# Pulsed Plasma Spraying of Liquid Feedstock for Coating Elaboration

Rat V., Mavier F., Bienia M., Lejeune M, Coudert J.F.

CNRS, University of Limoges, ENSCI, SPCTS UMR7315, European Ceramic Centre 12 rue Atlantis 87068 Limoges cedex, France, vincent.rat@unilim.fr

Self-sustained nitrogen pulsed plasma is studied by electrical and optical diagnostics. It is used to deposit coatings when the injection of suspensions of nanoparticles is synchronized with the arc voltage.

Keywords: pulsed plasma torch, plasma spraying, diagnostics, model

## **1** INTRODUCTION

Growing needs in energy demand from industrialized and emerging nations compel many researches to improve the efficiency of energy management by focusing on the development of renewable energy sources and by tackling ecological concerns. For example, fuel cells, thermal barrier coatings in gas turbine industry or photo-catalytic coatings require advanced elaboration processes capable manufacture nanostructured to ceramic coatings. These materials must have service properties, like specific finely structured architectures and graded properties (porosity/chemical composition). Such refractory materials are deposited by costeffective plasma spraying techniques possessing the advantage to treat materials with high rates (>kg/h) in high enthalpy medium (>10 MJ/kg). Ceramic nanostructured coatings can now be achieved whether nanopowders are injected or formed into arc plasma jet. Two emerging plasma spraving processes are currently under study, namely Suspension Plasma Spraying (SPS) and Solution Precursor Plasma Spraying (SPPS) [1]. In the former process, nanopowders are dispersed in a liquid with chemical additives avoiding particles agglomeration and are injected into plasma. In SPPS process, fully liquid chemical solutions containing the dissolved elements to deposit are injected in the plasma jet. Owing to plasma treatment, solid materials are in-flight synthesized and simultaneously sprayed onto a prepared substrate. The suspensions and solutions are usually injected either as a liquid jet (about 200 µm diameter) or as atomized droplet spray (5-80 µm droplet diameters).

Depending on heat and momentum transfers, droplets can be fragmented and vaporized, and

nanoparticles are subsequently plasma treated [2]. Controlling electric arc instabilities confined in non-transferred arc plasma torch is therefore a key issue to get reproducible coating properties. All studies are currently devoted to stabilize the arc by means of multielectrodes plasma torches. Alternatively, it is proposed to study self-sustained pulsed arc plasma jet associated with a synchronous injection of droplets containing nanopowders [3-4]. By adjusting the injection timing time-dependent enthalpv relatively to variations, heat and momentum transfers from plasma to materials are expected to be efficiently controlled. The electrical features of such a pulsed arc are presented and the enthalpy modulation is studied by means of optical emission spectroscopy. Temperature are interpreted measurements with а simplified time-dependent model of heat transfers inside the torch. The plasma treatment of droplets is also shown to be dependent on the injection timing. Coatings are also analyzed. At last, conclusion is given.

## 2 EXPERIMENTAL DESCRIPTIONS

## 2.1 EXPERIMENTAL DEVICES

A home-made plasma torch operates at atmospheric pressure in ambient air and is power supplied by a current regulated source. As shown in figure 1, the arc is ignited between the thoriated tungsten cathode tip and a water-cooled copper nozzle. The mean gas flow rate is maintained constant during experiments and is controlled by a mass flowmeter upstream the gas feeding line. The nitrogen gas is delivered to the cathode cavity with flow rates ranging between 2 and 4 standard litres per minute (slm). The internal diameter of the nozzle channel, D, can be changed between 3 and 4 mm. The arc current I, the mean arc voltage  $\overline{V}$ , and the heat losses to the electrodes  $Q_{loss}$  are measured, over a period of a few minutes. These values are used to determine the effective specific enthalpy,  $\overline{h}_L$ , available at the exit of the nozzle, L in length, such as  $\overline{h}_L = (\overline{V} I - Q_{loss})/q_m$  where  $q_m$  is the gas mass flow rate. The specific enthalpy  $\overline{h}_L$  represents a quantity which is averaged in time and also in the cross section of the plasma jet at the torch exit. The heat losses to electrodes are evaluated by means of calorimetric measurements of torch cooling water.



Fig.1: Simplified scheme of dc plasma torch

This set of measurements is also used to check the reproducibility of results. The instantaneous arc voltage, V(t) where t is time, is measured by using a data acquisition computer card piloted by Labview software at a sampling rate of 320 kS/s rate during 0.2 s, giving a maximum frequency of 160 kHz and a frequency resolution of 5 Hz in calculated power spectra.

Figure 2 presents the experimental set-up including the dc plasma torch, a fast-shutter camera, a pulsed laser diode, a spectrometer, a synchronization unit and an injector of droplets. Time-resolved imaging of plasma jet is performed by means of a fast-shutter camera (PCO, Kelheim, Germany) with 1392 x 1040 pixels resolution and which can be externally triggered. The imaging is associated with a 50 W laser diode designed for illumination applications (HiWatch, Oseir, Tampere, Finland) and permit to observe injected materials inside the plasma at the emission wavelength of 801 nm. The pulse duration is 1 µs.

Optical Emission Spectroscopy (OES) is carried out by using the IsoPlane spectrograph (Princeton Instruments, Trenton, USA). The focal length is 320 mm and the focal plane size is 27 mm wide x 14 mm high. The arrangement of optical components reduces optical aberrations. The spectrograph is equipped with a triple grating turret (68 mm x 68 mm grating size). It is associated with an Intensified CCD camera (PIMAX4 1024i, Princeton Instruments, Trenton, USA) with 1024 x 1024 pixels resolution (12.6 µm pixel size) including a fast gate intensifier (down to 3 ns). A UV objective (105 mm focal length, f/4 aperture ratio) is mounted on the spectrograph to image the plasma, providing a -0.3 magnification.



Fig. 2: Experimental setup

Lightfield software (64 bits, Princeton Instruments, Trenton, USA) is used to control spectroscopic devices and record the spectra.

The spectrometer is calibrated thanks to a tungsten ribbon lamp used as a standard source which is power supplied by a current regulated source.

A pyrometer is used to measure the tungsten ribbon temperature at given lamp current. The spectral radiance of the tungsten ribbon lamp is calculated for a given temperature by using the Planck's law and the spectral emissivity of tungsten. The spectrometer response to the tungsten ribbon lamp is known for given set of spectrometer parameters what enables to deduce the spectral radiance of the plasma.

The injection technology is based on drop-ondemand (DOD) method commonly used in the inkjet printing (Ceradrop, Limoges, France). The printing head contains 128 independent nozzles spaced by 0.5 mm and is controlled by LabView software. The liquid is ejected out of small orifices (diameter equal to 50  $\mu$ m) due to the pressure generated by a voltage pulse driven piezoelectric actuator. The drops have a diameter of 50 µm and the velocities in the range of 2 to 10 ms<sup>-1</sup>. The ejection frequency can be adjusted up to 20 kHz. The suspension used in the experiment is composed of titanium dioxide (90% TiO<sub>2</sub> rutile phase) powder and it consists of 42 wt.% of powder and 58 wt.% of water. The particle size distribution is mainly bimodal, i.e. 70 and 350 nm.

## 2.2 ARC VOLTAGE FEATURES

Undesired arc instabilities usually occur in dc arc torches for plasma spraying applications and have been studied for several decades [5]. Recent works are shown that they originate in complex coupling of different fluctuation modes. The well known retrike mode corresponds to random rearcing phenonema which are controlled by physical properties of the cold boundary layer (CBL) between the arc column and the anode wall in the arc channel. Local overheating of CBL leads to a dramatic increase of the electrical conductivity resulting in shunting the existing arc root and creating a new one at a different location [6]. The arc length is abruptly reduced and just after rearcing it increases again due to the plasma flow. This process is more or less randomly repeated with characteristic times of a few tens of  $\mu$ s so that the arc voltage waveform is roughly saw-tooth shaped.

The second important fluctuation mode, called Helmholtz mode, refers to as oscillation imposed by gas compressibility effects inside the cathode cavity. This mode is characterized by a strong oscillation with frequencies ranges between 3 and 5 kHz depending on operating conditions in common plasma torches (~20-50kW) used in plasma spraying. Pure acoustic oscillation modes can also be observed at higher frequencies but weakly affects the arc voltage. Unlike common torches where these modes are decoupled, the presented torch works in operating conditions allowing the coupling of Helmholtz and retrike modes.



Fig.3: Arc voltage signals: a) internal nozzle diameter d = 3.5 mm, I = 25 A, 2.7 slm  $N_2$ ,  $\overline{V} = 129 \text{ V}$ , f = 970 Hz, ; b) Mosquito mode: d = 4 mmI=15 A,  $2 \text{ slm } N_2$ ,  $\overline{V} = 73.7 \text{ V}$ , f = 1410 Hz(Time  $\tau$ , trigger signal)

Figure 3 depicts two arc voltage signals obtained for different operating conditions. In Fig. 3a, rearcing events (restrike) are superimposed to the lower frequency Helmholtz oscillation. In fig.3b where both modes are coupled following appropriate operating conditions, very repeatable sawtooth shape voltage signal is obtained. The arc length oscillates between positions in the nozzle corresponding to voltages changing between  $V_{min} = 40V$  and  $V_{max} = 110V$ .

The calculated power spectrum of the arc voltage displayed in Figure 4 exhibits a strong fundamental frequency of  $f_H=1410$  Hz with high quality factor (Q= $\Delta f/f_H=235$ ) and higher frequency harmonics.



Fig.4: Power spectrum of mosquito mode (Fig3.b)

This frequency can also be evaluated with the Helmholtz frequency, i.e.:

$$f_{\rm H} = K_{\rm H} \cdot \sqrt{\left(\gamma_{\rm g} P / \rho_{\rm p}\right)} \tag{1}$$

where  $\gamma_g$ , P, and  $\rho_p$  are respectively the isentropic coefficient of plasma forming gas, the pressure inside the cathode cavity, the mass density of plasma.

The constant  $K_H$  accounts for the torch geometry, namely the cross section area of the arc channel, the channel length and the volume of the cathode cavity [4].

In the so-called mosquito mode obtained with pure nitrogen (4.510<sup>-5</sup> kg.s<sup>-1</sup> mass flow rate) in Fig.3b, the mean arc voltage is  $\overline{V}$  =73.7 V, the arc current I=15 A and the mean specific enthalpy  $\overline{h}_{I}$  =13.4 MJ.kg<sup>-1</sup>.

The steep falling fronts of the voltage signal represent accurate events which are used to define rectangular pulses (see Figure 3b), delayed by an adjustable amount of time,  $\tau$ , ranging between 0 and 710 µs, which also

corresponds to a voltage threshold (see Fig.3b). Thanks to a synchronization device, these pulses are used to trigger the fast-shutter PCO camera, the laser diode and the ICCD detector, so that the plasma pictures and the spectrum are simultaneously recorded, for a given instantaneous voltage. The exposure time of the camera is  $\tau_{exp} = 30 \ \mu s$ . For the ICCD the exposure time,  $\tau_{gate}$ , is between 15 and 30  $\mu s$  for each received trigger. It is possible to accumulate N<sub>acc</sub> signals at a rate corresponding to the pulsed mode frequency that is 1410 Hz, so that the total exposure time is N<sub>acc</sub>. $\tau_{gate}$ . The number N<sub>acc</sub> is between 10 and 500 depending on operating conditions.

The same trigger voltage with appropriate  $\tau$  delay is used to eject droplets from the piezoelectric head. The laser diode can also be triggered.

# **3 RESULTS AND DISCUSSION**

### 3.1 TIME-RESOLVED OPTICAL EMISSION SPECTROSCOPY OF PLASMA

At nozzle exit, the identification of emitting systems of nitrogen plasma mainly highlights the first negative system of the molecular ion  $N_2^+$ , referenced to as  $N_2^+(1-)$  in the following. The second positive system of N<sub>2</sub> molecule and the violet system of CN molecule dominate downstream the nozzle exit where the plasma is cooled down by mixing with the ambient atmosphere and is recombining. Rotational temperatures are measured at nozzle exit from the simulation of the sequence  $\Delta v = v' - v'' = 0$ , where v is the vibrational quantum number and the single prime corresponds to an upper vibrational level and the double prime to a lower level. Spectra are fitted to experimental ones to deduce the rotational temperatures. Specair software [7] is used to simulate and fit the experimental spectra after the determination of the slit function.

The best-fit spectra allow estimating the measurements precision of  $\pm$  150 K for a measured value of 7500 K. Figure 5 depicts the spectra obtained at 1 mm from the nozzle for different time delays  $\tau$ , corresponding to different arc voltage levels, namely 105, 85,

75 and 62 V.



Fig. 5: Emission spectra at 1 mm from nozzle exit for different values of arc voltage. Rotational temperatures obtained are reported

Rotational temperatures vary between 6280 and 7540 K for arc voltages changing between 62 V and its maximum value around 105 V.

#### 3.2 INTERPRETATION OF MEASURED TEMPERATURES

Temperatures need to be interpreted in terms of specific enthalpy which is the quantity useful to quantify for example the heat transfers between plasma and materials. It can be shown that the heat conduction potential, defined as  $\varphi(T) = \int K(T') dT'$  where K and T are respectively the thermal conductivity and temperature, is related to the specific enthalpy. The use of thermodynamic data permits to establish the link between temperature and enthalpy. Figure 6 shows this dependence (full line). It results that enthalpy changes between 14.35 and 38.20 MJ.kg<sup>-1</sup>, i.e. a modulation ratio of 2.66. However, for a mean value of  $\overline{V}$  =73.7 V, the mean specific enthalpy obtained with calorimetric measurement gives  $h_1 = 13.4 \text{ MJ.kg}^{-1}$ .

Consequently, the interpretation of temperature measurements should consider an enthalpy profile effect to resolve this inconsistency. The molecular spectra results from measurements averaged in a cross section at the nozzle exit (xy plane in Fig.2). The Abel inversion is not performed because it requires several hundreds of inversions for a single spectrum that provokes noise amplification and increases significantly the residual obtained at the end of the fitting procedure. Actually, the measured temperature results from a measurement weighted by the local emission coefficient.

It is supposed that the specific enthalpy follows a parabolic profile, h(r) where r is the coordinate, compatible radial with measurements of  $(h_1, Q_{loss})$ . This assumption is backed by the laminar feature of plasma flow [3-4]. A corresponding temperature profile T(r) is obtained from thermodynamic data of nitrogen plasma. Assuming the local equilibrium, thermodynamic the radial distribution of the emission coefficient  $\varepsilon_{00}(r)$ of (0-0) band of  $N_2^+(1-)$  is calculated.



*Fig.6: Dependence of temperature on enthalpy. Full line: thermodynamic data, dashed line: temperature weighted by emission coefficient* 

According to this procedure, the measured temperature  $T_{\text{spectro}}$  is assimilated to the mean value given by:

$$T_{spetro} = \int_{0}^{R} T(r) \varepsilon_{00}(r) r dr / \int_{0}^{R} \varepsilon_{00}(r) r dr$$
(2)

where R is the radius of the plasma.

In Figure 6 is the reported this temperature weighted by the emission coefficient (dashed line). It can be seen that, for the measured temperatures 6280 and 7540 K, we respectively obtain 10 and 23 MJ.kg<sup>-1</sup>. The enthalpy modulation ratio is close the previous one, but enthalpies are shifted to lower values by considering the profile effect.

#### 3.3 MODEL OF ENTHALPY MODULATION

The interpretation of previous measurements can be carried out by means of a simplified model which establishes the relationship of the amplitudes and phase shift between the arc voltage and the specific enthalpy. It is also important because the material injection inside the plasma is triggered with the arc voltage whereas the local enthalpy is responsible for material treatment.

The available energy obviously depends on heat losses inside the arc channel. Thermal losses ( $Q_{loss}$ ) are due to electrode phenomena and convective/radiative heat transfers between the arc column and the wall. We suppose that the latter is proportional to the nozzle length L and the mean specific enthalpy at nozzle exit:

$$Q_{loss} = V_{elec}I + \alpha_{th}Lh_{L}$$
(3)

where  $V_{elec}$  and  $\alpha_{th}$  are respectively an equivalent arc voltage accounting for electrode phenomena and a heat transfer coefficient.

Calorimetric measurements with L changes permits to estimate  $V_{elec}=17\pm4V$  and  $\alpha_{th}=1.1\pm0.310^{-3}$  kg.m<sup>-1</sup>.s<sup>-1</sup>.

In the following heat losses due to electrode phenomena are supposed constant during voltage fluctuations and to be decoupled from convection and radiative heat transfers. We only consider heat exchanges with the walls in the arc channel and plasma convection.

By using quantities averaged over the channel cross section,  $S = \pi R^2$ , the energy conservation is written as:

$$\rho \frac{\partial h}{\partial t} + \rho u \frac{\partial h}{\partial z} = -p_{th}$$
(3)

z is the axial coordinate, with  $0 \le z \le L$ ,  $\rho$  and u are respectively the mass density and plasma velocity,  $p_{th}$  is the power per unit volume lost by heat transfer to the anode, so that  $p_{th}SL = \alpha_{th}Lh_L$ .

The enthalpy averaged over a cross section is supposed to be  $h_L = \overline{h}_L + h'$  where h' is the fluctuating component of enthalpy. The energy equation permits to obtain a simple first-order differential equation between h' and the fluctuating component of the arc voltage  $v'_{arc}$ :

$$\frac{dh'}{dt} + \frac{h'}{\tau_{th}} = \frac{v'_{arc}}{(q_m + \alpha_{th}L)\tau_{th}}I$$
(4)

where t is time,  $q_m$  the mass flow rate, and  $\tau_{th}$  a characteristic time of heat transfer given by:

$$\frac{1}{\tau_{th}} = \frac{q_m + \alpha_{th}L}{m_p}$$
(5)

where  $m_p$  is the plasma mass contained in the anode nozzle evaluated from the plasma mass density.

In the present operating conditions,  $\tau_{th}$  is about 130 $\mu$ s.

By using equation 5, the following transfer equation can be written:

$$\frac{\mathrm{H}(\omega)}{\mathrm{V}(\omega)} = \left(\frac{\mathrm{I}}{\mathrm{q}_{\mathrm{m}} + \alpha_{\mathrm{th}}\mathrm{L}}\right) \frac{1}{\mathrm{I} + \mathrm{j}\omega\tau_{\mathrm{th}}} \tag{6}$$

where  $H(\omega)$  and  $V(\omega)$  are the Fourier component of h'(t) and v'(t) respectively.

The periodic arc voltage of fig.3 b,  $T_o$  in period and  $\overline{A}$  in amplitude, is expanded in a Fourier series that is used, thanks to eq. 6 to define the time dependent enthalpy function, following:

$$h_{L}(t) = \overline{h_{L}} + \sum_{n=1}^{\infty} H_{n} \sin(\omega_{n}(t - \theta_{n})) (7)$$
  
with  $H_{n} = \frac{(-1)^{n+1}}{n\pi(q_{m} + \alpha_{th}L)} \frac{\overline{AI}}{\sqrt{1 + (\omega_{n}\tau_{th})^{2}}}$   
and  $\theta_{n} = \frac{T_{0}}{2\pi n} \arctan(\omega_{n}\tau_{th})$ 

where  $T_0=1/f_H=710 \ \mu s$  is the period of periodic arc voltage signal and  $\overline{A} = V_{max} - V_{min} = 70V$  the amplitude of arc voltage.

Figure 7 displays the simulated arc voltage and the calculated specific enthalpy (equation 7). An equivalent "thermal" voltage is defined as  $V_{th}=Q_{loss}/I$ , i.e.:

$$V_{th}(t) = V_{elec} + \alpha_{th} Lh_L(t)/I$$
 (8)



*Fig.7: Fluctuations of arc voltage, enthalpy and thermal voltage calculated from the model* 

We can note that the modulation ratio is about 2 with  $h_{max}=20$  and  $h_{min}=10$  MJ.kg<sup>-1</sup>. These values are close to those obtained by OES measurements when considering the profile effect. The enthalpy maxima are almost synchronous with the voltage maxima, the minimum values are delayed by about one third of period. The particular voltage of 62 V is almost synchronous with the minimum of enthalpy (therefore with the minimum of temperature). It seems that the minimum temperature remains above 6000 K even though the trigger voltage is not the minimum. Consideration of characteristic times of heat transfer  $(m_p/\alpha_h L)$  and of residence time  $(m_{n}/q_{m})$  has a low-pass filter effect on

enthalpy smoothing fast variations.

The decreasing branches of enthalpy corresponds to a plasma generated during the preceding period whereas the growing branches of enthalpy follow the arc voltage with a delay decreasing with time up to the maximum.

The mean value of thermal voltage is 36 V and fluctuates between 30 and 40 V.

### 3.4 INJECTION OF SUSPENSIONS IN PULSED ARC JET

The previous section shows that enthalpy is modulated with a ratio of approximately 2 at nozzle exit. This is confirmed when observing the arc jet for two different delays as shown in Figure 8.

In figure 8a where imaging is triggered at high voltage, the arc column is fully developed. In figure 8b, imaging is triggered at low voltage (around 55 V) which should be very close to the minimum of enthalpy as shown in Figure 7. At nozzle exit, in this case, a minimum of radiative emission can indeed be noted.



Fig.8: Time-resolved imaging of pulsed jet. a) imaging triggered at high voltage, b) imaging triggered at lower voltage

The interest to use such a pulsed plasma jet is twofold. First, if a pulsed injection of materials is associated with the plasma, it is expected to obtain reproducible heat and momentum transfers between materials and plasma and therefore to reach repeatable coating properties. Second, the modulation of enthalpy at nozzle exit is expected to influence the trajectories of materials in plasma plume and hence modulate heat transfers. This can be an additional experimental parameter, nonexisting in conventional plasma spraying of liquid feedstock, to treat materials more or less sensitive to heat transfers.

In the following, suspensions of  $TiO_2$  nanopowders are synchronously injected with the arc voltage by using the piezo-electric injection head as explained above.

The suspension flow rate injected is  $5.10^{-3}$  mL.min<sup>-1</sup> and the mass flow rate is  $2.810^{-3}$  g.min<sup>-1</sup>.

Figure 9 displays a picture of the plasma with synchronized injection of  $TiO_2$  suspensions (aperture time 125 µs). At about 30 mm, a substrate can intercept the plasma either to collect particles or to deposit a coating.



Fig. 9: Picture of pulsed arc jet with synchronous injection of  $TiO_2$  suspensions (exposure time 125  $\mu$ s)

At nozzle exit, the nitrogen plasma alone is observed with pink emissions of nitrogen. Suspensions droplets are perpendicularly injected with respect to the nozzle axis at about 4 mm from the nozzle exit. Upon the penetration of 50 µm droplets into plasma, they can undergo liquid fragmentation and vaporization. The breakup of a droplet is governed by the dynamic pressure applied by the plasma flow on droplet, surface tension effects and viscous forces. In conventional suspension plasma spraving in higher power plasma torches, the characteristic time of fragmentation is by far much higher than that of vaporization (~us and 0.1 ms respectively) [2]. In the present alternative process, the primary liquid fragmentation is absent because of low plasma velocity ( $\sim$ 50-100 m.s<sup>-1</sup>). This can be shown when evaluating the Weber number which compares the aerodynamic forces to the surface tension forces, i.e. We =  $\rho_{\rm p} v_{\rm r}^2 d_{\ell} / \sigma_{\ell}$  where  $\rho_{\rm p}, v_{\rm r}, d_{\ell}$ , and  $\sigma_{\ell}$  are respectively the plasma mass density (depending on enthalpy), the relative velocity between the plasma and the droplet, the diameter of droplet and surface tension of droplet. The Weber number is always weak, below 0.5. However, it has been observed a "thermal fragmentation" as shown in Figure 10. It depicts the injection of droplets, first, through a slit behind which the piezo-electric head is mounted, and second the interaction with plasma. The latter is not shown because the pulsed laser diode is used with an interferential filter centered at 801 nm. It can be seen that a droplet is isotropically fragmented, even in the reverse direction of plasma flow, what could not be possible in the case of pure momentum transfer.



Fig.10: Fragmentation of suspension droplet due to the plasma (exposure time 270  $\mu$ s)

The highly luminous region at the right hand side of the on-going droplet fragmentation corresponds to the plasma treatment of the previous droplet.

An estimation of the vaporization time can be given by using the property of linearity between the heat conduction potential and plasma enthalpy:  $\varphi(T) = a_{\varphi} h(T)$ . It follows:

$$\tau_{\rm vap} = \frac{\rho_{\ell} L_{\rm v}}{4N_{\rm u} a_{\phi}} \left[ 1 - \left( 1 + \frac{1 - x_{\rm m}}{x_{\rm m}} \frac{\rho_{\rm s}}{\rho_{\ell}} \right)^{-2/3} \right] \frac{d_{\ell}^2}{h_{\rm p}} \quad (9)$$

where  $\rho_{\ell}$ ,  $\rho_s$ ,  $L_v$ ,  $x_m$ , and  $h_p$  are respectively the mass density of liquid (water) and of solid phase, the latent heat of vaporization of water, the mass fraction powder in water, and plasma enthalpy. The constant  $N_u$  and  $a_{\phi}$  are respectively the Nusselt number and a proportionality constant between enthalpy and heat potential.

Equation (9) highlights its dependence on the plasma enthalpy; the order of magnitude of the vaporization time is about 100  $\mu$ s.

After vaporization of water, nanopowder are heated by the plasma what produces intense radiative emission of lines of titanium atoms (Ti I) and titanium ions (Ti<sup>+</sup>I). These metallic vapors appear in near UV domain (300-400 nm) and visible domain as seen in figure 9 (blue color).



spectral *Fig.11*: Synchronized image of droplet/plasma interaction at 12 mm from nozzle exit. Height is the y direction given by Fig.2.(y=0corresponds to the torch axis)

At higher distances, red/orange emissions are seen in Figure 9 which corresponds to red and orange-red systems of the TiO molecule [8]. The image is synchronized at high voltage (105 V) at 12 mm from the nozzle exit. For lower voltage (55 V), it is observed that molecular emissions of TiO occur farther downstream, i.e. at 20 mm, mainly in the plasma jet fringes of the (y=2mm). Consequently, it can be supposed that, first, the molecule formation starts in the fringes of the plasma plume with the atomic oxygen of air (Ti+ $O \rightarrow TiO$ ). Second, the modulation of enthalpy affects the heat treatment of nanopowders what delays the formation of TiO molecule.

#### **COATING DEPOSITION** 3.5

First attempts to deposit TiO<sub>2</sub> coatings are made onto stainless steel substrates bv performing synchronous injection with arc voltage. The surface of coatings obtained with and without synchronization is analyzed by scanning electron microscopy (SEM).

If no synchronization is performed, a very non-homogeneous coating is obtained with larges porosities, coarse melted zones which the characteristic size is much larger than the initial nanoparticle sizes (70-350 nm), but also very fine structures. With synchronization, a much more homogeneous surface coating is observed which has typical features of vapor condensation. This is consistent with spectroscopy studies where metallic and TiO vapors are seen. It is then supposed that the coating results from the association of condensed vapors and large melted zones which the proportion should depend on synchronization.





Fig. 12: SEM images of  $TiO_2$  coating surfaces for a) without synchronization, b) with synchronization

#### 4 **CONCLUSION**

Plasma spraying of liquid feedstock allows depositing finely structured ceramic coatings for many applications, such as for instance photo-catalytic coatings, fuel cells, thermal barrier coatings. The liquid phase is used as a carrier medium either to inject nanosized particles in the plasma core or to directly synthesize them in plasma. Reproducible plasma treatment is therefore of great importance to achieve desired coatings properties. That is why controlling arc instabilities must be performed. In this paper, we have proposed to generate a pulsed arc jet associated with a synchronous injection of droplets. Adjusting the timing injection should permit to reproduce and control the heat and momentum transfers, and coating properties.

A self-sustained pulsed nitrogen plasma jet is obtained by coupling two modes of arc instabilities. By means of time-resolved emission spectroscopy, the specific enthalpy at nozzle exit was shown to oscillate between 10 and 20 MJ.kg<sup>-1</sup>.

A time-dependent simplified model of heat transfers inside the torch has confirmed this modulation and has highlighted a phase shift between voltage and enthalpy fluctuations due to the characteristic time of heat transfer and of residence time of plasma inside the nozzle. This should be considered when triggering the injection of droplets for synchronization.

During the interaction between droplets containing nanosized particles of TiO<sub>2</sub>, metallic vapours are observed and TiO vapours as well. The comparison of SEM surfaces of coatings have shown more homogeneous microstructure when the synchronisation of injection is performed.

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### REFERENCES

[1] Killinger A, Gadow R, Mauer G, Guignard A, Vaßen R, Stöver D, J. Thermal Spray Technol. 20 (2011) 677-695.

[2] Fazilleau J, Delbos C, Rat V, Coudert J F, Fauchais P, Pateyron B, Plasma Chem. Plasma Process. 26 (2006) 371-391.

[3] Krowka J, Rat V, Coudert J F, J. Phys. D: Appl. Phys. 46 (2013) 224018.

[4] Krowka J, Rat V, Coudert J F, J. Phys. D: Appl. Phys. 46 (2013) 505206.

[5] Wutzke SA, Pfender E, Eckert ERG, AIAA. J. 5 (1967) 707-714.

[6] Nemchinsky V, IEEE Trans. Plasma Sci. 42 (2014) 4026-4030.

[7] Laux C O, Radiation and nonequilibrium collisional-radiatvie models (von Karman Institute Special Course on Physico-chemical Modeling of High Enthalpy and Plasma Flows, Rhode-Saint-Genèse, Belgium 4-7 June 2002).

[8] Pearse R W B, Gaydon A G, The identification of molecular spectra, John Wiley & Sons Inc., New York 1976.