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Editorial

Suspension and Solution Plasma or HVOF Spraying

Nanostructured materials offer significant improvements in engineering properties because their grain sizes are smaller than those of conventionally processed materials by a factor of almost 2 orders of magnitude (Ref 1). Since the mid-1990s, research has been conducted using thermal spray technology for the deposition of finely structured or nanostructured coatings (Ref 2, 3). To produce finely structured coatings by thermal spray techniques, four routes have been suggested:

- Spraying very complex alloys containing multiple elements that exhibit a glass forming capability when cooled down, with the undercooling temperature below the glass transition temperature. After deposition, upon subsequent heating in the 500 to 750 °C range, the metallic glass precursor transforms through a solid-state devitrification into multiple crystalline phases, and the resulting structures are nanoscaled (Ref 4, 5).
- Spraying conventional particles (in the 30 to 90 μm range) made of agglomerated nanoparticles. However, the operating parameter window for which particles are only partially melted (i.e., the molten part acts as a "cement" bonding unmelted nanograins) is very narrow (see the review of Lima and Marple, Ref 6). Coatings exhibit a two-scale grain-size architecture of nanograins (unmelted particles) and micrograins (melted material). These coatings have found application, for example, in thermal barrier abradable coatings made of partially stabilized zirconia.
- Spraying submicron-sized or nanosized particles via a suspension. A liquid carrier is used instead of a gas carrier (Ref 7-9). Once the suspension has been fragmented and the liquid vaporized by the plasma flow or the high-velocity oxyfuel (HVOF) flame, particles contained in the droplets are heated, accelerated, and deposited onto the substrate. They lead to the formation of splats that have equivalent diameters ranging between 0.1 and 2 μm and average thicknesses between 20 and 300 nm. The stacking of splats forms finely structured coatings. A new process consists of spraying a suspension of colloidal sol (Ref 10). It is also possible to use RF plasmas with axial injection of gas-atomized suspensions (Ref 11). RF plasmas allow high deposit purity, but the chemistry combination is difficult and nanostructure is not necessarily guaranteed. With conventional RF plasma torches, coatings are generally very porous. This can be an advantage for solid oxide fuel cell (SOFC) electrodes (Ref 12). On the other hand, when using supersonic nozzles downstream of the coil, fully dense coatings can be obtained (Ref 13).
- Spraying solutions of final material precursor. As with suspensions, the liquid undergoes rapid fragmentation and evaporation once injected into the plasma jet. This is followed by precipitation or gelation, pyrolysis, and melting resulting in the impact of molten droplets with average diameters ranging from 0.1 to a few micrometers (Ref 14-16). Here again, solutions can be sprayed with RF plasmas. It allows excellent control of chemical uniformity and stoichiometric control in a mixed or doped compound system. Functional oxide coatings have been deposited by starting from liquid inorganic precursors (Ref 17).

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In this issue, only the two last routes, suspension plasma spraying (SPS) and solution precursor plasma spraying (SPPS), are developed. Compared with conventional coatings, those manufactured from solutions or suspensions exhibit quite interesting features such as the absence of lamella boundaries, cracks, and porous microstructures along with nanometer-sized grains. Much work has been devoted to the following applications:

- Thermal barrier coatings (TBCs) (Ref 15, 16, 18-22) manufactured mainly implementing SPPS
- Solid oxide fuel cell components (Ref 7, 13, 23-26) implementing mainly SPS
- Wear-resistant coatings made of WC-Co (Ref 27) or ZrO_2-Al_2O_3 (Ref 28, 29) implementing SPS or ZrO_2-Al_2O_3-Y_2O_3 (Ref 30, 31) implementing SPPS
- Titania photocatalytic layers (Ref 32-34) implementing SPS
- SnO_2 layers (Ref 35) implementing SPPS

However, liquid injection within plasma or HVOF jets is quite different from particle injection by a carrier gas. In particular, differences exist in the fragmentation and vaporization mechanisms taking place, as well as the manner in which liquid droplets or liquid jets are produced. Indeed, mechanisms encountered in SPS or SPPS, especially with direct-current (DC) plasma jets, are by far more sensitive to arc root fluctuations than those encountered with conventional spraying. SPS/SPPS coating structures also depend strongly on liquid surface tension, viscosity, and composition. For both, particle and precursor treatment strongly depends on the location where fragmentation starts. For SPPS, the coating characteristics vary drastically with the precursor concentration and the heat and momentum transfers that droplets, resulting from liquid fragmentation, undergo. For SPS, the same dependency occurs when the influence of the precursor concentration is replaced by the suspension loading, the particle size distribution, the particle morphology, and so forth.

Numerous studies are still necessary to reach a better understanding of the involved phenomena, and for that the development of diagnostic techniques to quantify the in-flight temperatures and velocities of either the droplets or particles or to visualize the droplet/plasma interactions must be improved or developed anew.

From the viewpoint of the processes:

- The injection systems should be improved—atomizers producing calibrated streams of drops of average diameter smaller than 100 μm and with particle size and velocity distributions as narrow as possible. The flow rate should be adapted to produce layers at deposition rates acceptable from an economical point of view by industry.
- The suspension or solution surface tension and viscosity still need to be optimized (without overly increasing the quantity of energy required to vaporize the solvent). Indeed, surface tension and drop size control the fragmentation of the drops, which has to be limited in the jet fringes (except for axial injection). Moreover, potential contamination of materials by carbon from the solvents, when considering organic ones, has to be carefully studied.
- The absence of fragmentation of drops in the jet fringes, for radial liquid injection, would permit manufacture of fully dense or porosity-controlled layers.
- For SPPS, the effect of solution concentration seems to be a key parameter that has just begun to be studied.
- For SPS, the selection of the powder particle average size and size distribution (as narrow as possible) according to the plasma jet enthalpy and composition is crucial. In addition, it is necessary to minimize powder particle agglomeration. Up to now, the stabilization of metallic (Ni, for example) or cermet (WC-Co, for example) powder particles has not been thoroughly investigated.
- Plasma flow as stable as possible (for DC plasmas $\Delta V/V_{\text{mean}} < 0.2$) must be used to spray liquids.
- The spray pattern at short spray distance is also a key parameter to manufacture layers (coupling of injection parameters to kinematics) of controlled architecture.
- Coatings (mainly ceramic ones) produced up to now by SPS or SPPS present rather new and original architectures (in terms of pore network mostly) that must be studied and understood.
- The properties in service of SPS layers have been studied for thermal barrier coatings (TBCs) and exhibit interesting behaviors (for example, better resistance to thermal cycling than EB-PVD layers), but such studies have to be completed and developed at larger scales both for SPS and SPPS coatings.
- Modeling of the plasma jet interaction with the droplets, which is extremely difficult to conduct due to the very large number and the complexity of involved phenomena, must be developed.

To conclude I hope that in the future a few special issues will present the solutions developed to solve all these problems because these techniques are very promising for future industrial applications.

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