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Suspension and precursor solution plasma spraying by means of synchronous injection in a pulsed arc plasma

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ABSTRACT

Research has led to the development of nanostructured coatings by suspension plasma spraying (SPS) or solution precursor plasma spraying (SPPS). Both techniques open a new way to applications in the field of microelectronic devices. 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 droplet, resulting in an inhomogeneous treatment of the latter. This directly influences the texture and microstructure of deposits and subsequently their properties. Efforts to understand the origins of these instabilities have been made and have led to propose a new approach, i.e. an alternative to instabilities attenuations: the reinforcement and modulation of the instabilities. The adjustment of process parameters has allowed obtaining a pulsed laminar plasma and a modulation of its properties. This device is synchronized with an ink-jet print head to reproduce the same conditions of plasma/material interaction for each injected droplet. A home-made DC torch was made. His power of 1 kW is well below the standard torches (~30 kW for commercial torches) but is well adapted to the flow rate that can be delivered by the print head. This low powered home-made DC torch is used and operates with pure nitrogen as plasma forming gas. Aluminum nitrate aqueous solutions and TiO_2 suspensions are injected. The objectives of this work are firstly to characterize this pulsed plasma and its interactions with droplets to facilitate the understanding of heat and dynamics transfers. They are analyzed by time-resolved imaging and optical emission spectroscopy. Secondly, coatings are characterized by SEM, TEM and DRX analysis.

1. Introduction

The versatility and economics of thermal spray technologies is well known in the industrial field. They are introduced into manufacturing environments. Today, the majority of thermal spray applications are “passive”, in the field of protective coatings. The main function of the coating is to protect the substrate from heat, contact damage or corrosion, e.g. thermal barrier coatings (TBC). However, new opportunities are emerging with thick-film electronics and sensors manufacturing, e.g. semi-conductors like titanium dioxide or aluminum nitride which is known for applications as substrates for power circuits with high thermal conductivity. Thermal spray offers unique advantages: a high throughput manufacturing capability, a possibility of application for a wide variety of substrates and shapes, a possibility of three-dimensional structures capability using robotics arms and a cost-effective rapidly adaptable to existing infrastructure [1]. In this context, conventional plasma spraying technology is developing to master the coating at sub-micron and nanometer scale. For ten years, the liquid injection has been emerging, allowing the injection of nanomaterial in the plasma. In years to come, Solution Precursor Plasma Spraying (SPPS) and suspension plasma spraying (SPS) processes have the potential to become viable industrial technologies [2].

Further studies are still necessary to understand and improve these processes. One of commercial mono-electrode DC torch main drawback is due to the arc root random attachment at the anode wall resulting in strong voltage and power fluctuations. These fluctuations affect the plasma jet properties that impact on the particle trajectories and thermal treatment which influences the quality and reproducibility of coatings. Under the main influence of blowing, the arc is stretched and lengthened until an overheating instability suddenly shorten the arc resulting in an irregular saw-tooth shaped waveform. This fluctuating mode have been known for several decades and is reported as the so-called restrike mode. The arc instability is accompanied with some variations of hydrodynamic characteristics of the plasma jet particularly affecting the pressure in the rear part of the torch, where the cold gas is stored before entering the anode-nozzle region. These pressure variations are amplified by acoustic resonances due to the inner geometry

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Nomenclature

List of Symbols

a_φ	Coefficient of heat potential ($kg \cdot m^{-1} \cdot s^{-1}$)
C_D	Drag coefficient (dimensionless)
d_d	Diameter of the droplet (m)
h_d	Specific enthalpy of droplet ($J \cdot kg^{-1}$)
h_{ex}	Heat transfer coefficient ($W \cdot m^{-2} \cdot K^{-1}$)
$h_{p.}$	Specific enthalpy of plasma ($J \cdot kg^{-1}$)
$\overline{K}$	Average thermal conductivity of the plasma ($W \cdot m^{-1} \cdot K^{-1}$)
L_v	Latent heat of vaporization ($kJ \cdot kg^{-1}$)
Nu	Nusselt number (dimensionless)
Pr	Prandtl number (dimensionless)
Q°	Specific heat supplied per unit time by the plasma to a droplet ($J \cdot s^{-1}$)
r	Radius of the droplet (m)
Re	Reynolds number (dimensionless)
T_d	Droplet temperature (K)
T_p	Plasma temperature (K)
u_{vap}	Radial speed at which the sphere that contains the vapor inflate ($m \cdot s^{-1}$)
We	Weber number (dimensionless)
x_m	Mass fraction of TiO_2 powder (dimensionless)
Z	Ejection ratio (dimensionless)
γ	Surface tension ($N \cdot m^{-1}$)
η	Liquid viscosity ($Pa \cdot s$)
$\tau_{droplet}$	Delay of droplet emission (s)
τ_{acc}	Droplet acceleration time (s)
τ_{vap}	Droplet vaporization time (s)
ρ	Liquid density ($kg \cdot m^{-3}$)
ρ_l	Solvent density ($kg \cdot m^{-3}$)
ρ_s	Solid density ($kg \cdot m^{-3}$)
υ	Droplet velocity ($m \cdot s^{-1}$)
CCD	Charge-coupled device
DC	Direct current
DOD	Drop-on-demand
OES	Optical emission spectroscopy
SEM	Scanning electron microscope
SPPS	Solution precursor plasma spraying
SPS	Suspension plasma spraying
TEM	Transmission electron microscopy
TTL	Transistor-transistor logic
XRD	X-ray diffraction

of the torch, the lower frequency mode being known as the Helmholtz mode, commonly encountered in combustion devices. The Fourier spectrum of the voltage exhibits a strong and sharp peak that characterizes the Helmholtz and which frequency can be accurately predicted as a function of torch design and operating parameters [3]. By changing the torch design and by adjusting the operating parameters it is possible to merge the restrike and Helmholtz modes into a single one, for which the voltage wears an almost perfect periodic and triangular shape as presented in Fig. 1-a. Up to now, such a resonant mode has been obtained at a moderate power (1–2 kW) with a frequency of 1400 Hz. As the sound emitted by the torch recalls that of a mosquito, this will be referred as the mosquito mode in the following. Under such a mode, the flow properties are regularly space and time modulated (see Fig. 1-b) so that the resulting laminar and pulsed arc jet can be considered as a periodic emission of plasma gusts, each of them containing between 0.5 and 1 J of thermal energy, depending on the operating parameters [4]. A model based upon conservation equations has been developed and solved by using Fourier's series expansion [5]. The time-modulation of the specific enthalpy, averaged over the jet cross section, is theoretically highlighted, as shown in Fig. 2, with a modulation ratio, h_{max}/h_{min}, between 2 and 3 depending on operating conditions. The results are in rather good agreement with previous time-resolved temperature measurements obtained by optical emission spectroscopy [6]. Following [6] the temperature is modulated between 6000 and 7500 K with a period of 700 µs. This temperature range corresponds with molecular nitrogen dissociation, so that a change of specific enthalpy changes the amount of nitrogen atoms rather than the temperature. It can be seen in Fig. 2 that the maximum of enthalpy is in phase with that of voltage instead of the minimum of enthalpy that is delayed by a third of period with that of voltage. The model predicted also that the plasma speed is modulated in phase with specific enthalpy. This shows that the instant at which a droplet penetrates the plasma should be of great importance for its further thermal treatment and requires to be controlled as much as possible.

As a result, the following step is to choose an injection system able to dispense the precursor material in liquid form, which can be either a suspension or a solution. The basic idea is to synchronize droplet emission with a chosen arc voltage level to control heat and dynamics transfers from plasma to injected materials, that possibly could help for optimizing coatings properties. In this paper, a home-made resonant plasma torch is used together with a synchronizing device able to trigger a drop-on-demand (DOD) distributor. In this study two kinds of liquid have been injected, a suspension containing TiO_2 (rutile) and a solution of aluminum nitrate. The next section presents the experimental set up and procedure. Section 3 gives the results, with the presentation of plasma/droplet interactions for SPS and coatings characterization for SPS and SPPS. Section 4 starts a general discussion about this study and lastly, Section 5 gives a conclusion.

2. Experimental procedure

The overall arrangement is sketched in Fig. 3 that presents the print head, the plasma torch and the devices required for time resolved imagery and spectroscopy, the latter being used for in-flight diagnostics.

2.1. Torch parameters

The torch parameters are adjusted so that it works in the mosquito mode, for which the arc voltage signal wears the shape presented in Fig. 1. The plasma gas is nitrogen with a flow rate of 2 standard liters per minute (slm) or 0.042 $g \cdot s^{-1}$ and the arc current is 15 A. Once the resonant mode is locked, the voltage oscillates between 40 and 100 V at ~1400 Hz. The space and time averaged specific enthalpy is obtained from the energy balance of the torch (electrical and calorimetric measurements) and gives for the actual situation 14 ± 1 $MJ \cdot kg^{-1}$. These parameters are also listed in Table 1.

2.2. Synchronization device

The torch voltage is sampled by mean of a dividing bridge and sent to an electronic device able to generate a set of delayed TTL pulses that trigger the print head and the instruments that are used for the in-flight diagnostic (Fig. 3).

2.3. In-flight diagnostic

In-flight interactions are recorded by CCD camera (Pixelfly, PCO, Germany), coupled with a 50 W laser diode (HiWatch, Oseir, Tampere, Finland) to illuminate the droplets at the emission wavelength of 801 nm. Different collection optics can be mounted on the CCD camera providing different magnifications.

Optical emission spectroscopy (OES) is performed by using the Isoplane spectrograph (Princeton Instruments, Trenton, USA) associated with an Intensified CCD camera (PIMAX4 1024i, Princeton

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