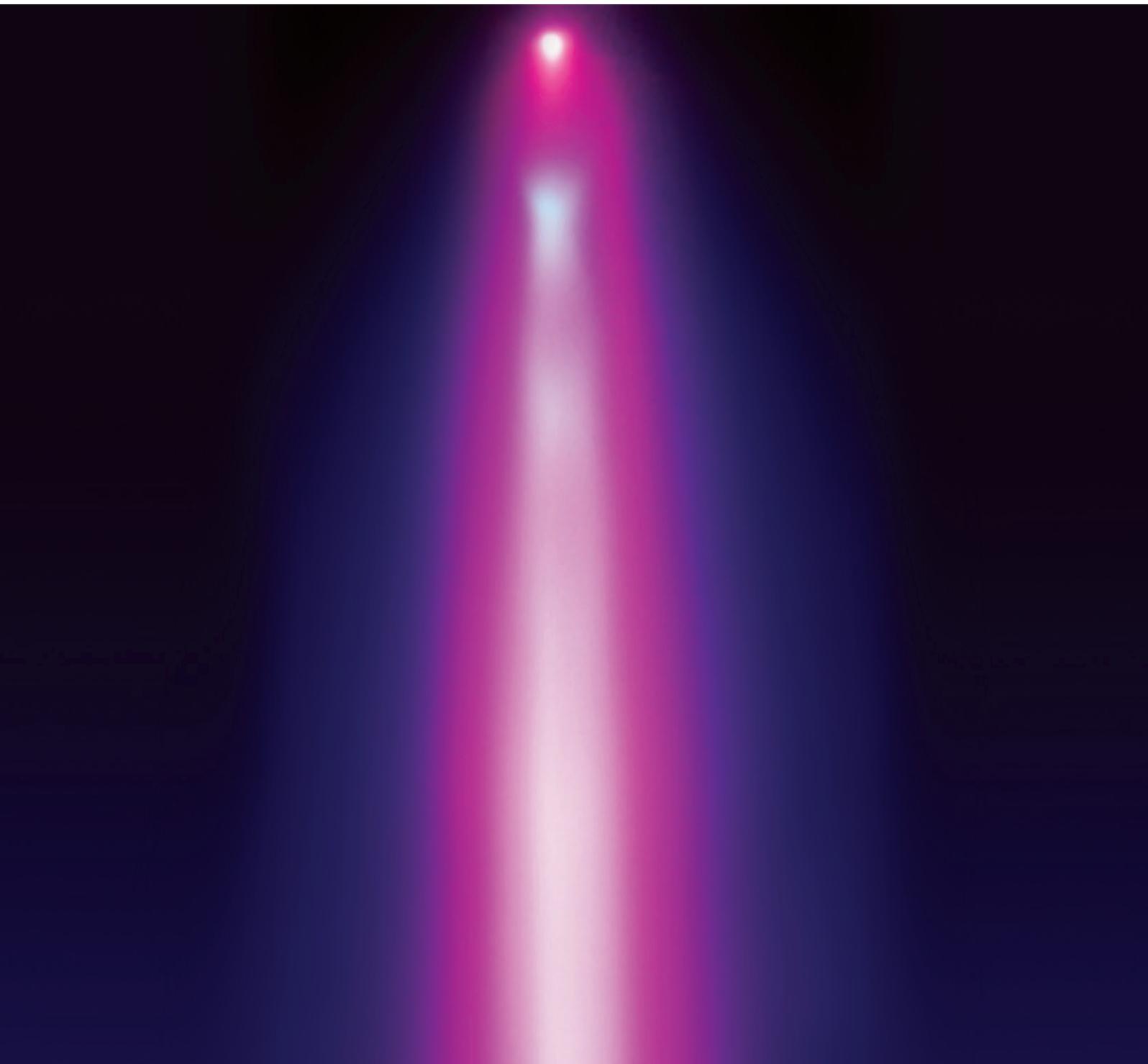


Solutions Flash

ChamPro LPPS Hybrid Technologies for application of unique, high-performance functional surfaces

SF-0014.2 – September 2016



Today's situation

Our well-established LPPS™ (Low Pressure Plasma Spray) process has been used for decades by industry to apply high quality, functional coatings on critical components for aircraft and industrial gas turbine engines, medical, and other specialized applications where coating quality and characteristics are critical. The coatings applied using the LPPS process are valued for their low levels of impurities and high densities, with structures that, in some cases, approach cast conditions. A typical coating thickness of an LPPS-applied coating is between 20 µm (0.0008 in) and 200 µm (0.008 in), although much thicker coatings are achievable. Typical chamber pressures range from 50 to 200 mbar.

The Oerlikon Metco solution

For the first time, thermal spray coatings unique structures and characteristics are achievable, extending thermal spray into previously unreachable regions. Collectively named LPPS Hybrid Technologies, Oerlikon Metco has developed three new chambered plasma spray technologies, each with unique process characteristics and that produce coatings

with unique properties and microstructures. These three new LPPS Hybrid technologies, PS-TF (Plasma Spray-Thin Film), PS-PVD (Plasma Spray-Physical Vapor Deposition) and PS-CVD (Plasma Spray-Chemical Vapor Deposition), bridge the missing gaps between traditional thermal spray coatings and thin film processes such as PVD and CVD.

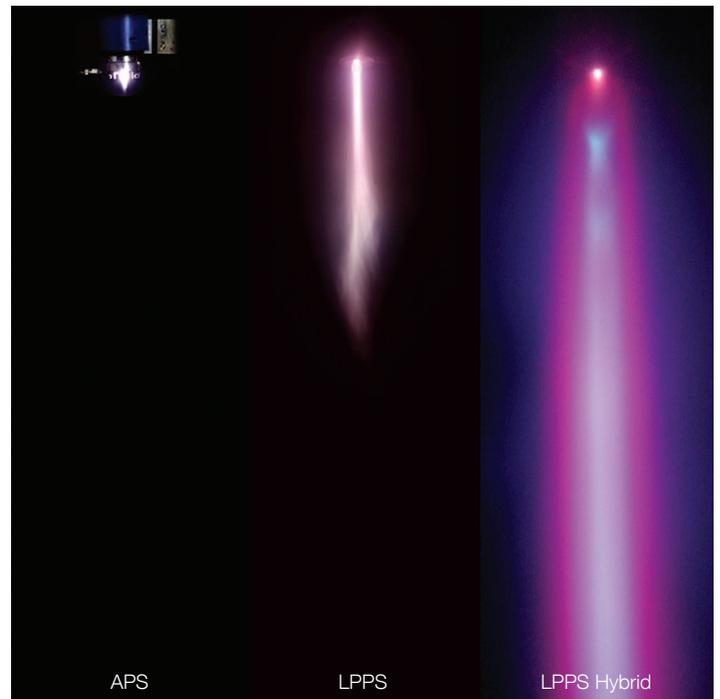
Solution description and validation

General description of LPPS Hybrid technologies

The LPPS Hybrid Technologies are an extension of Oerlikon Metco's ChamPro™ processes. Based on our long-proven and highly reliable LPPS process, an LPPS Hybrid system is designed with unique features that gives rise to the advanced process characteristics of LPPS Hybrid Technologies:

- Radically lower chamber pressures that are 50 to 100 times lower than those used for standard LPPS
- Plasma jet length as long as 2 m (6.6 ft)
- Plasma jet diameter of 200 to 400 mm (8 to 16 in)
- Plasma torch output up to 180 kW
- Capabilities to use powder feedstock materials, as well as liquid or gaseous precursor feedstocks, depending on the LPPS Hybrid Technology chosen
- Very flexible operating conditions
- Applies uniform coatings to relatively large areas

with unique properties and microstructures. These three new LPPS Hybrid technologies, PS-TF (Plasma Spray-Thin Film), PS-PVD (Plasma Spray-Physical Vapor Deposition) and PS-CVD (Plasma Spray-Chemical Vapor Deposition), bridge the missing gaps between traditional thermal spray coatings and thin film processes such as PVD and CVD.



Plasma jets at different ambient pressures: APS (atmospheric plasma spray), standard LPPS at 50 mbar and LPPS Hybrid at 1 mbar. The LPPS Hybrid plasma jet is an order of magnitude longer and significantly wider than a standard LPPS plasma jet.



A conventional plasma torch for ChamPro processes, such as the F4-VB shown on the left, has a maximum power output of 50 kW. An extended O3CP plasma spray gun, as shown on the right, as used for the LPPS Hybrid process, has a power output of 180 kW. This, combined with the low chamber pressure of the LPPS Hybrid process, give it its unique coating capabilities.

LPPS Hybrid system features

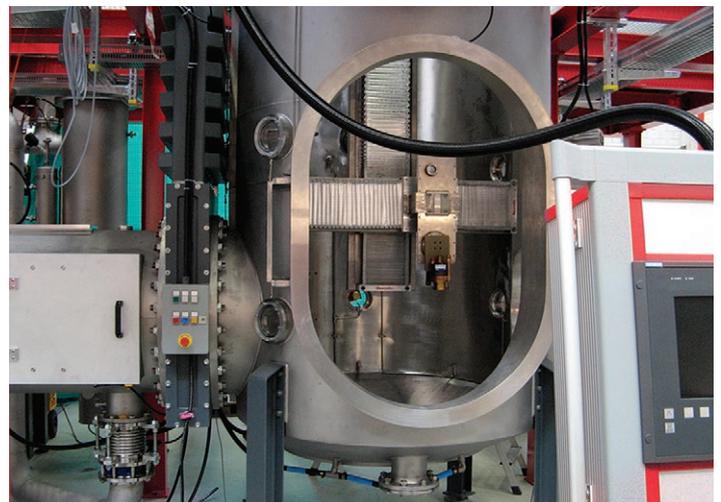
The system used for LPPS Hybrid Technologies is configured for maximum flexibility for a wide-range of applications:

- The large, vertically-oriented vacuum chamber is greater than 4000 l (282.5 ft³). The configuration of the chamber gives full advantage to the large plasma jet length, and permits large areas to be coated per coating pass.
- A separate load-lock with a sting manipulator allows parts to be loaded and unloaded quickly, without time lost to reestablish the vacuum.
- Gun movement is accomplished using a 4-axis, vertical gun manipulator, maximizing coating application flexibility.
- Spray distances from a few cm (1 – 2 in) to 1.3 m (approx. 4.25 ft) permit a wide range of coating conditions.
- A maximum of 180 kW vacuum plasma spray gun power output produces uniform coatings, even at the longest plasma jet length, and can produce a high-force plasma jet, allowing for vapor deposition capability and the coating of blind areas.
- The system configuration allows coating of large components, with large coated surface areas up to 700 x 700 mm (27.6 x 27.6 in), easily coating many different component geometries, such as turbine blades, tubes, large, flat plates, etc.
- Advanced MultiCoat™ system platform, controlling both the plasma spray and chamber environment, provides precision, flexible parameter development and superb reliability.

The system can be sized and customized with additional features to achieve the best efficiency for specific application requirements. Some of these customized features include multiple sting assemblies, preheat chambers, custom gun and part manipulation systems, sensor and monitoring equipment, etc.

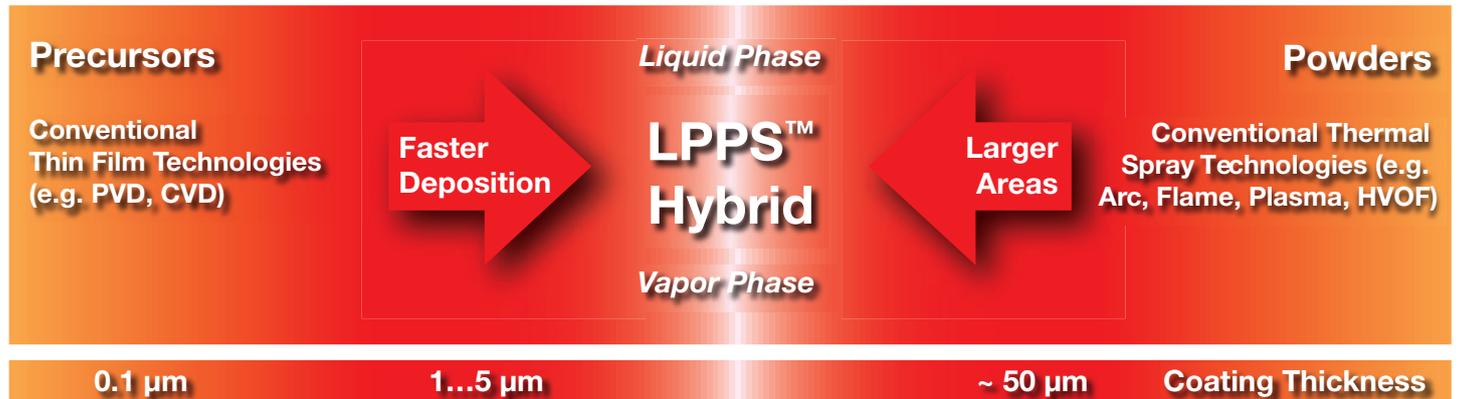


An LPPS Hybrid system with sting for part manipulation and load-lock unit.



View of the inside of the LPPS Hybrid chamber, showing the gun traverse unit.

A family of Hybrid process with unique coating regimes



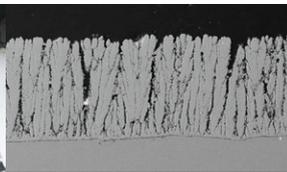
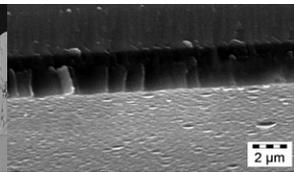
LPPS Hybrid Technologies closes the gap between PVD, CVD and conventional Thermal Spray technologies.

New coating regimes

The three LPPS Hybrid technologies are:

- **PS-TF** (Plasma Spray-Thin Film):
The PS-TF can produce thin, dense layers from liquid splats using a classical thermal spray approach but at high velocity and enthalpy.
- **PS-PVD** (Plasma Spray-Physical Vapor Deposition):
The PS-PVD process can produce thick, columnar-structured YSZ coatings (100 to 300 μm), using high gun enthalpy to vaporize specific types of feedstock materials.
- **PS-CVD** (Plasma Spray-Chemical Vapor Deposition):
The PS-CVD process uses modified conventional thermal spray components operated below 0.5 mbar to produce CVD-like coatings (< 1 to 10 μm) at higher deposition rates by using liquid or gaseous precursors as feedstock materials.

LPPS Technologies

	VPS/LPPS	PS-TF	PS-PVD	PS-CVD
Chamber pressure	50 mbar	1 mbar	1 mbar	0.5 mbar
Feedstock	Metallic powders	Metallic and ceramic powders	Ceramic powders	Liquid and gaseous precursors
State of deposit	Liquid	Liquid	Vapor	Vapor
Coating example	 MCrAlY	 LSM	 YSZ	 SiO _x

Comparison of LPPS Technologies: ■ Standard; ■ Hybrid

PS-TF (Plasma Spray – Thin Film) process description

The LPPS Hybrid Technology that is closest to standard LPPS is that of PS-TF in that it uses powder feedstock materials and applies them as classical thermal spray liquid splats onto the substrate. Where PS-TF differs, however, is that it takes advantage of the large dimension and high velocity of the LPPS Hybrid plasma jet to melt and accelerate the injected powder. Thin and dense metallic or ceramic coatings of thicknesses between 10 and 60 μm (0.0004 and 0.0024 in) can be produced quickly on large areas.

The larger spray pattern spreads the molten droplets over a wider surface on the substrate; therefore several coating passes are needed before full coverage can be attained. But this also serves to reduce the internal coating stresses and localized heat flux on the substrate.

PS-TF coatings are thinner than those produced using standard thermal spray processes, but thicker than those obtained using PVD or CVD. The coatings exhibit low porosity, with very small pores that are not interconnected.

PS-TF applications

The PS-TF process is ideal for applications where thin, dense, metallic or ceramic layers are required. Because internal coating stresses are generally low and any resulting porosity is small and not interconnected, PS-TF can be produced to create gas-tight layers for applications such as ion transport membranes.

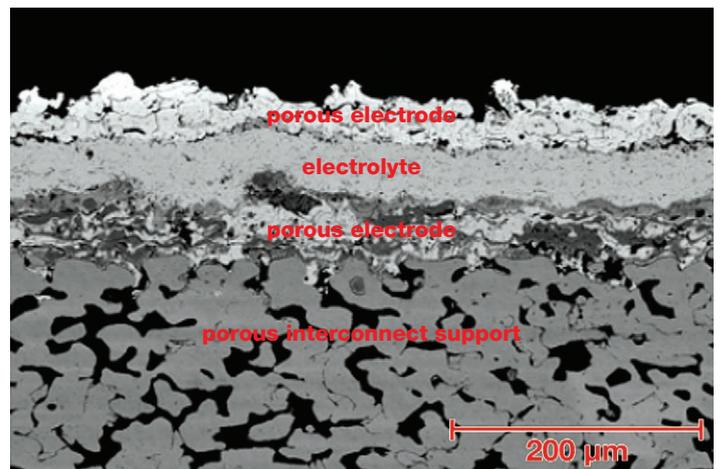
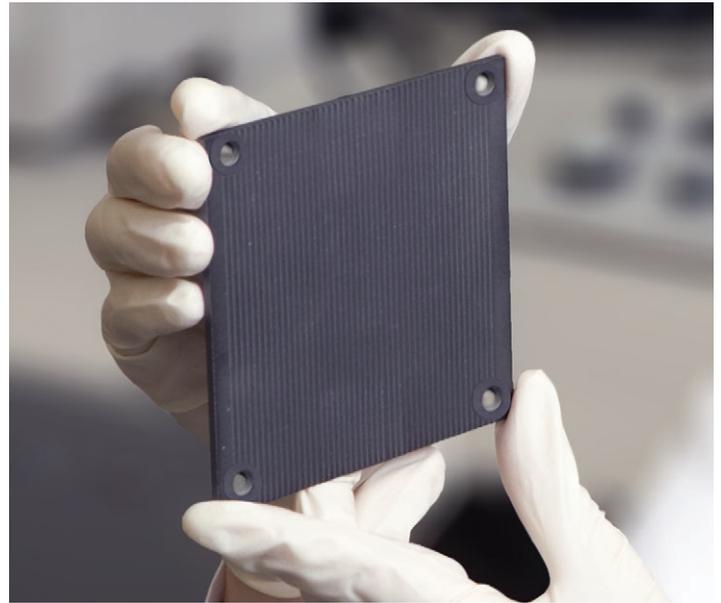
PS-TF coatings for Solid Oxide Fuel Cells (SOFC)

Solid Oxide Fuel Cells (SOFC) stack several thin ceramic layers—an anode layer, an electrolyte layer and a cathode layer—to form a single cell. Hundreds of these cells are connected in series to form an ‘SOFC stack’. Interconnects support the individual cells and allow fuel to reach the anode and oxidant to reach the cathode.

The structure, the purity, the quality and the uniformity of the ceramic layers is critical to the overall function and efficiency of the cell. While the anode and cathode are porous, electrically conductive layers respectively oxidize the fuel or reduce the oxidant, the electrolyte is an ion transport layer that should be gas tight. This layer must be very dense and without interconnected porosity to prevent leakage of the gases between the anode and the cathode. At the same time, the thinner this layer is, the higher the efficiency of the fuel cell.

With market demand for SOFCs rising exponentially, production methods that can reliably and cost effectively manufacture the individual cells in ever-increasing quantities is of high priority.

The use of LPPS Hybrid to apply the YSZ electrolyte layer and a dense LSM (lanthanum-strontium-manganate) diffusion barrier layer on the interconnect to effectively prevent chromium depletion of the interconnect substrate meet both stringent technological requirements and offers the commercial benefit of cost-efficient mass production.



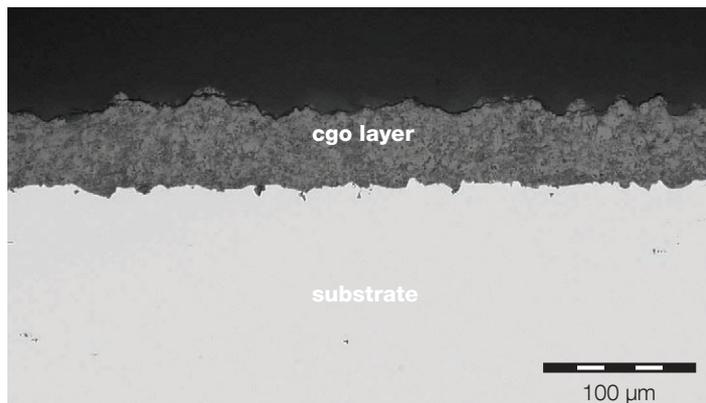
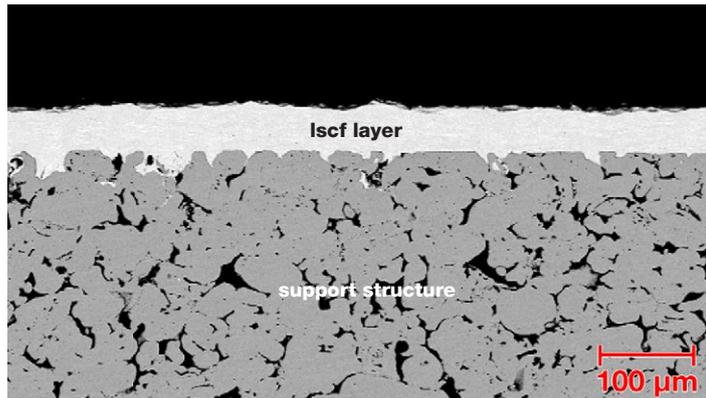
Top: A SOFC interconnect with an LSM coating. Bottom: cross-section of a multilayer system of a thermally sprayed SOFC. PS-TF applied electrolyte layer forms a gas-tight, ion transport membrane between the porous electrolyte layers.

Selective Ion Transport Membranes (ITM)

The promise of fuel cells notwithstanding, the use of fossil fuels for power generation remains ubiquitous. To reduce greenhouse gas emissions, the fuel is burned in an oxygen-rich environment, instead of air. The resulting combustion products, CO₂ and water can be reused to drive other power-producing equipment, or sequestered. However, oxygen production is a rather energy intensive proposition.

Oxygen-selective ITMs are proving to be a more efficient, less energy-intensive means of oxygen production. The use of PS-TF to produce perovskite LSCF (LaSrCoFeO) layers is showing excellent potential for this application. Thin, leak-tight layers have been demonstrated to efficiently transport oxygen. Further, PS-TF allows these layers to be applied rapidly to relatively large areas, thereby cost effective to produce.

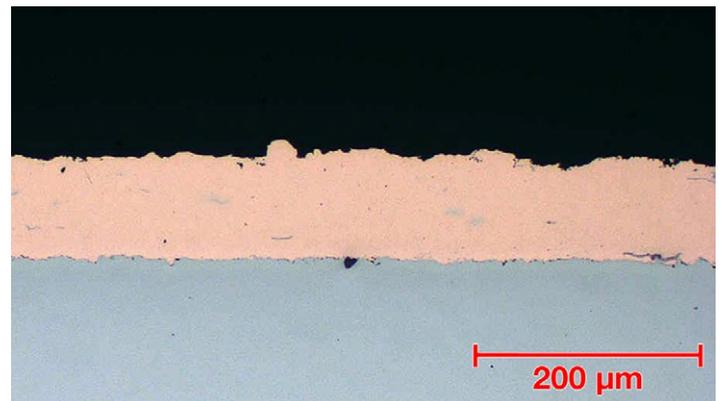
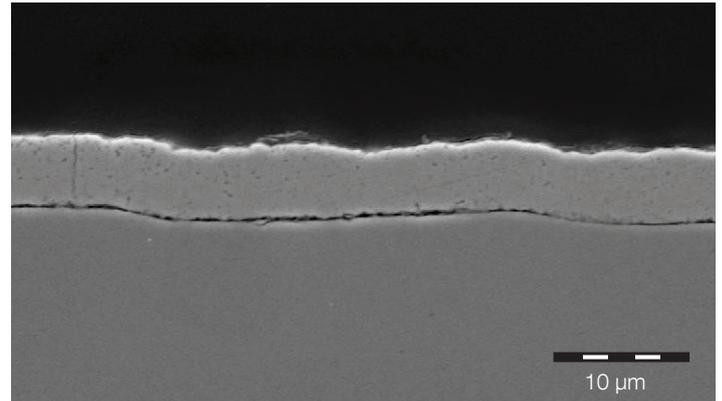
LSM (LaSrMnO) and CGO (CeGdO) applied using PS-TF have also proven successful for ion transport membrane applications.



Photomicrographs of PS-TF coatings for ITM applications. Above: LSCF coating on a porous metallic substrate, 40 μm (0.0016 in) thick. Below: CGO coating, 60 μm (0.0024 in) thick. In both cases, the coating is gas tight and of uniform thickness.

Metallic PS-TF coatings

Metallic coatings applied using PS-TF have little or no porosity. In fact, coating characteristics can approach as-cast conditions. Such coatings can be applied for various corrosion or electrical applications. Furthermore, PS-TF can apply coatings very quickly. For example, a zinc or zinc alloy coating for corrosion resistance can be applied 10 – 15 μm (0.0004 – 0.0006 in) thick on a 1 m² (10.8ft²) area in a few seconds.



Metallic PS-TF coatings. Above: A dense and smooth 10 μm (0.0004 in) zinc alloy deposited onto steel sheet. Below: A dense 100 μm (0.004 in) copper coating.

Summary of LPPS Hybrid PS-TF features

- The high kinetic energy and large plasma jet of the LPPS Hybrid process allows the application of dense and thin coating layers.
- Uniform coating thickness on thin and large substrates.
- Coatings are applied with minimal internal coating stresses.
- Low heat flux to the substrate prevents substrate deformation.
- Thin, high integrity coatings can be applied very quickly, often in just a few seconds or minutes per coated part.
- Capable of applying both metallic and ceramic coatings.
- Coatings applied are high purity.
- Uses readily available powder feedstock materials (fine particle size distributions are generally required), many of which can be supplied by Oerlikon Metco.
- Very thin electrolyte or other ITM layers can be applied on porous metallic and ceramic substrates with excellent results and full coverage.
- Applied electrolytes or ITMs are gas-tight, improving efficiency.

PS-PVD (Plasma Spray – Physical Vapor Deposition) process description

Another LPPS Hybrid process is PS-PVD. It uses a high energy plasma gun operated at chamber pressures of 1 mbar. The combination of high energy and reduced work pressure allows PS-PVD to either melt the powder feedstock material for deposition as liquid splats or vaporize the feedstock material for deposition as a condensate. Thus, the PS-PVD process fills the gap between conventional physical vapor deposition (PVD) technologies and standard thermal spray processes.

The possibility to vaporize feedstock material to produce layers results in new and unique coating microstructures. The properties of such coatings are superior to those of thermal spray and electron beam – physical vapor deposition (EB-PVD) coatings. In contrast to EB-PVD, the PS-PVD process incorporates the vaporized coating material into a supersonic plasma plume and is transported with a high flow onto the substrate. As a result of the forced gas stream of the plasma jet, parts with complex geometries such as multi-airfoil

turbine vanes can be coated with columnar thermal barrier coatings using PS-PVD. Even shadowed areas and areas that are not within the line of sight of the coating source can be coated with a homogeneous structure.

PS-PVD applications

Thermal Barrier Coating (TBC) solutions

Conventional thermal sprayed TBC coatings exhibit good thermal conductivity properties and are widely used. However, stresses within the coating caused by extreme operating temperatures and repeated thermal cycling limit the durability of the coatings in service.

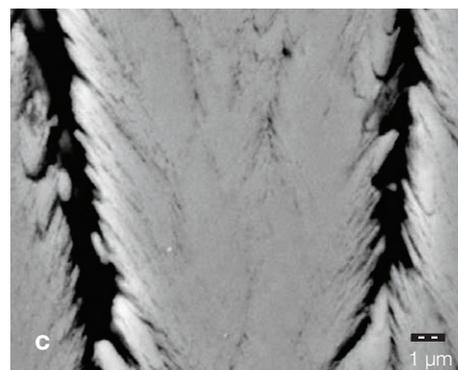
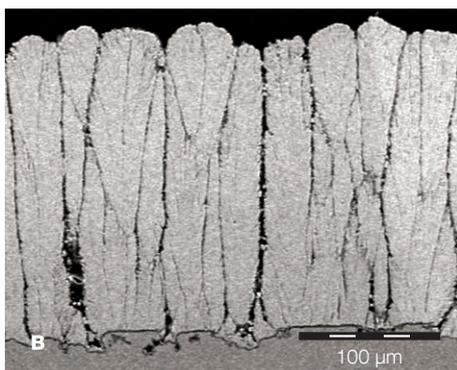
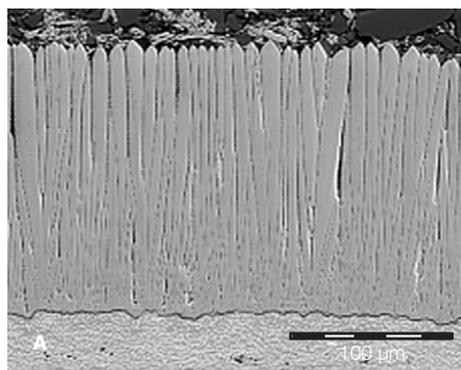
TBC coatings applied using EB-PVD have a specific columnar structure that is more strain tolerant at these high temperatures and stresses.

The drawbacks of conventional PVD processes are the high investment costs and the low deposition rates. For these reasons, this technology is mainly used for mass production of thin film applications or to produce thick TBC coatings on high-value, critical components such as hot-section turbine vanes for aircraft or industrial gas turbine engines.

However, conventional PVD is a line-of-sight process. Hence, only surfaces that are directly within the path of the coating source can be coated. Therefore, components with complex geometries and shadowed areas are very difficult to coat homogeneously.

Columnar structure formation: The high energy utilized with the PS-PVD coating process can vaporize the injected YSZ (yttria-stabilized zirconia) coating material to produce columnar TBC coating structures similar to those produced using the EB-PVD coating process.

The advantages of the PS-PVD process is that it can apply these columnar TBC coatings at a significantly higher deposition rate, and it can coat complex geometries with non-line-of-sight surfaces in one coating run. Both factors save cost and processing time.



SEM Photomicrographs of columnar-structured yttria-stabilized thermal barrier coatings A) Typical EB-PVD coating (courtesy of U. Schulz, DLR, Inst. of Materials Research, Cologne, Germany) B) A vapor-phase deposited, PS-PVD coating with a thickness of 150 μm (0.0059 in) on an MCrAlY bond coat. C) A magnified view of the columnar structure shown in image B.

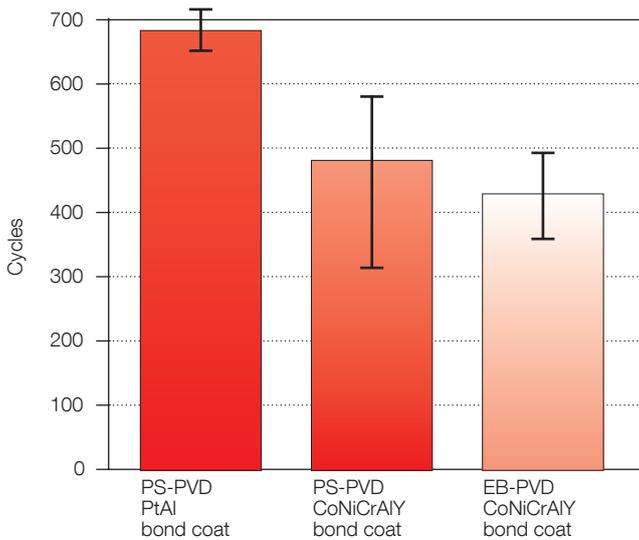
Comparative test results: Optimized columnar structured PS-PVD TBC coatings have been laboratory tested to compare them with EB-PVD.

The PS-PVD coatings exhibit outstanding endurance in furnace cycle testing, in some cases exceeding that of EB-PVD coatings.

Thermal conductivity testing also indicate that the PS-PVD coatings have a very low, stable thermal conductivity of 0.8 W/m·K (0.462 Btu_{IT}-ft/hr·ft²·°F).

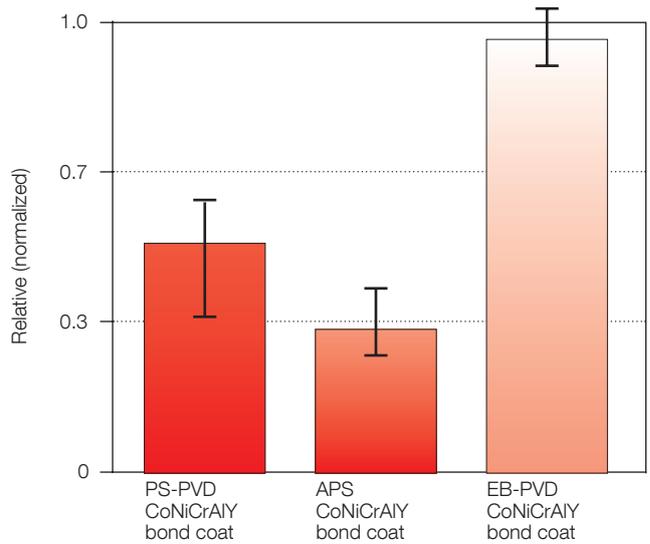
While the erosion resistance of PS-PVD coatings is significantly lower than those produced using EB-PVD, it is comparable, and even higher than the erosion resistance of atmospheric plasma sprayed (APS) TBC coatings with a ceramic top coat porosity of 15%.

Overall, these test results are quite favorable, indicating that PS-PVD coatings can provide excellent in-service results, in addition to potentially reduced coating application costs.



Furnace cycling testing

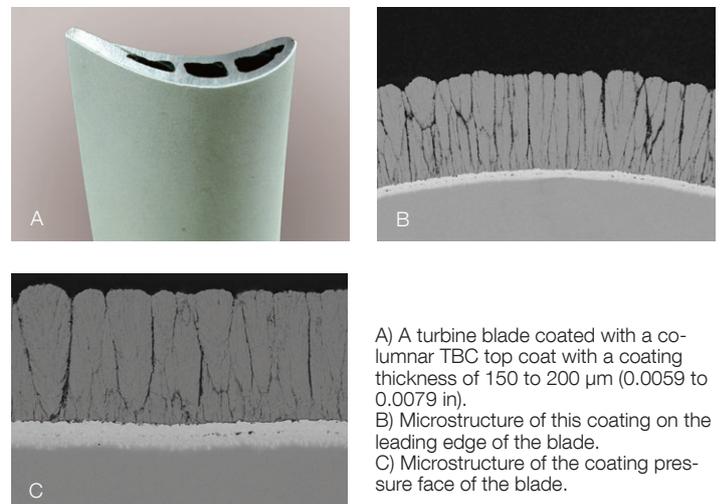
In atmosphere from room temperature to 1135 °C (2075 °F). Heat-up time = 6 min, hold time = 50 min, cool-down time = 4 min. The cycle is interrupted once each 24 h for 4 h at room temperature.



Erosion testing

Performed in accordance with GE Specification E50TF121

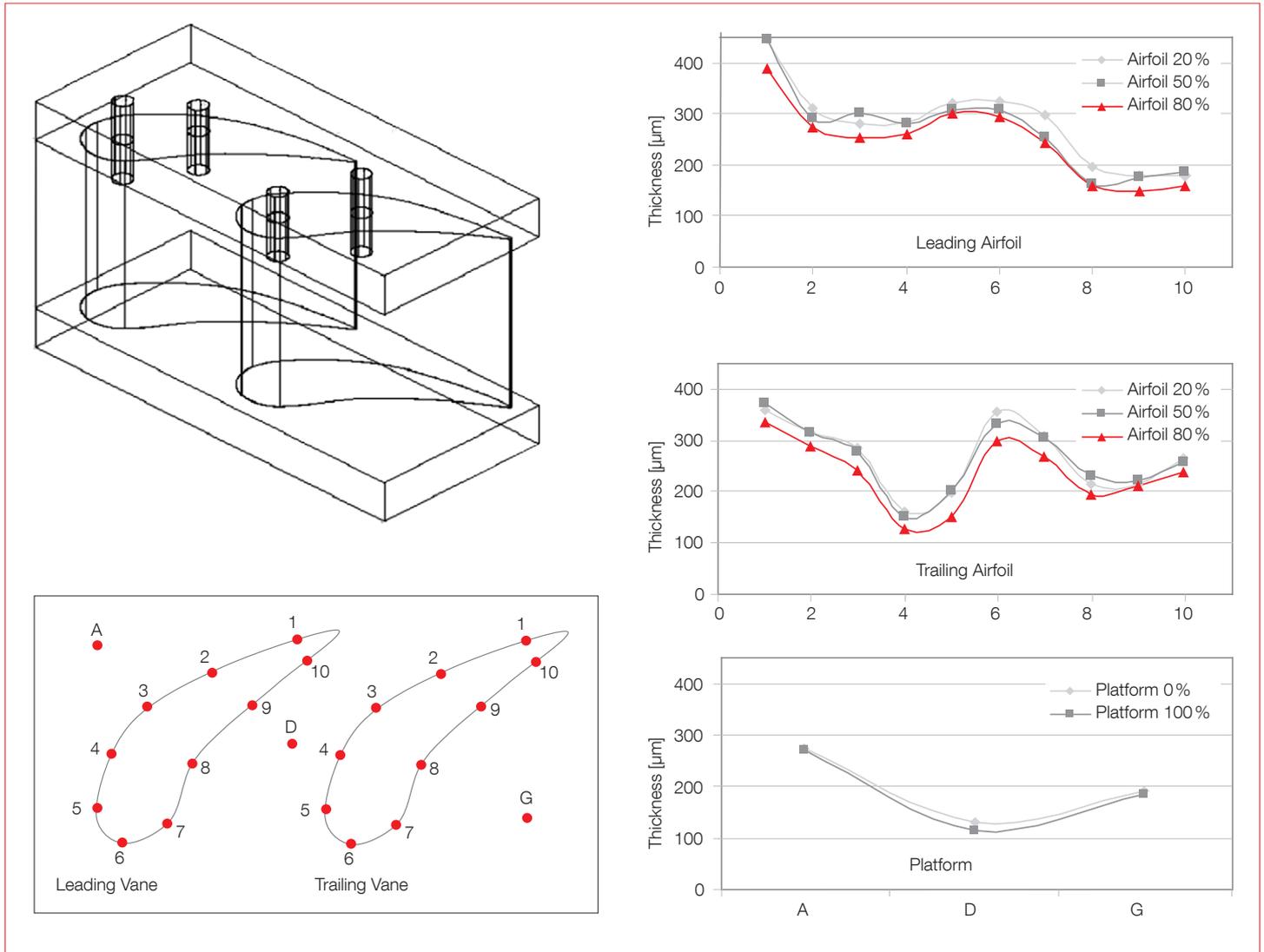
Uniform coating thickness: Simple gun and part motions ensure a homogeneous temperature distribution over the target surface. This, combined with a long broad plasma jet and low chamber working pressure ensures that coatings can be applied uniformly on large surfaces and on components with complex geometries.



Coatings on shadowed and blind surfaces:

Unlike conventional PVD processes, the PS-PVD process can coat areas that are not within the line of site of the coating source. Therefore, for many coating applications it

is possible to coat all surfaces, including shadowed and blind surfaces, in a single coating run, without the need for time-consuming part repositioning.



PS-PVD coating of a dummy turbine vane doublet for thickness measurements. Top-left: diagram of vane doublet. Bottom-Left: Thickness measurement points on the airfoils (numbered points) and platform (lettered points). Right: graphed results of thickness measurements showing coating thickness consistency. Three sets of measurements were taken along the vertical axis of the leading and trailing airfoils. Lower (0%) and upper (100%) platform thicknesses were measured.

Summary LPPS Hybrid PS-PVD features

- The high energy plasma gun operated at low chamber pressures can apply coatings as liquid splats, as a condensate from a vapor phase, or as a combination of both.
- Coating deposition rates are significantly faster than deposition rates achievable using EB-PVD, reducing processing time and coating costs.
- Lower capital investment than EB-PVD.
- Creates columnar structured YSZ TBC coatings.
- Resulting TBC coatings have higher resistance to thermal cycling than EB-PVC coatings, excellent thermal insulation characteristics and erosion resistance better than atmospheric plasma spray TBC coatings.
- Applies coatings of uniform thickness and structure, even on large flat areas and complex geometries.
- Non-line-of-site process can apply coatings to shadowed and blind surfaces in a single coating run eliminating time-consuming part repositioning and multiple coating runs.
- Uses readily available powder feedstock materials (fine particle size distributions are generally required), many of which can be supplied by Oerlikon Metco.

PS-CVD (Plasma Spray – Chemical Vapor Deposition) process description

Unlike the higher energy LPPS Hybrid processes, PS-CVD uses a plasma gun operating at low power (< 10 kW), low gas flows and low pressures with liquid or gaseous precursor materials to create a vapor out of chemical reactions that is propelled towards the substrate to be coated.

When liquid precursors are used, they are injected in the plasma gun, downstream of the point of plasma arc generation. When gaseous precursors are used, they can be injected in the gun or downstream into the plasma jet using a gas injection ring, or both.

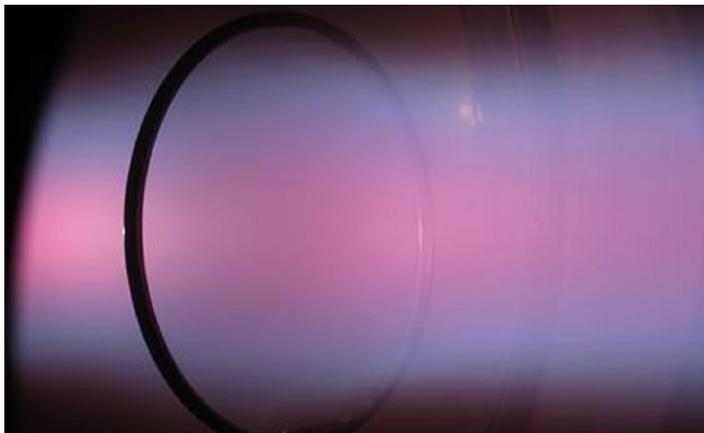
While low power, PS-CVD takes advantage of the high enthalpy and high ionization rate of the plasma jet to produce the deposition vapor, and new unique chemistries are possible.

Full-coverage coating thicknesses from 0.3 to 10 μm (12 to 400 μin) are possible, depending on the chemical composition of the vapor. Deposition rates are much higher than conventional CVD processes, making this a cost effective means of coating application when thin, sub-micron dense coatings are required.

PS-CVD applications

One of the most promising applications for PS-CVD is the application of silicon oxide (SiO_x) films. Thin, non-porous SiO_x films are valued for their chemical resistance, optical transparency, electrical insulation characteristics and compatibility with crystalline silicon substrates. As such, they have many applications in microelectronics and optoelectronics.

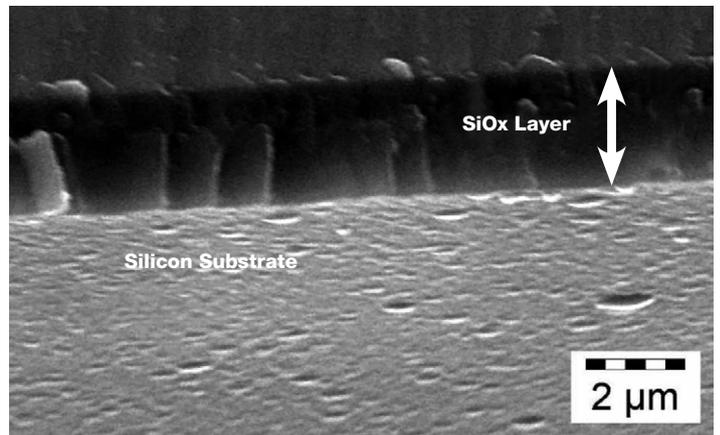
PS-CVD can be used to create such films on silicon wafers or steel components with diameters as large as 500 mm (19.7 in) using hexamethyldisiloxane (HMDSO or $\text{C}_6\text{H}_{18}\text{OSi}_2$) in an oxygen-enriched plasma jet. Such coatings have been applied at rates up to 35 nm/s (1.38 $\mu\text{in}/\text{s}$) with deposit efficiencies of about 50%.



The PS-CVD process exhibits a large, diffuse plasma jet with high enthalpy and high ionization rates. Note the injection ring for gaseous precursors.

Steel and zinc test coupons encapsulated in a PS-CVD-applied SiO_x film of about 2 μm (80 μin) demonstrated no corrosion after 3000 h in standard salt spray tests. Such coatings, which are hydrophobic in nature, could find use in applications such as solar panels where high deposition rates over large areas are needed.

Other possibilities for films applied using PS-CVD include the application of thin films of pure metals such as silver, aluminum or copper. Thin films of metallic oxides can also be applied. For example Al_2O_3 can be applied for electrical insulation or ZnO applied as a transparent-conductive oxide (TCO) film. The low energy of the PS-CVD process permits temperature management of the substrate during the coating process giving rise to the production of thin, homogeneous films on glass, wafers or thin metallic foils.



A film of SiO_x , approximately 2.5 μm (100 μin) thick, applied to a silicon substrate using PS-CVD.

Summary LPPS Hybrid PS-CVD features

- Uses a low power plasma gun (< 10 kW) with low gas flow rates and low chamber operating pressures.
- Uses liquid or gaseous precursors that chemically react with other feedstock elements or compounds to create the deposited chemistry.
- The plasma jet contributes high enthalpy and high ionization rates to drive chemical reactions.
- Applies uniform, full-coverage films with coating thicknesses of 0.3 to 10 μm (12 to 400 μin).
- Temperature-sensitive substrates can be coated, such as glass or metallic foils.
- Coats parts with diameters up to 500 mm (19.7 in).
- Faster application rates than conventional CVD processes, with good deposit efficiencies.

LPPS Hybrid customer benefits

Effective

- A family of processes (PS-TF, PS-PVD and PS-CVD), each of which offer uniquely flexible operating characteristics for a wide range of coating applications.
- Technology that “bridges the gap” between conventional thermal spray processes and standard thin film processes.
- Combinations of LPPS Hybrid Technologies can be used to produce new types of coatings.
- Some coatings applied using the LPPS Hybrid process outperform coatings applied using their thin film counterpart processes.
- Oerlikon Metco offers contract coating services for development or prototype work, with access to our LPPS Hybrid experts.

Environmental

- Use of sophisticated online sensor technology aids coating development and ensures the plasma environment is controlled within a tight process window.
- Chambered process with full filtration package keeps the environment clean and safe.
- High level of safety built into the system components.

Efficient

- Proven technology, based on our ChamPro LPPS design, is very reliable and fully supported by Oerlikon Metco.
- MultiCoat system platform controls the plasma process and chamber environment with excellent precision and reproducibility.
- Systems can be configured to maximize the production efficiency of specific coating applications.

Economical

- May apply coatings faster and at lower cost than comparative coatings produced by thin film processes such as PVD and CVD.
- Initial capital investment can be lower than comparable thin film coating equipment.
- Can be used for mass production applications.
- Coating applications using powdered feedstock materials are often available from Oerlikon Metco at competitive prices.

Contact Oerlikon Metco for more information on the benefits of LPPS Hybrid Technologies to apply unique thermal spray coatings for your application.

Information is subject to change without prior notice.

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