

HYDRODYNAMIC INVESTIGATION OF A LOW-PRESSURE PLASMA EXPANDED THROUGH A NOZZLE (PETN) FOR CERAMIC OXIDES DEPOSITIONS FROM NITRATE PRECURSORS.

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Abstract

Low-pressure plasma deposition (LPPD) is a suitable technique for plasma coating of various materials. In the specific case of the oxide deposition, the hydrodynamic aspect has a large influence in the final product, its morphology and nature. The Laser Doppler Anemometry (LDA) was used for the characterization of the flight-time of the solid and liquid particles, deduced from their velocity distribution along a specific tubular reactor with a convergent nozzle (cone). Velocity measurements have been performed in a low-pressure environment (1-10 mbar), and an O₂-Ar plasma in this reactor. For this hydrodynamic study of the reactor, the aqueous solution of lanthanum and manganese nitrates were previously vaporized by an ultrasonic nebulizer. The nebulized droplets were then introduced by a pulsed injection into the reactor.

INTRODUCTION

This work takes part of a new program for SOFC manufacturing by plasma processing, and focuses on LaMnO₃ thin film deposition in a low-pressure plasma [1]. Powder oxide formation from nitrate precursors have already been studied by plasma spraying. From a literature review, no low-pressure plasma coating process have been reported using nitrate aqueous precursors.

Laser Doppler Anemometry (LDA) analysis was largely used to help understanding particle-plasma interaction and the optimal location of the substrate. LDA system was operating in the back-scattering mode for all the measurements reported in this paper.

I- The experimental set-up and details

The reactor is made of pyrex glass and consists of a discharge part before the nozzle and a highly reactive part where the glow discharge couple with a substrate-holder made of stainless steel (after the nozzle). The reactor was described in detail previously [1-2].

Laser Doppler anemometers are non-intrusive optical instruments for the investigation of fluid flow structure in gases and liquids. The special properties of the source, making it so well suited for these measurements are the spatial and temporal coherence. The spatial coherence describes the ability of the light field to form interference fringes in space. The temporal coherence describes the monochromaticity of the light, [3-6].

The experimental set-up is composed of an argon laser ($\lambda = 5145 \text{ \AA}$, $P_{\text{max}} = 300 \text{ mW}$), a beam transmitter, the optical system and a photomultiplier, the acquiring system and a calculator. In this technique, the incoming beam from the laser is separated into two laser beams for the measurement of one velocity component (axial one in our case). At the same time, a frequency shift Bragg-cell (40 MHz) is added to one beam to allow for measurements of reversing flows. The two beams are then crossed forwards the transmitter. The crossing point of these beams has a volume of less than 0.1 mm^3 where the fringes are formed. This volume is the measurement volume. Particles which cross through these fringes scatter the monochromatic beam with a frequency shift which depends on their velocity (Doppler effect). The analysis of the scattered light leads then to the velocity measurement. Figure 1 shows our plasma reactor with the laser Doppler anemometry (LDA) equipment.

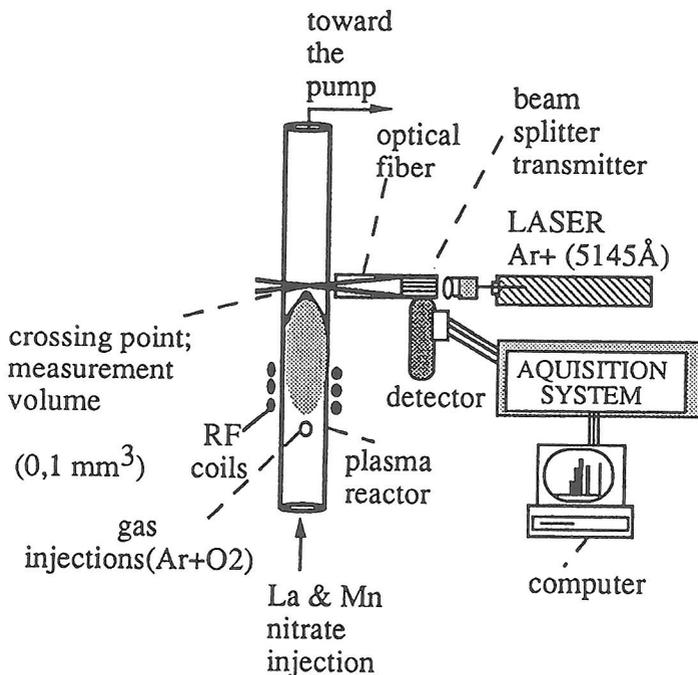


Figure 1 : LDA set up and the plasma reactor.

II- Measurement of velocities of the droplets in the plasma

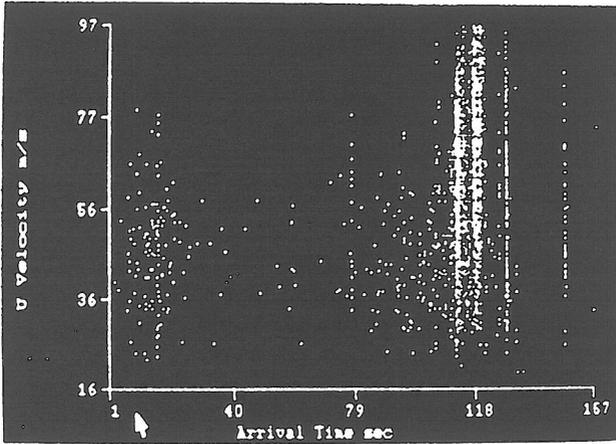
The plasma characterization in this specific tubular reactor with a convergent nozzle was carried out using LDA and OES analysis.[2] We present in this paper, the main results from LDA characterization.

II.1- Experimental parameters

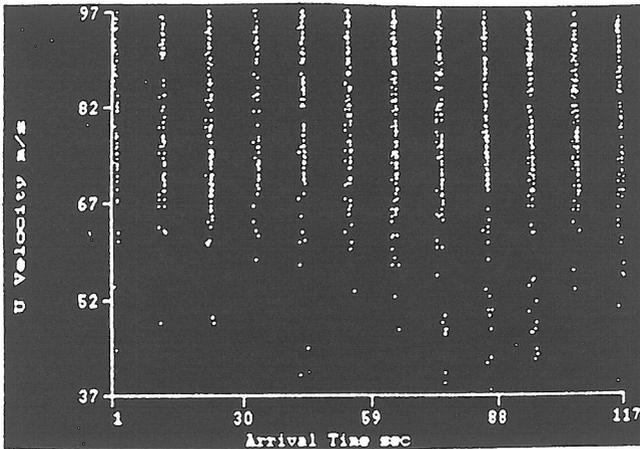
LDA measurements have been carried out at 2 mbar with nearly 100 sccm/mn flow rate of Ar+O₂ ($Q(\text{Ar}) = 50 \text{ sccm/mn}$, $Q(\text{O}_2) = 40 \text{ sccm/mn}$), during the injection of the liquid precursor ($\text{La}(\text{NO}_3)_3$ et $\text{Mn}(\text{NO}_3)_2$ with $10000 \mu\text{g/sccm}$ of La + Mn, 0.1-0.2 cc/mn) into the plasma reactor.

II.2- Results of the measurements and discussions

Figures 2-a and b illustrate two droplet injection systems to introduce liquid precursors. Figure 2-a shows a conventional liquid injection system using an electromagnetic valve. In this case the drops are introduced into the low pressure reactor one by one with no real control. Figure 2-b shows a new liquid injection system that we have developed, using an ultrasonic nebulizer to produce a mist and an electrovalve controlling the pulsed injection. As we can see in figure 2-b, the injection is completely regulated in this case and the velocity of the detected particles is in a smallest range.

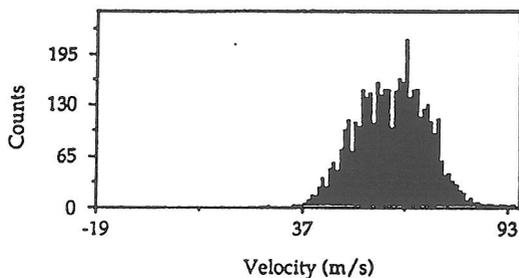


a)

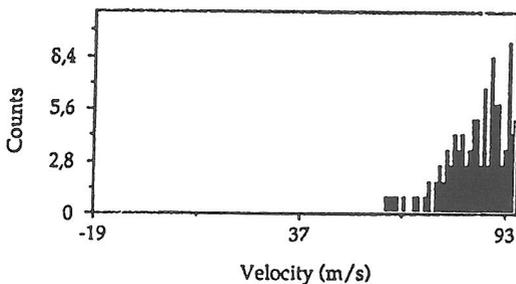


b)

Figure 2 : liquid injection control ; a) continous drops injection with an electromagnetic valve, b) pulsed droplet injection with an ultrasonic nebulizer and an electrovalve.



a) 0.5 cm from the exit of the nozzle
($V_{\text{mean}} = 65 \text{ m/S}$)



b) 3 cm from the exit of the nozzle
($V_{\text{mean}} = 88 \text{ m/S}$)

Figure 3 : Histograms of the axial particle population detected at two points along the reactor.

Droplets are introduced with a velocity of about 10 m/s into the low-pressure reactor and are then accelerated in the nozzle because of the mass conservation law and the pressure drop (1 mbar). Just passing through the nozzle, they reach an axial velocity of about 65-75 m/s and the density of the particles is higher because of the small diameter of the nozzle's exit where the population of detected particles reaches its maximum. As the analyzed point moves downstream from the exit of the nozzle, the particle density decreases as well as the particles diameters which become lower than the detectable diameter limit ($\approx 0.5 \mu\text{m}$). At the same time, the velocity increases up to 95 m/s (the upper velocity limit of our LDA set-up) and a shift of the histograms towards higher velocities is observed. Therefore we should be careful in using the average velocity values which are representative of a small amount of particles which can be detected (diameter $> 0.5 \mu\text{m}$ and velocity $< 100 \text{ m/s}$). Nevertheless these measurements indicate clearly an increase of particle velocities which can be explained by the high pressure drop between the two regions of the reactor during the injection of the droplets. The partial evaporation of droplets increases also the pressure inside the region before the nozzle. Pressure measurements in these two regions showed that the pressure is at least 3 times higher before the nozzle. A simplified calculation of a total evaporation of the solvent shows that this factor can reach almost 100. We consider that in the real case, the pressure drop factor, should vary between 4 and 10 during the unsteady flow stream (droplet injection). Table I summarizes a comparison between the theoretical and the experimental velocities along the reactor.

| | average velocity before the nozzle (m/s) | average velocity at the exit of the nozzle (m/s) |
|---|--|--|
| modelling; steady state flow stream (gas) | 20 | 45 |
| experimental measurement; unsteady state flow stream (particles) | 20-30 | 65-80 |

Table I. Theoretical and experimental velocities of the particles and gases.

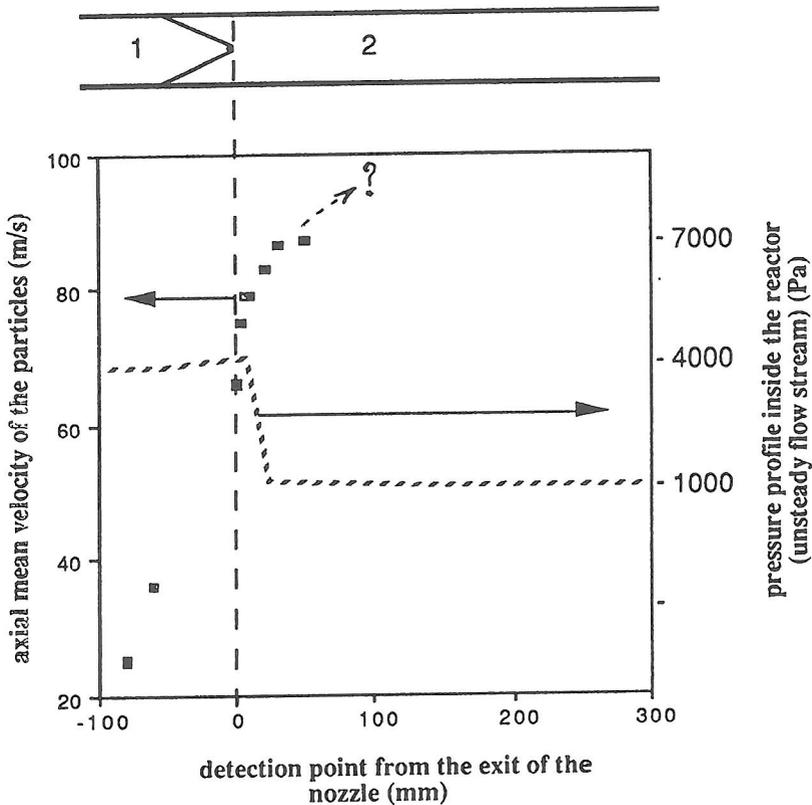


Figure 4: The experimental mean axial velocity profile combined to the pressure profile inside the reactor, during the injection (unsteady state).

CONCLUSIONS

The velocity distribution of detected particles along the reactor, leads to the following conclusions :

* the design of the reactor have a great influence on the particles velocities (nozzle's characteristics),

* as it could be supposed from the theoretical aspect, a strong acceleration was measured at the exit of the nozzle, owing to the gas expansion. The difference of the pressure between the two compartments of the reactor explains the strong acceleration of the gas and the particles at the exit of the nozzle.

* the density of detectable particles is maximal at the exit of the nozzle and decreases further, confirming a possible shrinking of droplets and solid particles by evaporation.

* this tool allows an on-line control of the droplet injection and shrinking along the reactor. This is of a great importance knowing that the velocity, the shrinking and the shape of the particles influence the adherence of the deposits to the substrate and their porosity.

* the modeling of the flow stream should be performed by taking into account a heterogenous phase in the flow stream with a partial evaporation of the droplets (compressible flow).

* the shock wave produced by a pulsed injection of a mist, participates in the dissociation of the evaporated solvent and the precipitated particles [1-2].

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