



HAL
open science

Determination of N and O Atom Density in Ar-N₂-H₂ and Ar-O₂-H₂ Flowing Microwave Post Discharges

T. Czerwiec, J. Gavillet, T. Belmonte, H. Michel, André Ricard

► **To cite this version:**

T. Czerwiec, J. Gavillet, T. Belmonte, H. Michel, André Ricard. Determination of N and O Atom Density in Ar-N₂-H₂ and Ar-O₂-H₂ Flowing Microwave Post Discharges. *Journal de Physique III*, 1996, 6 (9), pp.1205-1212. 10.1051/jp3:1996179 . jpa-00249518

HAL Id: jpa-00249518

<https://hal.science/jpa-00249518v1>

Submitted on 4 Feb 2008

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Determination of N and O Atom Density in Ar-N₂-H₂ and Ar-O₂-H₂ Flowing Microwave Post Discharges

T. Czerwiec^(1,*), J. Gavillet⁽¹⁾, T. Belmonte⁽¹⁾, H. Michel⁽¹⁾ and A. Ricard⁽²⁾

⁽¹⁾ Laboratoire de Science et Génie des Surfaces (**), Institut National Polytechnique de Lorraine, École des Mines de Nancy, parc de Saurupt, 54042 Nancy Cedex, France

⁽²⁾ Laboratoire de Physique des Gaz et des Plasmas (***), Université de Paris-sud, Bâtiment 212, 91405 Orsay, France

(Received 8 January 1996, revised 25 April 1996, accepted 3 June 1996)

PACS.52.70.Kz – Optical (ultraviolet, visible, infrared) measurements

PACS.82.40.Ra – Plasma reactions

PACS.82.40.Tc – Chemiluminescence and chemical laser kinetics

Abstract. — Number densities of N and O atoms have been determined using NO titration in Ar-N₂, Ar-N₂-H₂, Ar-O₂ and Ar-O₂-H₂ flowing microwave (2 450 MHz) post-discharges at 300 and 1500 Pa. The NO titration scheme is discussed from a kinetics point of view and applied to the high dilution of molecular gases in argon. The N/N₂ density ratio is enhanced by a factor 3 when small quantities of H₂ are introduced in Ar-N₂ discharges. The high O/O₂ density ratio obtained in Ar-O₂ post-discharges (0.5 to 0.6) are probably due to adsorbed H₂O that inhibits surface recombination of O-atom. The effect of H₂ addition in Ar-O₂ microwave discharge at 1500 Pa is to decrease the O atom density by homogeneous reaction involving H atoms and OH radicals.

1. Introduction

Flowing microwave post-discharges of reactive gases are studied for surface treatments without charged particles (electrons, ions) interactions. Such remote plasma processes have been performed in microelectronics to obtain Si₃N₄ and SiO₂ thin films [1,2] and in polymer treatments to increase the surface adhesion [3,4]. A flowing microwave post-discharge with N₂ and Ar-N₂ gas mixtures has been previously studied at high gas pressure ($5 \times 10^3 - 6.5 \times 10^4$ Pa) for steel surface nitriding [5]. The thickness and nitrogen content of γ' and ϵ iron nitride layers have been found to increase when a few H₂ was introduced into N₂ (Ar-N₂) to remove thin iron native oxide layers [6].

In the present work, the N atom density has been first determined by NO titration in Ar-N₂ and Ar-N₂-H₂ gas mixtures. Then, the O atom density has been deduced in Ar-O₂ and in Ar-O₂-H₂ gas mixtures by introducing NO in the post-discharge. Such a method, called the air-afterglow technique, has been previously proposed in oxygen post-discharge [7,8]. It is

(*) Author for correspondence (e-mail: czerwiec@mines.u-nancy.fr)

(**) Unité de Recherche associée au CNRS 1402

(***) Unité de Recherche associée au CNRS

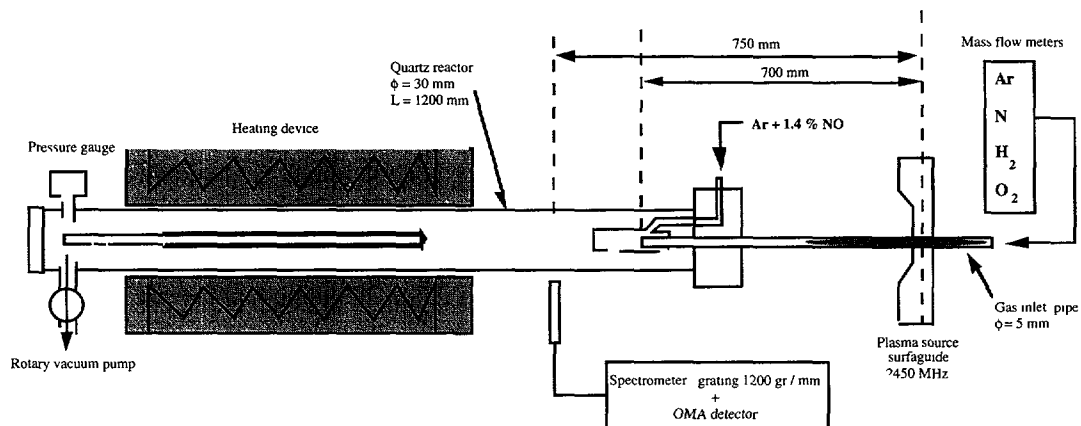


Fig. 1. — Experimental set-up for N and O atoms titration by NO.

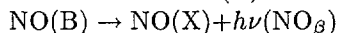
presently extended to Ar-O₂-H₂ gas mixtures by taking into account the possible influence of the different gases on this titration scheme.

2. The Experimental Set-Up

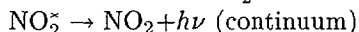
The same flowing microwave post-discharge reactor as described in references [5, 6] has been presently experimented. It is reproduced in Figure 1. The 2 450 MHz microwave plasma is produced in a quartz tube of 0.5 cm diameter with a surfaguide at a transmitted power of 130 W, a flow rate of 500-1050 sccm and a gas pressure of 300-1 500 Pa. The post-discharge runs into a reactor tube of diameter 2.8 cm at a distance of 70 cm from the surfaguide, corresponding to a post-discharge time $\Delta t \sim 10^{-2}$ s. Titration by NO is performed at the end of the 0.5 cm diameter quartz tube (75 cm from the surfaguide), in a mixing zone with a lateral exit of the flowing post-discharge (Fig. 1). The emission spectrum of the discharge and of the afterglow was analysed by using a Jobin-Yvon HR 640 spectrometer with a 1200 grooves mm⁻¹ grating and a photodiode array detector (IRY/1024).

3. N-Atom Density in Ar-N₂ and Ar-N₂-H₂ Post-Discharges

The N-atom density has been previously determined by NO titration [5]. The following reactions occur:



at low NO flow rates and:



at high NO flow rates.

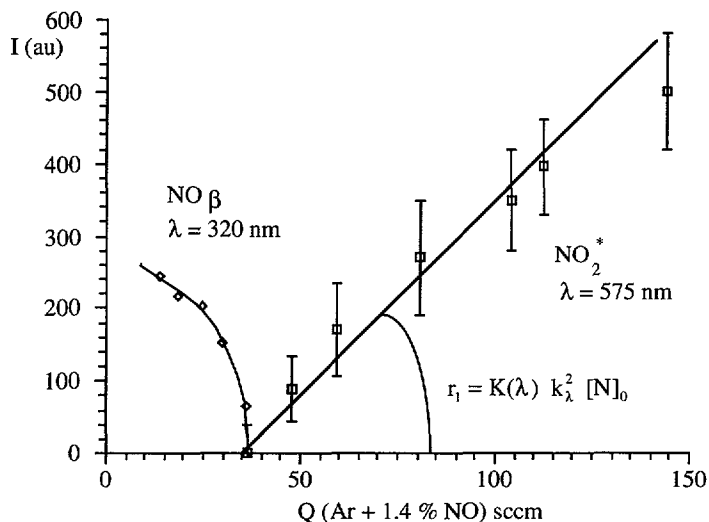


Fig. 2. — N-atom titration plot for an Ar-4% N_2 afterglow at $P = 300 \text{ Pa}$, $Q = 520 \text{ sccm}$ and $W = 130 \text{ W}$.

The colour change (extinction point) from the NO_β (violet) to the NO_2^* continuum (green) is produced as the two N and NO flow rates are equal in quantity. At this extinction point, all N-atom initially in the post-discharge have been converted into O-atom. The corresponding N-atom density $[N]_0$ can be written $[N]_0 = [O] = [\text{NO}]_{\text{ext}}$. By using an Ar-1.4% NO gas mixture, $[N]_0 = (7 \pm 0.4) \times 10^{13} \text{ cm}^{-3}$ has been obtained as reproduced in Figure 2 for an Ar-4% N_2 post-discharge at 300 Pa. The total gas flow rate was $Q = 520 \text{ sccm}$ and the 2 450 MHz microwave power was $W = 130 \text{ W}$. At 1 500 Pa of an Ar-5% N_2 post-discharge ($Q = 1050 \text{ sccm}$) at the same HF power, it has been determined $[N]_0 = (4.1 \pm 0.1) \times 10^{14} \text{ cm}^{-3}$. The $\frac{[N]}{[N_2]_i}$ density ratio (where $[N_2]_i$ denotes the density of N_2 with the discharge off), is 2.4% as for the experiment at 300 Pa. This relative density is calculated by assuming $T = 300 \text{ K}$ in the post-discharge.

The rate coefficients of reaction (a) - (d) are at $T = 300 \text{ K}$: $k_a = 3.7 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ [9], $k_b^{\text{Ar}} = 0.8 \times k_b^{\text{N}_2}$ [10], $k_b^{\text{N}_2} = (2.4 - 3.1) \times 10^{-34} \text{ cm}^6 \text{ s}^{-1}$ [10, 11], $k_c^{\text{N}_2} = 5.8 \times 10^{-32} \text{ cm}^6 \text{ s}^{-1}$, $k_c^{\text{Ar}} = 3.7 \times 10^{-32} \text{ cm}^6 \text{ s}^{-1}$ and $k_c^{\text{H}_2} = 6 \times 10^{-32} \text{ cm}^6 \text{ s}^{-1}$ [12]. The radiative loss frequency of NO_2^* is $\gamma_r = 2.5 \times 10^4 \text{ s}^{-1}$ [13] and the quenching rate coefficients are $k_d^{\text{Ar}} = 3.9 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$, $k_d^{\text{N}_2} = 6 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ and $k_d^{\text{H}_2} = 7.3 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ [14].

In writing reactions (a) - (d), it has been neglected the effects of collisions on $\text{N}_2(X, v)$ and $\text{N}_2(A)$ metastable molecules. Such excited molecules could play an important part in the early afterglow by heating the remaining electrons by superelastic collisions [15] and by producing excitation transfers [16]. In the present condition of late afterglow, these processes have been neglected. However, the $\text{N}_2(X, v)$ vibrational molecules are present with N-atom and can react with O-atom by:



The rate coefficient for reaction (e) is important for $v > 12$, $k_e(v > 12) = 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ [17], but as reaction (e) is followed by reaction (a) to restore O-atom, it has no effect on the presented kinetic schemes.

After the extinction point (for $[\text{NO}] > [\text{NO}]_{\text{ext}}$), the NO_2^* density is linearly increasing with $[\text{NO}]$ as shown in Figure 2. Such a variation can be explained by the following kinetics relation:

$$[\text{NO}_2^*] = \frac{[\text{O}][\text{NO}][\text{M}]k_c^{\text{M}}}{\gamma_r + [\text{M}]k_d^{\text{M}}} \quad (1)$$

By writing equation (1), the following two bodies reaction:



with $k_f = 5.6 \times 10^{-17} \text{ cm}^3 \text{ s}^{-1}$ [18] has been neglected for gas pressure $P > 100 \text{ Pa}$, since $[\text{M}]k_c^{\text{M}} > 2 \times 10^{-16} \text{ cm}^3 \text{ s}^{-1}$ for $\text{M} = \text{Ar}$. The radiative frequency γ_r can be neglected in equation (1) for $P > 100 \text{ Pa}$ since $[\text{M}]k_d^{\text{M}} > 10^6 \text{ s}^{-1}$ for $\text{M} = \text{Ar}$. Then, for high dilution of N_2 and H_2 molecular gases into argon, the intensity $I(\text{NO}_2^*)$ of the air afterglow continuum can be described by equation (2) in an Ar- N_2 gas mixture and by equation (3) in an Ar- N_2 - H_2 gas mixture:

$$I(\text{NO}_2^*) = K(\lambda)[\text{O}][\text{NO}] = K(\lambda)[\text{N}]_0[\text{NO}] \quad (2)$$

$$I(\text{NO}_2^*) = K(\lambda)[\text{N}]_0^{\text{H}_2}[\text{NO}] \quad (3)$$

with

$$K(\lambda) = k(\lambda) \frac{\sum_{\text{M}} k_c^{\text{M}}[\text{M}]}{\sum_{\text{M}} k_d^{\text{M}}[\text{M}]} \approx \frac{k_c^{\text{Ar}}}{k_d^{\text{M}}} k(\lambda) = 9.5 \times 10^{-22} k(\lambda) \quad (4)$$

$k(\lambda)$ is a calibration factor depending on spectrometer spectral response, on photon energy and optical emission probability of NO_2^* and $[\text{N}]_0^{\text{H}_2}$ is the initial N-atom density in the Ar- N_2 - H_2 gas mixture. Note that chemiluminescence with O_3 has not been considered here since, first substantial O_3 density only appears at high O_2 gas pressure and second, the NO-O_3 continuum is extending from 600 to 2200 nm [18] at larger wavelengths that presently used for NO_2^* detection: $\lambda = 575 \text{ nm}$.

The results obtained with an Ar-3.8% N_2 -0.2% H_2 gas mixture at $P = 300 \text{ Pa}$, $Q = 521 \text{ sccm}$ and $W = 130 \text{ W}$ are reproduced in Figure 3. First, it is found a sensitive increase of N-atom density with $[\text{N}]_0^{\text{H}_2} = (2.3 \pm 0.1) \times 10^{14} \text{ cm}^{-3}$ which is 3.3 higher than without H_2 . The increase of N-atom density with a few H_2 into N_2 has been previously analysed by LIF in DC N_2 - H_2 flowing post-discharge [19]. Recently, an increase of about 3 of N-atom density has been found in an Ar-10% N_2 -0.5% H_2 microwave post-discharge [20]. This seems to be connected to an increase of the discharge electric field and to a reduction of N-atom recombination on the post-discharge tube as a few H_2 is introduced into N_2 .

The slope of the $I(\text{NO}_2^*)$ variations with NO as determined in Figures 2 and 3 are $r_1 = K(\lambda)[\text{N}]_0$ and $r_2 = K(\lambda)[\text{N}]_0^{\text{H}_2}$, respectively. With $r_1 = 5.3 \pm 0.9$, $[\text{N}]_0 = (7 \pm 0.4) \times 10^{13} \text{ cm}^{-3}$, $r_2 = 16 \pm 2$ and $[\text{N}]_0^{\text{H}_2} = (2.3 \pm 0.1) \times 10^{14} \text{ cm}^{-3}$, it follows that:

$$\frac{r_2}{r_1} = \frac{[\text{N}]_0^{\text{H}_2}}{[\text{N}]_0} \quad (5)$$

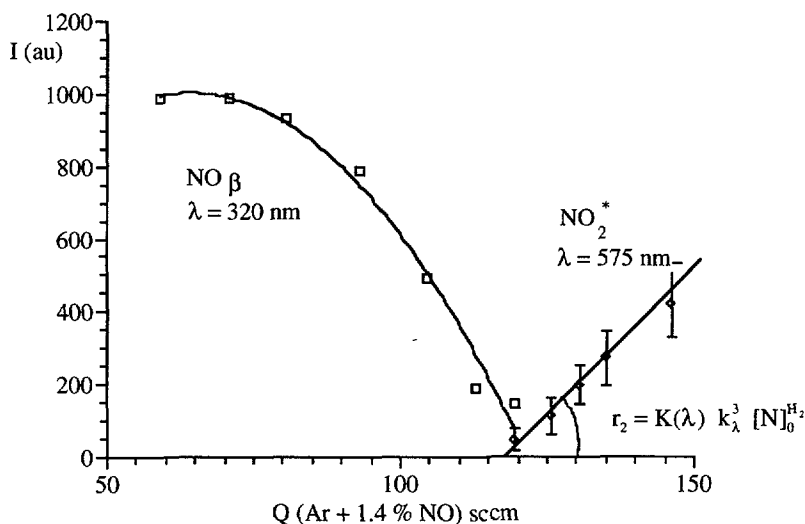


Fig. 3. — N-atom titration plot for an Ar-3.8% N₂-0.2% H₂ afterglow at $P = 300$ Pa, $Q = 521$ sccm and $W = 130$ W.

4. O-Atom Density in Ar-O₂ and in Ar-O₂-H₂ Post-Discharges

In Ar-O₂-H₂ post-discharge, the oxygen atoms coming from the discharge are reacting with NO to produce NO₂* by reaction (c). For high O₂ and H₂ molecular gases dilution into argon and by using the following rate coefficients in equation (4): $k_c^{O_2} = 5.6 \times 10^{-32}$ cm⁻⁶ s⁻¹ [12] for reaction (c) and $k_d^{O_2} = 5.4 \times 10^{-11}$ cm³ s⁻¹ [14] for reaction (d), it can be deduced that:

$$I(\text{NO}_2^*) = K(\lambda)[\text{O}][\text{NO}] \quad (6)$$

Variation of NO₂* intensity *versus* NO measured at the same wavelength with the same optical arrangement as above is reproduced in Figure 4 for an Ar-3.8% O₂-0.2% H₂ post-discharge at $P = 300$ Pa, $Q = 521$ sccm and $W = 130$ W. At this low H₂ percentage, the contribution of possible H₂O formed in the post-discharge has been neglected. The slope of NO₂* intensity *versus* Ar-1.4% NO flow rate is $r_3 = K(\lambda)[\text{O}]$ and by comparing with Figure 2 and Figure 3, it follows:

$$[\text{O}] = \frac{r_3}{r_1}[\text{N}]_0 = \frac{r_3}{r_2}[\text{N}]_0^{\text{H}_2} \quad (7)$$

With $r_3 = 120 \pm 10$, $r_1 = 5.3 \pm 0.9$, $[\text{N}]_0 = (7 \pm 0.4) \times 10^{13}$ cm⁻³, equation (6) gives $[\text{O}] = (1.6 \pm 0.5) \times 10^{15}$ cm⁻³. It results that the density ratio $C_0 = \frac{[\text{O}]}{[\text{O}_2]_i}$ (where $[\text{O}_2]_i$ denotes the density of O₂ with the discharge off) in the actual Ar-3.8% O₂-0.2% H₂ flowing HF post-discharge at 300 Pa is as high as 0.6. This value is considerably higher than those obtained in pure oxygen microwave post-discharges which normally ranges around 0.01 and 0.1 [21–24] and could only be compared to C_0 obtained in microwave discharge in O₂ [25]. Such high O atom density is probably due to the high argon dilution used in the present experiments and to the use of hydrogen.

It has been previously found that small amounts of molecular gases (N₂, H₂) increase the extent of dissociation of O₂ molecules in electrical discharges [22, 23]. In a microwave post-discharge at 70 Pa, Brown [22] observed an increase in C_0 up to 0.5 when traces of impurities

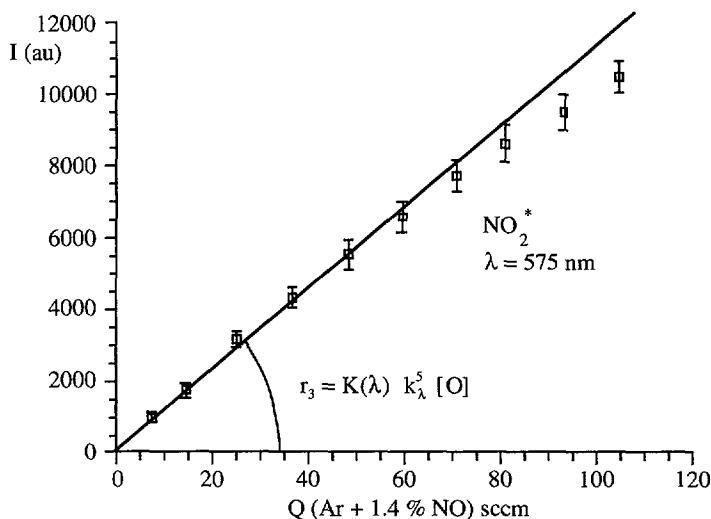


Fig. 4. — O-atom titration plot for an Ar-3.8% O₂-0.2% H₂ afterglow at $P = 300$ Pa, $Q = 521$ sccm and $W = 130$ W.

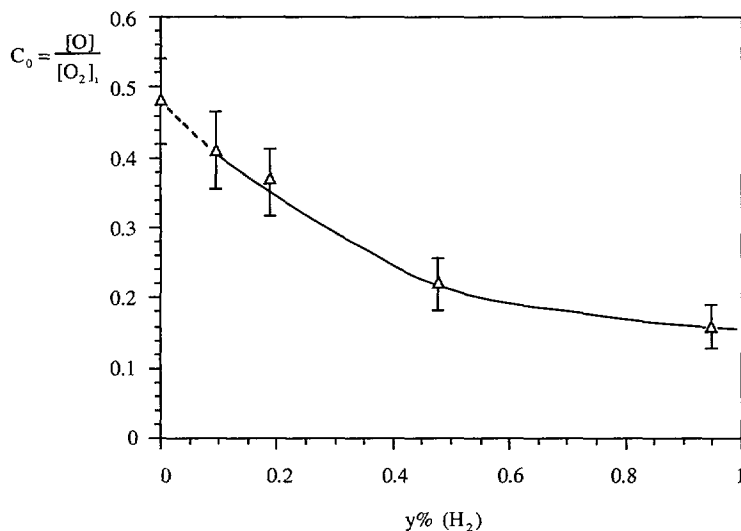


Fig. 5. — Relative O-atom density (C_0) versus hydrogen percentage (y %) for an Ar-1.2% O₂- y % H₂ microwave discharge at $P = 1\,500$ Pa, $1\,039.5 \leq Q \leq 1\,049.5$ sccm and $W = 130$ W.

such H₂O or H₂ were injected in the O₂ discharge. As it is reproduced in Figure 5 for the present experiment at 1 500 Pa ($1\,039.5 \leq Q \leq 1\,049.5$ sccm), the oxygen atom density in the Ar-1.2% O₂- y % H₂ post-discharge is decreasing from $[O] = (2.1 \pm 0.4) \times 10^{15} \text{ cm}^{-3}$, $C_0 = 0.48$ as $y(\text{H}_2) = 0$ to $(7 \pm 1) \times 10^{14} \text{ cm}^{-3}$, $C_0 = 0.16$ as $y(\text{H}_2) = 1\%$. This behaviour was also observed by increasing the pressure at constant mass flow rate and constant H₂ addition in O₂ [22]. The high initial C_0 value may be due to impurities such as water vapour adsorbed on the reactor

walls [28]. Moreover, the destruction of O atoms may be either by heterogeneous (surface recombination) or by homogeneous (gas phase) reactions. The decrease of O-atom density in introducing H₂ in the high pressure Ar-O₂ gas mixture could be explained by homogeneous reaction involving H atoms and OH radicals such as:



with $k_g = 4.3 \times 10^{-32} \text{ cm}^6 \text{ s}^{-1}$ [26] and $k_h = 2.9 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ [27].

5. Conclusion

The O-atom density determination by NO titration has been discussed from kinetic point of view for the complex post-discharge in Ar-O₂-H₂. Addition of small quantities of H₂ to Ar-N₂ mixture has been investigated for N-atom density determination and consequences on O-atom density determination is also discussed. It can be concluded that N-atom density is significantly enhanced by H₂ addition by a factor 3 in Ar-3.8% N₂-0.2% H₂ at 300 Pa ($Q = 520 \text{ sccm}$). Both Ar-N₂ and Ar-N₂-H₂ mixtures can serve as references for O atom titration by NO in Ar-O₂ or Ar-O₂-H₂ post-discharge. Relative O-atom densities as high than 0.5-0.6 has been determined in Ar-O₂ post-discharge at 300 Pa ($Q = 520 \text{ sccm}$) and 1 500 Pa ($Q = 1\ 039.5 \text{ sccm}$). This is probably related to H₂O settled on the reactor walls that inhibits the surface recombination of O-atom. It has been found a sensitive decrease of O-atom density as H₂ is initially introduced in an Ar-O₂ gas mixture. Works are in progress to analyse the kinetics processes in Ar-O₂-H₂ gas flowing post-discharges.

Acknowledgments

The authors wish to express their thanks to J.P. Prelot for his technical support.

References

- [1] Kulisch W., Remote plasma-enhanced chemical vapour deposition with metal organic sources gases: principles and applications, *Surf. Coat. Technol.* **59** (1993) 193.
- [2] Tsu D.V., Parsons G.N., Lucovsky G. and Watkins M.W., Optical emission and mass spectroscopic studies of the gas phase during the deposition of SiO₂ and a-Si: H remote plasma-enhanced chemical vapour deposition, *J. Vac. Sci. Technol. A* **7** (1989) 1115.
- [3] Normand F., Marec J., Leprince Ph. and Granier A., Surface treatment of polypropylene by oxygen microwave discharge, *Mat. Sci. Engn. A* **139** (1991) 103.
- [4] Normand F., Granier A., Leprince Ph., Marec J., Shi M.K. and Clouet F., Polymer treatment in the flowing afterglow of an O₂ microwave discharge, *Plasma Chem. Plasma Proc.* **15** (1995) 173.
- [5] Ricard A., Oseguera-Pena J., Falk L., Michel H. and Gantois M., Active species in microwave post-discharge for steel-nitriding, *IEEE Trans. Plasma Sc.* **18** (1990) 940.
- [6] Malvos H., Michel H. and Ricard A., Correlation between active species density and iron nitride layer in Ar-N₂-H₂ microwave post-discharge, *J. Phys. D* **27** (1994) 1328.
- [7] Clyne M.A.A. and Nip W.S., Reactive Intermediates in the gas phase, D.W. Setser Ed. (Academic Press, 1979).

- [8] Piper L.G., Caledonia G.E. and Kennealy J.P., Rate constants for deactivation of N_2 ($A^3\Sigma_u^+$, $v' = 0, 1$) by O, *J. Chem. Phys.* **75** (1981) 2847.
- [9] Michael J.V. and Lim K.P., Rate constants for the N_2O reaction system: thermal decomposition of N_2O ; $N + NO \rightarrow N_2 + O$; implication for the $O + N_2 \rightarrow NO + N$, *J. Chem. Phys.* **97** (1992) 3228.
- [10] Baulch D.L., Drysdale D.D. and Horne D.G., Homogeneous gas phase reactions of a H_2 , N_2 , O_2 system (London Butterworths, 1973).
- [11] Gross R.W.F. and Cohen N., Temperature dependence of chemiluminescent reactions. II Nitric oxide afterglow, *J. Chem. Phys.* **48** (1968) 2582.
- [12] Young R.A., Black G. and Slinger T.G., Reaction and deactivation of O (1D), *J. Chem. Phys.* **49** (1968) 4758.
- [13] Hakala D.F. and Reeves R.R., Ruby laser induced emission from NO_2 , *Chem. Phys. Lett.* **32** (1976) 510.
- [14] Donnelly V.M., Keil D.G. and Kaufman F., Fluorescence lifetime studies of NO_2 . III Mechanisms of fluorescence quenching, *J. Chem. Phys.* **71** (1979) 659.
- [15] Colonna G., Gorse G., Capitelli M., Winkler R. and Wilhelm J., The influence of electron-electron collisions on electron energy distribution functions in N_2 post-discharge, *Chem. Phys. Lett.* **213** (1993) 5.
- [16] de Benedictis S., Dilacce G. and Simek M., Time resolved LIF spectroscopy on N_2 (A) metastable in a He/ N_2 pulsed RF discharge, *Chem. Phys.* **178** (1993) 547.
- [17] Gordiets B. and Ricard A., Production of N, O and NO in N_2 - O_2 flowing discharges, *Plasma Sources Sci. Technol.* **2** (1993) 158.
- [18] Sutoh M., Morioka Y. and Nakamura M., Absolute rate constant for the chemiluminescent reactions of atomic oxygen with nitric oxide, *J. Chem. Phys.* **72** (1980) 20.
- [19] Amorim J., Baravian G. and Ricard A., Production of N, H and NH active species in N_2 - H_2 dc flowing discharges, *Plasma Chem. Plasma Proc.* **15** (1995) 723.
- [20] Bockel S., Amorim J., Baravian G., Ricard A. and Stratil P., Spectroscopic study of active species in dc and hf flowing discharges in N_2 - H_2 and Ar- N_2 - H_2 mixtures, *Plasma Sources Sci. Technol.* (1996) to be published.
- [21] Granier A., Pasquiers S., Boisse-Laporte C., Darchicourt R., Leprince P. and Marec J., Characterization of a low pressure oxygen discharge created by surface waves, *J. Phys. D* **22** (1989) 1487.
- [22] Brown R.L., Effects of impurities on the production of oxygen atoms by microwave discharge, *J. Phys. Chem.* **71** (1967) 2492.
- [23] Mearns A.M. and Morris A.J., Use of the nitrogen dioxide titration technique for oxygen atom determination at pressures above 2 Torr, *Chem. Eng. Symp. Ser.* **112** (1971) 37.
- [24] Kaufman F. and Kelso J.R., Catalytic effects in the dissociation of oxygen in microwave discharges, *J. Chem. Phys.* **32** (1960) 301.
- [25] Brake M., Hinkle J., Asmussen J., Hawley M. and Kerber R., Dissociation and recombination of oxygen atoms produced in a microwave discharge, *Plasma Chem. Plasma Proc.* **3** (1983) 63.
- [26] Tsang W. and Hampson R.F., Chemical kinetic data base for combustion chemistry, Part. I: Methane and related compounds, *J. Phys. Chem. Ref. Data* **15** (1986) 1087.
- [27] Baulch D.L., Cobos C.J., Cox R.A., Frank P., Hayman G., Just Th., Kerr J.A., Murrells T., Pilling M.J., Troe J., Walker R.W. and Warnatz J., Summary table of evaluated kinetic data for combustion modelling, *Combust. Flame* **98** (1994) 59.
- [28] Collart E.J.H., Baggerman J.A.G. and Visser R.J., On the role of atomic oxygen in the etching of organic polymers in a radio-frequency oxygen discharge, *J. Appl. Phys.* **78** (1995) 47.