oerlikon metco

Solutions Flash

Thermal Spray coating solutions for solid oxide fuel cells
Perovskite coatings ■ Dense, thin electrolytes ■ Insulating layers

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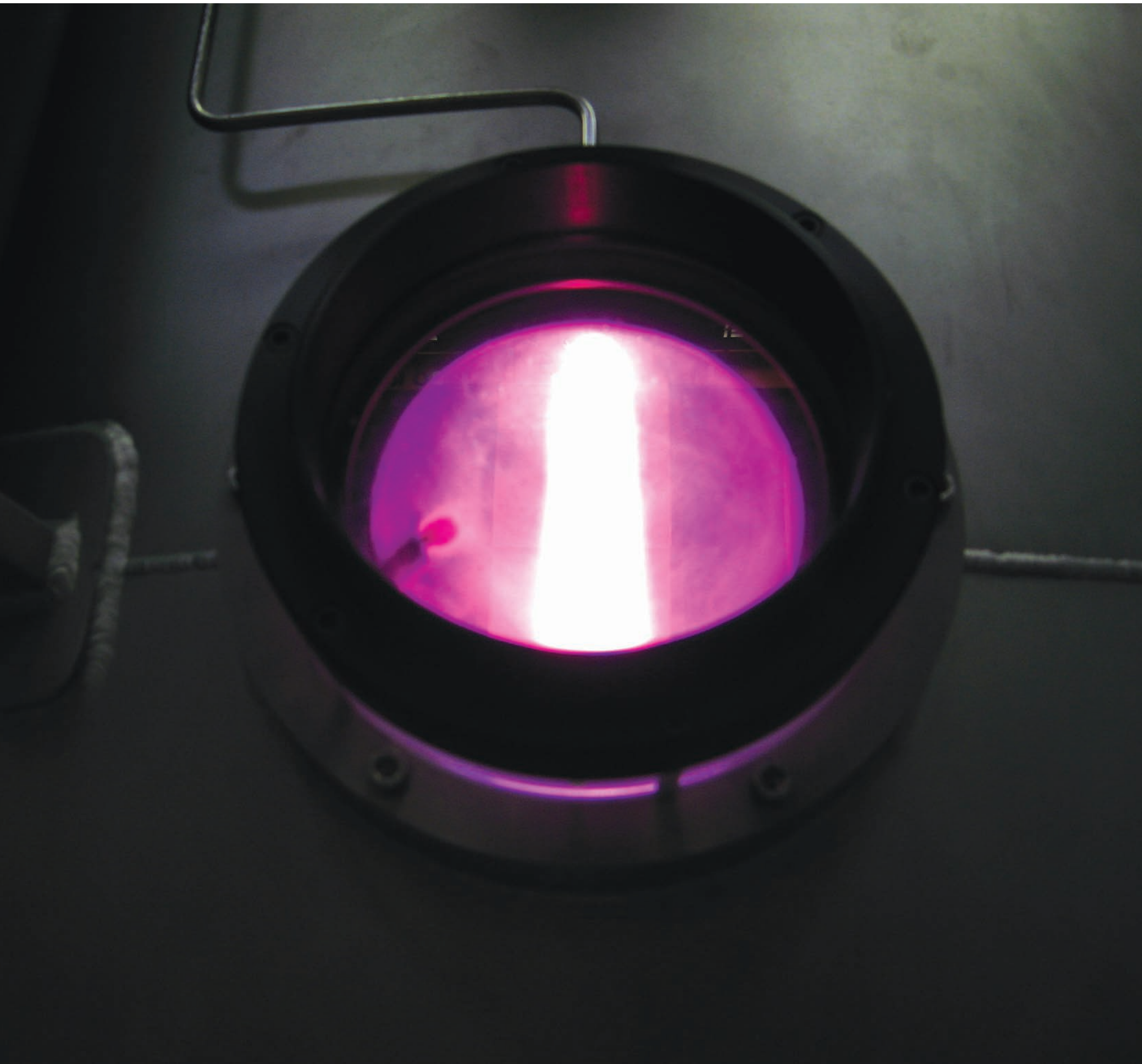


Today's situation

Fuel cell technology brings the promise of a more eco-friendly energy source as a result of lower and cleaner emissions, and improved economics through high output efficiencies. These devices are electrochemical in nature, meaning that they convert fuel directly into electricity. The common types of fuel cells, named for the type of electrolyte they employ, are phosphoric acid (PAFC), molten carbonate (MCFC), proton exchange membrane (PEM) and solid oxide (SOFC). Because of their different materials and operating temperatures, they have varying benefits, applications and challenges, but all share the potential for high electrical efficiency and low emissions.

Solid Oxide Fuel Cells operate at high temperatures between 600 and 1000 °C (1112 and 1832 °F). Of all types of fuel cells, SOFCs deliver the highest electrical efficiency of about 50 % (Figure 1). As they do not use a catalyst, they can be designed to use various types of fuels, making them very flexible for a variety of applications.

SOFCs have been developed for applications such as:

- Distributed Power Generation
- Combined Heat and Power (CHP): Micro and Industrial
- Auxiliary Power Units (APU) for the transportation market
- The success of the SOFC depends, to a large extent, on coatings, and cost-effective thermally sprayed coating solutions have already proven to be important tools to improve the lifetime and efficiency of SOFCs:

Insulating layers to improve thermal cycling behavior

Plasma sprayed insulating layers, in combination with metal solder, have the potential to significantly improve the thermal cycling behavior of a stack compared to conventional solutions using glass solder.

Prevention of chromium evaporation from interconnects

To prevent degradation of the cell and extend the useful service life, functional coatings are applied to the chromium-based interconnect. Atmospheric plasma sprayed coatings have the potential to provide excellent technical and cost-effective industrial solutions to protect the cathode from chromium poisoning.

Dense, thin electrolytes – the key for success

The electrolyte of a SOFC must be absolutely dense and as thin as possible to attain a highly efficient and powerful cell. For metal-supported cells, where sintering of the electrolyte is not an option, plasma sprayed coatings offer a viable solution.

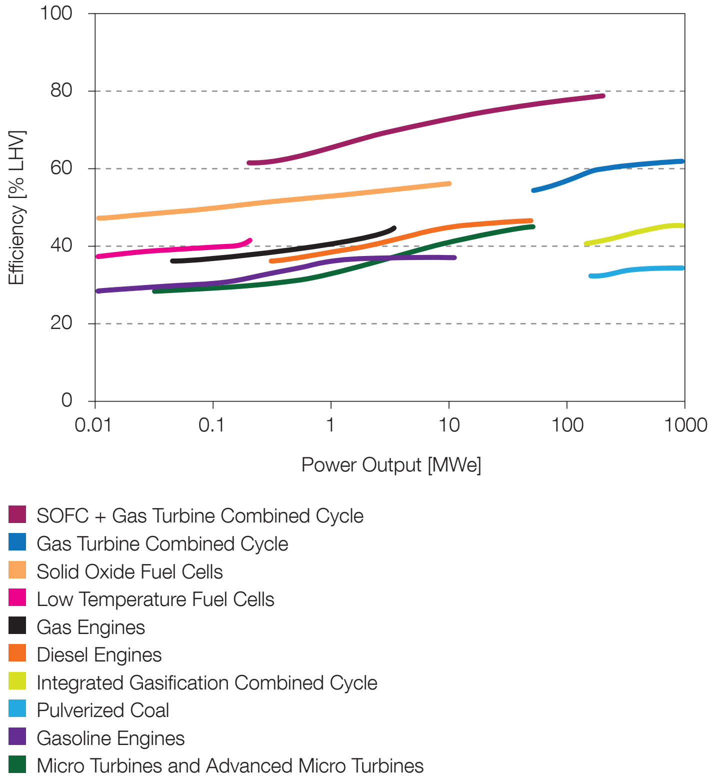


Figure 1. Efficiency of different power generation systems.
(source: California Advanced Reciprocating Internal Combustion Engines Collaborative, Workshop Proceedings, July 2001)

The Oerlikon Metco solution

Oerlikon Metco has developed high efficient coating solutions for various functional layers on SOFC components using new thermal spray technologies. Perovskite coatings, insulating layers and porous electrode layers can be effectively deposited by means of Atmospheric Plasma Spraying (APS) and the TriplexPro™-210 plasma spray gun. Moreover, Oerlikon Metco's PS-TF (Plasma Spray-Thin Film) process produces cost-effective, very dense and thin electrolyte coatings of yttria-stabilized zirconia (YSZ).

Solution description and validation

Oerlikon Metco SOFC material solutions

Oerlikon Metco has a long history for development and in-house manufacture of unique, high quality materials for specialized markets. For SOFC applications, we offer a broad portfolio of stocked and made-to-order ceramic powders designed to very stringent standards. Included in this portfolio are the following materials, all of which can be adjusted to meet specific customer needs:

Products available in production quantities

Type	Product	Chemistry	Particle Size
LSM	Metco 6800	$(La_{0.8}Sr_{0.2})_{0.98}\,MnO_{3-\sigma}$	-45 +15 µm
	Metco 6801		-53 +22 µm
YSZ	Metco 6613	8mol% YSZ	-20 µm
LSCF	Metco 6830	$La_{0.6}\,Sr_{0.4}\,Co_{0.2}\,Fe_{0.8}\,O_3$	-25 +5 µm
	Metco 6830A		-45 +15 µm
	Metco 6831	$La_{0.78}\,Sr_{0.4}\,Co_{0.2}\,Fe_{0.8}\,O_3$	-25 +5 µm
	Metco 6831A		-45 +15 µm
MCO	Metco 6820	$Mn_{1.5}\,Co_{1.5}\,O_4$	-45 +15 µm

Products available in experimental or pilot quantities

CGO	MCF
LSCC	ScSZ (Ce doped)

Overview of thermal spray application technologies for SOFC solutions

TriplexPro-210 Plasma Spray Technology

The TriplexPro-210 is a universal, all-purpose plasma gun that incorporates three essential design elements:

- Cascaded arc chamber
- Divided arc current
- Use of standard, exchangeable nozzles and adjustable three-port powder injection

Together, these features make the TriplexPro-210 the most versatile gun on the market today.

Cascaded arc chamber

Over 20 years ago, Oerlikon Metco pioneered the cascaded anode approach to control and stabilize the arc voltage. Oerlikon Metco has now refined and enhanced this fundamental technology in the design of the TriplexPro-210. The key benefits of a cascaded anode gun are:

- Higher voltage, lower amperage operation
- A large reduction of power oscillation
- Reduction of the influence of gas flow and type on the arc behavior

The cascade fixes the length of the electric arc and provides the arc with a starting path over a series of electrically neutral rings (neutrodes) within the arc chamber. Once the gun is ignited, only the common front anode (nozzle) is electrically connected to the power supply. The fixed arc length stabilizes the plasma plume and eliminates the very high amplitude power oscillations in the 3 to 5 kHz range that are inherent in plasma guns without arc stabilization. As the amplitude and frequency of the oscillation is directly linked to the heating and flight path of each powder particle, the stable plume produced by the TriplexPro-210 significantly increases deposit efficiency and the consistent quality of the coating.

Figure 2. A) TriplexPro-210 and B) detailed view inside the torch of the cascaded arc design and divided arc current

Divided arc current

The TriplexPro-210 divides the total current equally between three electrodes, which provides the key benefits of improved gun component life and coating processing rates through:

- Uniform heating of the plasma gas
- Less erosion of the anode at arc attachment points
- Defined location of arc attachments
- Three arcs operating at a higher overall voltage have the advantage of stable gun operation over longer periods

The three arcs of the TriplexPro-210 have a magnetic repulsion separation of 120 degrees, which generate a symmetrical plume with defined zones of preferred powder injection.

Exchangeable nozzles

The TriplexPro-210 can operate with different nozzles, injectors and injector holders to maximize the usable range of the gun: Each nozzle is designed for a specific function and can be easily exchanged. Oerlikon Metco has leveraged the design freedom resulting from the unique arc control design of the gun by offering nozzles that cover the normal parameters as well as extended parameter ranges for unique operational conditions as shown in Figure 3. The stability offered by three distinct plasma arcs permits a wide variety of uniform plasma plumes as shown in Figure 4. As the arc attachment for these plumes are always at the same location, powder injection conditions are reproducible, very stable and can be adjusted to optimize a given spray parameter.

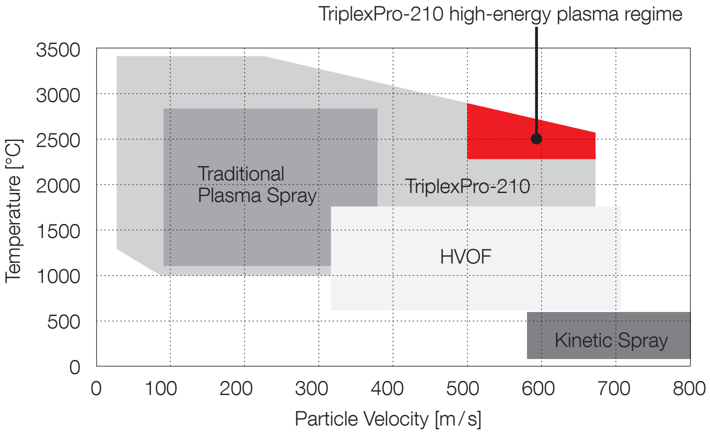


Figure 3. Particle velocity vs. particle temperature diagram that shows the broad application range of the TriplexPro-210 vs. other thermal spray processes and traditional plasma spray.

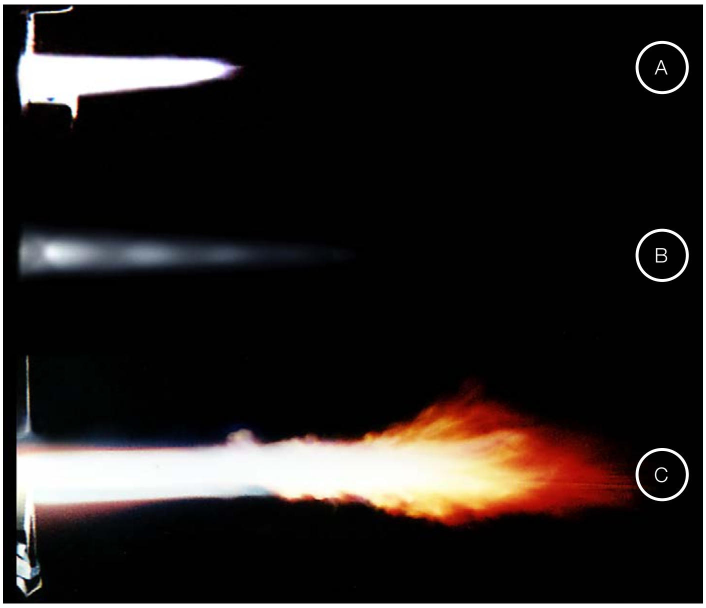


Figure 3. The versatility of the TriplexPro-210 Plasma Spray Gun is demonstrated by these very different plasma jets. A) Standard jet with 9 mm nozzle, B) High velocity jet [> mach 1], C) High enthalpy jet.

The benefits of TriplexPro-210 technology for SOFC applications

In addition to the various coating functions that include

- Insulating function (dense layer)
- Prevention of chromium-evaporation (dense layer)
- Plasma sprayed anode or cathode (porous layer),

the quality and reproducibility of the coatings produced using TriplexPro-210 technology are very important criteria for SOFC applications. In addition, it is essential that the layers will not be contaminated during the process, such as that which could occur by metal transfer from the gun's electrode or nozzle.

The main features of the TriplexPro-210 technology are:

- Stable arcs with defined location of arc attachment that are constant and reproducible relative to the powder ports
- Higher voltage and lower amperage operation for a considerably reduced rate of nozzle erosion at the arc attachment points
- Higher feed rates and deposit efficiencies, reducing processing cost and time,

The combination of these features can be considered a quantum leap in plasma spray and make the TriplexPro-210 an ideal tool for SOFC applications. With several hundred thousand SOFC interconnects currently coated per annum with a LSM layer using the TriplexPro-210, this technology is to be an important contributor to the SOFC industry by making the cells more efficient, reliable and economical.

LPPS Hybrid technologies

The Oerlikon Metco LPPS™ (Low Pressure Plasma Spray) technology is well-established as a versatile coating tool for various industrial applications, such as medical, aero gas turbines and industrial gas turbines. New LPPS Hybrid Technologies takes this further with placement between the conventional thin film processes, such as PVD and CVD, and the conventional thermal spray processes as illustrated in Figure 5. Using radically lower work pressures (50 to 100 times lower than traditional LPPS), the properties of the plasma jet differ distinctly from the standard LPPS regime. The plasma jet is extended to a length of more than 2 m (6.6 ft) and a diameter between 200 and 400 mm (7.9 and 15.7 in), as shown in Figure 6.

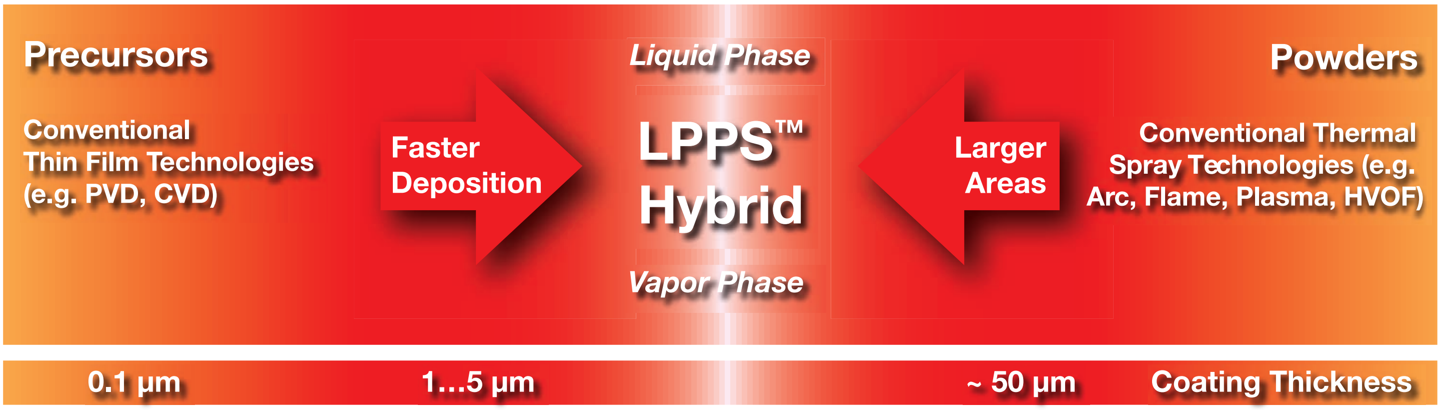


Figure 5. LPPS Hybrid technologies closes the gap between PVD, CVD and conventional Thermal Spray technologies.

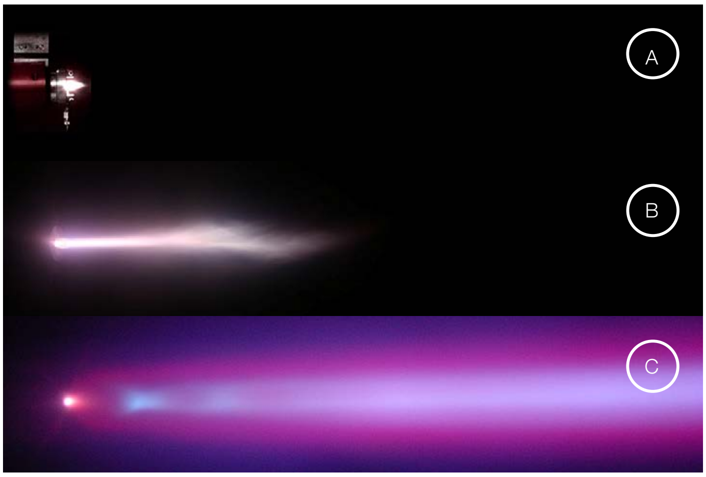


Figure 6. Plasma jets at different ambient pressures
A) APS (atmospheric, B) LPPS at 50 mbar and C) LPPS at 1 mbar.

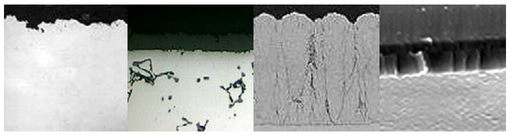
	LPPS Technologies			
	VPS/LPPS	PS-TF	PS-PVD	PS-CVD
Chamber pressure	50 mbar	1 mbar	1 mbar	0.5 mbar
Feedstock	Metals	Metals, Ceramics	Ceramics	Liquid & Gaseous Precursors
State of deposit	Liquid	Liquid	Vapor	Vapor
Coating example				
	MCrAlY	LSM	YSZ	SiOx

Figure 7. LPPS Technologies: ■ Standard; ■ Hybrid

New Coating Regimes

These hybrid technologies (Figure 7) include:

- PS-PVD (Plasma Spray-PVD) 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-CVD) 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.
- PS-TF (Plasma Spray-Thin Film) can produce thin, dense layers from liquid splats using a classical thermal spray approach but at high velocity and enthalpy.

Of these hybrid technologies, the PS-TF process has proven to be an effective tool for SOFC manufacture. The unconventional plasma conditions in the PS-TF regime give rise to the deposition of very thin and dense layers of ceramic and metallic coatings. Typically, an area of 1 m^2 (10.8 ft^2) can be coated with a 10 µm (0.0004 in) thick ceramic layer in about 1 minute.

PS-TF can be used within a broad range of operating conditions in terms of chamber pressure, plasma gas, power input, spray distance and component geometry, thereby having the flexibility to produce different types of coatings with a variety of characteristics.

Benefit of PS-TF technology for SOFC applications

The main advantages of the PS-TF technology for SOFC applications include:

- The ability to apply thin layers very fast (10 µm thick coating to an area 1 m^2 in about 1 min) is a prerequisite and benefit for a reliable, mass production process.
- The capability to apply dense layers of metallic and ceramic coatings — a highly successful solution to apply the dense, YSZ electrolyte directly on the anode of metal-supported cells.

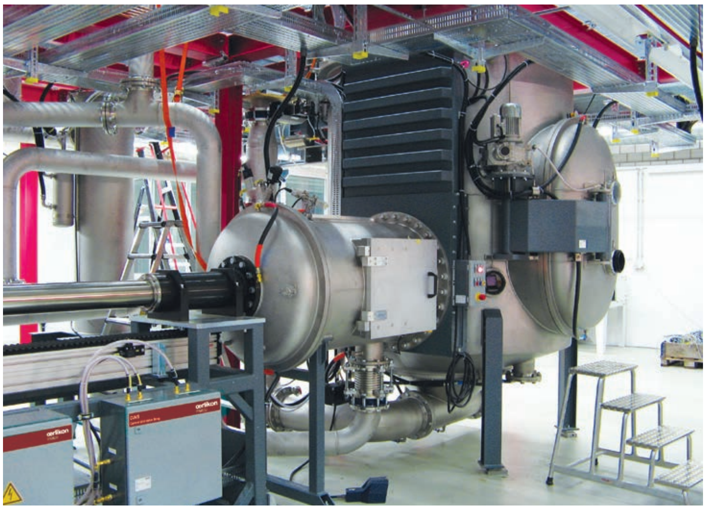


Figure 8. The Oerlikon Metco LPPS-Hybrid System used to apply PS-TF coatings.

Thermal spray coating solutions for solid oxide fuel cells

LSM coatings with TriplexPro-210

Nowadays, several hundred thousand SOFC interconnects like those shown in Figure 9 are coated each year with an LSM (Lanthanum-Strontium-Manganate) layer to prevent chromium evaporation from the metallic interconnect material. The preferred technology to produce such coatings is atmospheric plasma spray using the TriplexPro-210 spray gun. The advantages of this technology are:

- The ability to apply dense coatings with excellent reproducibility
- High spray rates and deposition efficiencies
- An absolutely constant process over a long period (200 hours of spray time without a drop in voltage)
- Minimal impurities in the coating from the electrodes and the nozzle of the plasma torch

These LSM coatings are dense and state-of-the-art, having an applied coating thickness of approximately 50 µm (0.002 in) and quite a uniform coating thickness distribution as shown in Figure 10.

It can be assumed that such a uniform coating thickness distribution can also be achieved on more complicated geometries. By minimizing the coating thickness variation on the interconnect, the total coating thickness can be reduced. This decreases the quantity of coating material needed and further reduces the processing time.

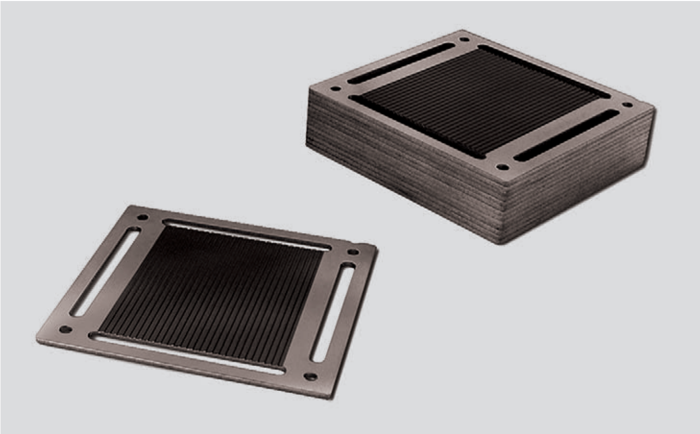


Figure 9. SOFC interconnects coated with the TriplexPro-210 plasma spray gun.

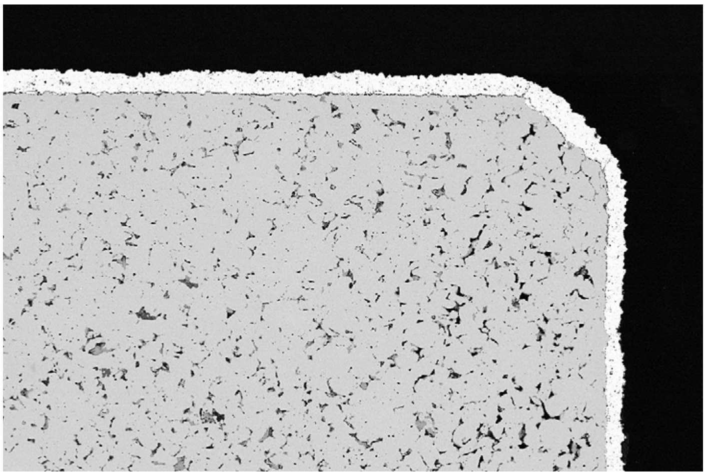


Figure 10. "State-of-the-art" LSM coating, applied on an interconnect made out of P/M CrFeY, using the TriplexPro-210.

LSM coatings with PS-TF

Ceramic LSM coatings applied using the PS-TF™ technology are dense, thin and uniform over a wide surface area of 300 mm (11.8 in) width. The results obtained, so far, are very promising. As shown on the two cross-sections of Figure 1, the applied coating is absolutely dense.

In addition to the benefit of extending the useful life of a SOFC, the coating quality and the high spray rate and deposit efficiency make it very clear that this technology is advantageous for the mass production of SOFCs. X-Ray crystal structure analyses of the different coatings reveal information about the phase structure of the LSM layer compared to the powder used. The phase structures show that the original perovskite structure of the powder is preserved using both thermal spray techniques, with only minor variation in the intensity and width of the three main peaks.

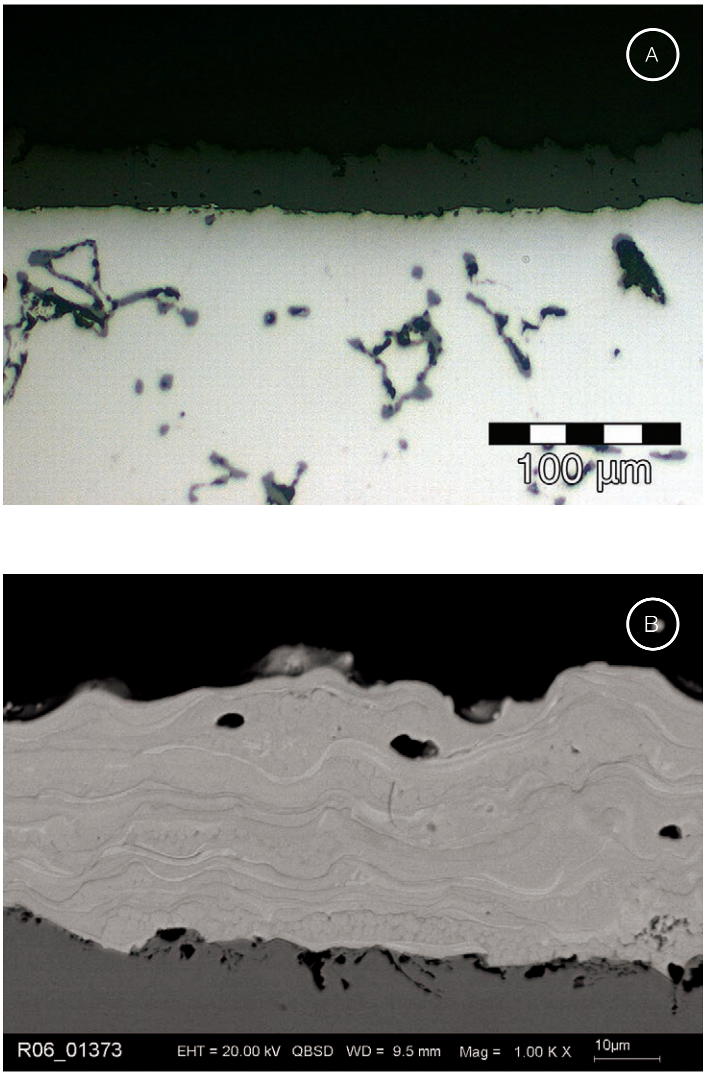


Figure 11. LSM coating sprayed with PS-TF A) light microscope B) SEM image

YSZ electrolyte applied with PS-TF

Electrolytes for SOFCs must be dense to prevent cross-contamination between the anode and cathode, and thin to maximize efficiency. A common material for these electrolytes is YSZ (yttria-stabilized zirconia), which also can be doped with scandium. Conventional thermal spray technologies cannot produce dense ceramic coatings with a thickness below 50 µm because the resulting coating porosity is too high. However, the unique characteristics of the PS-TF technology makes this possible, as shown in Figure 12.

Small pores can be observed in the cross-section of the YSZ coating; however, they are obviously not interconnected. Such a coating is obtained using the Oerlikon Metco O3CP plasma gun at a high power of 120 kW and a coating chamber pressure of 1.5 mbar. In this case, the powder feed rate was 60 g/min. These results, combined with the fact that an area of 1 m^2 can typically be deposited with a 10 µm thick ceramic coating in about 1 minute, make PS-TF a very productive and cost-effective solution for the application of the SOFC electrolyte layer.

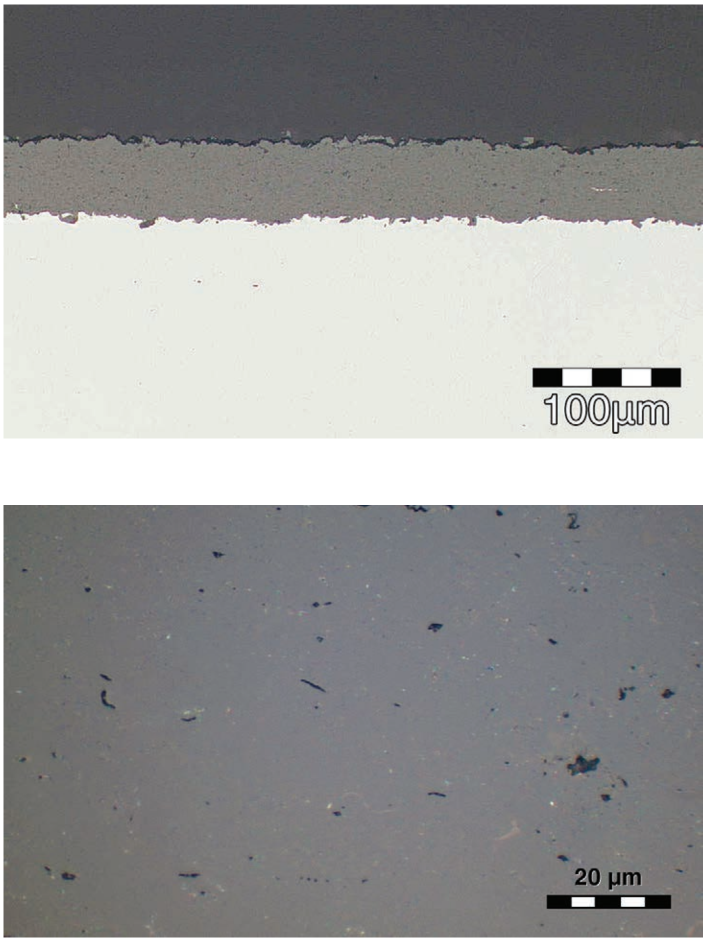


Figure 12. Micro-section applied using PS-TF at different magnifications.

Customer benefits

Effective

- Available materials portfolio of high quality materials formulated specifically for SOFC applications
- Produces thin, dense, full-coverage coatings quickly
- Capable of applying the full range of coating materials, including metallic, ceramic and cermet materials.
- Coats large surface areas.
- Suitable for mass production.
- Wide-range of operating conditions for a variety of SOFC coating applications.

Environmental

- Oerlikon Metco coating solutions support the success of eco-friendly SOFC technology.
- Best use of the resources and materials employed.

Economical

- Fast application of coatings saves production time.
- Can be used for mass production applications.
- Oerlikon Metco coating solutions contribute to increased lifetime and performance of SOFCs, while saving production costs.

Efficient

- High deposit efficiencies and deposition rates for efficient mass production of SOFCs.
- Proven and reliable coating application technologies, fully supported by Oerlikon Metco.
- MultiCoat™ system platform controls the plasma process and chamber environment with excellent precision and reproducibility.
- Coatings applied using the TriplexPro-210 are deposited faster and more efficiently than with any other plasma spray technology.
- Considerable reduction in scrap rates compared to other plasma spray processes.
- PS-TF can apply multiple SOFC layers with a single, unique process.
- Many coatings applied using the PS-TF process outperform coatings applied using other processes.
- Systems can be configured to maximize production efficiency of specific coating applications.

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