Pulsed arc plasma jet synchronized with drop-on-demand dispenser

F Mavier\(^1\), L Lemesre, V Rat, M Bienia, M Lejeune and J-F Coudert

\(^1\) Univ. Limoges, CNRS, ENSCI, SPCTS, UMR 7315, F-87000 Limoges, France.

fabrice.mavier@etu.unilim.fr

Abstract. This work concerns with the liquid injection in arc plasma spraying for the development of finely structured ceramics coatings. Nanostructured coatings can be now achieved with nanopowders dispersed in a liquid (SPS: Suspension Plasma Spraying) or with a salt dissolved into a liquid (SPPS: Solution Precursor Plasma Spraying) injected into the plasma jet. Controlling electric arc instabilities confined in non-transferred arc plasma torch is therefore a key issue to get reproducible coating properties. Adjustment of parameters with a mono-cathode arc plasma allows a new resonance mode called “Mosquito”. A pulsed arc plasma producing a periodic regular voltage signal with modulation of enthalpy is obtained. The basic idea is to synchronize the injection system with the arc to introduce the liquid material in each plasma oscillation in the same conditions, in order to control the plasma treatment of the material in-fly. A custom-developed pulsed arc plasma torch is used with a drop-on-demand dispenser triggered by the arc voltage. A delay is added to adjust the droplets emission time and their penetration into the plasma gusts. Indeed, the treatment of droplets is also shown to be dependent on this injection delay. A TiO\(_2\) suspension and an aqueous solution of aluminium nitrate were optimized to get ejectable inks forming individual droplets. The feasibility of the process was demonstrated for SPS and SPPS techniques. Coatings from the suspension and the solution were achieved. First synchronized sprayings show a good penetration of the droplets into the plasma. Coatings show a fine structure of cauliflowers shapes. The synchronization of the ejection allows a control of morphology and a better deposition efficiency. Further investigations will find the optimal operating parameters to show the full potential of this original liquid injection technique.

1. Introduction

In the field of thermal spray coating processes, research has led to the development of nanostructured coatings by suspension plasma spraying (SPS) and precursor solution plasma spraying (SPPS). Liquid injections are promising techniques with the potential to become industrially viable [1,2]. However, a better control of plasma/material interactions is necessary. Mono-electrode DC plasma torches indeed generate strongly fluctuating plasma that modifies the thermal and dynamic transfers to the injected suspension droplets, resulting in an inhomogeneous treatment of the latter. This directly influences the texture and microstructure of deposits and subsequently their properties [3,4].

Efforts to understand the origins of these instabilities have been made. Previous works have shown that these instabilities are mainly due to the effects of compressibility of the plasma gas in the cathode cavity effects, belonging to the instability mode called Helmholtz mode. Other fluctuations are due to successive phenomena of elongation, breakdown and restrike of the electric arc, also called "restrike mode". In alternative to instabilities attenuations, a new approach is proposed: the reinforcement and
modulation of the instabilities [5]. The adjustment of process parameters has allowed obtaining a pulsed laminar plasma with a modulation of its properties. A low powered DC torch is used and operates with pure nitrogen as plasma forming gas. This device is synchronized with a drop-on-demand injection system to reproduce the same conditions of plasma/material interactions for each injected droplet [6]. Aluminum nitrate aqueous solutions and TiO$_2$ suspensions are injected to make homogeneous coatings with a controlled microstructure and chemical composition. The objectives of this work are (i) to characterize and understand plasma / droplet heat and dynamics transfers and (ii) to highlight the influence of the synchronization on the coatings obtained.

2. Experimental setup

2.1. The pulsed arc plasma

The spray depositions in this study are carried out using an experimental DC torch, custom-developed at the University of Limoges, working in the “Mosquito” pulsed mode. In figure 1 we can see a pulsed arc plasma and a modulated arc voltage signal. CCD camera shows individual plasma gusts emitted at the same frequency as arc voltage oscillations. The plasma gas is nitrogen. The current is 15 A and arc voltage oscillates between 40 and 100 V at ~1400 Hz. The average specific enthalpy obtained by performing a calorimetric measurement on the water cooling system of the torch is 13 MJ.kg$^{-1}$. The operating torch parameters are shown in table 1.

![Figure 1](https://example.com/figure1.png)

**Figure 1.** Imaging of a plasma jet in the “Mosquito” pulsed mode, camera aperture time: 60μs (a), arc voltage signal in the pulsed mode (b).

| Table 1. Plasma spraying operating parameters. |
|-----------------------------------------------|
| Parameter           | Value       |
|---------------------|-------------|
| Current             | 15 A        |
| Average enthalpy    | 13 MJ.kg$^{-1}$ |
| Anode nozzle diameter | 4 mm       |
| Plasma gas          | Nitrogen    |
| Flow rate           | 2slm        |
2.2. The drop-on-demand (DOD) dispenser

A drop-on-demand dispenser is used to inject the liquid material (a suspension or a solution). The dispenser nozzle where the droplets are emitted is fixed on the top (around 10 mm) of the plasma torch nozzle exit (figure 2). The diameter of the droplets is 80 μm. The DOD dispenser is a glass capillary. The ejection is actuated by a piezoelectric crystal to generate an individual droplet for each pulse trigger. For this study, aluminum nitrate aqueous solutions and TiO$_2$ suspensions were used. The suspension is a 15 vol% commercial aqueous suspension of rutile with submicronic particles with a bimodal distribution of 70 and 350 nm (Ceradrop, France). The aluminum nitrate solution is custom-made according to a method which is described in the results section.

![Image of DOD dispenser](image)

**Figure 2.** Picture of optimized ink ejection test at 1400 Hz without plasma, standard camera no synchronized, aperture time: 125μs.

2.3. Synchronization setup

The torch voltage is sampled by means of a dividing bridge and sent to an electronic synchronization device able to generate a set of delayed TTL pulses that trigger the drop-on-demand dispenser and the instruments that are used for the in-flight diagnosis (figure 3).

In-flight interactions are recorded by a CCD camera, coupled with a 50 W laser diode to illuminate the droplets at the emission wavelength of 801 nm. Optical emission spectroscopy (OES) is performed by using an Isoplane spectrograph (Princeton Instruments, Trenton, USA) associated with a high resolution Intensified CCD camera (PIMAX4 1024i, (1024 x 1024 pixels, 12.6 μm pixel size, Princeton Instruments, Trenton, USA). The camera, laser and OES are triggered by the synchronization system. A standard camera (Nikon D7100), not synchronized, is used for imaging.
Figure 3. Schematic view of the synchronous injection system “Mosquitorch”.

The spraying distance is fixed to 33 mm from the torch nozzle exit. This distance has given the best results in previous tests. Substrates are 25×25×1 mm mirror-polished stainless steel squares. The effective deposition time is fixed to 1 min to limit excessive thermal expansion stresses.

2.4. Coatings characterization
Coating morphologies and elemental composition are characterized on a scanning electron microscope (SEM, XL30, Philips, The Netherlands) coupled with an electron dispersion spectrometer (EDS). Imaging and diffraction pattern with transmission electron microscopy (TEM, JEOL2010, UK) are also used to characterize crystallinity and crystallite sizes. The structural characteristics of the coatings are determined using X-ray diffraction (XRD) with Cu Kα radiation (Siemens D 5000, Germany). The resulting diffractograms are indexed with JCPDS-ICDD database.

3. Results and discussion
3.1. Ink optimization and ejection tests
The propagation velocity of the acoustic wave within the glass capillary of the DOD microdispenser is estimated with this equation [7]:

\[ a = \frac{c}{\sqrt{1 + \frac{KdC_1}{Eh}}} \tag{1} \]

where \( c \) is the speed of sound in the fluid \( (\text{m.s}^{-1}) \); \( K=\varepsilon^2\rho \) \( (\text{GPa}) \); \( C_1 \) a correction factor; \( d \) the tube diameter \( (\mu\text{m}) \); \( h \) the thickness of the wall \( (\mu\text{m}) \); \( E \) glass Poisson’s ratio.

This velocity is used to estimate an order of magnitude of the time taken by the wave between the excitation of the piezoelectric component and the ejection of a droplet to the orifice. This time is estimated at 18 µs, less than a Mosquito period of 700 µs. Therefore, the operating frequency of the
Mosquito is compatible with the DOD dispenser as the generation of two consecutive droplets does not cause disturbance.

The solution is prepared from aluminum nitrate salt 27 wt% (Al(NO₃)₃·9H₂O, 98%, Alfa Aesar, Germany) dissolved into deionized water. The suspension and the solution are optimized to fit the viscosity and surface tension requirements of the DOD dispenser given by the manufacturer. In addition, the ejection ratio Z, which involves Reynolds (Re) and Weber (We) numbers, must be in a range of 1 – 10 (equation 4) [8].

\[
Re = \frac{\rho vr}{\eta} \quad (2) \quad We = \frac{\rho v^2 r}{\gamma} \quad (3)
\]

\[
Z = \frac{Re}{\sqrt{We}} = \sqrt{\frac{\rho \gamma r}{\eta}} \quad (4)
\]

where \( \rho \) is the droplet density (kg.m\(^{-3}\)); \( \gamma \) the surface tension (N.m\(^{-1}\)); \( r \) the radius of the droplet (µm); \( \eta \) the viscosity (Pa.s).

Surface tension of fluids is controlled by a tensiometer (DCAT11, DataPhysics Instruments, Germany) and viscosity by a rheometer (ARG2, TA Instruments, USA). The commercial suspension has already been optimized for \( Z=3.3 \) and was used as purchased. In the case of the solution, glycerol (99+%, Alfa Aesar, Germany) is added to increase the viscosity of the initial solution (1.7 to 5.1 mPa.s) and a surfactant is added to decrease the surface tension (76.5 to 41.6 mN.m\(^{-1}\)) which leads to a ratio of ejection \( Z=8.8 \).

After these adjustments, the actuation pulse waveform sent to the piezoelectric printhead is optimized in order to get a stable ejection. An ejection is considered stable if a single spherical droplet is obtained without filaments or satellite droplets and whose velocity and trajectory are the same for all ejected droplets. In addition, preliminary studies showed that the droplets velocity must be higher than 2 m.s\(^{-1}\) to obtain a good penetration of the droplets inside the plasma gusts emitted by the pulsed arc torch as shown in figure 1. For this study, the pulse is optimized to eject droplets at 2.5 m.s\(^{-1}\). A cooling system with a copper holder and a cold water flow is used to prevent a temperature elevation of the DOD dispenser. Indeed, the temperature fluctuation strongly impacts viscosity which is the predominant term in the ejection ratio.

3.2. \( \text{TiO}_2 \) by SPS: In-flight diagnosis

Compared to conventional injection, e.g. mechanical injection, which delivers a continuous stream, drop-on-demand (DOD) systems allow isolating the droplets injection with the same experimental behavior thanks to the synchronized emission and acquisition. A regular jet of individual droplets is emitted from the DOD dispenser above the plasma jet, at the same frequency as the plasma gusts. In the first moments after the ejection, the droplet meets a gust of plasma resulting from the resonance mode. The temperature was measured between 6500 and 8000 K depending on the injection delay [9]. When a droplet arrives on the torch axis, it is fragmented in all directions, even at counter flow (figure 4). We suggest that this step is a thermal fragmentation because of low plasma velocity (~66 m.s\(^{-1}\)) and a Weber number below 0.5 (0.04-0.48). Indeed, mechanical fragmentation occurs when \( We > 12-14 \). Acceleration time of a droplet in the plasma is estimated at 800 µs while vaporization time is estimated at 200 µs, which implies that vaporization takes place more rapidly than acceleration.
Figure 4. Synchronous injection of TiO$_2$ suspension in the pulsed plasma. Time-resolved imaging synchronized with droplet emission driven at the torch voltage frequency (laser shot: 20μs).

After fragmentation and vaporization, the droplet vapor seeds the plasma gust. Visually (figure 5) near the injection point blue light emission from plasma caused by the injected material is observed, which was attributed to titanium vapor by emission spectroscopy analysis. Titanium vapor is observed because heat transfer is efficient with nitrogen as plasma forming gas and the first excited states of titanium atoms are relatively low (<4eV). At larger distance, plasma gusts become orange corresponding to titanium oxide emission (TiO). Indeed, titanium oxide molecular bands are observed at 12mm from the nozzle exit of the plasma jet that could suggest that TiO forms with the in-flight oxidation of titanium atoms (figure 5).

Figure 5. (a) Picture recorded with a standard camera; aperture time: 125 μs, no triggering. (b) Spectral mapping of light sampled at 12 mm from the torch exit following the line of sight.

3.3. TiO$_2$ by SPS: Coatings characterization
Two sets of TiO$_2$ coatings are investigated: coatings with and without synchronization injection. Coatings obtained without synchronized injection means that each injected droplet undergoes a different treatment and the injection is not mastered. They show a large panel of particles: submicronic fine structures of cauliflowers shapes, splats, molten particles and spherical particles from 10
micrometers (figure 6). XRD indexation shows only rutile phase (JCPDS No. 04-016-2838) for coatings with synchronized and non-synchronized injection.

![Image](image1.png)

**Figure 6.** Synchronous injection of TiO₂ suspension in the pulsed plasma. Time-resolved imaging synchronized with droplet emission driven at the torch voltage frequency (laser shot: 20μs).

Coatings with a synchronized injection show a much better homogeneity, a large majority of the surface is composed with cauliflowers shapes (figure 7) suggesting the synchronization allows a control of the treatment and ultimately the morphology of the coating.

![Image](image2.png)

**Figure 7.** SEM picture × 750 top surface coating of TiO₂ with non-synchronized injection (left) and synchronized injection (right).

The thickness of the deposits is 10 microns. Cross-sections show a very porous columnar base (figure 8). High magnification shows grains from few tens of nm and a finer porosity in each cauliflower structure. TEM diffraction patterns confirm the presence of rutile, no amorphous phases are visible. Two crystallite sizes are observed: large grains of tens of nanometers [30-80 nm] and small grains <10 nm (figure 9). This high specific surface could be interesting for photocatalytic applications.
3.4. AlN by SPPS: Coatings characterization

Solution sprayings permits to obtain a fine structure similar to previous results by SPS. XRD confirms the presence of cubic aluminum nitride only (JCPDS No. 04-004-8344). The formation of nitride could be due to the use of nitrogen as plasma gas and the nitrate as precursor. First coatings obtain without synchronization show a structure less heterogeneous in comparison to the previous study by SPS. Some micrometrics splats and voids are observed (figure 10). Coatings with synchronized injection show a better homogeneity with no splats and no voids, the fine structure of cauliflowers shapes is the majority of the coating (figure 11). In addition, coatings with synchronized injection show a significant reduction in deposited material losses in the periphery of the substrate due to poor penetration into the plasma jet. The coatings have larger thickness: 9 microns for synchronized injection against about 5 microns to non-synchronized, with a much more even thickness distribution. The synchronizing effect on the morphology of the deposit is less impressive than for SPS tests, but it allows much more morphology control and a greater deposition efficiency.
A larger magnification on coatings with synchronized injection shows a fine structure of cauliflowers shapes from ~1 µm similar to TiO$_2$ by SPS, probably due to an aluminum vapor condensation on substrate and spherical structures of a few micrometers, perhaps originating from a nucleation in-flight process (figure 12). Candidato and al. show similar cauliflowers shapes by SPPS method, only with high concentration of dissolved precursors. They proposed that these microstructures are formed in-flight by a nucleation phenomenon [10]. Our future investigations will identify the formation process of these structures and optimize the operating parameters, e.g. spraying distance, to see if other morphologies and crystalline structures are possible via the synchronous injection process.
4. Conclusion
A process combining atmospheric plasma spraying and inkjet drop-on-demand injection was developed. A pulsed arc plasma is generated with an arc plasma torch custom-developed at the University of Limoges. The principle is to inject each droplet in each plasma oscillation to control the dynamic and the enthalpy transfer to the material in order to increase the quality of the coatings. Inks have been optimized for injecting individual droplets at the same frequency as the plasma on the axis of the torch. In-flight diagnosis shows a good penetration of droplets in each plasma gust. The droplet travels to the torch axis and seeded the plasma gust creating a vapor by thermal fragmentation. First coatings with synchronized injection were made with an aqueous nano-suspension of TiO$_2$ and an aqueous aluminum nitrate solution. The results show a fine structure of cauliflowers shapes of a few micrometers in width and grains sizes of a few nanometers. Synchronization increases the homogeneity and the deposition efficiency of the coatings. Futures studies should be investigating the photocatalytic activity of our coatings. The use of an anatase suspension and adjusting operating parameters to maintain the crystalline species should be considered. Investigations will be identifying the optimizing parameters to show the full potential of this original process.

References
[1] Fauchais P, Vardelle M, Goutier S and Vardelle A 2015 Key Challenges and Opportunities in Suspension and Solution Plasma Spraying Chem. Plasma Process 35 511–525
[2] Sampath S 2010 Thermal Spray Applications in Electronics and Sensors: Past, Present, and Future Journal of Thermal Spray Technology 19 921–949
[3] Etchart-Salas R 2007 Suspension Plasma Spraying. Analytical and experimental approach of the phenomena imply in the reproductibility and the quality of the deposits Thesis (University of Limoges)
[4] Etchart-Salas R, Rat V, Coudert J F, Fauchais P, Caron N, Wittman K and Alexandre S 2007 Influence of plasma instabilities in ceramic suspension plasma spraying J. Thermal Spray Technol. 16 857–865
[5] Rat V and Coudert J F 2010 Pressure and Arc Voltage Coupling in Dc Plasma Torches: Identification and Extraction of Oscillation Modes Journal of Applied Physics 108 (4)
[6] Krowka J, Rat V and Coudert J F 2013 Resonant Mode for a Dc Plasma Spray Torch by Means of Pressure–voltage Coupling: Application to Synchronized Liquid Injection Journal of Physics D: Applied Physics 46 (22)
[7] Fromm J 1984 IBM J. Res. Dev. 28 322–333
[8] Ainsley C, Reis N and Derby B 2002 Freeform fabrication by controlled droplet deposition of...
powder filled mels Journal of materials science 37 3155–3161

[9] Rat V, Krowka J and Coudert J F 2015 Modulation of the specific enthalpy of a pulsed arc plasma jet Plasma Sources Sci. Technol. 24 045009

[10] Candidato Jr. R T, Sokołowski P, Nana G L, Constantinescu C, Denoirjean A and Pawłowski L 2016 Possibility of Developing Hydroxyapatite Coatings with High Purity by Solution Precursor Plasma Spray Process (To be published)

Acknowledgments
The French National Research Agency is thanked for financial support in the frame of PLASMAT program (ANR-12-JCJCJS09-0006-01). The Electric Arc Association (AAE) is thanked for financial support.