in CO_2 and H_2, 1:1 mixture, *versus* gas flow rate and constant total inlet pressure.

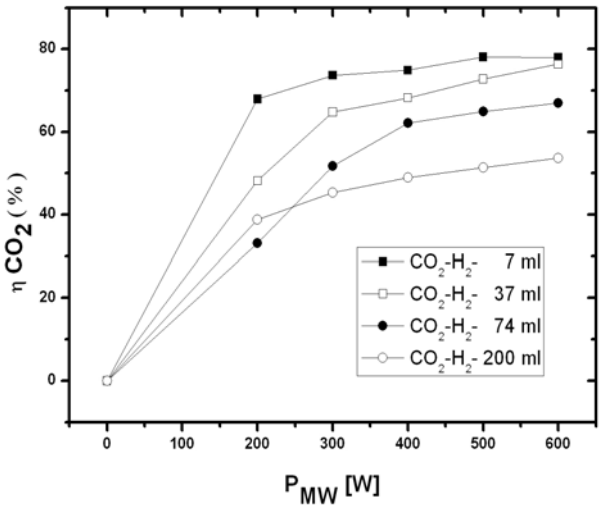

Fig. 6 – The percentage of CO_2 dissociation in microwave discharge plasma produced in CO_2 and H_2.

The experimental results show that the presence of the hydrogen within the CO_2 microwave discharge decrease the η dissociation coefficient. The system is no more saturated and with the increase of microwave radiation power more carbon dioxide is dissociated. A possible explanation of this decreasing is the decrease of the electron temperature that can be measured by Langmuir probe. The excitation and ionization process of the molecular hydrogen introduced in the CO_2 discharge by electron – molecule collisions may lead to electron cooling.

4. CONCLUSIONS

The microwave discharge plasma dissociates the CO_2 in carbon monoxide and oxygen. The high dissociation efficiency up to 90% of carbon dioxide can be obtained within microwave plasma discharge at relatively low pressure when reverse reactions are less probable. The dissociation efficiency decreases with increasing of the gas flow rate and its corresponding pressure.

Acknowledgments. This work was supported by the project: "Preparing doctoral students for professional development and insertion by facilitating access to scholarships and providing additional training recommended by best practice models from Europe", POSDRU contract 107/1.5/S/78342 project co-funded from European Social Fund through Sectorial Operational Program Human Resources 2007–2013.

The POSCCE-O 2.2.1, SMIS-CSNR 13984-901, No. 257/28.09.2010 Project, CERNESIM, is also gratefully acknowledged for the infrastructure used in this work.

REFERENCES

1. S.V Krupa, R.N Kickert, Environ. Pollut., **61**, 263–393 (1989).
2. R. Hackman, H.Akiyama, Ieee T. Dielect. El. In., **7**, 657–686 (2000).
3. U.Kunico, Chang Jen-Shih, Ieee T. Dielect. El. In., **7**, 602–614 (2000).
4. J. L. Hueso, J. Phys. Chem. A, **109**, 4930-4938 (2005).
5. I.N. Kosarev, N.L. Aleksandrov, S.V. Kindysheva, S.M. Starikovskaia, A.Yu.Starikovskii, J. Phys. D: Appl. Phys., **40**, 4493–4502 (2007).
6. Jianhong Zhang, Jizhong Sun, Ye Gong, Dezhen Wang, Tengcai Ma, Yue Liu, Vacuum, **83**, 133–137 (2009).
7. Fridman A, *Plasma chemistry*, ch.5, Cambridge University Press, New York 2008
8. I A Kossyi, A Yu Kostinsky, A A Matveyev, V P Silakov, Plasma Sources Sci. Technol., **1**, 207–220 (1992).
9. R.W.B Pearse, A.G. Gaydon, *The identification of molecular spectra*, 3rd Edition with Supplement, Chapman & Hall Ltd., London, 1965.
10. A. Fowler, A.G. Gaydon, Proc. R. Soc. Lond. A., **142**, 362–369 (1933).