Effect of suspension characteristics on in-flight particle properties and coating microstructures achieved by suspension plasma spray

E Aubignat1,2, M P Planche1, A Allimant2, D Billières3, L Girardot4, Y Bailly4 and G Montavon1,5
1IRTES-LERMPS, UTBM, 90010 Belfort cedex, France
2Saint-Gobain C.R.E.E., 84300 Cavaillon, France
3Saint-Gobain Coating Solutions, 84000 Avignon, France
4Institut FEMTO-ST, UMR 6174, CNRS, Université de Franche-Comté, 90000 Belfort, France

Abstract. This paper focuses on the influence of suspension properties on the manufacturing of coatings by suspension plasma spraying (SPS). For this purpose, alumina suspensions were formulated with two different liquid phases: water and ethanol. Suspensions were atomized with a twin-fluid nozzle and injected in an atmospheric plasma jet. Suspension injection was optimized thanks to shadowgraphy observations and drop size distribution measurements performed by laser diffraction. In-flight particle velocities were evaluated by particle image velocimetry. In addition, splats were collected on glass substrates, with the same conditions as the ones used during the spray process. Scanning electron microscopy (SEM) and profilometry analyses were then performed to observe the splat morphology and thus to get information on plasma / suspension interactions, such as particle agglomeration. Finally, coatings were manufactured, characterized by SEM and compared to each other.

1. Introduction
Suspension plasma spraying (SPS) is a coating manufacturing process that aims at injecting a suspension (solid particles of about 1 µm or less, dispersed in a liquid phase) in a high-energy plasma flow. Particles are heated, accelerated towards a substrate, flattened and subjected to a rapid solidification. Layer after layer, a coating develops to provide functional properties to the substrate on top of which it is built [1][2][3]. Figure 1 depicts the principle of SPS. This variation of the conventional plasma spray process that injects, with a carrier gas, coarser particles (order of magnitude: 30 µm in diameter) is able to achieve coatings with finer thickness (from 10 to 100 µm instead of hundreds of µm) and microstructure. The particle size reduction leads to a size reduction of pores embedded in the coating and created mostly by particle stacking defects [4]. Moreover, submicrometer-sized particles having lower kinetic and thermal inertia, their velocity and temperature decrease rapidly and thus, their spreading on the substrate is lower than larger particles (i.e., their flattening ratio is smaller). This results in a granular microstructure [5] rather than a lamellar one encountered with conventional plasma spraying.

ghislain.montavon@utbm.fr
Though this emerging process has been studying since the mid-1990’s and achieving a fast-growing interest, it has no industrial applications yet and still needs some developments due to the complex phenomena, such as suspension fragmentation and liquid phase evaporation, that occur in the plasma which are not totally understood and controlled. The suspension injection is a particularly challenging point of the process because it is necessary that particles follow an optimal trajectory inside the plasma in order to be correctly treated. Besides, due to low momentum quantity, suspension droplets and then submicrometer-sized particles are extremely sensitive to plasma instabilities.

Aiming for an optimized injection, various strategies have been considered by the scientific community:

- Axial injection within the plasma torch [6] should be "ideal" for a complete thermal and kinetic treatment of particles, such as the one encountered in the High Velocity Oxy Fuel (HVOF) process [7]. However, this approach requires an adapted torch geometry that allows internal injection. Such configurations are generally more complicated, and costly, than classical plasma torches. Moreover, internal injection increases the risk of clogging.

- In the same manner as conventional powder, suspension can also be radially injected. Suspension droplets can only penetrate the plasma if their momentum is superior to the plasma one [8]. With this type of injection, a part of the suspension, more or less important, may not be injected in the hot central zone of the plasma core and a distribution of trajectories is observed for penetrated particles. This is why injection conditions must be adjusted in order to fulfill at best this requirement.

Since radial suspension injection can be easily implemented on most existing plasma spray equipments, it is the object of numerous studies. Among them, two main techniques are met:

- Mechanical injection [9][10][11]: most of the time, the suspension is stored under pressure in a reservoir and is forced through a capillary injector of a given internal diameter. The suspension is injected in the form of a liquid jet. This type of injector is easy to handle and allows a good penetration of the suspension thanks to the important momentum quantity of the liquid jet. However, as all the input parameters (internal diameter, pressure and suspension flow rate) are correlated, for given plasma flow and injector, the suspension flow rate cannot be varied. The injection is also much localized and there is a risk of clogging at the injector exit.

- Atomization [12][13]: a coaxial twin-fluid nozzle (as shown on Figure 2) is usually used to generate a stream of fine droplets. The co-current gas fragments once the suspension and serves as a carrier so that droplets penetrate the plasma flow before being breaking up a second time. Atomizer geometry is more complex, its control more difficult but the mass flow is independent from the chosen plasma flow. Freedom in adjusting the injection conditions allows exploring a broader spectrum of coating microstructures achievable with this technique, which has brought the choice on this kind of injector for this study.

The behavior of atomizers adapted to SPS process, and phenomena that arise in the plasma, are still not fully understood. This is why two suspensions, an aqueous and an ethanol-based one, whose properties were characterized, were selected to understand how droplets are generated by a home-made twin-fluid atomizer. Based on previous studies, shadowgraphy [11] and laser diffraction [14] were used to characterize the nozzle and optimize the suspension injection. In-flight diagnosis was also carried out to get information on particle velocities and molten state, just before impact on the substrate. SEM analyses of coatings obtained with the two selected suspensions are finally presented and hypotheses are developed, based on the diagnosis observations, in order to give a possible explanation to the difference of noticed morphology.
2. Experimental setups and methods

2.1. Suspension plasma spray conditions

An \( \alpha \)-alumina feedstock powder (P152SB, Aluminium Péchiney, France, \( D_v(50) = 1.6 \ \mu m \), SSA = 2.4 m\(^2\).g\(^{-1}\)) was added either to distilled water or to ethanol. A solid mass load of 20 wt.% was chosen, corresponding to a volume fraction of 0.06. An ammonium salt of polyacrylic acid (noted PAA, from Coatex, France, Mw = 2000-2500 g.mol\(^{-1}\), pH = 7-8) and a phosphoric ester (Beycostat C213, CECA, France) were added respectively to aqueous and alcoholic suspensions to achieve good dispersion, checked by zeta potential measurements and sedimentation tests. Rheology measurements were performed and showed that suspensions with such low volume fraction could be assimilated to the liquid phase: viscosity does not go over a few mPa.s whatever the liquid phase. Surface tensions of liquid phases were also measured. Suspension characteristics are given in Table 1.

| Liquid phase | Dispersant (wt.%\(^a\)) | Mass density (kg.m\(^{-3}\)) | Surface tension (x10\(^3\) N.m\(^{-1}\)) |
|--------------|-------------------------|-------------------------------|------------------------------------------|
| Water        | PAA (0.2%)              | 1176                          | 82.5 ± 0.3                               |
| Ethanol      | Beycostat (0.5%)        | 940                           | 24.0 ± 0.1                               |

\(^a\) Weight percentage of dispersant is indicated in relation to mass of powder.

During the spray process, suspension was stored in a pressurized tank, under magnetic stirring to avoid sedimentation issues, and was delivered through a home-made twin-fluid atomizer, supplied with argon as atomizing gas. Properties of the spray can be adjusted by varying the input liquid and gas pressures that directly act on flow rates and velocities. The spray unit consists in an atmospheric plasma ProPlasma torch (Saint-Gobain Coating Solutions, Avignon, France), used in a “high performance” mode and equipped with a 6.5 mm diameter anode. The torch was attached to a 6-axis robotic arm. The atomizer is positioned perpendicularly to the torch axis, at 10 mm from the torch axis and 6 mm downstream the anode face.

| Plasma | Intensity (A) | Ar/H\(_2\):Total gas flow rate (slpm) | Enthalpy (x10\(^5\) J.kg\(^{-1}\)) | Effective power\(^a\) (kW) |
|--------|--------------|-------------------------------------|-----------------------------------|---------------------------|
| 1      | 600          | 48/12:60                            | 13.0                              | 19                        |
| 2      | 600          | 50/10:60                            | 11.4                              | 17                        |

\(^a\) Effective power is defined as the total electric power supplied to the plasma torch minus the thermal losses due the torch cooling.
Two sets of plasma operating spray parameters, given in Table 2, were used in conjunction with the different liquid phase used for the suspension formulation: the ethanol-based suspension, easier to evaporate, was injected in the plasma whose enthalpy is the lowest.

2.2. Characterization of the atomizer and the injection

A shadowgraphy technique (SprayCam, Control Vision Inc, USA) was used to observe on the one hand, the atomized jet generated by the twin-fluid nozzle without the plasma, and on the other hand, the suspension injection in the plasma and the droplet trajectory. The area of investigation was (22 × 16.5) mm² allowing the detection of drops and particles > 30 µm. The system is able to acquire up to 10 images per second. The software ImageJ (www.scion.org) was used to process images, to quantify the spray width and to superpose some images in order to highlight the quality degree of the injection in the plasma by revealing droplets, which did not penetrate the plasma. Droplet size distributions were measured using an optical instrument based on laser diffraction (Spraytec, Malvern Instruments Ltd, Malvern, UK). This measurement rests on the Mie scattering and uses a 10 mm diameter laser beam whose wavelength is 670 nm. Distributions with median size $D_{v}(50)$ from 2.5 to 125 µm are measurable.

2.3. In-flight diagnosis

In addition to suspension injection observations via shadowgraphy, some in-flight diagnoses were carried out to qualify by other means the quality of injection and to understand what happens between the moment that drops are injected into the plasma and the moment they impact the substrate.

2.3.1. Particle Image Velocimetry (PIV). PIV [15] is a technique able to measure the velocity of features (droplets and particles) and to give simultaneously a visual overview of the injection inside the plasma. It consists in acquiring with a CCD camera two successive images of a cross section of the plasma flow containing particles, by illuminating them with extremely short laser pulses (7.3 ns @532 nm in this case), turned into light sheets. The light sheets are positioned in order to include both the torch and atomizer axes. According to the particle velocities and displacements, a time of 200 ns between the two laser pulses, and so images, was taken on. The velocity of a small set of particles can be estimated measuring its displacement observed from the first image to the second one. This is done thanks to an algorithm analyses based on cross-correlation. The plane chosen for this experiment was including both plasma torch and atomizer axes. The spatial resolution of this experiment is 23 µm per pixel. Insight 3G software (TSI Inc., USA) was used for image acquisitions, instantaneous displacement field determinations and instantaneous velocity field derivation. The average velocity vector fields were calculated and plotted using two software TECPLLOT (Tecplot Inc., Bellevue, WA, USA) and Mathematica (Wolfram, USA). More details on diagnosis were given in a previous work [16].

2.3.2. In-flight particle collection. Particles were collected in the same injection conditions as for coating manufacturing; in particular, suspension flow rate was kept identical. Glass substrates at ambient temperature were selected for their easy implementation of the tests. They passed only once in front of the plasma torch, at the spray distance and at a relative speed of about 15 m.s$^{-1}$ in order to get separated splats and to allow further analyses. Samples were then observed by scanning electron microscopy (SEM) and a zone of 180 × 130 µm² per sample was characterized with an interferometric profilometer to measure particle dimensions (surface and thickness). To eliminate noise, splats whose diameter was below 1.6 µm (corresponding to 5 pixels on images) were not taken account for the analysis.

2.4. Coatings

Some coatings were manufactured using the alumina suspensions described in Table 1, plasma parameters of Table 2 and optimized suspension injection conditions. They were sprayed on rotating
aluminum plates (5 × 30 × 40 mm³), preheated with the plasma flow at 150°C, at least. Coatings were sprayed at a distance of 35 mm from the plasma torch exit, moving at a relative speed of 2 m.s⁻¹. Coating morphology was finally observed by SEM.

3. Results and discussions

3.1. Optimization of the suspension injection

Before the coating manufacturing by SPS process, the selected home-made atomizer must be characterized in order to check whether it could be convenient for this process. Shadowgraphy observations were first performed, shown on Figure 3 and Figure 4.

For a large range of gas and liquid pressures, observations revealed that the home-made nozzle generates atomized jet whose spray cone angles are sufficiently fine so that the whole spray pattern can penetrate the plasma flow, symbolized by pink circles. It can also be noticed the spray is a little bit finer in case of ethanol compared to water.

Since the sprays observed in free atmosphere seem to be adequate for SPS process, that is to say sprays with fine cone angle and well-defined geometry without outlying secondary droplets, some injection tests were then carried out with the two alumina suspensions. Figure 5 and Figure 6 present the results, obtained with the same gas and liquid pressures for both suspensions. In both cases, image overviews bring out that all the droplets penetrate the plasma flow. Once again, the ethanol-based jet appears to be a little finer. Besides, few millimeters after the liquid injection, droplets are too small to be detected on images, which is consistent with a good treatment leading to fragmentation of droplets and liquid evaporation phase. In parallel, spray beads were also manufactured to confirm the quality of the injection and neat lines of molten alumina were obtained and very little overspray was observed on either side far from the spray bead.

To finalize the spray characterization, droplet size distributions were measured by laser diffraction with the same conditions as for injection tests. The results, presented in Figure 7, show that droplets are smaller in case of ethanol with a median diameter in number of 28 µm compared to 44 µm for water, containing respectively 260 and 1260 alumina particles. This is concordant with its lower surface tension that requires less energy to break out drops.
3.2. Contribution to the understanding of phenomena occurring into the plasma

Now that optimal conditions were found for a proper injection of suspensions, attention was focused on particle treatment achieved by the plasma. Particle velocities were measured for the two suspension conditions. Figure 8 and Figure 9 present the velocity vector profiles obtained. It was not possible to calculate vectors in the plasma due to too high emittance, whence a lack of high velocity vectors in this zone.

Considering the important velocities, it appears that droplets and then particles seem to have penetrated in the plasma in both cases. For the alcoholic suspension, the field seems more homogeneous with vectors all over the area of investigation. Given that alcoholic droplets are initially smaller, less dense and evaporate faster, alumina particles get quickly rid of the solvent and then, are carried away by the plasma flow. On the contrary, aqueous droplets penetrate the plasma and follow a trajectory close to the torch axis, thanks to their higher momentum. Concerning the particle velocity value, it is equivalent for both cases (a maximum around 500 m.s\(^{-1}\) with an uncertainty of the measurement of about 10\%). However, it should be noted that these vector fields are not correlated with a number of particles: particles with highest velocities are not representative of particles that contribute most to the coating building.
PIV measurements give information on particle velocities and trajectories but data on particle temperatures, or at least, their melting state, are also very useful to understand the phenomena occurring inside the plasma. This can be achieved thanks to particle collection onto a substrate: a pancake-like splat is sign of a totally molten particle whereas if the particle is not correctly flattened, it is an indication that the particle was not treated by the plasma or already solidified before the impact. The size of the collected particles could also give some explanation to what happened to particles in the plasma, such as agglomeration. Figure 10 gives the SEM observations performed on particle collection with the two suspensions.

These observations revealed the presence of some splats correctly molten and splashed for both cases. It also showed the presence of numerous fine and spherical particles. These particles may have already cooled down before the impact on substrate. In any case, it is difficult for such fine particles to spread due to their lack of momentum quantity. On higher magnification, it is noticed that some particles have agglomerated during their stay in the plasma as grain boundaries are still visible. Moreover, this particle agglomeration led to porosity creation.

Splats surface were measured by profilometry and an equivalent diameter was calculated for each surface measured. A histogram of diameters was plotted on Figure 11 and Figure 12 shows the average diameter and the number of particles analyzed.
These results highlight that particles arriving on the substrate have same dimensions whether the suspension is water or ethanol-based with an average diameter of 3 µm, which supposes that these two suspensions are fragmented in the same manner by the plasma. Assuming a squashing rate of about 2 [17], most particles have not agglomerated. However, a such size distributions of splats could lead to voids as it is explained in [18].
Finally, coating microstructures were manufactured with the same injection conditions as for injection tests and were observed by SEM (cf. Figure 13 and Figure 14).

![Figure 13. Coating microstructure obtained with the alumina aqueous suspension.](image1)

![Figure 14. Coating microstructure obtained with the alumina alcoholic suspension.](image2)

It is found that the coating with the aqueous suspension is denser than the one with ethanol. Moreover, the deposition efficiency is lower for water. As said previously, aqueous droplets follow a trajectory close to the torch axis, which has for consequence a better stacking with less porosity. On the other hand, because of lower vaporization enthalpy and boiling point of ethanol and despite the difference of plasma enthalpy (cf. Table 2), surface coating temperature is higher in case of alcoholic suspension injection. This could enhance the sticking of particles, which explains the higher deposition efficiency.

**Conclusions**

This study presents some phenomena occurring inside plasma during SPS coating manufacturing using an aqueous suspension and an alcoholic one. Atomized jets generated by a home-made twin-fluid nozzle were observed by shadowgraphy. Their fine spray cone angle led to a proper injection into the plasma. Droplet size measurements showed that ethanol droplets are slightly smaller than water ones, consistent with the difference of surface tension. Velocity vector fields were obtained by PIV. They showed that in case of alcoholic suspension, particles were carried away by the plasma flow all over the area of investigation, whereas aqueous droplets travel close to the torch axis. They also revealed particle velocities of more than 500 m.s$^{-1}$ at spray distance, equivalent for both suspensions. In-flight particle collections were also performed, which showed that particles arriving on the substrate had approximately the same dimensions whatever the suspension. The average splat diameter of about 3 µm suggested that most particles did not agglomerate, although agglomeration is not totally excluded according the SEM observations. Finally, the morphology of resulting coatings was observed by SEM. The deposition rate of the coating produced with the aqueous suspension is much lower. However, it appeared denser than the alcoholic one. The difference of porosity rate could be explained by a difference of particle trajectories inside the plasma, whereas the difference of deposition efficiency comes from the surface coating temperature, higher in case of ethanol, which can favor the sticking of particles. Nevertheless, further work should be carried on to confirm this hypothesis, such as PIV measurements on a plane perpendicular to the twin-fluid atomizer and also at its exit. This work demonstrates that different microstructures, more or less porous, can be obtained by changing the suspension liquid phase. Thus, coatings satisfying requirements of several applications can be manufactured just by adapting the suspension composition.
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