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Suspension Plasma Spraying of Zirconia Coatings: Process and Coating Structure

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Abstract: Suspension plasma spraying (SPS) permits to manufacture finely structured coatings (nano- or submicron-sized) coatings. Compared to conventional plasma spraying, SPS exhibit several major differences: i) a more pronounced sensitivity to arc root fluctuations; ii) a shorter spray distance; iii) a higher thermal flux transmitted from the plasma flow to the substrate. Several operating parameters play relevant roles in the suspension processing and the coating architecture.

Keywords: Suspension Plasma Spraying, suspension injection, coating structure

1. Introduction

Several emerging technologies include in their design finely structured layers (nano- or micron-sized) such as environmental barriers for photocatalytic applications (anatase-TiO₂, γ -Al₂O₃, etc.), electric insulation for solar energy generators (Al₂O₃, (MgO)₂(Al₂O₃)₂(SiO₂)₅, etc.), ionic and electronic conductions for Solid Oxide Fuel Cells (SOFC) (ZrO₂-7Y₂O₃, perovskites, etc.), etc. Those layers should be manufactured on large surfaces and should ideally exhibit thicknesses ranging from 10 to 50 μ m, average values. Moreover, those layers should also exhibit a large variety of architectures, from dense and gas-tight ones to very porous ones.

Producing finely-structured "thick" layers by thermal spraying, in particular plasma spraying when considering refractory feedstock, requires reducing the feedstock particle average size. Conventionally, those particles are carried out to the plasma jet *via* a carrier gas and injected radially a few millimeters downstream from the exit of the plasma torch. In such a configuration, the momentum imparted to the particles has to be of the same order than the momentum density imparted to the plasma flow. When reducing the average particle diameters, the particle velocity has to be increased in order to maintain as constant as possible the particle momentum. While the decrease in the injector internal diameter to increase the carrier gas velocity reaches technological difficulties that cannot be solved (injector plugging), the increase in the carrier gas flow rate leads to the plasma jet disruption by the cold carrier gas flow as the required flow rate reaches very high values (in the order of one fourth of the plasma forming gas mass flow rate) when considering injected particle diameters smaller than 5 μ m.

Suspension Plasma Spraying (SPS) [1-2] aims at circumventing the previously detailed technological limitations. In this process, a stabilized suspension, made of a liquid, solid particles and a dispersant, is injected within the plasma flow. The liquid is very quickly vaporized and the individual particles, or the particle

agglomerates, depending on the average size of the solid feedstock, are heated and simultaneously accelerated towards the substrate surface where they impact, spread and solidify, analogously in a first approximation to larger particles, to form a layer.

2. Major mechanisms occurring in SPS

Two technological routes can be used to inject a liquid within a plasma flow, either pneumatic injection (based on a secondary atomization of a liquid stream within a dedicated nozzle by a secondary plasma gas flow) or mechanical injection (based on the injection within the plasma flow of a continuous liquid stream). From the first route results a divergent stream of liquid droplets (characterized by broad particle size and velocity distributions) which heavily disturb the plasma flow and which does not lead to a homogeneous treatment of the droplets into the plasma flow, resulting in layers exhibiting heterogeneous, non-cohesive and porous structures. The second route is based on pressurized tanks associated to an injector of diameter varying from 50 to 300 μ m, depending on the characteristics of the liquid and its flow rate. This permits to sow the plasma jet with a liquid without disturbing the flow. The droplet treatment which results is hence more homogeneous, as are the structures of the produced layers. This second solution will be exclusively considered in the following.

The suspension can be injected either radially [1] or axially [3] to the plasma flow, depending on the plasma torch design. In the following, only the case of a radial injection will be considered and discussed, that is to say suspension plasma spraying implementing a direct current stick-type cathode plasma torch.

Several natures of liquid can be used as carrier. The first developments used de-ionized water [1-2] but most of the works nowadays consider ethanol since the enthalpy of vaporization of this latter fluid is lower than that of water (0.84 MJ.kg⁻¹ to be compared to 2.26 MJ.kg⁻¹). Of course, one has to consider also the other sources of

energy dissipation corresponding to vapor molecular decomposition and atomic ionization before mixing with the plasma flow species.

The required condition for the continuous liquid stream to penetrate the plasma flow is that its momentum density has to be higher than the one of the plasma flow, that is to say:

$$\rho_{\text{liquid}} V_{\text{liquid}}^2 > \rho_{\text{plasma}} V_{\text{plasma}}^2 \quad (1)$$

where ρ_{liquid} and ρ_{plasma} represent the specific mass of the carrier and the plasma, respectively, and V_{liquid} and V_{plasma} the velocity module of the liquid and the plasma, respectively.

Upon penetration within the plasma flow, the liquid stream will encounter two mechanisms, fragmentation and vaporization [4]. In a first approximation, one can say that whatever the characteristic dimension of the liquid stream fragmentation occurs before vaporization; the characteristic time of this latter mechanism being two order of magnitude higher than the one related to fragmentation. This signifies that the liquid stream encounters fragmentation upon penetration within the plasma flow to form liquid droplets. Those droplets evaporate in a second time. Indeed, the fragmentation occurs for a liquid flow characteristic dimensionless Weber number, We , higher than 12-14 [4]. We represents the ratio of inertia forces to surface tension ones and is expressed as follows:

$$We = \frac{\rho_{\text{liquid}} \cdot \Delta V^2 \cdot d_{\text{liquid}}}{\sigma_{\text{liquid}}} \quad (2)$$

where ρ_{liquid} represents the liquid specific mass, d_{liquid} the liquid stream characteristic dimension (average diameter), σ_{liquid} the liquid surface tension (considered in the calculation at ambient temperature in contact with air at ambient pressure) and ΔV the difference in velocities between the liquid stream and the plasma flow. From a practical point of view, such a threshold of 12-14 for the dimensionless Weber number is reached at the fringes of the plasma jet. This signifies that depending upon their momentum liquid droplets will penetrate more or less into the plasma flow. For the ones with lower momentums, they will very likely travel at the fringes of the flow where the solvent will be evaporated but the droplet content will be poorly treated. The fragmentation of the liquid stream at the earliest interactions with the plasma flow is also promoted by the plasma instabilities which result mostly from the arc root fluctuations [5].

The suspension characteristics also affect the fragmentation mechanism [6]. Indeed, the higher the suspension surface tension and dynamic viscosity, the more delayed the fragmentation.

The suspension injection velocity, that is to say the suspension stream momentum density, constitutes a third major operating parameter for suspension injection. Indeed, this velocity will drastically influence the dispersion of the droplet clouds within the plasma flow [7]: the higher the suspension injection velocity, the lower

the dispersion angle of the droplet cloud within the plasma flow. Decreasing the droplet cloud dispersion angle within the plasma flow permits to decrease the droplet flow pattern upon impact onto the substrate while increasing the homogeneity of their treatment within the plasma flow.

When considering the processing of droplets by the plasma flow, one has to consider the solid particle average size. Either the suspension is made of nano-sized particles (about 200 nm, average diameter) or of micron-sized particles (about 1 μm , average diameter). Considering a suspension of nano-sized particles, one can envisage the following scenario [6]: **i**) once fragmentation of the liquid stream has occurred, solvent begins to evaporate; **ii**) the evaporation of the solvent leads to the formation of micron-sized aggregates made of nano-sized particles; **iii**) these aggregates are not stable within the plasma flow and desegregate into smaller aggregates; **iv**) the smaller ones are very likely totally or partially vaporized whereas the larger ones melt to form small liquid particles which impact, spread and solidify to form flattened lamellae of equivalent diameters in the order of the micrometer. One can envisage the following scenario for the processing of a suspension made of micron-sized particles [6]: **i**) once fragmentation of the liquid stream has occurred, solvent begins to evaporate; **ii**) the evaporation of the solvent leads to the formation of aggregates constituted by a few particles; **iii**) these aggregates melt and form liquid particles which impact, spread and solidify to form flattened lamellae of equivalent diameters in the order of a few micrometers.

As the vaporization of the liquid phase and the dissociation and ionization of resulting species very significantly decreases the enthalpy of the plasma, this leads to a very significant decrease in the plasma core size: the interaction time between the plasma flow and the droplets / particles is decreased. Moreover, as the particles to be processed exhibit small diameters, their thermal inertia as well as their inertia are much lower than they are for larger particles and their velocity and temperature very quickly decrease when they exit the plasma jet and interact with the surrounding colder atmosphere. As a result, the stand-off distance has to be adjusted compared to conventional plasma spraying. Depending on the operating parameters, the suspension characteristics and the particle sizes, the stand-off distance varies from 35 to 50 mm. A consequence of this relatively short stand-off distance is the increase in the heat flux transmitted from the plasma and the recombined gases to the substrate. The higher heat fluxes transferred to substrates due to shorter stand-off distances will modify the sprayed layer characteristics as solidification kinetic of the first deposited layers will be lowered compared to conventional plasma spraying. This significantly modifies their structure which evolves, at the microscopic scale, from a layered architecture for conventional plasma spraying to first a dendritic and then a granular one for suspension plasma spraying (**Fig. 1**) [8].

Collected flattened particles onto polished substrates are characterized by [6]: i) almost the absence of peripheral projections around the lamellae. This signifies that the dimensionless flattening Sommerfeld number, K_f , is lower than 6 [9]; ii) the absence of intralamellar cracks within the lamellae, *a contrario* to Al_2O_3 lamellae collected under conventional plasma spray conditions, indicating that the residual quenching stress developing within the lamellae upon rapid solidification and cooling is lower than the intrinsic mechanical resistance of Al_2O_3 .

The most surprising is very likely to be able to collect a significant quantity of such lamellae onto a substrate. Indeed, the condition for the in-flight particles to impact the substrate instead of following the gas stream flowing parallel to the substrate surface due to their low inertia is that their dimensionless Stokes number be higher than 1. The dimensionless Stokes number is defined as follows:

$$St = \frac{\rho_p d_p^2 V_p}{\mu_g e_{BL}} \quad (7)$$

where ρ_p represents the particle specific mass, d_p its average diameter upon impact and V_p its impact velocity. μ_g is the gas dynamic viscosity and e_{BL} the average thickness of the boundary layer developing at the substrate surface. This signifies that, depending on the particle size distribution resulting from the suspension stream fragmentation and the processing of the liquid droplets within the plasma jet, particles will impact more or less farer from the gun centerline axis. From a practical point of view, the larger particles characterized by dimensionless Stokes numbers higher than 1 will impact in the center of the particle flow pattern whereas the ones characterized by dimensionless Stokes numbers close to 1 will impact at the periphery of the particle flow pattern. From this specific particle flow pattern, proportionally more extended compared to conventional plasma spraying, results the following coating manufacturing sequence [7]: **i)** the bottom part of the deposited layer results from the stacking of small lamellae issuing from the periphery of the particle flow pattern; **ii)** the intermediate part of the deposited layer, representing most of the thickness due to the density of larger impinging particles, is then built-up; **iii)** the upper part of the deposited layer results once again from the stacking of small lamellae issuing from the periphery of the particle flow pattern. Such a sequence generates specific inter-pass stacking defects as depicted in **Fig. 2.a**. When adjusting suspension injection conditions to reduce the droplet dispersion within the plasma flow (**Fig. 2.b**) and when adjusting plasma torch operating mode from the restrike to the takeover one (**Fig. 2.c**) to reduce even further these dispersions [7], the density of stacking defects can be reduced. Finally, the adjustment of the kinematics of the spray torch in front of the substrate permits to reduce these inter-pass stacking defects and to produce typical structures as the one depicted in **Fig. 2.d**. Such a coating architecture is characterized by the absence of detectable inter- and intra-lamellar

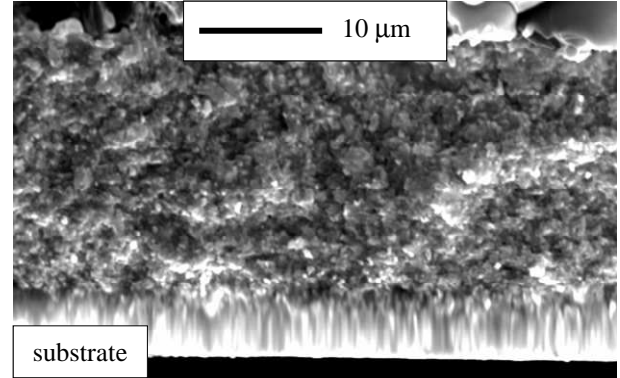


Fig. 1. SPS ZrO_2 layer architecture (micron-sized particles, ethanol-based suspension, suspension load: 20 wt.%, $\text{Ar-H}_2\text{-He}$ plasma, 40-10-50 SLPM, arc current intensity: 500 A, anode internal exit diameter: 6 mm, stand-off distance: 40 mm) [8].

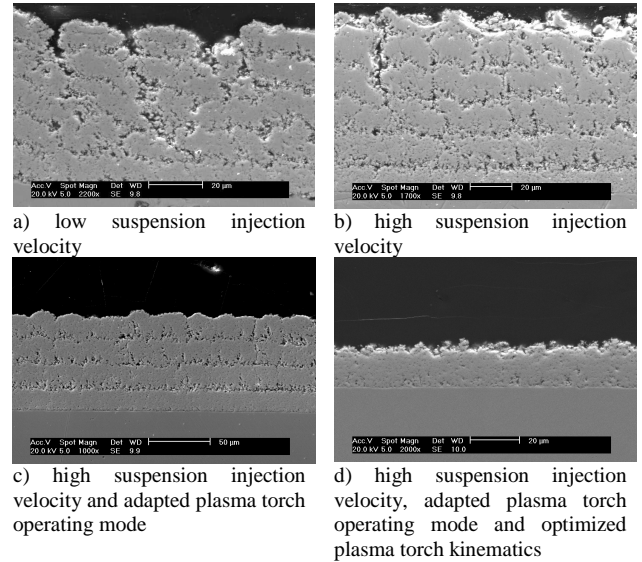


Fig. 2. Typical SPS ZrO_2 coating architecture manufactured by suspension plasma spraying [7].

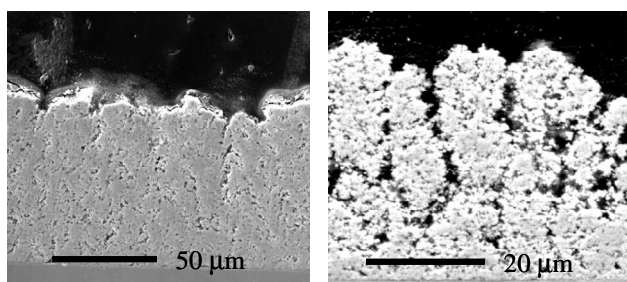
cracks (considering the picture resolution, this corresponds to crack sizes larger than $0.15 \mu\text{m}$).

3. Effects of suspension characteristics on ZrO_2 coating architecture

A stabilized suspension is made of: i) a liquid carrier (water or ethanol are the most used ones); ii) a dispersant (electrostatic, stearic or electrostearic dispersant); iii) solid precursor particles, either nano-sized or micron-sized.

Depending on their manufacturing process, solid precursors will exhibit different particle morphologies, average sizes and particle size distributions. Those characteristics will influence the suspension characteristics, for example in terms of the dispersant mass fraction. Moreover and as already underlined in section 2, the droplet treatment by the plasma flow and its evolution towards molten particles will depend upon the

average sizes of the solid precursor particles. In such a way, the particle size distribution of the precursors will play a relevant role into their treatment by the plasma flow and hence onto the layer manufacturing mechanism. Beside the average size itself (nano- or micron-sized particles), two cases have to be considered, either a broad particle size distribution or a narrow one. When operating a suspension made of a solid precursor with a narrow particle size distribution, the treatment of the droplets and then of the resulting molten particles will be similar. This will result in a homogenous coating architecture. On the opposite, when operating a suspension made of a solid precursor with a broad particle size distribution, the treatment of the droplets and then the resulting molten particles will be dissimilar. In particular, some small aggregates made of the smallest particles will be easily vaporized since in this case, the plasma operating parameters will have been optimized to process larger particle diameters. This could result in the stagnation of vapors in the vicinity of the substrate which would generate stacking defects leading to heterogeneous structures. These effects are illustrated in Fig. 3 which displays two coating architectures manufactured from two suspensions made of solid precursors exhibiting dissimilar particle size distributions: the broader the particle size distribution, the more heterogeneous the coating architecture [6-8].



a) sedimented agglomerated nano-particles of particle size distribution ranging from 1 to 2 µm
 b) agglomerated nano-particles of particle size distribution ranging from 0.2 to 2 µm

Fig. 3. ZrO₂ coating architectures manufactured from two suspensions made of solid precursors exhibiting dissimilar particle size distributions [8].

Conclusion

SPS present a large interest to manufacture under atmospheric conditions "thick" (10 to 50 µm) finely-structured layers onto large surfaces.

This process, under development, requires a very tight control of the operating conditions and pertinent technological solutions. Among the major extrinsic operating parameters to be considered, one can cite: **i)** the mechanical (pneumatic) injection which proved to less

perturb the plasma flow and permit a more homogeneous treatment of the suspension within the plasma jet; **ii)** the characteristics of the suspension. Ethanol as liquid carrier, compared to de-ionized water for example, requires less energy to be vaporized; **iii)** the particle size distribution from which derives in part the coating pore architecture. Narrow particle size distribution will promote dense coatings whereas broad particle size distributions will promote porous coatings; **iv)** the injection conditions which aims at providing the suspension stream with a momentum density higher than the plasma flow momentum density. The higher the suspension energy density, the lower the dispersion of the fragmented droplet cloud within the plasma flow and the more homogeneous the droplet plasma treatment; **v)** the arc root fluctuations which significantly affect the suspension plasma treatment. The take-over operating mode has to be favored by selecting mono-atomic plasma gas species; **vi)** the short stand-off distance which increases the thermal transfer to the substrate and modifies in turn the coating architecture; **vii)** the kinematics which has to be optimized to reduced the stacking defect density.

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