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

Liquid suspension spray

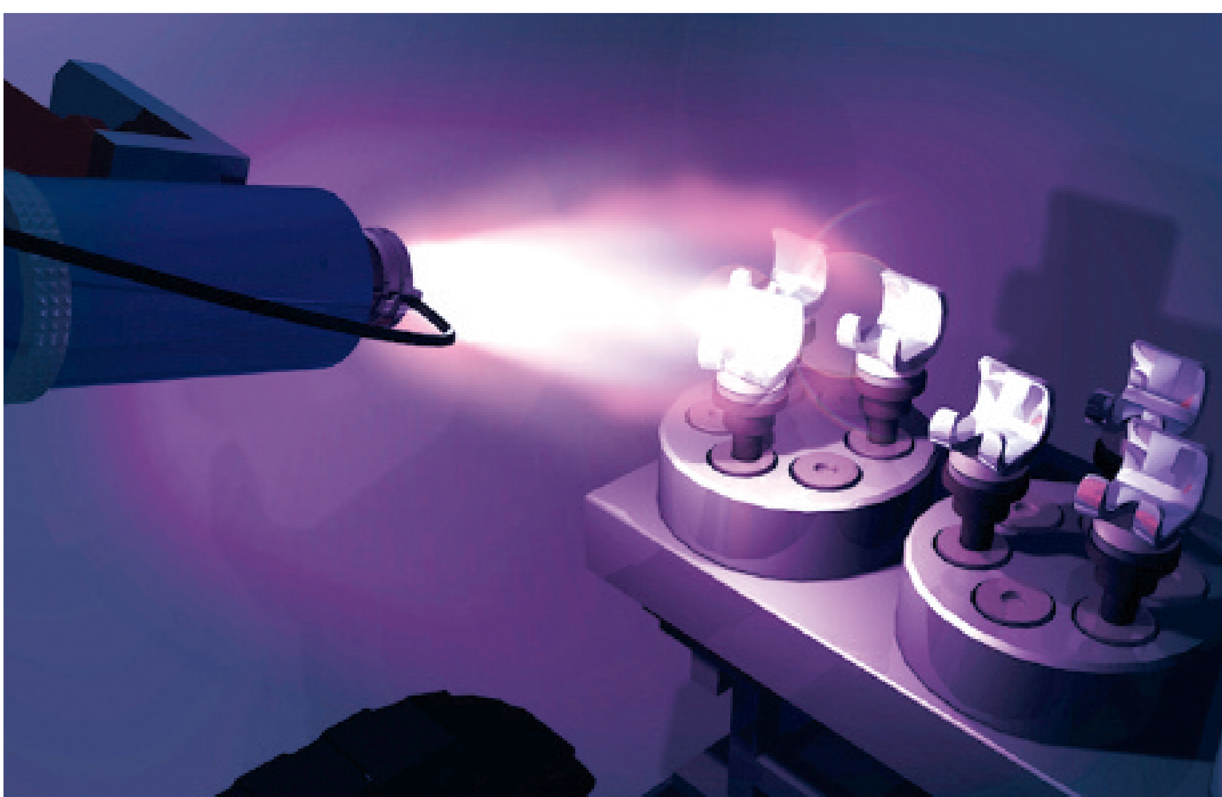
New challenges, new opportunities

There has been steadily growing industrial interest in coatings that fall into the category of liquid suspension plasma spray. This new technology makes it possible to develop coatings with finer powder, which have several advantages compared to traditional coatings. The engineers of Sulzer Metco have developed a new prototype feeder that allows the transportation of this fine powder and that can be combined with all existing guns from the division.

Traditional plasma applied coatings use a feedstock of powdered material in a typical size range of 30 to 150 microns, these materials are pneumatically transported and injected into the plasma plume. As our understanding of thermal-spray coatings increases, we see that there are several significant advantages to producing coatings with a finer grain size, based on grain boundary effects that first become measurable when the powder is in the submicron size range.

The shift towards finer powders has created the requirement for new methods of powder transport and injection that solve both practical engineering hurdles and the health and safety issues of working with submicron powders. While liquid suspension powder feeding is not new, there is a growing need for practical, robust design solutions to make this method commercially viable.

F4 plasma gun spraying medical implants.



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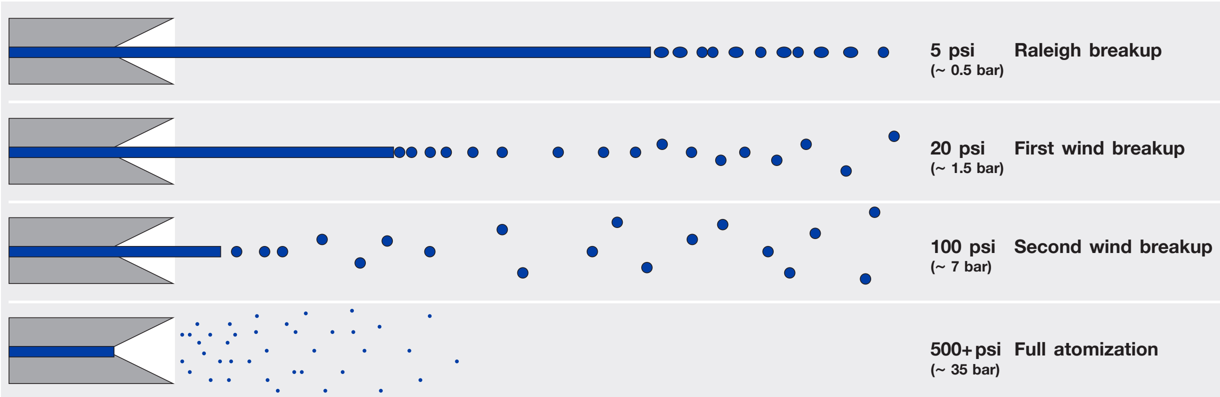


1 Droplet breakup regime as a function of increased supply pressure.

Principles of liquid feeding

Suspending or dissolving the coating material in a liquid addresses the problem of handling superfine powders that are not only extremely difficult to feed but can permeate human skin tissue and thus pose a health risk. Our customers, considering the safety and welfare of their employees, are actively investigating liquid feedstock as the means to achieving new coatings with submicron characteristics.

Unlike powder feeding, which uses a fluidized gas stream or carrier gas to transport and inject powder into a process plume to form a coating, liquid feeding uses a liquid-based medium to transport and inject the coating material in one of three forms:

- preparation in which the powder particles are suspended in a liquid medium, preferably water or ethanol (the most common form of liquid-based feedstocks);
- solution in which the material to be deposited to form the coating is dissolved in a liquid medium, again preferably water or ethanol; or
- precursor in which the liquid medium comprises chemicals that react in the process plume to form the coating materials in situ.

The liquid medium is injected into the thermal-spray plume and breaks up into tiny droplets before the liquid is heated and vaporized. Once the liquid is processed, the remaining coating material can be heated, melted, and accelerated to the substrate to form a coating. The effects that using a liquid-based medium will have on the process plume must be considered. The additional energy required to both heat and vaporize the liquid results in quenching, while some liquids, such as alcohol, will actually add some heat back from combustion. If there is too much mass flow of liquid, the plume will have either insufficient energy remaining to process the powder (in the case of water) or excess energy (in the case of alcohol).

Injection of a liquid-based feedstock into a thermal-spray plume introduces another challenge with regard to atomization. Ideally, the stream of liquid as it is injected into the plume must break up into small droplets to aid in processing the liquid. If the droplets are too small they may not penetrate the plume at all. If the droplets are too large they may not process quickly enough.

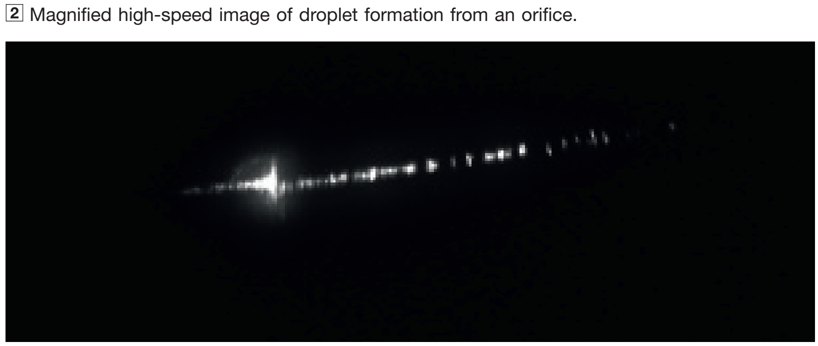
Atomization is a pressure-driven means by which a liquid stream will break apart after exiting an orifice. The principle can be observed almost everyday in shower heads and water fountains: the higher the pressure, the higher the flow and the smaller the droplets. Even automotive fuel injectors work on the same principle. There are three methods of atomization:

- pressure-based atomization, where a liquid is forced through an orifice under pressure to break up into droplets;
- gas-assisted atomization, where a gas under pressure is used to aid in the stream breakup as it exits an orifice (commonly used to disperse liquids in spray cans); and
- mechanically assisted atomization where a mechanical means is used to agitate the liquid as it exits an orifice.

Evaluation and testing of all three methods showed that a simple pressure-based system alone yielded the best results for liquid injection into thermal-spray plumes based on total mass flow required, ability to control droplet size, achievable droplet breakup regime, and complexity. Experimentation and testing showed that the ideal droplet breakup regime for injecting a liquid feedstock into a thermal-spray plume ranged from first- to second-wind breakup 1. This produced droplets from about 50 µm to as large as 200 µm, which encompasses the typical powder particle size range used in plasma guns.

Magnified high-speed images 2 of a 0.008" (0.2 mm) injector orifice producing first- and second-wind breakup of water droplets were made, and they compared

2 Magnified high-speed image of droplet formation from an orifice.



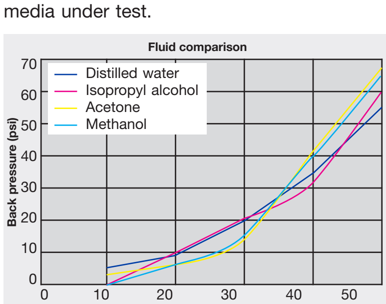
3 Liquid feed prototype system used to spray customer-driven applications.

well with the theoretical data. The injector is a replaceable ceramic insert in a stainless-steel housing. As the stream exits the injector, the stream almost immediately breaks up into droplets and starts to disperse within a few millimeters of the exit. This condition is ideal for radial injection into a plasma plume.

Feeder development

Sulzer Metco experimented with different technologies for controlling liquid flow while conducting a number of internally and externally funded customer-driven programs for developing different liquid-based coating applications. Based on the experience gained, a simple pressure-based prototype liquid feed system was developed for testing 3. The feeder is now used to support customer development applications with various plasma guns including the Triplex*Pro*™-200.

4 Flow vs. pressure curve for several liquid media under test.



The specifications for the feeder were defined by the limits imposed by the operating principles of liquid feeding, described previously. Injector orifice sizes range from 0.004" (0.1 mm) to as large as 0.012" (0.3 mm), depending upon the volumetric flow rate and droplet breakup regime needed for an application. The desirable flow range was from about 10 ml/min to as high as 80 ml/min—which then determined that the required pressure range for the feed system should be from about 5 psi to 100 psi. Measurement of flow vs. pressure for several different liquids 4 showed that the pressure flow curve remains fairly constant regardless of which liquid medium is used. These results simplified the requirements.

During development a major issue that affects the reliability of a liquid feed system was discovered. The injection orifice was prone to clogging as a result of agglomeration of the fine particulates. The main cause of the agglomeration was primarily from residual droplets of liquid suspension remaining in the injector or feed lines after shutdown. These droplets would dry out and, when liquid flow was resumed, flakes from the dried residue would partially or fully clog the injector. Clogging and inconsistent flow were also found to occur in another situation. The injector got hot when the plasma gun ran with no liquid feeding. Subsequent activation of the liquid flow led to clogging when the liquid medium evaporated.

To solve the clogging problem, a novel purge-misting system was incorporated into the feed system to flush the injector and maintain a constant flow with moist gas whenever the suspension feed was off. The moistened gas prevented any drying or agglomeration and kept the injector clean. Just using a dry gas purge or even a pure liquid purge did not prevent all occurrences of clogging. Incorporating the purge mister provides a consistent and repeatable flow of liquid that can be maintained for long periods of time.

It was also discovered during the development, that properly prepared suspensions are critical to the operation of the system. It is necessary to use surfactants and dispersants to maintain the suspension in the correct concentrations and thereby minimize any tendency for agglomeration or settling of the solids. The allowable concentration level is also limited by the physical behavior of the fluid. High-solid loading results in non-Newtonian behaviors that can cause variations in droplets sizing and clogging in the injector orifice as well as in the filters used to prevent contaminants from entering the feed line.

The last important feature is the need to provide adjustable geometry for locating the liquid injector relative to the plasma gun plume. It was discovered early on that the interrelationship between droplet breakup, mass flow, and orifice sizing required the injector location to be adjustable both radially and axially. The adjustable injector, along with its purge-misting system, was designed as a single device that can be readily mounted onto any plasma gun 5.

Parameter development

Considerable testing was performed with different feedstock liquids and submicron powders. Tests were conducted with the liquid feed system 3 and injection setup 5 to understand what effects on developing spray parameters liquid feedstocks might have. One central question was whether parameter development had to start from the beginning or whether there was a shortcut from existing powder-based spray parameters.

The principles of feeding provide some insight into the development of spray parameters. If one considers the effect on the plume energy the liquid presents, it is possible to correct for the difference. If a spray parameter exists for a specific application or spray material, the parameter can be adjusted by adding current flow or removing current flow. These adjustments compensate for the quenching effects of water or the added net energy from using alcohol. Testing with various liquids and suspended media showed that this was a feasible means of obtaining at least a starting point for optimization.

Working out the particle physics, it becomes clear that the submicron or smaller particles are going to track the plume energy state almost exactly in terms of velocity and temperature. This lack of latency in the particles requires some adjustment to determine ideal spray distances. Specifically, the range of deposition is much smaller with liquid-based feedstock than with conventional powder spraying. Where conventional spraying affords a range of spray distances measured in inches, suspension spraying with submicron particles is measured in fractions of an inch. Due to the quenching effects, spray distances can also be considerably shorter then with conventional powder spraying and are often in the 2–3 inch range as opposed to the typical 4–8 inch range.

Design of coatings

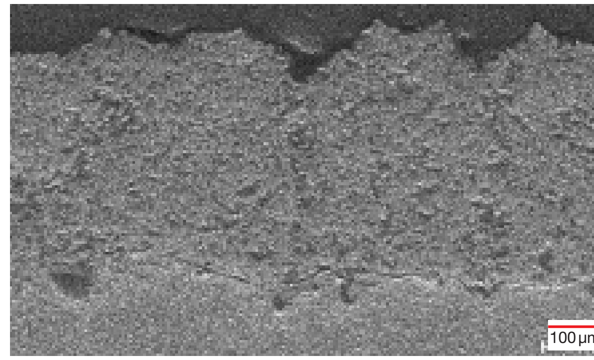
Consider liquid-based spraying as enhanced thermal spray. Thermal spray, in essence, is a means of assembling material on a micron-sized basis. This unique method of additive manufacturing produces material qualities not found in nature or in any other manufacturing process. For this reason, thermal spraying has found a wide range of applications. Liquid-based spraying extends thermal spraying into submicron and even nano-sized assembly, further augmenting the unique properties of thermal spray.

It is generally accepted today that the myriad of grain boundaries in a thermal-spray coating provide some ductile qualities, because each grain boundary affords some relative movement among the grains. The larger percentage of grain boundaries created in submicron and nano-structured coatings produces coatings that are more damage tolerant due to these grain boundaries.

The grain boundaries also serve as imperfections in the coating structure that inhibit thermal transfer. They provide thermal-barrier coating materials such as yttria-stabilized zirconia (YSZ) additional thermal-barrier qualities. The increase in damage tolerance plus the reduction of thermal conductivity should make for improved and thinner thermal-barrier coatings extending their application. One such example showing—a high magnification cross-sectioned microstructure—was sprayed with submicron-sized YSZ particles suspended in methanol with a 9MB gun configured with an adjustable injector holder 5.

The coating structure 6 shows some unique characteristics beyond just having a submicron-sized structure. Note the vertically aligned regions of porosity that can emulate vertical cracks. Features like this, as well as surface profiles similar to the substrate profile, provide new opportunities for coating development.

A greater number of grains at the surface also translates to increased surface area that could increase reactivity in coatings such as titanium suboxide and electrolytic coatings for solid-oxide fuel cells (SOFCs). The performance of sputter targets with regard to sputter rate can also theoretically be improved.



6 Microstructure of suspension plasma-sprayed yttria-stabilized zirconia.

5 Adjustable liquid feed injection setup for a 9MB plasma gun.

Other distinct characteristics of submicron- and nano-structured coatings include hydrophobic properties suitable for enhancing chemical resistance in wet environments. This quality would create thermal-spray coatings with improved corrosion resistance in both hot and cold environments.

The expertise and knowledge gained in the development of liquid feed capability provide Sulzer with the ability to support customer needs as liquid suspension plasma spraying evolves into commercial applications.

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