Mechanisms of heat transfer between a droplet and a plasma jet in Suspension Plasma Spraying.

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**Abstract.** This article describes a small-scale modeling investigation of the suspension plasma spraying process. The heat transfer between a droplet of pure water and an Ar/H\(_2\) plasma jet was analyzed. The low dwell time of the droplet in the flow before impacting the substrate leads to consider radiation as not the main mechanism while convection and conduction were enhanced as the droplet became deformed.

**Key words:** suspension plasma spraying, heat transfer, conduction, radiation, deformation, vaporization, modeling, small scales

1. **Introduction**

Obtaining higher efficiency rates or increasing the lifetimes of functional industrial parts requires the development of new materials such as ceramic coatings. For many years now, the industry has relied upon surface treatment processes by deposition of various materials to improve these parameters. Since the end of the 1990’s, the processing of nanostructured materials has been performed using thermal spraying processes [1-4]. The characteristic length of the various physical processes (electronic, mechanical, optical…) is included in this scale field, in which the structural organization plays a main role. Moreover, it confers enhanced properties to the specific coatings.

Among the various processes, plasma spraying is well adapted to ceramic coating deposition. Conventional plasma spraying uses a micrometer-sized powder, injected with a carrier gas into the plasma plume, to produce thick layers, generally from 100 µm to close to or greater than a millimeter. Nanomaterials can be deposited by such adapted plasma spraying, but their small particle mass requires a liquid media, like water or ethanol, to increase the particle momentum and ensure penetration into the plasma jet. The nanoparticles are put in suspension and pushed into the plasma jet by pressure via an injector located close to the torch exit. After vaporization of the media, the particles are treated in the plasma plume, impact the substrate and thus generate a coating through piling of lamellae.

This process, represented in **Figure 1**, is a concentration of complexity through a succession of physical phenomena (liquid jet fragmentation, vaporization, heating, agglomeration…) detailed in [5].
All these multiphase phenomena play important roles both in a reduced space scale (where the short stand-off distance ranges from 30 to 50 mm) and the associated time scale (from a few microseconds for the primary fragmentation to a few milliseconds for the vaporization phenomenon).

The in-situ analysis of the succession of phenomena is particularly difficult because of the high plasma jet velocity with important gradients, the significant radiation from the plasma due to the high temperature, again with high gradients which lead to composition, thermodynamic properties and transport coefficient gradients, and the liquid which rapidly changes into gas at low temperature.

For these reasons, modeling can be one way of investigating this process. To this end, previous papers have put forward numerical investigations in the first steps of the interactions (penetration and fragmentation) between an argon/hydrogen plasma flow and a continuous jet of pure water [5-8]. These studies have shown the possibility of modeling the hydrodynamic interactions between the two fluids leading to the liquid fragmentation without use of an analytical model, merely solving the NAVIER-STOKES equations involving VOF (Volume of Fluids) methods to track the interface [9] [10]. At each step (in space and time), the equations, described in [5], are resolved which causes the interfaces to move between liquid and gas and then to a scattered liquid phase in case of breakup.

Based on this, the next step, i.e., heating of the droplet, is described here. The aim of the present work was to determine the mechanisms of heat transfer, especially its activation, between the as-fragmented droplet and the surrounding gas. We start by focusing our interest on previous investigations concerning heat transfer in suspension plasma spraying.

Suspension plasma spraying has been intensively studied generally through shadowgraph imaging analysis [11-14] or infrared imaging [15] but also by numerical approaches [16-23]. These investigations deal with the breakup of the droplets in particular. In fact, few studies concern the heat transfer between liquid droplets and a plasma jet where low temperature phase transformation can appear rapidly.
Concerning particle-loaded droplet heat transfer, KASSNER et al [24] proposed the mechanism depicted in Figure 2 with the following assumed stages: evaporation of the liquid and particle agglomeration, heating of the solid ceramic particles to the melting temperature, particle melting, heating of the liquid particle to the evaporation temperature, and finally, evaporation of the ceramic. For the sake of simplification, the droplet break-up at the beginning of the injection as well as during the dwell time in the plasma until evaporation of the fluid has been left out. The single steps from one stage to another are thus assumed to be separate. To reach the next stage, a defined energy amount for the phase transformation L is needed, or alternatively to reach the temperature for the next phase transformation Q. This energy comes from the plasma by radiation and convection during a short required time for the energy transfer.

The following parts of this paper describe the investigations concerning the first stage of this model in an attempt to understand how the heating of the droplet leads to its evaporation. First, a description of the global experimental conditions is proposed. From these parameters, we extracted local conditions concerning on the one hand the plasma plume as the surrounding atmosphere of one droplet and on the other hand the size and position in the plasma flow of one characteristic water droplet. They were the result of previous studies referenced in the section “Local experimental conditions”.

After that, modeling investigations concerning different physical phenomena were carried out and were analyzed separately to describe their influence upon the droplet behavior. The evaporation was not taken into account due to the short calculation time.

2. Experiments and modeling

2.1. Global experimental conditions

The following analyses were based upon the injection of a water jet into a plasma plume. The operating conditions of the plasma are summarized in Table 1. An explanation of these choices can be found in [5] [25] [26] and are not detailed here. Using a mixture with hydrogen implied that the downstream plasma flow fluctuated and presented stretching and shrinking with hot gas puffs and a modification of the gas velocity. These instabilities led to different liquid treatments depending on the instantaneous state of the plasma [25] [27] with various degrees of penetration of the liquid in the jet and different trajectories. The suspension parameters are listed in Table 2. In the first approximation, the liquid was not loaded with the particle.

2.2. Assumptions and model

The investigations presented here require determining the characteristics of the plasma flow, such as its composition, velocity and temperature, in addition to the droplet size and velocity distributions. Such calculations have been carried out by CARUYER et al [7] using a Computational Fluid Dynamic (C.F.D.) library solving the compressible and multiphase Navier-Stokes equations. For the sake of simplicity, all details concerning how to write and solve the fluid mechanics equations can be found in [6], [7] and [9]. The basic assumptions of the calculations both under steady-state or time-dependent conditions are detailed in [8], [28] and [29]. As explained in these articles, the arc root motion was simulated by the 3-D simple Joule effect model. In addition, the flow scale was considered to be larger than the size of the mesh grid, in order to perform resolved scale multiphase flow simulation by a volume-of-fluid interface tracking approach.

In section 4.3, the CFD code was also used with the following calculation conditions. Computations were carried out in 2D configuration for a shorter calculation time and because of agreements with 3D test case results. This increased the accuracy of the mesh without having a high number of cells. The mesh size around the droplet was 50 nm, which means that there were 400 cells in the diameter of the droplet. In order to have a Courant number lower than 0.3 (required for stability reasons by the interface tracking algorithm), the time step was $2.5 \times 10^{-11}$ s. The domain size was 200 µm long and 100 µm large (Figure 3).
Table 1: Spraying operating conditions

| Parameter                        | Value         |
|----------------------------------|---------------|
| Plasma torch                     | SULZER METCO F4-VB |
| Nozzle diameter (mm)             | 6             |
| Plasma gas mixture               | Argon / Hydrogen |
| Plasma gas flow rate (slpm)      | 45 / 15       |
| Arc current intensity (A)        | 500           |
| Mean voltage (V)                 | 76            |
| Thermal efficiency (%)           | 52            |
| Standoff distance (mm)           | 40            |

Table 2: YSZ suspension parameters

| Parameter               | Value     |
|-------------------------|-----------|
| Media                   | water     |
| Injection pressure (Pa) | $2.5 \times 10^7$ |
| Diameter of the injector (µm) | 200 |

Figure 3: Definition sketch of the calculation domain with the initial droplet position.

The low dimension of meshes was a high assumption regarding the mean free path of the plasma which certainly implied an important error percentage for the calculation of the gas characteristics. Nevertheless, close to the droplet and inside it, the mean free path of the molecules was larger because of a lower temperature leading to validity of the continuity equation.

After 20 µm in the y-direction, the mesh became exponential, to reduce the computational time. The left side was the input side, with a 500 m.s$^{-1}$ condition for the gas velocity and the right side was the output side. The top boundary had a sliding condition, while the bottom boundary presented a planar symmetry in order to be able to divide the number of cells by 2. In order to properly calculate the Laplace pressure and capillary effects, an accurate representation of the interface properties was implemented for the local normal and curvature by [30]. Indeed, without this method and even with a quite thin mesh, spurious oscillations of the interface could be induced, which would disturb the interface in an artificial and non-physical way.

3. Local experimental conditions

Based on the previous calculations, the following figures show the characteristics of the plasma flow. These characteristics were the results of long time calculations since they correspond to mean values integrating the fluctuations of the plasma (due to the arc root motion). First of all, Figure 4 shows that the as-fragmented droplets were completely immersed in an atmosphere of plasma at a high temperature, more than 9000 K close to the centerline (Figure 5) while the surrounding gas
flowed at more than 500 m/s (Figure 6) if the fragmentation was assumed to end 10 mm from the torch exit and close to the centerline.

Figure 4: Average weight percentage of plasma gas versus surrounding air.

Figure 5: Average calculated temperature field (K)

At this position in this environment, the liquid shape was assumed to be completely fragmented into small droplets following the size distribution in Figure 7. This figure shows that the main population of the fragmented droplets (defined by their near-spherical shape) had a diameter close to 20 µm regardless of the time [31]. Still-existing ligaments were not incorporated in these distributions.

Figure 6: Average calculated velocity field (K)

Figure 7: Size distribution of the droplets at different times of the unsteady plasma flow.

4. Analysis of the heat transfer mechanism

Evaporation of the liquid requires the activation of heat transfer. In this section, the evaporation was not taken into account and the investigations concerned the different mechanisms of heat transfer, that of the radiation, and that of convection assuming a spherical droplet. Finally, the mechanism of non-spherical droplet deformation was investigated.

4.1. Radiation

The highest black body emission intensity is in the wavelength range centered around 0.25 µm. Considering the spectral absorption coefficient of the different plasma gas species [32]. Figure 8 indicates that the radiation was free to heat droplets in the frequency range $0.5 \times 10^{13} – 3. \times 10^{15}$ Hz
(wavelength from 0.6 to 0.1 µm) and moreover, Figure 9 shows at which wavelength the liquid water could absorb the radiation when its environment was at different black body temperatures [33]. The heating was efficient in two wavelength ranges, one from around 0.06 µm to 0.2 µm, the second from 1 µm to 10 µm. So the common range for efficient heating was between 0.1 and 0.2 µm. From this, Table 3 shows the integrated power upon the entire wavelength range considering the plasma as a black body radiating at the different temperatures. In [34], GIRARD et al. calculated the dwell time it takes for a mean droplet to reach the substrate: it was less than 100 µs. So, Table 3 also indicates the energy absorbed by a 20-µm water droplet flowing in the plasma jet during this dwell time. We must add that plasma radiation is lower than that of a black body at the same temperature so that the values of absorbed energy in table 3 are overestimated.

Table 3: Integrated available power and absorbed energy by a 20 µm sized water droplet in 100 µs.

| Temperature (K) | Integrated power (W) | Absorbed energy (J) |
|-----------------|----------------------|---------------------|
| 10 000          | 0.028                | 2.8 10^{-6}         |
| 11 000          | 0.063                | 6.3 10^{-6}         |
| 12 000          | 0.129                | 1.29 10^{-5}        |

From the model previously proposed by KASSNER [24], the energy required for heating and evaporating a 20-µm sized water droplet was around 1.10^{-5} J. When comparing these two energies, it appeared that the available radiation energy of the plasma was not high enough to completely evaporate the droplet. Radiation is only one activation mode to start this process. But as Basu et al. explained in [35], it takes more than 200 µs to start the significant vaporization of the fuel droplet. In SPS, the dwell time is only 100 µs for the 20-µm water droplet before reaching the substrate. Consequently, radiation is not the main mechanism for heating the droplet.

4.2. Convection for a spherical droplet

This section describes how to determine whether the convection mechanism is efficient during the flight of the droplet between the fragmentation position and the impact onto the substrate. This mechanism has been completely detailed in [34]. Here, we only mention the main conclusions. Due to heat transfer, each droplet receives energy from the plasma which leads to vaporization. Assuming that the droplet is spherical, the interface phase transformation velocity is more than 0.1 m/s. Due to the phase transformation above the boiling temperature, the steam might expand with a speed of around 160 m/s. This is a lower limit of the boiling phenomenon.
On the contrary, the water vaporization is not a supersonic phenomenon if the heating occurs by convection. So the vapor speed is less than the sound speed in steam (evaluated to 440 m/s at 100°C) and so the evaporation time is more than 38 µs. During this lapse of time, the plasma jet and steam are in interaction with each other. Calculations of their volume momentum show that the momentum of steam is higher than that of plasma (respectively 90 and 15 kg m s\(^{-1}\) m\(^{-3}\) for steam and plasma). This implies that if the boiling is uniform, the steam pushes the plasma, and prevents it from touching the droplet. Consequently, heat transfer does not occur between the hot plasma and the cold droplet, but through a layer of steam, from a hot source to a cold target. This is also one of the conclusions made by Basu et al \[35\]. Then, considering the position where the momentums of the plasma jet and of the steam sphere are equal, it can be deduced that the steam radius (including the liquid droplet) is close to 18.3 µm leading to a steam thickness of 8.3 µm (Figure 10).

In conclusion, if the droplet remains spherical during its flight, heating by convection cannot be considered to be the main mechanism due to the steam sphere around it. Based on this, the next section is dedicated to the deformation of the in-flight droplet.

4.3. Deformation of a droplet.
The following figures present different parameters for a droplet immerged in a plasma flow at different calculation times (t= 0.25 µs, 1 µs, 2.25 µs and 4.25 µs). The initial time corresponds to the beginning of the plasma flow appearing at the left side of the domain. Of course in this case, no thermal effect is taken into account due to the low calculation time.
Figure 11 shows the shear stress beginning to appear around the droplet with an asymmetry between its left side, its upper side and its right side. As a consequence, the shear stress on the interface accelerates the external layer of the liquid, which rotates over the center of the droplet. As the time increases, the internal velocity grows (Figure 12) and leads to an accumulation of the fluid on the right side (downstream) of the droplet with the beginning of the interface geometry deformation, as shown in Figure 12, Figure 13 and Figure 14. While this appendix appears, the external layers continue to be accelerated and transform the spherical droplet into a kind of medusa shape, much thinner and with a higher surface contact with the plasma. This higher surface contact leads to a greater drag force, and thus to a greater dynamic pressure from the upstream side inside the droplet (Figure 15).

![Figure 13: Droplet shape immersed in the plasma flow at 2.25 µs.](image1)

![Figure 14: Droplet shape immersed in the plasma flow at 4.25 µs.](image2)

![Figure 15: Internal pressure of a droplet immersed in the plasma flow at 4.25 µs.](image3)

![Figure 16: Boiling temperature of water versus pressure.](image4)

According to Figure 16 [35], the boiling temperature of the water varied depending on the pressure. Consequently, the droplet that immerged in the plasma flow could boil from 363 K to 383 K. This pressure distortion accelerated the boiling phenomenon, and this temperature difference led to an energy saving of approx. $4.2 \times 10^{-7}$ J for a 20-µm diameter droplet. This value is low, representing around 3% of the latent heat but it is enough to accelerate the process of the droplet heating.
5. Conclusions
The present article has been dedicated to investigating the heat transfer between a water droplet and the plasma jet surrounding it. The objective of these studies was to understand in which way the boiling phenomenon appeared in order for only the nanoparticles to reach the substrate.

Different mechanisms have been considered: radiation, convection around a spherical droplet and deformation of the droplet due to shear stress. Radiation could have an influence on the heating but is not enough efficient to boil completely a droplet while convection to a spherical droplet had no influence at all due to a thick layer of steam encompassing the liquid droplet.

Another mechanism was identified due to the deformation of the droplet before boiling because of the shear stress from the plasma flow. This shear stress also led to an internal flow inside the droplet, mixing the droplet temperature. Moreover, the deformation increased the surface exchange resulting in a more efficient heating. As only water droplets were considered, further studies will integrate the influence of ceramic particles inside the liquid jet via modification of the chemical and physical properties of the liquid. Finally, we will also consider how change of the liquid phase influences the plasma flow.

References
[1] GITZHOFER F., BOUYER E., and BOULOS M., 1997, Suspension Plasma Spraying, U.S. Patents, 5, 609, 921
[2] KARTHIKEYAN J.J., BERNDT C.C., TIKKANEN J., REDDY S., HERMAN H., 1997, Plasma Spray Synthesis of Nanomaterial Powders and Deposits, Surf. Coat. Technol., 238 (2), pp. 275-286.
[3] KARTHIKEYAN J.J., BERNDT C.C., REDDY S., WANG J.Y., KING A.H., HERMAN H., 1998, J. American Ceram. Soc., 81 (1), pp. 121-128.
[4] BOUYER E., GITZHOFER F., BOULOS M., 1996, “Parametric Study of Suspension Plasma Sprayed Hydroxyapatite”, Proceedings of the ITSC 1996, (Ed.) C.C. Berndt, (Pub.) ASM International, pp 683-691.
[5] MEILLOT E., VINCENT S., CARUYER C., DAMIANI D., CALTAGIRONE J.P., 2013, J. Phys. D: Appl. Phys., 46 (22).
[6] MEILLOT E., DAMIANI D., VINCENT S., CARUYER C., CALTAGIRONE J.P., 2013, Analysis by Modelling of the Plasma Flow Interactions with a Liquid Injection, Surf. Coat. Technol., 220, pp. 149-156.
[7] CARUYER C., VINCENT S., MEILLOT E., DAMIANI D., CALTAGIRONE J.P., 2011, Effects of plasma conditions on the fragmentation and the atomization of a liquid jet, ILASS – Europe 2011, Proceedings of 24th European Conference on Liquid Atomization and Spray Systems, ESTORIL, PORTUGAL, September 2011
[8] CARUYER C., VINCENT S., MEILLOT E., CALTAGIRONE J.P., 2010, Modeling the First Instant of the Interaction Between a Liquid and a Plasma Jet with a Compressible Approach, Surf. Coat. Technol., 205, pp. 974–979.
[9] VINCENT S., BALMI GER E. G., CALTAGIRONE J.P., MEILLOT E., 2010, Eulerian-Lagrangian multi-scale Methods for Solving Scalar Equations - Application to Incompressible Two-phase Flows. J. Comput. Phys., 229, pp. 73–106.
[10] LOPEZ J., HERNANDEZ J., GOMEZ P., FAURA F., 2005 J. Comput. Phys., 208 pp. 51–74.
[11] DAMIANI D., TARLET D., MEILLOT E., 2014, A Particle-Tracking-Velocimetry (PTV) Investigation of the Injection of Liquid Solution in a Thermal Plasma Jet, J. Thermal Spray Technol., 23 (3).
[12] DAMIANI D., MEILLOT E., CARUYER C., VERT R., 2011, Méthodes optiques pour la visualisation des écoulements dans les plasmas, 14ème Congrès Français de Visualisation et de Traitement d’Images en Mécanique des Fluides, Lille, France,21 - 25 novembre 2011.
[13] MEILLOT E., DAMIANI D., CARUYER C., VINCENT S., CALTAGIRONE J. P., 2011, IEEE Trans. Plasma Sci., 39 (11)
[14] ETCHART-SALAS R., 2007, Projection par plasma d’arc de particules submicroniques en suspension. Approche expérimentale et analytique des phénomènes impliqués dans la reproductibilité et la qualité des dépôts. Ph. D. Thesis (in French), Limoges University, 2007.
[15] SOYSAL D., ANSAR A., 2013 Surf. Coat. Technol., 220, pp. 187-190.
[16] MARCHAND C., VARDELLE A., MARIAUX G., LEFORT P., 2008 Surf. Coat. Technol., 202, 4458–4464.
[17] MARCHAND C., CHAZELAS C., MARIAUX G., VARDELLE A., 2007 J. Thermal Spray Technol. 16 (5-6) pp. 705-712.
[18] SHAN Y., COYLE T.W., MOSTAGHIMI J., 2007 J. Thermal Spray Technol., 16 (5-6), pp 698-704.
[19] SHAN Y., COYLE T.W., MOSTAGHIMI J., 2007 J. Thermal Spray Technol., 16 (5-6), pp 736 – 743.
[20] QIAN L.J., LIN J.Z., H.B. XIONG, 2011 Int. J. of Thermal Sci., 50, 1417-1427.
[21] XIONG H.B., QIAN L.J., J.Z. LIN, 2012 J. Thermal Spray Technol., 21 (2) pp. 226-239.
[22] CHEN X., PFENDER E., 1982 Plasma Chem. and Plasma Process. 2, 2, pp 185-212.
[23] PFENDER E., LEE Y.C., 1985 Plasma Chem. and Plasma Process., 5, 3, pp 211- 237.
[24] KASSNER H., VASSEN R., STÖVER D., 2008, Study on Instant Droplet and Particle Stages During Suspension Plasma Spraying (SPS), Surf. Coat. Technol., 202, pp. 4355 - 4361.
[25] COUDERT J.F., RAT V., 2010, The role of torch instabilities in the suspension plasma spraying process, Surf. Coat. Technol., 205, pp. 949-953.
[26] JANISSON S., VARDELLE A., COUDERT J.F., FAUCHAIS P., MEILLOT E., 1999, Analysis of The Stability of DC Plasma Gun Operating With Ar–He–H2 Gas Mixtures, in: Annals of the New York Academy of Sciences, 891, pp. 407–416.
[27] FAZILLEAU J., DELBOS C., RAT V., COUDERT J.F., FAUCHAIS P., PATEYRON B., 2006, Phenomena Involved in Suspension Plasma Spraying. Part 1: Suspension Injection and Behavior, Plasma Chem. Plasma Process, 26 pp. 371-391.
[28] MEILLOT E., VINCENT S., CARUYER C., CALTAGIRONE J.P., DAMIANI D., 2009, From D.C. time-dependent thermal plasma generation to suspension plasma spraying interactions, J. Thermal Spray Technol, 18 pp. 857–86.
[29] CARUYER C., VINCENT S., MEILLOT E., CALTAGIRONE J. P., DAMIANI D., 2010, Analysis of the unsteadiness of a plasma jet and the related turbulence, Surf. Coat. Technol., 205 pp. 1165–70.
[30] PIANET G., VINCENT S., LEBOI J., CALTAGIRONE J.P., ANDERHUBER M., 2010, Simulating compressible gas bubbles with a smooth volume tracking 1-fluid method, Int. J. of Multiphase Flow, 36 pp. 273-283.
[31] CARUYER C., 2011, Modélisation de nanomatériaux injectés par voie liquide dans un jet de plasma pour la fabrication de nanostructures, Ph. D. Thesis (in French), Université de Bordeaux 1, 4329, 2011.
[32] CRESSAULT Y., ROUFFET M.E., GLEIZES A., MEILLOT E., 2010, Net Emission of Ar-H2-He Thermal Plasmas at Atmospheric Pressure, J. Phys. D: Applied Phys., 43.
[33] MESENBRINK M., 1996, Complex indices of refraction for water and ice from visible to long wavelengths. Ph. D. Thesis. Florida State University, March 1996.
[34] GIRARD F., MEILLOT E., VINCENT S., CALTAGIRONE J.P., BIANCHI L., Understanding of heat and mass transfers between plasma jet and colloidal droplets in Suspension Plasma Spraying process, Surf. Coat. Technol., submitted, in progress.
[35] BASU S., SAHA A., KUMAR R., 2012, Thermally Induced Secondary Atomization of Droplet in an Acoustic Field, Applied Physics Letters 100, 054101.