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T. Czerwiec (1,*), J. Gavilet (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 (***) University of Paris-Sud, Bâtiment 212, 91405 Orsay, France

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Abstract. — Number densities of N and O atoms have been determined using NO titration in Ar-N$_2$, Ar-N$_2$-H$_2$, Ar-O$_2$ and Ar-O$_2$-H$_2$ 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/N$_2$ density ratio is enhanced by a factor 3 when small quantities of H$_2$ are introduced in Ar-N$_2$ discharges. The high O/O$_2$ density ratio obtained in Ar-O$_2$ post-discharges (0.5 to 0.6) are probably due to adsorbed H$_2$O that inhibits surface recombination of O-atom. The effect of H$_2$ addition in Ar-O$_2$ 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 Si$_3$N$_4$ and SiO$_2$ thin films [1,2] and in polymer treatments to increase the surface adhesion [3,4]. A flowing microwave post-discharge with N$_2$ and Ar-N$_2$ gas mixtures has been previously studied at high gas pressure ($5 \times 10^8 - 6.5 \times 10^4$ Pa) for steel surface nitriding [5]. The thickness and nitrogen content of $\gamma'$ and $\epsilon$ iron nitride layers have been found to increase when a few H$_2$ was introduced into N$_2$ (Ar-N$_2$) 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-N$_2$ and Ar-N$_2$-H$_2$ gas mixtures. Then, the O atom density has been deduced in Ar-O$_2$ and in Ar-O$_2$-H$_2$ 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

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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 2450 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 300-1500 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:

$$N + NO \rightarrow N_2 + O \quad (a)$$
$$N + O + M \rightarrow NO(B) + M \quad (b)$$
$$NO(B) \rightarrow NO(X) + h\nu(NO_\beta)$$

at low NO flow rates and:

$$O + NO + M \rightarrow NO_2 + M \quad (c)$$
$$NO_2 \rightarrow NO_2 + h\nu \ (\text{continuum})$$
$$NO_2 + M \rightarrow NO_2 + M \quad (d)$$

at high NO flow rates.
The colour change (extinction point) from the NO\(_{\beta}\) (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 \([N]_0 = [O] = [NO]_{ext}\). By using an Ar-1.4\% NO gas mixture, \([N]_0 = (7 \pm 0.4) \times 10^{13}\) 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 \(Q = 520\) sccm and the 2 450 MHz microwave power was \(W = 130\) W. At 1 500 Pa of an Ar-5\% N\(_2\) post-discharge (\(Q = 1050\) sccm) at the same HF power, it has been determined \([N]_0 = (4.1 \pm 0.1) \times 10^{14}\) cm\(^{-3}\). The \([N]_0\) density ratio (where \([N]_0\) represents 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 \(T = 300\) K in the post-discharge.

The rate coefficients of reaction (a) - (d) are at \(T = 300\) K: \(k_{\text{Ar}} = 3.7 \times 10^{-11}\) cm\(^3\) s\(^{-1}\) [9], \(k_{\text{H}_2} = 0.8 \times 10^{11}\) cm\(^{-1}\) [10], \(k_{\text{N}_2} = (2.4 - 3.1) \times 10^{-34}\) cm\(^6\) s\(^{-1}\) [10, 11], \(k_{\text{N}_2} = 5.8 \times 10^{-32}\) cm\(^6\) s\(^{-1}\), \(k_{\text{Ar}} = 3.7 \times 10^{-32}\) cm\(^6\) s\(^{-1}\) and \(k_{\text{H}_2} = 6 \times 10^{-32}\) cm\(^6\) s\(^{-1}\) [12]. The radiative loss frequency of NO\(_2^*\) is \(\gamma_r = 2.5 \times 10^4\) s\(^{-1}\) [13] and the quenching rate coefficients are \(k_{\text{Ar}} = 3.9 \times 10^{-11}\) cm\(^3\) s\(^{-1}\), \(k_{\text{N}_2} = 6 \times 10^{-11}\) cm\(^3\) s\(^{-1}\) and \(k_{\text{H}_2} = 7.3 \times 10^{-11}\) cm\(^3\) s\(^{-1}\) [14].

In writing reactions (a) - (d), it has been neglected the effects of collisions on N\(_2\) (X, v) and 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 N\(_2\) (X, v) vibrational molecules are present with N-atom and can react with O-atom by:

\[
N_2(X, v) + O \rightarrow NO + N
\]
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 \( \text{NO}_2^* \) density is linearly increasing with \([\text{NO}]\) as shown in Figure 2. Such a variation can be explained by the following kinetics relation:

\[
[\text{NO}_2^*] = \frac{[\text{O}][\text{NO}][M]k_c^M}{\gamma_r + [M]k_d^M} \tag{1}
\]

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

\[
\text{O} + \text{NO} \rightarrow \text{NO}_2^* \tag{f}
\]

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

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

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

with

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

\( k(\lambda) \) is a calibration factor depending on spectrometer spectral response, on photon energy and optical emission probability of \( \text{NO}_2^* \) and \([\text{N}]_0^\text{H}_2\) is the initial N-atom density in the \( \text{Ar-N}_2-\text{H}_2 \) gas mixture. Note that chimiluminescence with \( \text{O}_3 \) has not been considered here since, first substantial \( \text{O}_3 \) density only appears at high \( \text{O}_2 \) gas pressure and second, the \( \text{NO}-\text{O}_3 \) continuum is extending from 600 to 2200 nm [18] at larger wavelengths that presently used for \( \text{NO}_2^* \) detection: \( \lambda = 575 \text{ nm} \).

The results obtained with an \( \text{Ar}-3.8\% \text{N}_2-0.2\% \text{H}_2 \) 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 \( \text{H}_2 \). The increase of N-atom density with a few \( \text{H}_2 \) into \( \text{N}_2 \) has been previously analysed by LIF in DC \( \text{N}_2-\text{H}_2 \) flowing post-discharge [19]. Recently, an increase of about 3 of N-atom density has been found in an \( \text{Ar}-10\% \text{N}_2-0.5\% \text{H}_2 \) 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 \( \text{H}_2 \) is introduced into \( \text{N}_2 \).

The slope of the \( I(\text{NO}_2^*) \) variations with \( \text{NO} \) 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:

\[
\frac{r_2}{r_1} = \frac{[\text{N}]_0^\text{H}_2}{[\text{N}]_0} \tag{5}
\]
In Ar-O_2-H_2 post-discharge, the oxygen atoms coming from the discharge are reacting with NO to produce NO\(^2\) by reaction (c). For high O_2 and H_2 molecular gases dilution into argon and by using the following rate coefficients in equation (4): 
\[ k^c_{02} = 5.6 \times 10^{-32} \text{ cm}^{-6} \text{ s}^{-1} \] [12] for reaction (c) and 
\[ k^d_{02} = 5.4 \times 10^{-11} \text{ cm}^{-3} \text{ s}^{-1} \] [14] for reaction (d), it can be deduced that:

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

Variation of NO\(^2\) 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% O_2-0.2% H_2 post-discharge at \( P = 300 \text{ Pa}, Q = 521 \text{ sccm} \) and \( W = 130 \text{ W} \). At this low H_2 percentage, the contribution of possible H_2O formed in the post-discharge has been neglected. The slope of NO\(^2\) 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:

\[ [\text{O}] = \frac{\tau_3}{\tau_1} [\text{N}]_0 = \frac{\tau_3}{\tau_2} [\text{N}]_0^\text{H}_2 \] (7)

With \( \tau_3 = 120 \pm 10, \tau_1 = 5.3 \pm 0.9, [\text{N}]_0 = (7 \pm 0.4) \times 10^{13} \text{ cm}^{-3} \), equation (6) gives \([\text{O}] = (1.6 \pm 0.5) \times 10^{15} \text{ cm}^{-3}\). It results that the density ratio \( C_0 = \frac{[\text{O}]}{[\text{O}_2]} \) (where \([\text{O}_2]\) denotes the density of O_2 with the discharge off) in the actual Ar-3.8% O_2-0.2% H_2 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 compared to \( C_0 \) obtained in microwave discharge in O_2 [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 (N\(_2\), H\(_2\)) increase the extent of dissociation of O\(_2\) 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
such H$_2$O or H$_2$ were injected in the O$_2$ 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% O$_2$-y% H$_2$ post-discharge is decreasing from [O] = (2.1±0.4)×10$^{15}$ cm$^{-3}$, $C_0 = 0.48$ as $y(H_2) = 0$ to (7±1)×10$^{14}$ cm$^{-3}$, $C_0 = 0.16$ as $y(H_2) = 1%$. This behaviour was also observed by increasing the pressure at constant mass flow rate and constant H$_2$ addition in O$_2$ [22]. The high initial $C_0$ value may be due to impurities such as water vapour adsorbed on the reactor.

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**Fig. 4.** — O-atom titration plot for an Ar-3.8% O$_2$-0.2% H$_2$ 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% O$_2$-y% H$_2$ microwave discharge at $P = 1 500$ Pa, 1 039.5 $\leq Q \leq$ 1 049.5 sccm and $W = 130$ W.
and, 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 H\textsubscript{2} in the high pressure Ar-O\textsubscript{2} gas mixture could be explained by homogeneous reaction involving H atoms and OH radicals such as:

\[
\begin{align*}
O + H + M & \rightarrow OH + M \quad \text{(g)} \\
O + OH & \rightarrow O_2 + H \quad \text{(h)}
\end{align*}
\]

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-O\textsubscript{2}-H\textsubscript{2}. Addition of small quantities of H\textsubscript{2} to Ar-N\textsubscript{2} 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 H\textsubscript{2} addition by a factor 3 in Ar-3.8\% N\textsubscript{2}-0.2\% H\textsubscript{2} at 300 Pa (\( Q = 520 \text{ sccm} \)). Both Ar-N\textsubscript{2} and Ar-N\textsubscript{2}-H\textsubscript{2} mixtures can serve as references for O atom titration by NO in Ar-O\textsubscript{2} or Ar-O\textsubscript{2}-H\textsubscript{2} post-discharge. Relative O-atom densities as high than 0.5-0.6 has been determined in Ar-O\textsubscript{2} post-discharge at 300 Pa (\( Q = 520 \text{ sccm} \)) and 1 500 Pa (\( Q = 1 039.5 \text{ sccm} \)). This is probably related to H\textsubscript{2}O 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 H\textsubscript{2} is initially introduced in an Ar-O\textsubscript{2} gas mixture. Works are in progress to analyse the kinetics processes in Ar-O\textsubscript{2}-H\textsubscript{2} gas flowing post-discharges.

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