Metco has left the Sulzer Group and is now part of the Oerlikon Group.

oerlikon metco

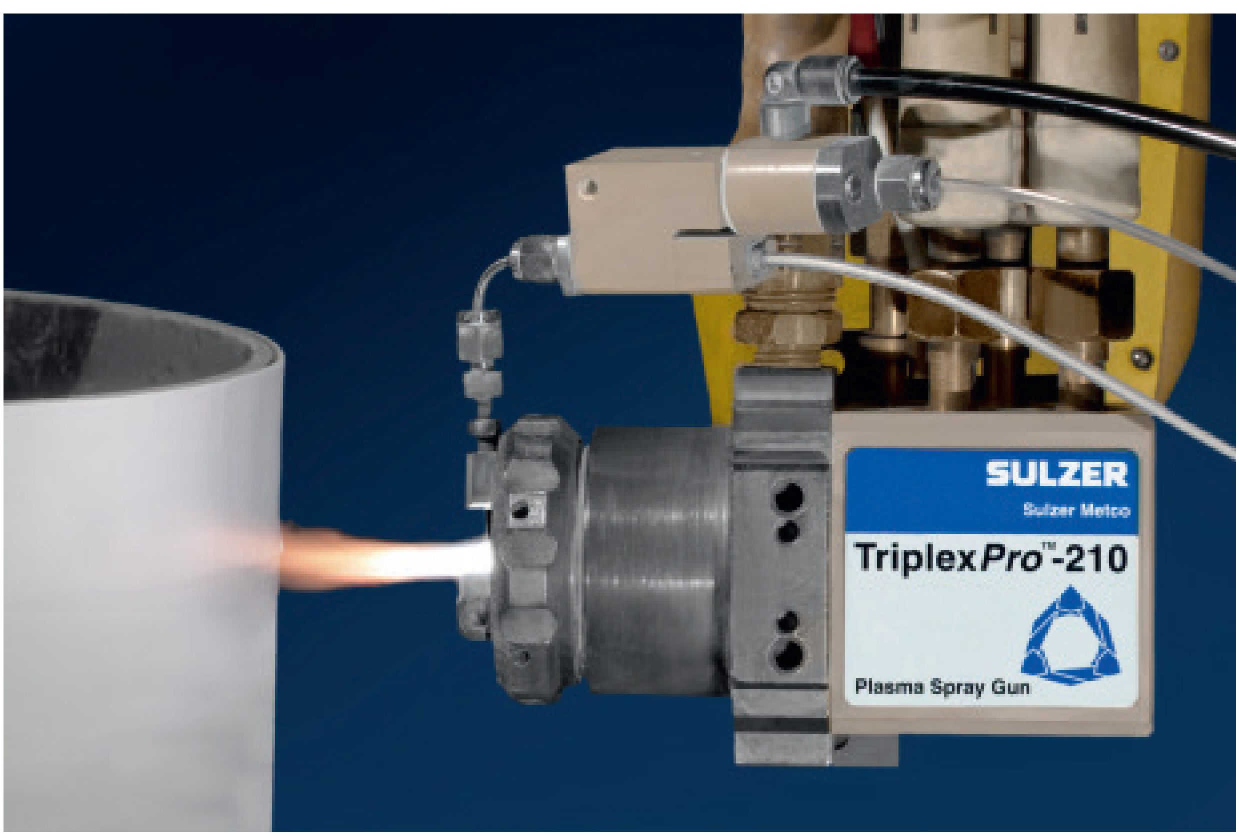
Thermal spray technology for microstructured coatings

Suspension spraying—an emerging coating technology

Microstructured coatings are needed for new applications and improved performance. Sulzer Metco develops suspension spray technologies that produce microstructured coatings with cost-effective thermal spray processes. The first results show the great potential of this new technology for demanding applications like thermal-barrier coatings or solid-oxide fuel cells.

Coatings with designed micro- and nanoscale structures are becoming increasingly popular because of their improved physical and mechanical properties. The range of applications that can benefit from such coatings is broad, and these applications use various deposition methods. Current coating methods that produce designed microstructures—such as physical vapor deposition (PVD)—have the combined disadvantages of being high cost and providing a slow deposition rate. The popular coating technologies atmospheric plasma spraying (APS) and high-velocity oxy fuel spraying (HVOF) are favored because of their versatility, their rapid deposition rate, and their relatively low

Thermal spray equipment adapted for liquid suspensions is versatile and economical.
More information on plasma spray guns: **www.sulzer.com/plasma-spray-guns**



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cost. However, they are not yet capable of producing microstructured coatings (overview in 1).

Suspension spraying is an emerging coating technology that produces fine-structured coatings in the micro- and potentially nanoscale while capitalizing on the desirable features of APS and HVOF processes. Suspension feedstocks can cover the full range of chemical material compositions already produced by Sulzer Metco—from ceramics and metal oxides to metal alloy–carbide blends.

Overcome the limitations of gas-based powder feeders

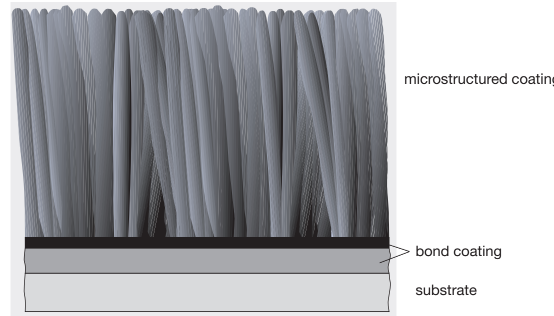
Conventional APS and HVOF technologies cannot produce fine-structured coatings because the feedstock powder must be greater than about 10 microns in size. Such particles, when melted by the plasma or flame, are deposited as «splats» that are much larger than the micron scale. This is the limitation of the gas feed systems that deliver the powder to the plasma or flame.

Sulzer develops suspensions that are optimized for the liquid feed equiment.

One way to overcome this drawback is to use agglomerated particles. These are large enough to be fed but will break into fine raw particle sizes in the plasma jet upon injection. Sulzer already offers this process in a newly developed low-pressure plasma spray (LPPS) technology. The plasma spray physical vapor deposition (PS-PVD) process at 1 mbar work pressure combined with a high-power gun evaporates the fine agglomerated powder and transports the vapor along the plasma jet onto the substrate. This process results in new and unique coating microstructures similar to electron-beam physical vapor deposition (EB-PVD) columnar structures (Fig. 2). Additionally, due to the forced gas stream of the plasma jet, complexly shaped parts with non-line-of-sight areas—such as multiple airfoil turbine vanes—can be coated with columnar thermal-barrier coatings.

Another way to overcome this limitation is to use fine-particle suspensions with a liquid carrier feed system in place of a gas carrier feed system. APS and HVOF torches are versatile and simple systems. They can be easily modified to accommodate liquid suspensions by substituting existing gas-based powder feeders with liquid-based suspension feeders. Sulzer Metco's liquid feeder prototype 5MPE-SF was described in the *Sulzer Technical Review 2/2011*.

Suspension and liquid feed systems must work together in an overall design to produce coatings with repeatable characteristics. Sulzer Metco develops suspensions that are optimized in performance for the prototype liquid feed equipment and achieve the desired properties of the micro- and nanoscale structures of the functional layers produced.



2 Coatings with designed microstructures have specific microscopic morphologies (e.g., the size and shape of the deposited particles and the pores) in order to achieve desired coating properties. Columnar structures with vertical cracks can for example compensate thermal expansion differences between the coating and the substrate (used in thermal-barrier coatings).

Liquid suspensions have unique challenges

Suspensions consist of solid particles dispersed in a liquid medium. In coating applications, these are particles of the coating material to be deposited. The liquid medium's function is to carry the particles from a feed hopper to the torch. Suspensions for coating applications must have a high degree of consistency to ensure stable and repeatable deposition rates, efficiencies, and physical properties.

Suspension consistency is difficult to establish because suspensions are inherently unstable unless certain measures are taken. Particles have a natural tendency to settle and stick together forming larger clusters or agglomerates (see infobox). This behavior is detrimental to

1 Comparison of PVD and thermal spraying.

PVD (Physical vapor deposition)		**Thermal spraying**	
In PVD processes, a vapor is condensed on the substrate. It is possible to coat large areas and multiple parts as well as to create microstructures. The downsides are higher investment costs and lower deposition rates.		The melted feedstock is applied with a spray gun onto the substrate. Thermal spraying processes are versatile and rapid, but the conventional gas-based powder feeders create structures larger than micron scale. The spray pattern is generally small and has to be moved to coat parts.	
Types:		**Types:**	
EB-PVD Electron-beam PVD	**PS-PVD** Plasma spray PVD	**PS** Plasma spraying	**HVOF** High-velocity oxy-fuel spraying
The coating material is evaporated from ingots with a focused electron beam.	The feedstock is evaporated with a high-energy plasma gun.	The feedstock is melted in a high-temperature plasma jet at different spraying environments: **APS:** Atmospheric plasma spraying (ambient air). **HPPS:** High-pressure plasma spraying **LPPS:** Low-pressure plasma spraying	A combustion flame heats and propels the particles at near supersonic speeds but at reduced temperatures.
The deposition rate and the material utilization efficiency are higher than conventional PVD.	This process fills the gap between the conventional PVD technologies and thermal spray processes.	Plasma spraying is the most flexible of all the thermal spray processes and has sufficient energy to melt materials such as ceramics and metals.	HVOF can deposit very dense coatings.

How suspensions sediment

Particles in liquid suspensions used for coatings typically range in size from a few microns down to 0.01 microns, or 10 nanometers. The suspended particles settle over time, which is called sedimentation. While smaller particles do not settle as quickly as larger particles, they tend to stick together more readily due to electrostatic attraction, thus forming agglomerates. These clustered particles sediment in the same way that large single particles do. Sedimented particles are problematic for spray processes because they can clog the narrow orifices in the suspension feeder.

the operation of the liquid feed equipment and hinders the achievement of stable and repeatable material flow. For good flow, the particles in the suspension must be well dispersed and homogeneous throughout the coating operation. Although the stirring agitator in the liquid feed hopper assists in mixing, the suspension itself must be designed to resist settling and agglomeration.

Keeping particles separated

In an ideal suspension, the particles are fully separated, or dispersed, in the liquid. If the particles are small and separated, the sedimentation process is much slower. The problem of agglomeration is counteracted by a combination of chemical and mechanical processes:

- The agglomerates are pulled apart in the liquid through various types of high-energy mixing.
- The particles are treated in order to prevent them from sticking together. This is commonly achieved using a class of chemical compounds called dispersants.

One example is the use of a dispersant that imparts either a positive or a negative surface charge to the particles to keep them separated through electrostatic repulsion. Well-dispersed suspensions also benefit from reduced viscosity, which allows them to flow more easily in a pressurized feed system.

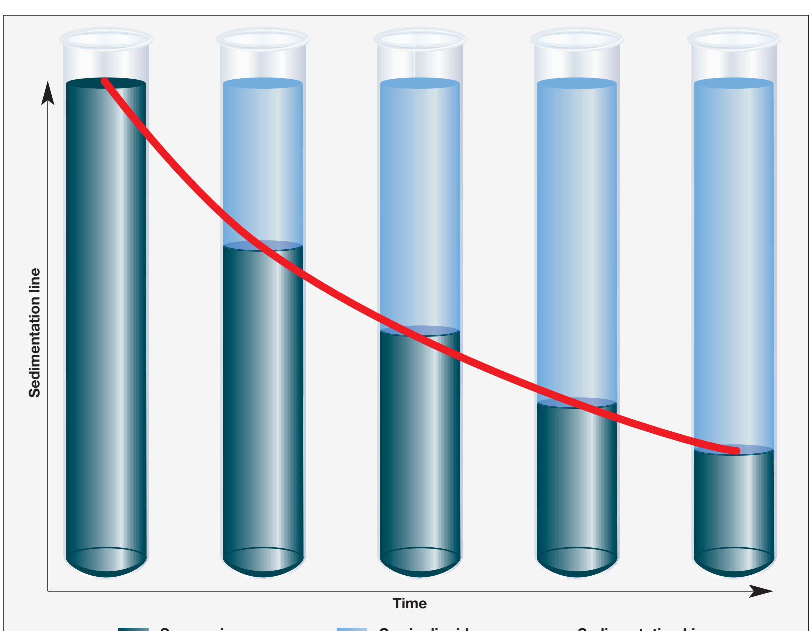
Spray tests with the optimized suspensions demonstrated the high performance of the coatings.

Choosing suitable solids content and liquid types

The solids content of suspensions (called loading) typically varies from 1–30%, but it can potentially be higher. A high solids loading is economical because it minimizes both the volume of suspension required and the coating deposition time. However, the practical maximum for solids loading is also determined by the design of the suspension feed system and the ability of the torch to process the material.

Although many kinds of liquids may, in principle, be used for suspensions in thermal spray, the most common ones are alcohols, water, ethylene glycol, and various mixtures thereof. Alcohols are preferred, because they do not cool the plasma as much as water. However, the flammability of alcohols raises safety concerns. The cooling effect of suspensions is a primary challenge in suspension plasma spray. A substrate needs to be brought closer to the torch to intercept the melted particles where the plasma is hottest. This reduced working distance makes it more difficult to coat complexly shaped parts such as turbine blades.

3 The sedimentation rate is measured by resting the suspension in a glass container and observing the clear liquid phase over time. There is a sharp interface between the growing clear liquid layer at the top and the settling suspension containing the particles at the bottom.



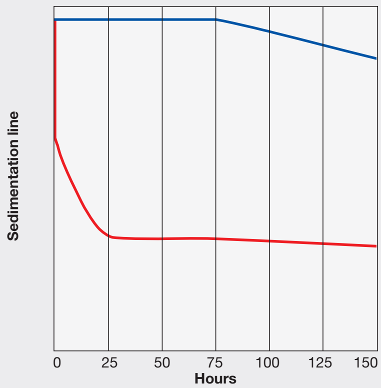
Optimizing suspensions

In order to develop applicable suspensions, Sulzer Metco measures the sedimentation rate (Fig. 3) and the viscosity as the primary indicators of dispersion and stability. Well-dispersed suspensions have slower sedimentation rates and lower viscosity than aggregated or poorly dispersed systems that involve the same materials. Suspensions with agglomerated particles have higher viscosity because of molecular bonding mechanisms (interparticle bridging) that resist turbulent flow. With reduced agglomeration, the individual particles are unbound and the suspension flows more easily.

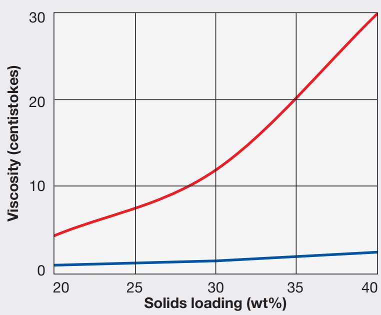
Dispersants can have a dramatic effect on suspension stability. Sulzer Metco

Experimental results

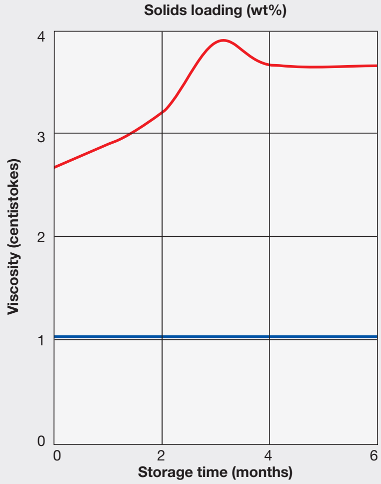
Sulzer Metco evaluated the behavior of suspensions and the effect of dispersants. The suspension tested contained 0.3-micron zirconium oxide stabilized by yttrium oxide particles (commonly referred to as yttria-stabilized zirconia, or YSZ) in ethanol.



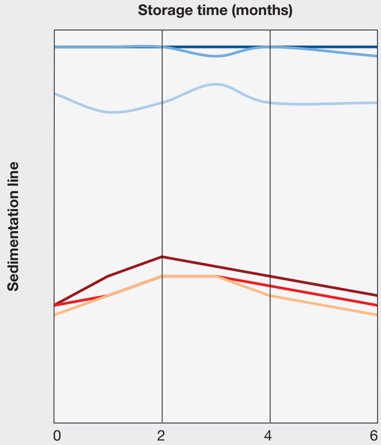
The sedimentation rate is much slower with the use of a dispersant. With a dispersant, the suspension is still in the early phase of sedimentation after 144 hours. This short-term level of stability is suitable for use for the time frame of a spray session.



A high solid content increases the viscosity of the suspension. With a dispersant, the viscosity is significantly lower and the range of possible solid loadings is increased.

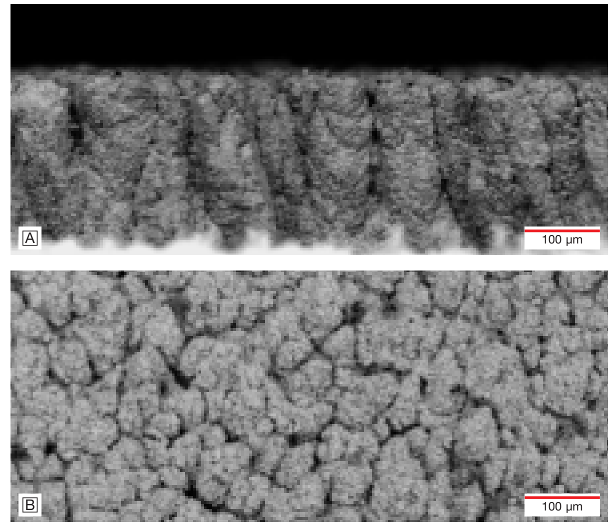


Commercial suspensions must be able to retain or recover their properties upon simple remixing after storage, as one would do with a can of paint. A suspension without dispersant that is remixed at one month intervals shows a marked increase in viscosity from its original "fresh" condition. With a dispersant, the suspension recovers its original low value when it is remixed at various times throughout the test storage period of six months.



The settling rates (both with and without the dispersant) were not significantly affected by remixing through the storage period.

The last two plots indicate that the potency of the dispersant did not deteriorate during the storage period.



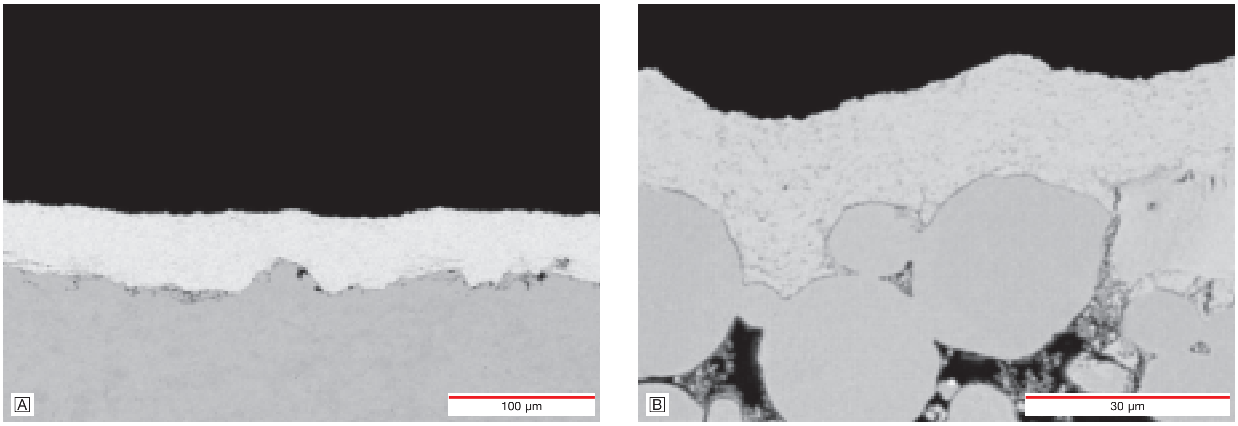
4 Sulzer Metco uses suspension plasma spray to create columnar microstructures on various materials. This example shows a 7 wt% Y_2O_3 stabilized ZrO_2 coating in side view A and top view B.

investigated these effects with a series of experiments (see infobox). The results enabled Sulzer Metco to optimize the suspensions. The following spray tests with these suspensions demonstrate the performance of the coatings.

High-performance thermal-barrier coatings

Ceramic materials such as yttria-stabilized zirconia are used as thermal-barrier coatings in gas turbine engines. Their low thermal conductivity can reduce the thermal load on the components by as much as 300 °C. Thermal-barrier coatings are usually produced by APS and electron-beam PVD (EB-PVD). In demanding areas, such as in the hot section of the turbine, columnar microstructured coatings produced by EB-PVD provide improved mechanical properties, particularly, improved strain tolerance. Cooler, less-demanding components use APS to produce denser coatings with vertical cracks that also provide high strain tolerance.

Sulzer Metco has produced suspension plasma spray coatings using a liquid feed prototype system adapted to a Triplex*Pro*™-210 torch. The preliminary



5 Sulzer Metco suspensions produced thin and dense SOFC coatings with suspension HVOF technology. The 14 wt% Y_2O_3 stabilized ZrO_2 coating was applied to a steel substrate A and a porous substrate B to show the good coverage of the coating.

experiments successfully demonstrated the capability of producing columnar microstructures composed of a variety of materials, including zirconium oxide stabilized with:

- Yttrium oxide (Fig. 4)
- Cerium oxide
- Dysprosium oxide

The performance of suspension plasma spray coatings and their structures such as dense, vertically cracked thermal-barrier coatings are being actively studied. They will be compared with standard APS coatings and similar microstructured coatings produced by other methods such as EB-PVD and PS-PVD.

Efficient electrolyte coating for solid-oxide fuel cells

Solid-oxide fuel cells (SOFCs) are used for power generation and can be manufactured in a wide variety of sizes from a few watts to several kilowatts of power. An SOFC is composed of several multilayer systems, each comprising an anode (YSZ/NiO), electrolyte (YSZ), and cathode (LSCF, lanthanum strontium cobalt ferrite). Usually such multilayer systems can be produced on porous metallic supports, which bring the mechanical stability of the cell to the system. The operating temperature of these devices is in the range of 750 to 900 °C. The electrolyte, which is one of the main parts of the cell, must be thin (preferably less than 20 microns) to efficiently conduct the ions, and it must be dense to form a gas-tight seal between the gases of both the anode and cathode.

The benefit of suspension HVOF technology over conventional HVOF, APS, and suspension plasma spray is the potential to produce coatings that are both very thin and very dense. This is mainly because of the high particle velocity and the increase of the heat transfer into the particles from the additional combustion heat passed on by the organic carrier liquid of the suspension. As the powder feedstock in suspension-based processes is very fine, the minimum coating thickness to achieve dense coatings is much lower than for all the standard processes.

Suspension HVOF technology can produce coatings that are both very thin and very dense.

Promising results

Sulzer Metco investigated the application of HVOF suspension technology for SOFC coatings. For the experiments, the liquid suspension was injected directly into the combustion chamber of a modified Diamond Jet™ 2700 spray gun.

The coatings on a flat steel substrate and on a porous substrate (Fig. 5) are compliant to the morphology and are shown to be free of cracks and delaminations. The coating on the porous substrate is promising because the pores beneath the coating have not been blocked. Thus, they allow fuel gases to contact the coating electrolyte.

The preliminary trials show the potential that HVOF suspension technology has for SOFC applications. Sulzer is currently investigating several SOFC materials:

- Lanthanum strontium manganite
- Manganese cobalt oxide
- Zirconium oxide stabilized with 14% yttrium oxide

Further trials will show the possibilities of HVOF suspension coatings for other SOFC applications where dense coatings are required such as chromium evaporation barrier coatings or porous coatings such as cathode layers.

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