RADIATION FROM AN INDUCTIVELY COUPLED PLASMA IN THE NEAR-UV TO NEAR-IR SPECTRAL REGION FOR A TITAN-TYPE N_2-CH_4 MIXTURE.

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ABSTRACT

An inductively coupled plasma torch, working at atmospheric pressure, is used to create N_2-CH_4 Titan-like plasma (98%N_2 - 2%CH_4). The operating frequency and power are 64 MHz and 3 kW respectively. This kind of apparatus allows obtaining plasma in chemical and quasi-thermal equilibrium. The spectral measurements cover the [320-840] nm range and are performed inside the induction coil. Each interesting spectrum is calibrated and compared to the line-by-line spectral code SPARTAN used for the simulation of the radiative emission of entry-type plasma.

Finally, a discussion is proposed about the nucleation phenomenon which is occurred in the ICP torch with the N_2-CH_4 plasma. Preliminary studies show the synthesis of nanostructured carbon on the quartz tube.

1. INTRODUCTION

The study of Titan, largest satellite of Saturn, is of great scientific interest because its atmosphere is mainly composed of methane, nitrogen and also acetylene and organic species. The composition, well known from the US missions Voyager1 (1980) and Voyager2 (1981), could be an element for the origin of life on Titan.

The European Huygens probe on board the Cassini mission (NASA, ESA, ASI) has successfully performed a descent through the atmosphere of Titan on 14 January 2005.

This mission and all the Titan projects require complex studies to know the properties of the atmosphere surrounding a probe during its hypersonic speed journey, primarily to size the thermal surface protection. Studies performed in laboratories are necessary, they are based on the development of models and experimental validations. Several types of experiments are used: shock-tubes, arc-jets and inductive sources at atmospheric pressure or at reduced pressure.

The LAEPT has an inductively coupled plasma torch (ICP-T64) which works at atmospheric pressure and which is used to create N_2-CH_4 Titan-like plasma.

The outline of the paper is as follows. In section 2, the characteristics of the experimental set-up are given. In section 3, after a discussion concerning the sustained conditions of the plasma when methane is injected into a pure nitrogen plasma, experimental spectra in the range [320-840] nm are presented and an estimation of the axial temperature is given. In section 4, a discussion is proposed about the nucleation phenomenon which is occurred in the ICP torch with the N_2-CH_4 plasma. Preliminary studies show the synthesis of nanostructured carbon on the inner surface of the quartz tube. The chemical equilibrium composition of a N_2-CH_4 Titan-like plasma (98%N_2 - 2%CH_4) is given through the calculation code based on the Gibbs free energy minimization. Finally, the perspectives of this preliminary study will be given.

2. EXPERIMENTAL SET-UP

The ICP-T64 torch present at the L.A.E.P.T. (Thermal Plasmas and Electrical Arc Laboratory) in Clermont-Ferrand, France, is a classical ICP torch able to work with different kinds of plasma gas (air, argon, CO_2, N_2 and gas mixtures). A seven-turn induction coil, made in Inconel, cooled by air is used to sustain the N_2-CH_4 plasma. In order to ignite the plasma, a metallic wire is plunged into the confinement quartz tube of the plasma gas to realize the initial ionisation.

The main features of the experimental set-up and operating conditions are reported in Tab.1 and Fig.1, respectively. The plasma is generated through the induction coil by a radio frequency (RF) of 64 MHz delivering a power up to 3 kW. The plasma is confined within a 28-mm cylindrical and vertical quartz tube. The plasma gas is injected at a fixed mass flow rate of 0.2 $g.s^{-1}$.

The optical set-up, placed at 34.3 cm from the plasma axis, leads to a spatial resolution of 1mm. Spectral lines intensities are measured with a 0.50 m focal length Czerny-Turner monochromator connected to a CCD detector (1242×1152 pixels, each pixel having a width of 22.5 micrometers). An 1200 grooves/mm grating is used. Its apparatus function $\Delta\lambda_{app}$, assimilated to a Gaussian profile with a Full Width at Half Maximum (FWHM), is calculated from the following relation :

$$\Delta\lambda_{app} = FWHM\ f_P D^{-1} \qquad (1)$$

where FWHM is expressed in pixels, D^{-1} represents the gratings dispersion (1.56 nm/mm) and f_p defines the pixel dimension (22.5 µm). The calculated value of $\Delta\lambda_{app}$ gives 0.14 nm for an entrance slit equal to 100 µm.

Table 1. Main features of the experimental set-up.

Inductively coupled plasma
Manufacturer/type: Défi Systèmes/ICP T64
Power supply: 64 MHz, 2.1 kW
Tuning: Automatic adaptation
Inductor: Seven-turn air-cooled coil
Plasma gas flow rate: 0.222 $g.s^{-1}$
Operating pressure: atmospheric pressure
Torch: 28 mm internal diameter quartz tube

Optical set-up
Spectrometer: Chromex 500 IS
500 mm focal length
Czerny-turner mounting
Entrance slit: e = 100 µm
Gratings: 1200 $grooves.mm^{-1}$
Detector: CCD EEV 1152×1242 pixels
Spatial resolution: 1 mm
Apparatus function: 0.14 nm

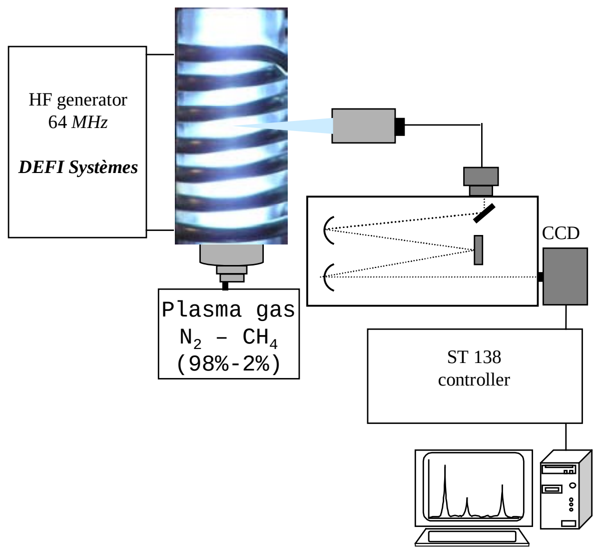

Figure 1. Plasma torch and detection experimental set-up.

The measured emission spectra must be corrected from the spectral response of the optical device, which include lens, monochromator and CCD detector. So, a calibration in intensity, between 300 and 800 nm, is necessary to take into account all these effects. A tungsten lamp (PHILIPS WI14) is used to cover the range [300 – 800] nm. The calibration procedure is realized in the same conditions as for experimental spectral acquisitions ones.

3. EXPERIMENTAL SPECTRA

Optical emission spectroscopy is the simplest non-intrusive method for plasma diagnostics. The analytical zone is limited between the fourth and the fifth induction coil where the luminous response is the greatest. Each spectrum corresponds to one acquisition of one second and the electronic noise is automatically subtracted.

One particularity of the Titan atmosphere plasma created in the ICP-T64 torch is the difficulty to have a sustainable plasma. At first, the plasma was ignited with pure nitrogen, and when the methane was injected the plasma generally was cut. It has been observed also that there was a loss of injected power, about 1 kW, when the methane was added. This effect is mainly due to the automatic adaptation of impedance but it is worth noting that there is no problem of extinction when the plasma changes to Titan atmosphere to pure nitrogen. The studies have been improved to understand this unusual behavior of this kind of plasma. So, the transport coefficients have been considered and calculated in equilibrium conditions at a pressure of one atmosphere.

The well-known solution of the Boltzmann equation due to Chapmann and Enskog [1,2] assumes two-body interactions between chemical species. This interaction can be described by a potential interaction between two particles. By successive integrations, we obtain collision integrals which are the basic data of the transport coefficients [1,2]. Several interaction types have to be taken into account:
- Neutral-neutral collisions are with a Lennard Jones potential [3,4] and data to determine the collisions integrals [5] and empirical combining rules [2].
- Charged-neutral collisions. In this case, the resonant charge exchange occurs for some collision integrals. This inelastic process is the dominant process [6]. From Dalgarno [7] the charge exchange cross section can be written versus the relative speed g of the two interacting particles and two parameters A and B. For the other collisions between neutral and charged particles, we consider them as elastic and that the charge particle generates a dipole in neutral particle during the collision [8].
- Charged-charged collisions. The collisions (repulsive or attractive) between two charged particles are described by a shielded Coulomb potential [9].
- Electron-neutral collisions. The values for the collisions integral can be found in literature or can be estimated [3].

To calculate the electrical conductivity, we used the third-order Sonine approximation of the Chapman-Enskog method [10,11]. To calculate the viscosity assuming that it is due to the heavy chemical species, we used the formulation given in

[1]. The thermal conductivity λ_{tot} can be separated into four terms with a good accuracy [10,12]:

$$\lambda_{tot} = \lambda_{tr}^{e} + \lambda_{tr}^{h} + \lambda_{\mathrm{int}} + \lambda_{react} \quad (2)$$

where λ_{tr}^{e} is the translational thermal conductivity of electrons, λ_{tr}^{h} the translational thermal conductivity of heavy species particles, λ_{int} the internal thermal conductivity and λ_{react} the chemical reaction thermal conductivity.

Thermal conductivity of electrons at the third approximation order is given by [10,11].

The translational thermal conductivity due to the heavy species in the second-order approximation can be written as [13]. The internal conductivity due to the effect of internal degrees of freedom is taken into account with the Eucken correction [1, 10,11]. We use the formulation of the chemical reaction thermal conductivity developed by Butler and Brokaw [14].

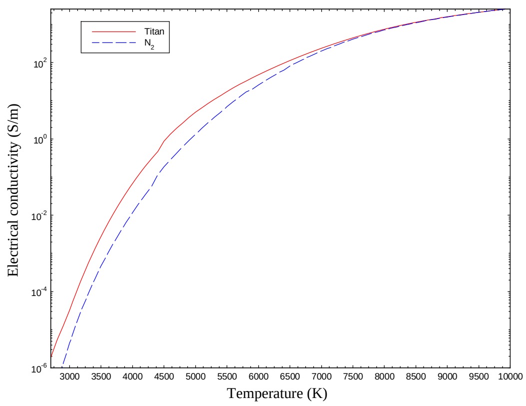

Figure 2. Evolution of the electrical conductivity as a function of temperature.

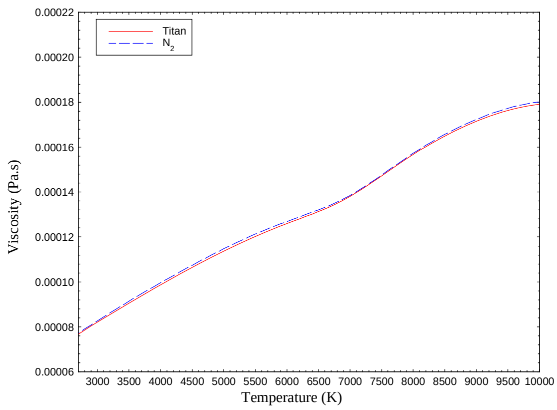

Figure 3. Evolution of the viscosity as a function of temperature.

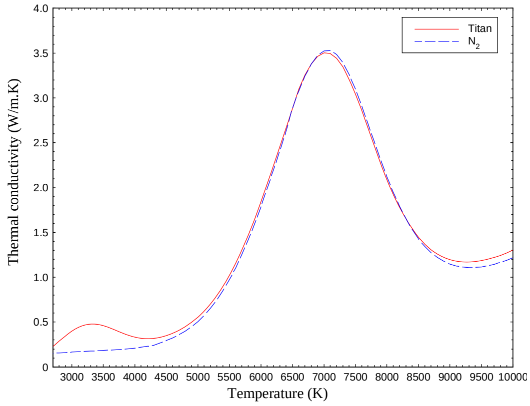

Figure 4. Evolution of the thermal conductivity as a function of temperature.

First explanations can be given by considering the different physical properties of the two plasmas (pure N_2 and Titan compositions).

Fig.2-3-4 report the differences observed for the electrical conductivity, the viscosity and the thermal conductivity of the two plasmas between 2700K and 10000K.

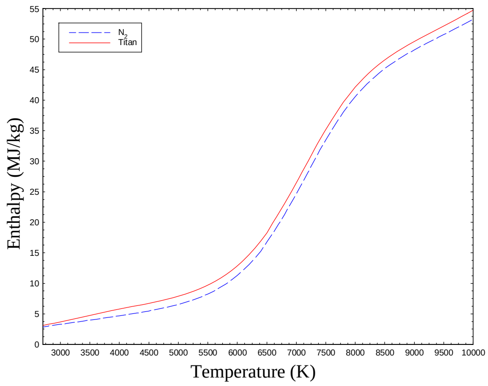

Figure 5. Evolution of the specific enthalpy as a function of temperature.

As the viscosity doesn't seem to be an influent parameter, the two others may explain the difficulty to have a viable plasma when methane is added. Moreover, the Fig.3 shows a light difference of viscosity for the two gases . Concerning the enthalpy (Fig.5), no significant differences appear. So, no real clear conclusion can be today brought on the specific behaviour of the plasma when methane is added. However, it must be noted that there is no more problem when the torch is ignited directly with the gas mixture. For a temperature of 3500K, the Fig.2 shows a factor around 2 on the electrical conductivity. Is this parameter inducing a non stability of the plasma flow or this effect due to a behaviour of the electric supply ?

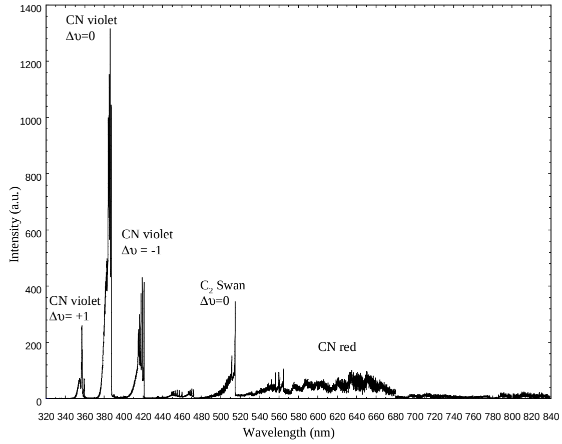

Figure 6. Experimental emission spectra for a Titan atmosphere plasma at atmospheric pressure.

Fig.6 reports a recorded spectrum (without Abel inversion) from the plasma formed with a Titan-like atmosphere in the range [320 – 840] nm. The spectral response of the monochromator has been taken into account but the spectrum is not calibrated in intensity. The CN violet (Δv=0) molecular emission is predominant and the C_2 emission is also present. No atomic line is observed in the spectral domain. Very few papers are available in the literature concerning spectra issued from ICP torch with a mixture of Titan like plasma. One can only mentioned the works done by the Von Karman Institute (VKI) in Brussels, Belgium, with the minitorch working at lower pressure. In order to make a comparison, Fig.7 represents spectra obtained by the VKI [15]. CN violet ((Δv=+1,0,-1), CN red and C_2 (Δv=0) is also observed but with a more important relative contribution of CN violet (Δv=0).

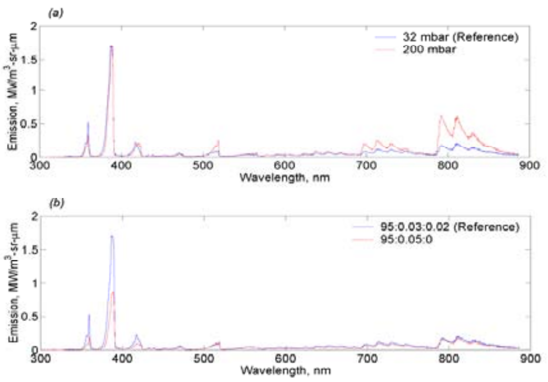

Figure 7. Effect of pressure (a) and mixture composition (b) on the measured spectra: the reference spectra was measured for a pressure equal to 32 mbar and a mixture composition of xN_2:xCH_4:xAr=0.95:0.03:0.02 (mole fraction) [15].

Fig.8 represents the radial evolutions of the intensity of CN and C_2 peaks respectively and Fig. 9 shows the result of the application of Abel inversion. The geometrical method is used in order to apply the Abel inversion.

It can be noted that the application of Abel inversion is easily practicable for the CN system. For the C_2 system, the presence of a plateau of intensity in the axis of the plasma leads to some difficulties in order to apply the Abel inversion.

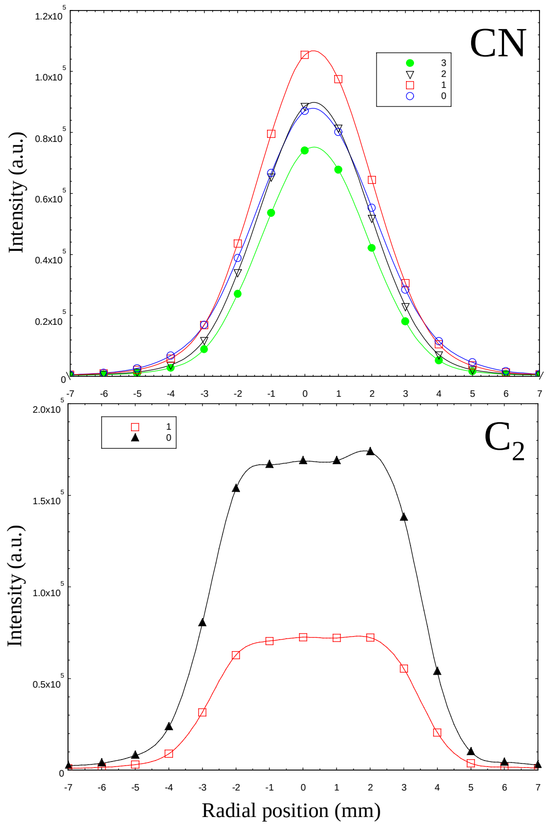

Figure 8. Emission profile measured over the plasma diameter for the first four band heads of the CN violet system (~388 nm) and the first two band heads of the C_2 swan system (~510nm).

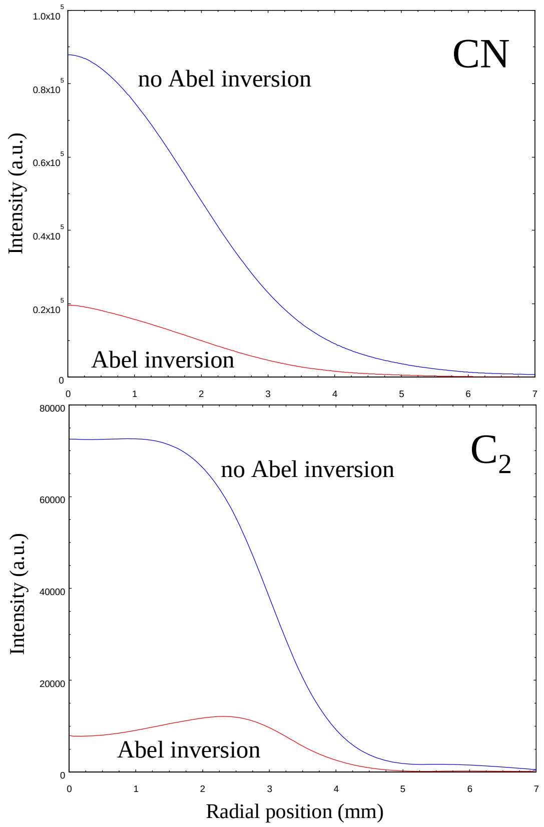

Figure 9. Example of the application of Abel inversion for the band head of the CN violet system (~388 nm) and the C_2 swan system (~510 nm).

In order to estimate the temperature, the spectra of the C_2 Swan system and the CN violet system ($\Delta v=0$) has been considered and the SPARTAN code [18] used.

Fig.10 reports the best agreement obtained by the comparison between the experimental spectrum at the centre of the plasma for the C_2 Swan system and the synthetic one. As it is considered that the plasma is at or close to thermal and chemical equilibrium, two temperatures have been estimated in order to have the best agreement, the rotational temperature (T_r) and the vibrational one (T_v). The obtained values are T_r=3200K and T_v=3700K.

Fig.11 reports the results concerning the CN violet system. When the experimental spectrum is observed, one can conclude that there is a strong absorption of the lines, especially for the first band head (0-0). So, in order to take into account this absorption, the following calculations are made :

- Estimation of T_v and T_r followed by the calculation of emission ε_n and absorption α_n coefficients using the line-by-line code SPARTAN.
- Calculation of the slab emitted intensity (Eq. 2)

$$I = \varepsilon_n / \alpha_n \times \left(1 - \exp(\alpha_n \times l)\right) \qquad (2)$$

- Convolution with a gaussian apparatus function simulating the slit.

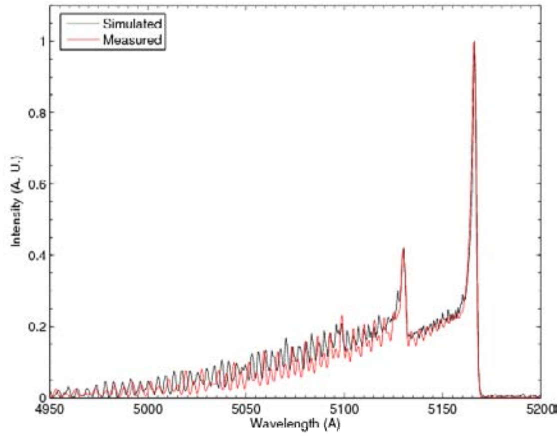

Figure 10. Simulation of the radiative emission of the C_2 Swan system over the ICP torch axis.

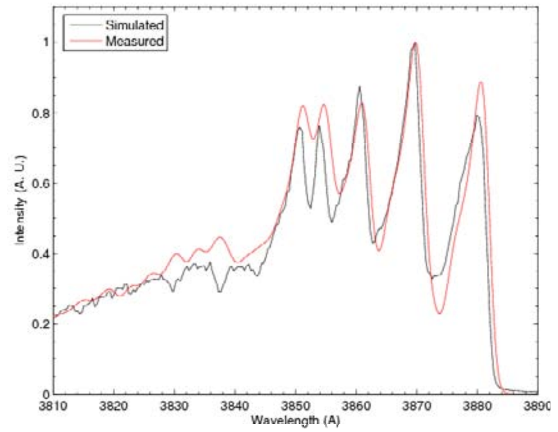

Figure 11. Simulation of the radiative emission of the C_N violet system over the ICP torch axis for the $\Delta\upsilon=0$ transitions (best agreement obtained).

The agreement between simulation and experience is not ideal, as it can be seen in Fig.11. The best agreement gives T_r=3200K and T_v=3700K with a somehow large uncertainty of 500K. However, this first estimation of temperature, based on the molecular spectra, leads to acceptable results and is a good starting point for future investigations. It is worthy to note that owing to the large uncertainty on the temperatures, it is possible that a thermal equilibrium (T_r=T_v) might be reached in the plasma.

As the temperature is altogether relatively low, it is of interest to increase it. Two solutions have been envisaged if it is considered that the applied power is fixed:

- Does a small amount of argon can significantly increase the temperature ?
- Does a lower mass flow of the plasma gas is possible ?

Fig.12 represents the evolution of the calculated specific enthalpy of the plasma when different percentages of argon is added to the initial composition of the Titan plasma. It can be observed that a small proportion of argon does not significantly increase the temperature of the plasma (< 200 K). An extreme example is given for a mixture with 50% of argon and the variation of temperature does not exceed 1000 K. As a conclusion, the addition of argon is not a pertinent parameter to increase the temperature of our plasma.

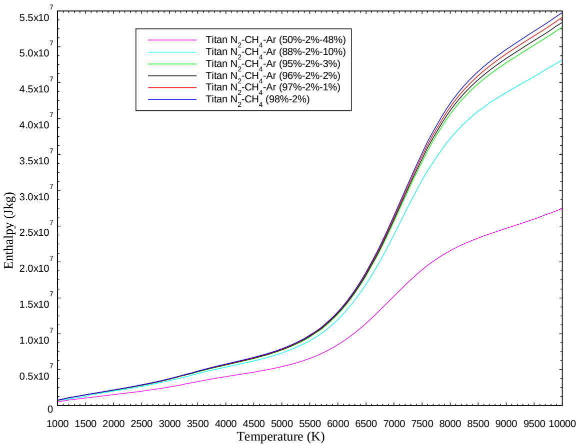

Figure 12. Influence of the addition of argon on the temperature of a Titan plasma if the specific enthalpy is fixed.

The other solution would consist to decrease the total mass flow of the gas plasma keeping the same initial gas composition. In order to have an evaluation of the incidence of this parameter, some assumptions must be made :

- the applied power is constant,
- the transferred energy from the inductor to the plasma is constant,
- the plasma is considered at equilibrium at a temperature of 3700 K.

The following simple energy equation is used :

$$P = \dot{m}\,\Delta H \qquad (3)$$

where P is the transferred power (J.s^{-1}), ΔH is the gain in specific enthalpy (J.kg^{-1}) and $\dot{m}$ the mass flow (kg.s^{-1}).

As P represents the transferred power in the plasma, and which is known is only the applied power, the value of the efficiency of the coupling must be evaluated. So, we can proceed as follows : From the value of the enthalpy (Fig.12) corresponding to 3700K and by considering that the power is completely transferred to the plasma, we obtain the value of a “theoretical” mass flow. Then, if we compare with the experimental mass flow, one obtains a value of efficiency near 55%. As the classical values vary between 40% and 70% of the applied power, our result seems coherent. From this, we can then estimate the influence of the mass flow on the temperature of the plasma (Fig.13). A reduction of the mass flow is of interest in order to increase the temperature of the Titan plasma if the plasma electric supply accepts this condition.

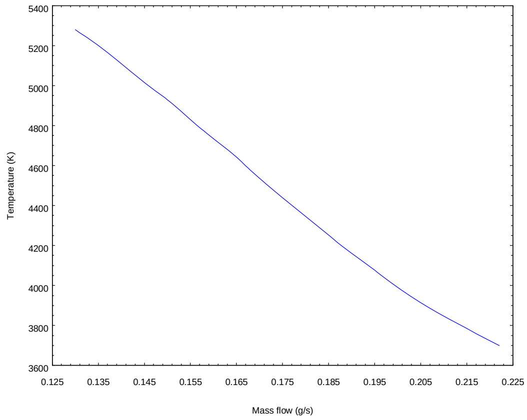

Figure 13. Influence of the mass flow on the temperature of a Titan plasma if the applied power is fixed.

4. DISCUSSION ABOUT THE NUCLEATION PHENOMENON

When the ICP torch works with a Titan like atmosphere, it is observed inside the quartz tube the formation and deposition of “black soot” on the injector (Fig.14) and also on the walls of the quartz tube. It can be noted that the rotation of the deposit follows the movement of vortex of the gas flow.

Figure 14. Photographs of the deposition on the injector protection (left) and on the walls of the quartz tube (right).

In order to determine what kind of particles was formed in the Titan plasma, an analysis of the soot has been realized by the Laboratory of Inorganic Materials (LMI) at Clermont-Ferrand by using Scanning Electron Microscopy (SEM) with field effect (CASIMIR society). Fig.15 and Fig.16 show the appearance of two types of morphologies more or less dense including one composed of spherical nano-particles (Fig.16) at different points of the device.

It must be noted that, in a lot of studies related to the characterization of Titan plasma, it is observed depositions on the wall of the plasma confinement and formation of aerosols. In the first case, a brown deposition can be detected which is attributed to HCN [19]. The second case concerns the formation of dusts which are named “tholins”. These tholins, which are mainly composed with C, H and N species, can appear as a yellow powder or with a very dark color [20,21]. However, our configuration seems to be different than the others with a black color for our deposition. The analysis of the powder must be continued in order to determine the chemical composition of this type of soot.

The studies which have been realized on carbon nano-particles synthesis [22] shows similar images to that of Fig.16. This particular aspect which represents the type of the carbon compounds nano-structured is called “ruffled paper structure”.

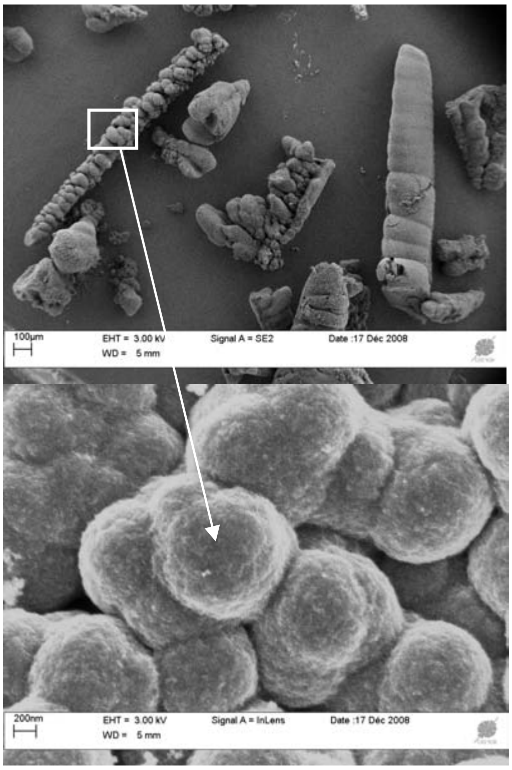

Figure 15. Photographs of one type of morphology observed by SEM with a scale of 200nm.

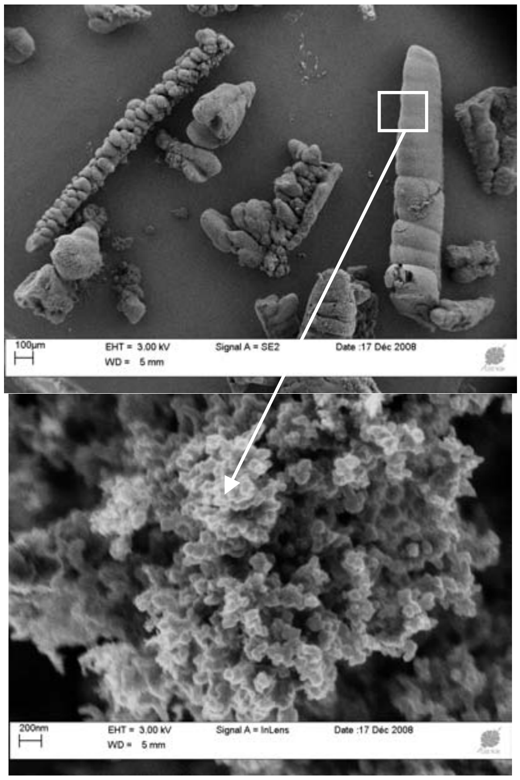

Figure 16. Photographs of the other type of morphology (nano-structured carbons) observed by SEM with a scale of 200nm.

From the calculation of the plasma composition based on the Gibbs free energy minimization, one can give a first explanation about the presence of carbon in the plasma torch (Fig.17).

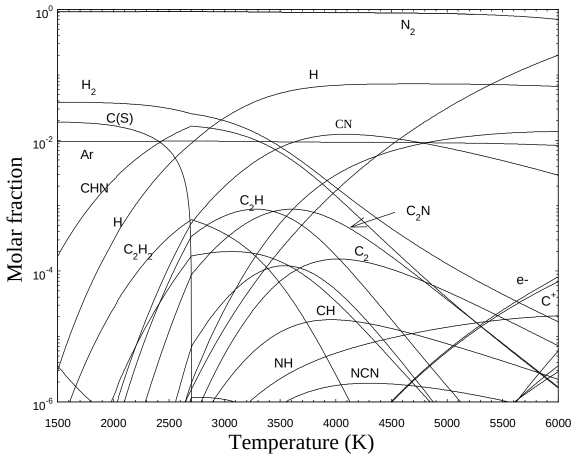

Figure 17. Chemical composition (molar fraction) of a N_2(98%)-CH_4(2%) plasma at equilibrium and atmospheric pressure as a function of temperature.

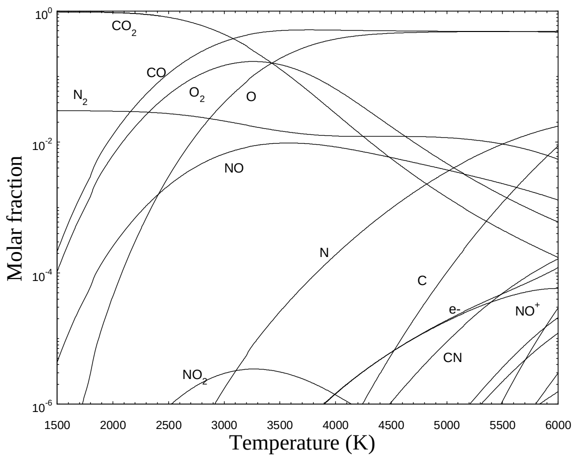

Figure 18. Chemical composition (molar fraction) of a CO_2(97%)-N_2(3%) plasma at equilibrium at atmospheric pressure as a function of temperature.

As it can be observed in the Fig.17, there is the presence of a graphite phase [C(S)] until a temperature of 2700K. So, it confirms the formation of C on the walls of the quartz tube and on the injector which is placed just under the first inductor coil. By comparison with a Mars plasma which has been studied in a previous work [16,17] and where no formation of carbon has occurred, the Fig.18 shows also the fact that there is no formation of carbon species. This absence is mainly due to the presence of O_2.

4. CONCLUSION

The first investigations [23] on the study of a Titan like atmosphere plasma formed with an inductively coupled plasma torch lead to interesting observations and results, especially the formation of carbon species. It was also shown that the addition of methane strongly disturbed the plasma and explanations about this change of behaviour have to be carried out.

Temperature has been estimated but only at the centre of the plasma. Further works have to be done in order to determine the radial evolution of temperature and if a weak departure from thermal equilibrium exists in this kind of plasma. For this, the addition of a very small percentage of argon in the plasma would be interesting as we could have atomic lines to determine the atomic excitation temperature.

A new optical diagnostic has to be added to the experimental set-up in order to determine the electronic density (Mach-Zehnder Interferometer). Moreover, it would be of interest to realize kinetic calculations to confirm that the chemical equilibrium is reached inside the inductor where the optical measurements are recorded.

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