

Quo Vadis Thermal Spraying?

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This paper is devoted to thermal spraying and presents the state of our current knowledge, as well as the following research or development needs: spraying heat sources, *i.e.*, flame, high-velocity oxifuel flame (HVOF), detonation gun (D-Gun), and plasma torches; particle heat and momentum transfer (measurements and modeling), process on-line control, powder morphologies, and injection within the hot jet and reactions with environment; coating formation, *i.e.*, particle flattening and solidification, splat layering, residual stresses, coating microstructure, and properties; and reliability and reproducibility of coatings.

Keywords control, diagnostics, microstructures, review, splat formation, splat layering, spray processes

1. Introduction

Thermal spraying is a group of processes in which finely divided metallic and nonmetallic materials are deposited in a molten or semimolten state on a prepared substrate.^[1,2] The heat source is a combustion flame, a plasma jet, or an arc struck between two consumable wires. In this process, the substrate can be kept at relatively low temperature by specific cooling devices.

1.1 Process Development

Thermal spraying has been practiced since the early 1900s, when Dr. Schoop (refer to the Master Patent for Schoop Technology^[3]) introduced the technique with a flame as the heat source. In the beginning, it was limited to low melting-point materials such as tin and lead and was progressively extended to steels. To avoid unmelted particles in the spray jet, wire-flame spraying was developed, where the wire feedstock was drawn by drive rolls into the rear of the gun. Here again, the materials' melting temperature was limited to 1500 to 1600 °C.

After the introduction of plasma spray torches by Thermal Dynamic Corp. (Lebanon, NH), in 1957, plasma spraying was an attractive option, at first, for the aeronautics industry, especially NASA, and later for the aircraft industry. The use of the plasma jet dramatically extended the technology possibilities to any material that could melt; *i.e.*, the difference between its melting and decomposition or evaporation temperatures was preferably greater than 300 K.

Later on, the use of soft vacuum^[4] or controlled (neutral) atmosphere^[5] made it possible to suppress some important drawbacks of atmospheric plasma spraying (APS), at the expense of a much higher investment (more than one order of magnitude). These controlled environments permitted dense coatings with almost no oxidation to be achieved, as well as coatings that ex-

hibited excellent bonding and cohesive strength. Plasma spray technology has also evolved with the following.

- The high gas velocity direct current (d.c.) arc torches were developed by Pratt and Whitney with the Gator Gard in the early 1970s (licensed to Sermatech^[6]) and in the late 1980s by Browning with the high-energy, high-velocity Plazjet (licensed to a Japanese company^[7] and now commercialized by Tafa).
- The radio frequency (RF) induction plasma spray torch produces low-gas velocities and, thus, allows the spraying of particles with diameters over 100 μm. This technology was introduced by Boulos^[8] and is now commercialized by Teckna in Canada.
- The twin wire arc was introduced and still plays the dominant role in wire spraying. Compared to earlier open flame wire spraying, the arc process is capable, at reduced cost, of higher deposition rates of electrically conductive materials having a high melting temperature, for example, molybdenum.^[9]

Almost in parallel to plasma spraying, Union Carbide (now Praxair Surface Technologies, Inc., Indianapolis, IN) marketed the trademarked D-Gun^[10,11] producing premium coatings, especially metallic and cermet ones, which have long been the goal of all other coating processes, *i.e.*, higher density, improved corrosion barrier, higher hardness, better wear resistance, higher bonding and cohesive strength, almost no oxidation, thicker coatings, and smoother as-sprayed surfaces. However, the detonation gun (D-Gun) process was available only as a service.

In the 1980s, the high-velocity oxifuel flame (HVOF, Jet Kote, Doloro-Stellite, Goshen, IN) was introduced. In this device, the high pressure was produced continuously due to combustion in a pressurized water-cooled chamber,^[11] from where the combustion gases expanded through a nozzle as they exhausted and accelerated to the atmosphere. Many designs of HVOF torches became available,^[11] with the combustion pressure increasing from 0.4 to 1.35 MPa, and values up to 4 MPa are envisaged. High-velocity air fuel (HVAF) torches were also designed^[12] where pressures of 0.8 MPa were achieved, with high inlet air pressure (1 MPa) providing most of the burner cooling, *i.e.*, only 10% of the energy was lost in the cooling system.

1.2 Economic Need for Thermal Spraying

In general, coatings of high performance materials—metals, alloys, ceramics, or cermets—are applied to relatively easy-to-

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Nomenclature	
d	particle diameter (m)
D	splat diameter (assumed to be disk shaped) (m)
K	Sommerfeld parameter: $K = \sqrt{We} \cdot \sqrt{Re}$ (—)
ℓ	mean free path (m)
Ra	mean roughness (μm)
Re	Reynolds number of the particle, $Re = \frac{\rho_p \cdot v_p \cdot d}{\mu_p}$ (—)
T_c	critical preheating temperature of the substrate: if $T_s > T_c$, splats on smooth surfaces are disk shaped (K)
T_s	substrate surface temperature (K)
v_p	particle velocity (m/s)
We	Weber number of the particle: $We = \rho_p \cdot v_p^2 \cdot d / \sigma_p$ (—)
ρ_p	particle specific mass (kg/m^3)
μ_p	molten particle viscosity ($\text{kg}/\text{m}\cdot\text{s}$)
σ_p	surface tension of the droplet (J/m^2)
ζ	flattening degree: $\zeta = D/d$ (—)
Abbreviations	
1-D	one-dimensional
3-D	three-dimensional
A/C	adhesion/cohesion
APS	atmospheric plasma spraying
CCD	charged coupled device camera
CFD	computational fluid dynamics
CVD	chemical vapor deposition
d.c.	direct current
D-Gun	detonation gun
HVAF	high velocity airfuel flame
HVOF	high velocity oxifuel flame
i.d.	internal diameter
IR	infrared
PVD	physical vapor deposition
RF	radio frequency
SHS	self-propagating high-temperature synthesis

work and more economical base materials. The base material/coating combination can be tailored to provide resistance to heat, wear, erosion, and/or corrosion, as well as unique sets of surface characteristics. Coatings are also used to restore worn and poorly machined parts to original dimensions and specifications. Historically a surfacing technology, plasma spraying, has moved from coating to a materials processing technology (e.g., Smith and Novak^[13] and Thorpe^[14]).

As stated by Kassabji *et al.*,^[15] “higher product value to users and continuous improvement of the value chain (including plant yield and new products introduction) are keys to further market expansion. Within this process, at product’s parts level, ‘bulk’ capabilities are mature and both new ‘multi-materials’ or ‘surface engineering’ features will be the driving forces.”

In spite of competing processes (chemical vapor deposition

(CVD), physical vapor deposition (PVD), *etc.*) and certain drawbacks, thermal spray process sales are increasing regularly (almost by 10% per year since 1990^[15]). The growth will probably continue during the beginning of the next century, because spraying techniques are relatively harmless to the environment and the full potential of thermal spraying as an alternative to more conventional coating techniques (e.g., hard chromium) for processing “multimaterials” or for free forming and repairs is still undiscovered.^[15] However, this development could be enhanced with increased quality of coatings and process reliability. It demands improved process understanding and on-line control with a real time closed-loop control.^[16,17]

1.3 The Five Subsystems of Thermal Spray Processes

To understand better how coatings will be developed in the near future, it has to be kept in mind that coating properties depend on five subsystems on which the operator can exercise some control. These are listed below:

1. flame or plasma jet formation linked to the torch design, the forming gas composition and mass flow rate, the dissipated power, and many other process parameters;
2. powder and its injection; coating properties depend closely on the powder chemical composition, particle size distribution and morphology (linked to the powder manufacturing process), and injector internal diameter, shape, length, position, and tilting as well as on the hose length and “trajectory” between the powder feeder and injector;
3. composition of enveloping atmosphere, *i.e.*, air or inert gas at a pressure equal to, or lower than, 10^5 Pa;
4. substrate material and preparation, including cleanliness and roughness, oxidation state, preheating time, and temperature, as well as temperature control during and after spraying; and
5. relative motion of the torch and substrate, which controls the coating thickness per pass and, partially, the heat transferred to the coating and substrate.

The first and second items are linked to the particle trajectory distribution within the plasma jet and, thus, to the particle velocity and temperature distributions upon impact, which are key parameters for coating formation.

The third item controls the jet length and is especially important for plasmas, where the entrained oxygen dissociation at 3500 K efficiently cools down the jet in its fringes and controls particle oxidation in-flight.

The fourth and fifth items are linked to the coating A/C, phase structure, and residual stress distribution, among other parameters.

This paper is a status report of the present understanding and knowledge of thermal spray processes with the aim of establishing future research and development needs.

2. Flames and Plasma Jets Formation

2.1. Combustion Processes

2.1.1 Flame Spray Processes. Although very frequently used, traditional (low-velocity) flame spraying is a much forgot-

ten process. No major research has been performed during the last decade, despite the fact that this process is responsible for about 25% of the turnover in the thermal spray business.^[18] However, the DPV 2000 on-line diagnostic process control tool (developed by NRC Canada^[19]) for measuring the temperature, velocity, size, and position of the particles in the flame has shown a rather poor reproducibility for this common process.^[20] The process variation on an industrial day-to-day basis has a significant influence on the behavior of sprayed powders, as well as on the properties of the resulting coatings. For instance, variations of up to 50% in both resistance to erosion and tensile strength and around 10% in porosity have been observed.^[20] According to significant industrial use, a systematic study of the process and gun design would be an important issue.

Special guns have been designed by different companies to spray polymer powders, at least those where the melting point is below about 280 °C (*e.g.*, Ref 21 to 24). However, as far as we know, it does not seem that such guns have been optimized. Thus, to what extent can polymer particles be in contact with the flame? How is the carrier gas (air or nitrogen), which in turn heats the particles, heated by the flame? Such studies are important because polymer spraying is a one-coat process that acts both as the primer and the sealant.^[25] Thermal spraying is well suited for large structures, which otherwise could not be dipped in a polymer suspension or sprayed with electrostatic high-voltage guns. Moreover, such coatings can be easily repaired. Thus, the market for this process seems to be wide open.

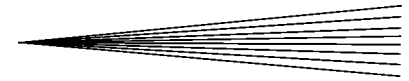
2.1.2 D-Gun Process. For a long time, D-Gun technology has been the reference standard in producing metallic and cermet coatings. However, as it was available only as a service, no research work was published on the process. With the transformations that occurred in the former USSR, Russian equipment and literature on the subject became available in the mid-1990s.^[11,26,27] A one-dimensional (1-D) model describing the gas dynamics of the detonation coating process was developed^[26] and applied to calculate parameters of gas and particles during the detonation spraying of WC-Co particles with an oxygen-propane mixture. It has shown the importance of the composition of the fuel mixture and the location where particles are loaded with respect to the particle impact velocity. The importance of both parameters was confirmed from the analysis of alumina coatings sprayed with oxygen-hydrogen or oxygen-acetylene mixtures.^[27] It was also shown that the particle size, fuel/oxygen ratio, diluent gas percentage, and location of the particle injection play an important role in particle velocity; and these characteristics are linked to the wear resistance of the coating. The effect of the detonation on the crystal phase content of coatings has also been investigated. Compared to HVOF or plasma spray processes, much work, some of which is in progress, is necessary to better understand the phenomena of the D-gun process.

2.1.3 HVOF Process. The HVOF process, in a fashion similar to the D-gun, is based on high-pressure combustion. As the particle velocities are a function of the chamber pressure,^[11] by using higher oxidant content and fuel pressure, impact velocities similar to those of D-Gun could be achieved, in principle. Since the first HVOF torch (Jet Kote system) operating at 0.41 MPa, different torches have been designed with operating pressure up to 1.35 MPa (Terojet, Eutectic Castolin, CH). Besides gas fuels such as propylene, propane, methane, and hydrogen, liquid fuels such as kerosene have been used. The HVAF guns using air in-

stead of oxygen have also been developed with kerosene as the fuel. In fact, the concept of guns has evolved, along with a better understanding of the system, through modeling^[28-30] and measurements.^[31-33] Compared to the developments up to the mid-1990s, the trends with respect to the torch design are a decrease in particle temperature and increase in their impact velocity. Measurements have shown that increasing the volume fraction of the melted phase in particles results in higher oxidation of coatings^[32] and/or higher tungsten carbide decomposition.^[33] The following six solutions have been developed to reduce the particle temperature and to increase their velocity.

1. Injection of particles in the fully expanded, even overexpanded, gas at the barrel entrance just downstream of the de-Laval nozzle.^[11,34] Part of the thermal energy is transformed to kinetic energy by the convergent-divergent nozzle, and particles are less heated but more accelerated. In this case, compared to processes where the powder is injected axially in the high-pressure hot gas, the powder feeder is pressurized below 0.2 MPa and longer barrels can be used without clogging.
2. Increase in the barrel length^[11] and use of a conical barrel instead of a straight one.^[35,36]
3. Increase in the combustion pressure. With oxygen, however, the tank pressure is limited to 1.8 MPa, and, in conjunction with long barrels, high combustion pressures result in high heat losses and, thus, in lower deposition efficiencies. Therefore, a compromise in the combustion pressure is necessary.
4. New torch design.^[34,37] Such torches use kerosene and oxygen and can work at 4.2 MPa. The flame is "shock stabilized" and burning occurs in the short 8 mm diameter bore. The powders are injected into an overexpanded area and allow gravity feed. At such chamber pressures, the particle velocity can be very high (over 1000 m/s^[34]), and, for example, an Inconel 625 coating is fully dense with no oxidation.^[34]
5. New HVAF torches,^[12] which seem to be an attractive alternative to HVOF. At 0.8 MPa combustion pressure and above, the fully expanded jet temperature is below the melting point of Inconel or WC-Co^[34] and high velocities can be achieved for the particles. Moreover, as the compressed air used for combustion provides a major portion of the burner cooling, only 10% of the energy is lost in the cooling system corresponding to 90% of thermal efficiency. Owing to the lower temperature and high velocity, no decomposition or oxidation processes of WC-Co particles occur in HVAF spraying, resulting in a 100% retention of WC-Co particles and a complete absence of W₂C. In contrast, in the HVOF process, oxidation and decomposition can occur.^[38]
6. Use of HVOF or HVAF multiple and single wire spraying systems. Wires are fed at the barrel exit. The coating so-formed contains smaller particles than its powder counterpart owing to the intense shearing action of the flame jet. High throughput can be achieved and makes this technique a competitive alternative to arc spraying,^[34] but at the expense of a higher coating oxidation and a higher cost.

Finally, as far as we know, contrary to the available information for flames, plasmas, and wire arcs, no paper deals with the reproducibility of the HVOF and HVAF processes.



2.2 Arc and Plasma Processes

2.2.1 Plasma Spraying. There is much data available, as detailed below, that deals with d.c. plasma-spraying torches.

- A. For the stick-type hot cathode conventional d.c. torches, the main efforts were devoted to the following five points.
 1. Cathode erosion arises mainly due to the diffusion of thorium dopant toward the cathode tip and its evaporation.^[39,40] The possibility of using more stable dopants such as LaB_6 ^[41,42] has been suggested.
 2. Anode erosion has significant consequences on coating properties.^[43] The study of arc-root fluctuations can help to predict when erosion becomes detrimental to the coating.^[44,45]
 3. Design of the torch nozzle has led to an improvement of heat and momentum transfer to the injected particles.^[46]
 4. The use of ternary Ar-H₂-He plasma-forming gas mixtures increases both the thermal conductivity of the plasma gas (better heat transfer) and its viscosity over 10,000 K (to delay the mixing of the jet with the surrounding air and to lengthen the jet core).^[47,48] The influence of such mixtures on electrode erosion has also been studied.^[49]
 5. It has been shown that the electrical connection to the anode nozzle influences the plasma torch efficiency.^[50] However, it does not seem that commercial torches take this factor into account.
- B. Nonconventional plasma torches were also developed and commercialized in the following fashions.
 1. Various small rotating torches,^[51] which spray inside cylinders (diameter >50 mm), have been created.
 2. Microplasma spraying torches,^[52] with jet diameters between 2 and 4 mm and lengths between 30 and 50 mm, can be used to coat a restricted surface area or spray on narrow strips. Such torches spray mainly nonrefractory metals and alloys.
 3. Torches with axial injection have been commercialized. Those torches improve the heat transfer to particles that are difficult to melt or to particles larger than those used in conventional torches. They use either three cathodes, the powder being fed between them,^[53] or a gas-tunnel type torch, which is switched off once the main torch is ignited.^[54] Such torches allow the spraying of very dense oxide coatings.
 4. Torches with three cathodes and a segmented anode (*e.g.*, the TRIPLEX from Sultzer-Metco CH)^[55] have been developed. The arc current is distributed between the three cathodes, so that erosion is less than that of a single cathode torch. The arc has a controlled length owing to the segmented anode, thereby resulting in very low voltage fluctuations.
 5. Plasma spray systems with two external anodes, constituted of two d.c. plasma torches,^[56] which are placed symmetrically to stabilize the anode spot of the arc, have been designed. The powder is injected before the two plasma jets, issued from the anode torches and behaving as a gaseous anode, to improve the momentum and heat transfer to particles.
 6. Torches working with pure argon, but with a long plasma

column stabilized by vortices, resulting in voltages in the range of 60 to 80 V with 500 to 600 A.^[57]

7. Water plasma torches with a consumable graphite electrode and an external rotating anode are still used to spray high quantities (10–20 kg/h) of oxides or metals.^[58,59] According to the low quantity of vaporized water to produce the plasma, very high enthalpies are achieved with temperatures up to 25,000 K and velocities over 3000 m/s.^[60] Work is now in progress to suppress the drawbacks of such torches such as the consumable cathode and external anode.
- C. Plasma torches allowing the achievement of high velocities (>300 m/s) have also been designed.

All torches presented previously, except the water plasma torches, produce plasma jets with high temperatures (10,000 to 14,000 K in the jet core) and a low density (1/30 to 1/40 that of the cold plasma-forming gas), resulting in fully molten particles upon impact with velocities below 300 m/s. They are not very well suited to atmospherically spray materials that are sensitive to oxidation. To reduce particle oxidation, higher particle velocities with lower temperatures have to be achieved.

1. High power stick-type cathode torches (≈ 100 kW) working with high flow rates (>100 slm) of Ar-He plasma-forming gas and especially designed nozzles to achieve supersonic flows have been designed. Due to the He high viscosity, the acceleration of the particles is much better than with Ar-H₂ plasmas, and, moreover, the jet length is increased.^[2] These torches are used to spray metals or chromium oxide for anilox rolls.
2. Vortex-stabilized torches with button-type cathodes working with a rather low current (<400 A) and voltages up to 500 V^[7,61,62] have been used. The plasma jet temperature is lower^[63] (<9000 K); thus, the gas viscosity and density are higher than with stick-type torches, and the powders are more accelerated. High velocities arise from dissipated powers (150 to 250 kW), resulting in denser coatings with high powder throughputs (>10 kg/h). According to the lower plasma temperature, supersonic jets can be easily achieved.^[64] When using cold well-type cathodes, air can be used as the plasma gas^[65] and steels can be sprayed with a limited oxidation when the particle size is over 25 μm in diameter. Their short residence time and the colder plasma limit their melting and, thus, reduce the volume fraction of liquid phase. High throughputs up to 20 kg/h are also possible.
- D. Several new spraying processes are also now currently used, examples of which follow.
 1. Underwater plasma spraying, which has been developed to achieve a high corrosion-proof surface treatment. One of the aims of this technique is, for example, an extended life of off-shore structures. Studies were devoted to the internal shape of the nozzle shield where particles are melted and propelled toward the substrate as well as the distance, often called clearance, between the nozzle shield extremity and substrate.^[66–69] Dense coatings of metals or alloys, obtained either by injecting powders or wires in the plasma jet, were achieved with neither cracks nor peeling,

despite the fast cooling of each coating pass by the surrounding water, making this technique very promising.

2. High-pressure plasma spraying is now used to increase the plasma enthalpy, in order to achieve better melting of refractory materials within controlled atmosphere chambers. Special torch nozzles have been studied to work at pressures up to 0.3 MPa. This makes it possible to produce shorter plasma jets than at 0.1 MPa, but with a higher enthalpy and almost the same thermal efficiency.^[70,71]

2.2.2 RF Plasma Spraying: Torches Allowing Use of Bigger Particles (up to 150 μm). Because the internal diameter of a 50 kW RF plasma torch is around 50 mm compared to 6 to 8 mm for the same d.c. torch, it is clear that the plasma velocity is 15 to 25 times lower than that achieved in d.c. torches. This results in longer residence times of the particles in the jet, which allow the spraying of larger metal particles, thereby reducing drastically their initial oxide content. Moreover, with such torches, the particles are injected axially into the plasma, thereby optimizing their acceleration and heating. The use of large particles is also particularly interesting for the preparation of monotapes for metal matrix composites.^[8] The best spraying conditions are achieved in a soft vacuum (≈ 40 to 50 kPa). Such pressures help to keep the oxide content of coatings very low but make the equipment more expensive. Many torches adapted to different plasma-forming gas and with different power levels are now available.^[72]

Supersonic RF Plasma Torches. When spraying with d.c. plasma jets at chamber pressure < 30 kPa, the heat and momentum transfer to the particles is seriously reduced by the Knudsen effect.¹ To overcome this problem, supersonic induction plasma spraying has recently been developed.^[73] This consists of an RF plasma torch equipped with an integrated de-Laval nozzle below the coil, with a vertical throat diameter of 10 mm for a torch inner diameter (i.d.) 35 mm. With the axial particle injection in the upper part of the torch, where the pressure is 47 kPa, and a spraying chamber pressure of 6 kPa, particles are fully molten and their impact at higher velocity with the supersonic flow improves the coating density.

2.2.3 Wire-Arc Spraying: Equipment Improvement. In wire-arc spraying, the atomized molten particle size is mainly influenced by the flow of the atomizing gas as well as its turbulence intensity. This has been clearly demonstrated by recent measurements of particle size distributions^[74] as well as arc voltage and current fluctuations,^[75] which are induced by the turbulent intensity of the atomizing flow. Such studies have demonstrated the existence of correlations between, on the one hand, the arc voltage and current fluctuations, and, on the other hand, coating properties. The propelling gas injection and nozzle design^[75,76] have been modified to optimize coating properties. The analysis of voltage and current fluctuations has also allowed a better understanding of the dynamic nature of the flow process and the development of control algorithms.^[77]

New Applications. If, at first, the main application of wire-arc coatings was the protection against corrosion, many other

applications are now used. For example, the development of automated thermal spray systems to spray in-field applications: steel bridge decks, civil works structures, ships, *etc.*;^[78] new composite coatings for enhanced corrosion protection of steel structures;^[79] arc-sprayed mold making for plastic products;^[80] arc-sprayed self-lubricating coatings;^[81] and the use of cored wires in which, for example, hard materials are covered with a metallic sheath.^[82] Cored wires widens greatly the applications of arc spraying, such as, for example, NiCrAlY bond coats for thermal barriers, which have higher bond strengths than those plasma sprayed (up to 1.5 times higher).^[83]

3. Heat and Momentum Transfer to Particles, Powders, Injection, and Reaction with Their Surrounding Atmosphere

Most of the studies have been devoted to plasma spraying and HVOF, a very few being related to D-guns^[26,27] and almost no studies reported on flames. Thus, this section will mainly deal with plasma jets and HVOF.

3.1 Flame or Plasma Flows with Particles

3.1.1 Modeling. Heat and momentum transfer between a high-temperature flow and a single particle received a lot of attention in the 1980s. The paper by Boulos *et al.*^[84] presents an overview of our current knowledge. It takes into account the heat propagation phenomenon in the particles and all the corrections needed under thermal plasma conditions, *e.g.*, steep temperature gradients in the boundary layer surrounding the particle, Knudsen effect, and vaporization.

The acceleration and melting of particles can be predicted, provided temperature and velocity distributions of the flow are known, which can be done either by modeling and/or measurements.

In HVOF, Oberkampf and Tallpalikar^[85,86] have assumed an axisymmetric geometry. The combustion of propylene was modeled by a one-equation and an approximate equilibrium chemistry model that accounted for dissociation of the combustion products. They considered full coupling between the interior and the exterior flow fields. The numerical algorithm used an Eulerian/Lagrangian approach for the gas and solid phases, both phases being coupled through momentum and energy exchange terms. More recently, this model was extended to three-dimensional (3-D) to represent a setup with a curved air cap used for coating interior surfaces.^[30]

For d.c. plasma jets, no reliable model presently takes into account the arc column, with its attachment at the anode-nozzle wall, which is a full 3-D unsteady-state problem. All models calculate, at the nozzle exit, velocity and temperature distributions matching the plasma gas-mass flow rate and its enthalpy. The most popular model for the plasma flow is the k - ϵ turbulence model with, if necessary, the correction of Launder and Sharma to account for low Reynolds numbers occurring in the plasma core. The initial simplified approach, in which particle effects have been de-coupled from the plasma flow, has been extended to iterative techniques to include loading effects.^[87] The LAVA code^[88] incorporates the particles and their stochastic distribution. This code can also take into account nonequilibrium effects, *i.e.*, when electrons and heavy particles have different

¹ Knudsen effect occurs when the mean free path ℓ in the plasma is no longer small compared to the particle size d . To use the fluid dynamic equations, it is requested that $\ell/d < 100$. As ℓ is inversely proportional to the gas density, ℓ increases when the pressure decreases and the heat and momentum transfers to particles are reduced.

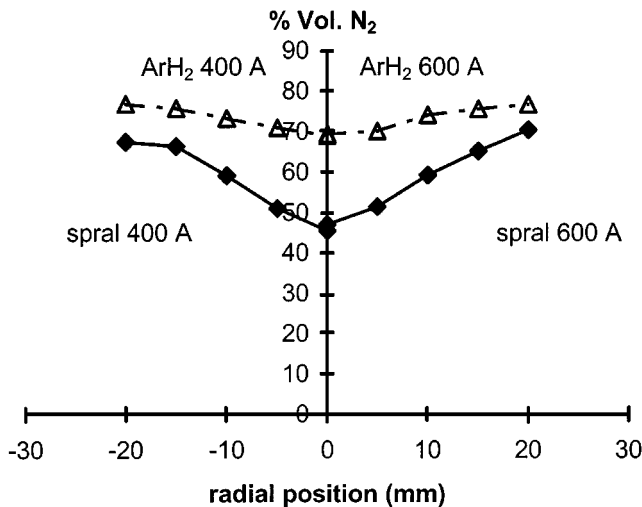
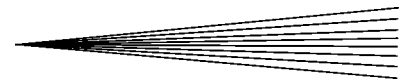


Fig. 1 Influence of the arc current on surrounding air entrainment for Ar-H₂ (45/15 slm) and Spral 22 (60 slm) plasma jets; nozzle i.d. 7 mm and 80 mm from the nozzle exit^[97]

temperatures. However, in most cases, the particles are injected through a tube orthogonal to the plasma jet and the problem is 3-D, which adds to its complexity. Such calculations have been recently performed^[89-91] by extending the ESTET code,^[92] developed for plasma heating to plasma spraying.

A realistic model should also take into account the large-scale entrainment of the very dense ambient gas into the low density plasma jet, a phenomenon probably enhanced by the arc root fluctuations inducing some type of piston flow. The mixing with the plasma of the entrained cold gas bubbles, which are 20 to 40 times denser than the former, is very slow and the turbulent plasma jet must be treated as a two-phase mixture.^[93]

The development of these codes, especially for plasma jets, has become possible only because calculations of transport properties of plasma gases used for spraying (Ar, Ar-He, Ar-H₂, Ar-H₂-He, and N₂-H₂) and of the surrounding air^[94] can be carried out. To avoid overcomplex calculations when air is mixed with the plasma gas, mixing rules are used.^[95]

The development of these calculations of transport properties has allowed Air Liquide to patent the ternary mixture Ar/He/H₂ called Spral,^[47,48,96] which increases the plasma-jet core viscosity and its heat-transfer coefficient. Such a mixture delays the mixing of the surrounding air with the plasma gas, compared to a classical Ar-H₂ mixture.^[97] This is illustrated in Fig. 1 where the nitrogen originating from the surrounding air is measured 80 mm downstream of the torch exit with an enthalpy probe, coupled with a mass spectrometer. Moreover, compared to an Ar-H₂ mixture, Spral improves the lifetime of the torch electrodes.^[98]

For RF plasmas, the flow calculations are simpler, as is the powder injection due to the torch symmetry and the powder axial injection. The effect of the metallic probe injection on the electromagnetic fields is generally neglected, but that of the cold carrier gas is taken into account.^[99]

3.1.2 Measurements. Modeling is backed by measurements of the plasma jet and particle diagnostics.

To characterize the plasma jet, emission spectroscopy, laser scattering (Rayleigh and Thompson), Coherent Anti-Stokes

Raman Scattering, enthalpy probes coupled with mass spectrometry, and laser strobe imaging^[100,101] are all used. The obtained results have demonstrated the nonequilibrium effects, the surging and whipping of the plasma jet due to arc-root fluctuations, the engulfment process for the surrounding air entrainment,^[102] and the importance of the design of the plasma-forming gas injector close to the cathode tip on the flow temperature^[63] and velocity distributions.^[44]

For particles in-flight, fast pyrometry (50 ns), laser Doppler anemometry and sizing laser anemometry, emission, and absorption spectroscopy to follow the vapor cloud surrounding a single particle in-flight^[100-106] are used. The main results are as follows: the particle injection has a drastic influence on the particles' trajectory velocity and temperature distributions; the fast particle evaporation,^[107] occurring either with rather low boiling temperature materials or heat propagation phenomenon in refractory materials,^[106-108] greatly modifies the heat transfer and cools the plasma by the resulting intense radiation; and the plasma jet fluctuation changes at frequencies between 2 and 10 kHz the mean trajectory of the particles and their heating.^[109]

3.2 On-Line Control

The properties of coatings depend strongly upon the molten state and velocity of the particles upon impact.^[110,2,17] In order to evaluate on-line the state of the key physical process variables, sensors based on the measuring techniques presented in the previous section have been developed to monitor these characteristics. They have been designed to resist the harsh environment existing in spray booths and give reliable information over time.

3.2.1 DPV 2000 Technar CN. The setup developed by Moreau *et al.*^[19,111,112] is a robust easy-to-use optical sensor allowing particle temperatures prior to their impact to be determined by using a fast (100 ns) two-color pyrometer, while their velocities are measured by a time-of-flight technique. An optical-fiber linear array, located in the same sensor head, is used to monitor the hot jet particles and characterize the trajectories of the sprayed particles. The radiation from the hot particles is detected by a camera that permits the measurement of the orientation and width of the particle jet relative to the plasma gun. The corresponding dimensions of the measurement volume are about 3.9 mm length × 280 μm height × 500 μm width (dimensions are with respect to the centerline of the plasma torch).

Under industrial conditions, the torch is positioned in front of the sensor head for 1 min; then, the piece is coated and the torch comes back in front of the sensor head for a 1 min measurement.^[113] The data are saved on a PC disk. This setup makes it possible to (1) determine when the load effect becomes important;^[112] (2) compare guns working with the same macroscopic parameters in different booths;^[113] (3) measure the time necessary before reaching stability of the particle spraying conditions;^[113] (4) correlate the particle parameters upon impact with the structure of plasma-sprayed coatings;^[114] (5) increase the reproducibility of the spraying process;^[20] (6) check the long-term stability of plasma spraying;^[115] and (7) correlate the information about particles in-flight to the coating deposition efficiency, coating microstructure, and diffusivity.^[116,117]

Such measurements are more sensitive to process variation than the classical control system of keeping constant the plasma

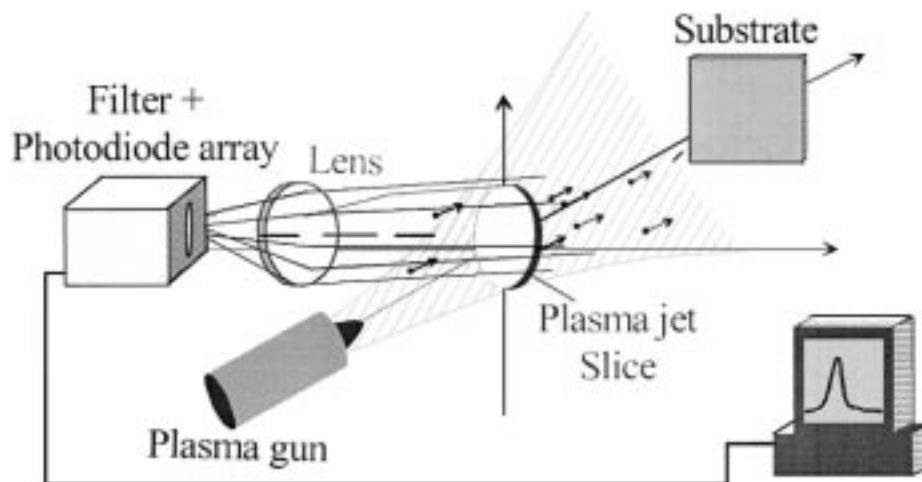


Fig. 2 Schematic view of the experimental setup for the sensing of particle spray

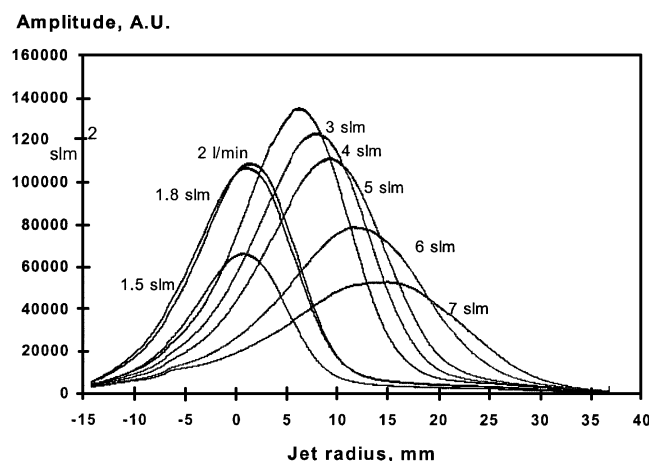


Fig. 3 Effect of the carrier gas flow rate on the radial distribution of alumina powder (22 to 45 μm). Ar-H₂ (45/15 slm) d.c. plasma, $I = 600$ A, nozzle i.d. 7 mm, and internal injection 2 mm upstream of the nozzle exit with a 1.8 mm i.d. injector. Measurements performed 70 mm downstream of the nozzle exit

power and gas flow rate. They are also very sensitive to the powder carrier gas flow-rate variation.

3.2.2 In-Flight Particle Pyrometer. A similar but simpler system has been developed by Swank *et al.*^[118] The sensor head forms a measurement volume, which is pencil shaped, 5 mm in diameter, and approximately 50 mm long. This allows the determination by two-color pyrometry of the mean temperature of particles crossing the measurement volume. It has been used on NiAl particles in-flight in a plasma jet^[118] and on alumina droplets resulting from an arc spray.^[119]

3.2.3 Video Cameras. Recently, a three-intensified sensor color high-speed video camera has been proposed to measure simultaneously particle temperatures and velocities.^[120] Stratronics proposes an imaging two-color pyrometer, using a Charged Coupled Device (CCD) camera and allowing the measurement of particle temperature distributions from 600 to 2700 K with an accuracy on the order of 10%. The system provides simultaneously two images at short and long wavelengths.^[121]

A promising imaging technique using a fast nonintensified CCD camera^[122,123] has been proposed by Vattulainen *et al.* This allows measurement of particle trajectory, velocity, and temperature.

3.2.4 Use of a 1-D Detector Array. A CCD camera, with its associated computer and software, is more expensive (almost one order of magnitude) than the 1-D detector equipment now under development. The experimental setup of Vardelle *et al.*^[91,124] to determine the hot particle spray position within the plasma jet, and its spread, is shown in Fig. 2. The measurement technique is based on the real-time detection of the thermal radiation emitted by particles. The system comprises a lens, 60 mm in diameter, and a computer-controlled 1-D detector array, consisting of 1024 photo-diodes. A slice, 50 mm in diameter and 100 μm thick, of the particle jet is focused on the photo-diode array. An interferential filter centered at 514.5 nm with a pass band equal to 3 nm makes it possible to eliminate the lines emitted by the plasma gas and the plasma light reflected by the particles. The time sequence for data acquisition is 13 ms, which permits recording 70 spectra per second or a time-averaged recording over a time ranging between 0.013 and 120 s.

The collected data are analyzed in real-time mode with commercial software. The data processing consists of subtracting the background light and then determining the maximum amplitude of radiation intensity and its position along the plasma-jet diameter. Recording such signals along the torch axis allows the particle character to be determined. The amplitude of the recorded light signals depends equally on the number of particles, their size, and temperature. For a set of plasma spray conditions, the comparison of these data with stored reference data enables corrective actions to be made when a drift is observed.

For example, Fig. 3 shows the effect of the carrier gas flow rate on the radial distribution of hot alumina particles in an Ar-H₂ plasma jet. Measurements performed in an industrial booth during 1 week have shown the good reliability of the setup, which allows any drift of the particle injection to be corrected, conditions either due to carrier gas flow-rate variation or a decrease of the torch power due to electrode erosion (Section 3.4).

3.3 Powders

Powder with the same chemical composition and size distribution from different suppliers can have a very different morphology owing to the different powder manufacturing methods used. Thus, thermally sprayed coatings exhibit significant variations, even though the starting powders appear to be equivalent with respect to the chemical composition and particle size distribution.^[125] This has been demonstrated for plasma spraying,^[126–130] HVOF,^[131–133] and D-gun.^[132,134]

Particle morphology plays an important role in pneumatic feeding. Its flowability is not necessarily the only criterion; the powder mass flow rate also depends directly on its apparent density,^[135] which is highest with dense spherical particles such as those made denser by RF plasmas.^[136] Morphology is also important for the particle behavior upon penetration within the plasma jet,^[108] for example, with the de-agglomeration of agglomerated particles. The homogeneity of the particles^[126,128] is a key parameter for coating behavior, especially at high temperatures. For complex compositions, such as those resulting in quasi-crystalline coatings, there is also a close link between processing, phase structure, and coating properties.^[137,138] Finally, it must be kept in mind that powder characterization is not necessarily straightforward; for example, the characterization of particle size distribution^[139] may vary depending on the particle morphology.

New powder manufacturing techniques seem to be very promising. Reactive powders, for example, with carbon and metal, allow carbide coatings by self-propagating high-temperature synthesis (SHS) to be produced during particle heating in the plasma jet.^[140,141]

A second example concerns agglomerated particles with carbon short fibers, which allow coatings with a better resistance against wear by abrasion and a better adhesion compared to those obtained with “pure” materials to be produced.^[142]

The mechanofusion process, a third powder manufacturing technique, results in size reduction and shape spheroidization for brittle and irregularly shaped powders. Strong mechanically bonded Ni/Al composite powder with a uniform phase distribution was produced by this process.^[143] Steel particles covered with an alumina shell 3 to 4 μm thick were fabricated and the resulting coatings exhibited a uniform distribution of alumina grains (in the range 0.1 to 1 μm) in a steel matrix.^[144]

A fourth example concerns suspension plasma spraying of fine (<10 μm) or even ultrafine (<100 nm) particles, which are axially fed into an induction plasma through an atomization probe. The atomization of the suspension results in droplets about 20 μm in size. Owing to their long residence time (>1 ms), they are flash dried in the plasma and then melted. They can be either collected as powders or directly sprayed onto a substrate. This allows polyphase particles to be achieved and the preparation of immiscible phases or composite particles with a great flexibility in material composition.^[145] When starting with nanosized particles ($d < 150$ nm) within the suspension, it is even possible to obtain thin coatings with nanosized grains.

3.4 Powder Injection

Importance of Injection Control. In most cases in thermal spraying, particles are introduced into the plasma flow by means

of a carrier gas flow through an injector. Injection parameters control, to a large extent,^[146,147] (1) the distribution of particle trajectories in the plasma jet and, thus, their acceleration and heating, and (2) the deposition efficiency.

The carrier gas mass flow rate must be adjusted so that the maximum number of particles penetrate the plasma flow and have the optimum acceleration and heating. The mass flow rate depends on the injector geometry, diameter, and location; the hot jet momentum and density; and the particle size distribution of the material feedstock. For example, any reduction of the power dissipated in the flame or plasma jet due to the erosion of the nozzle or anode modifies the mean trajectory of the particles if the carrier gas flow rate is kept constant. In plasma spraying, a change of 0.1 mm of the distance between the injector exit and the torch axis modifies the particle mean trajectory.

If there is a general appreciation that injection parameters can be important, very few investigations conducted under controlled and documented conditions are available.^[146–149] In addition, the injection conditions must be stable in order to make the spray process consistent and reproducible. Instabilities in powder injection may arise from the feeding system and, for d.c. plasma interaction with the plasma jet. The latter is linked to the plasma spray procedure and depends on the fluctuations of the plasma flow resulting from the anode arc-root motion. The time constant of this process ranges between 0.5×10^{-4} and 0.5×10^{-3} s. Instabilities linked to the powder gas feeder have longer time constants, approximately 0.1 to 100 s and more. These instabilities can result from the feeder type, which delivers an interrupted or inconsistent flow of powder, or from various feeding problems such as gas leakage, curves, and bends in the piping system, agglomeration of the powder in the hose and plugging,^[149] etc. Of course, the morphology and the density of the powder can enhance these problems.

The balance between the rate of change of momentum when injecting a particle and the drag force from the jet flow acting on it determines its trajectory.^[91] Most studies have been performed on injection in plasma jets; however, the general trend should be the same for HVOF with radial injection. In plasma jets, the optimum trajectory is an angle of 3 to 4° relative to the torch axis.^[108] However, particles have a size distribution as well as a velocity distribution, and, owing to collisions with the injector wall and between themselves, their injection velocity vector does not necessarily point in the direction of the injector axis.

Setup to Characterize Particle Injection. To study these phenomena, the 3-D CFD code ESTET^[89–91] has been used to calculate particle trajectories in the injector and then in the plasma jet. Cold-particle trajectories outside the injector or in the plasma jet have been measured^[146] using a setup based on the burst counting of scattered light, by particles passing through a focused detection beam, as shown in Fig. 4.

A uniform laser sheet orthogonal to the plasma jet axis was generated by an oscillating mirror (2400 Hz). The laser beam was provided by an argon laser with standard input of 2 W (TEM₀₀ mode). The laser sheet scanning had a standard height of 50 mm centered on the torch or injector axis. The scattered light was focused on the entrance slit of a monochromator, adjusted at the laser source wavelength (514.5 nm) with a band pass filter of less than 0.1 nm. The scattered light was detected with a 1024 linear photo-diode array connected to a computer for

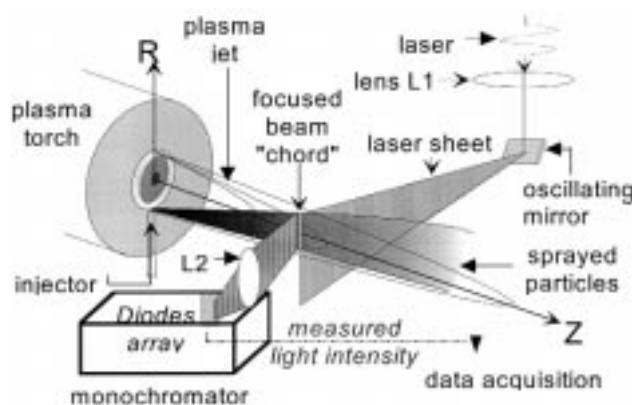


Fig. 4 Schematic view of the experimental setup to follow cold particle trajectories

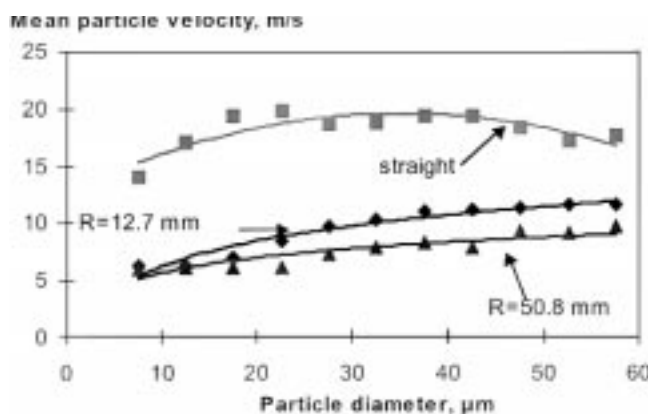


Fig. 5 Mean particle velocity computed vs particle diameter for ZrO_2 powder injected in different tubes. Carrier gas flow rate: 4 slm. Length of the straight part of the curved injector: 35 mm, and i.d.: 1.8 mm, with two different curve radii: 12.7 and 50.8 mm

data acquisition. Hot particles were detected by the setup described in Fig. 2 (Section 3.2).

Most Important Results Related to Injection. The obtained results are presented in detail in Ref 150, and only the six main points will be emphasized.

1. Inside the injector, the flow is generally turbulent ($3000 < Re < 8000$), and there is little dependence of particle velocity on the particle's size at the injector exit. The collisions with the injector wall, especially for particles where diameter d is below $20 \mu m$, are responsible for the particle jet divergence at the injector exit. This does not result in size segregation of the particles within the jet, as confirmed by measurements performed in a small volume (a cylinder $160 \mu m$ in diameter and $160 \mu m$ in length).^[151]
2. The use of a straight or curved injector results in some differences at the injector exit, as illustrated in Fig. 5. The latter shows the calculated velocities of zirconia particles with different diameters at the exit of straight or curved injectors with two different radii of curvature (12.7 and 50.8 mm) followed by a 35 mm long straight section. As con-

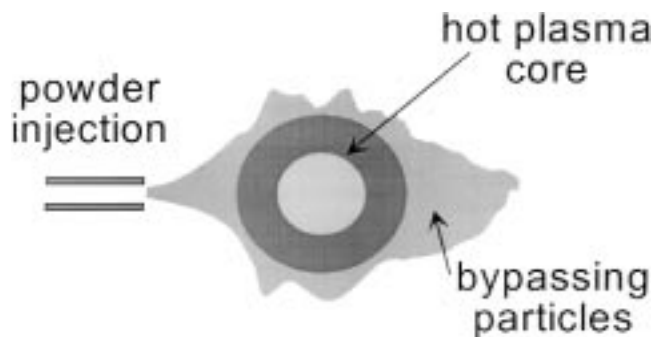


Fig. 6 Scheme of the particle bypassing the plasma jet

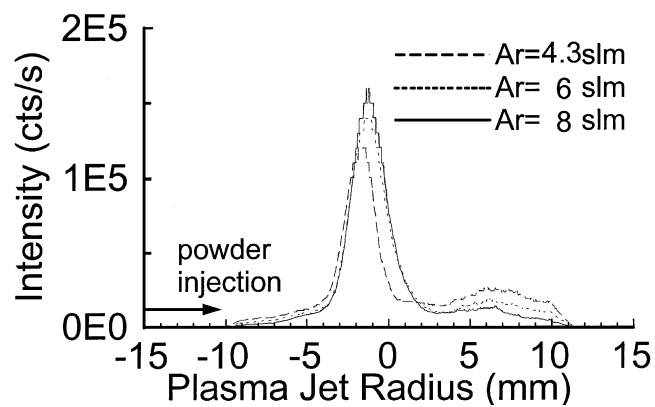


Fig. 7 Cold zirconia particles (fused and crushed $-45 +5 \mu m$). Radial distribution at $z = 10$ mm when injected in an Ar- H_2 (45/15 slm) plasma jet, $I = 600$ A, nozzle i.d. 7 mm, and external injection with a 1.8 mm i.d. injector

firmed by measurements, the bend results in a reduction of particle velocity. Particles are driven to the outside of the curve, where the gas velocity is lower and wall collisions are enhanced.

3. Owing to the divergence of the trajectories, some particles, especially particles $< 20 \mu m$, bypass the plasma jet, as schemed in Fig. 6. Their quantity increases when the carrier gas flow rate is beyond or below that resulting in the optimum mean trajectory (6 slm), as shown in Fig 7. Particles bypassing the plasma jet are sucked downstream by it. They are then entrained with a lower velocity (Fig. 8) and they can create defects in the coating when they stick to it because they are usually still in a solid or plastic state.
4. Internal injection allows a better heat and momentum transfer to particles compared to external injection. However, in internal injection the plasma jet is more disturbed by the cold carrier gas than it is with external injection. This is illustrated in Fig. 9 which shows the predictions obtained with the ESTET C.F.D. code.^[152]
5. These measurements have also confirmed the drastic influence of the plasma jet fluctuations (at frequencies between 2 and 20 kHz). They act mainly on the particle trajectories, a lower momentum of the jet resulting in a mean particle

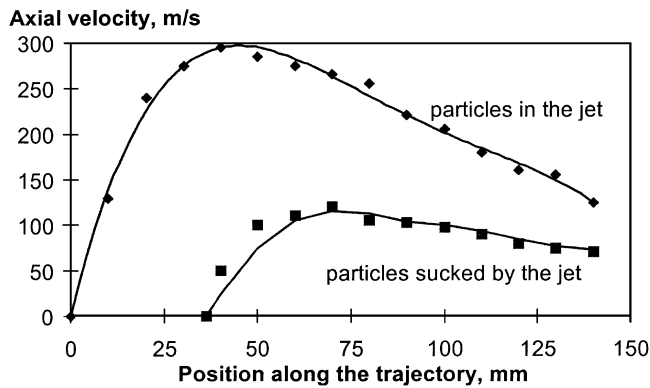


Fig. 8 Alumina particles ($-45+5\ \mu\text{m}$) mean velocity along their mean trajectory with the bypassing particles traveling in the jet periphery sucked into the jet flame further downstream. Same conditions as those depicted in Fig. 7

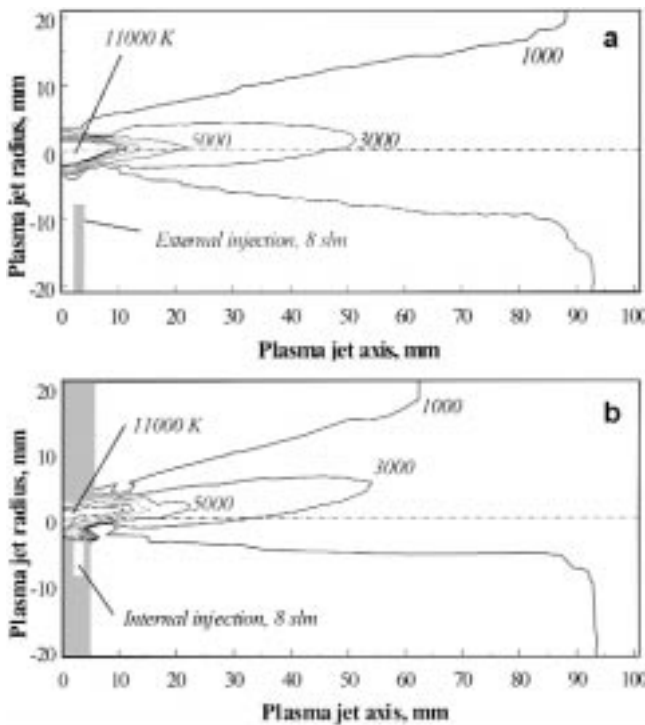


Fig. 9 Modeling of a plasma flow interacting with a powder carrier gas Ar-H₂ (55/15 slm). d.c. plasma torch with a 7 mm nozzle i.d., where an effective thermal power of 13.5 kW is dissipated; powder injector 1.8 mm in i.d.; and 8 slm of Ar carrier gas. (a) external injection and (b) internal injection

trajectory crossing the jet axis and a higher plasma jet momentum resulting in particles barely crossing it.

- Finally, the pipe between the torch and the powder feeder plays an important role with its length and path, as well as the powder feeder position relative to the torch.^[153] Naturally, the regularity of the powder feeding and its mass control, independent of the carrier gas flow rate, are also key issues, the regularity being linked to the powder feeder and powder flowability and apparent density.^[134]

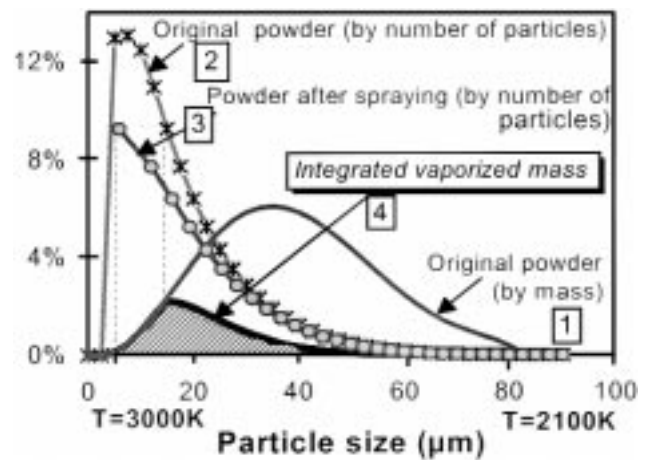


Fig. 10 Size distribution of an iron powder before and after thermal treatment. Computed total vaporized mass fraction: 17%. Used plasma gas Ar-H₂ (45/15 slm), $I = 380\ \text{A}$, nozzle i.d. 7 mm, and external powder injection

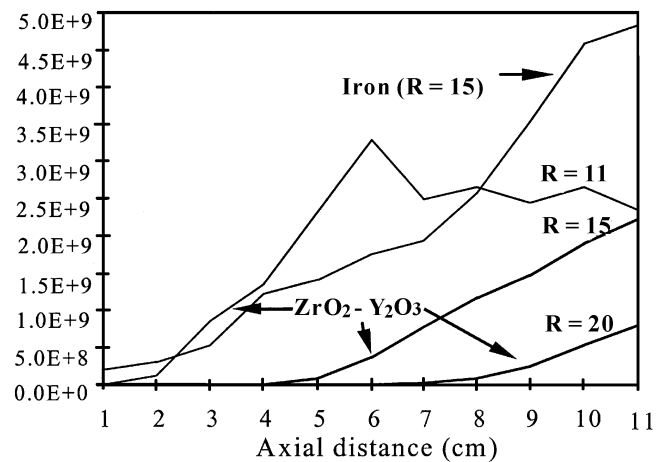


Fig. 11 Number concentration (cm^{-3}) of iron and ZrO₂-Y₂O₃ particles less than $1\ \mu\text{m}$ in diameter collected at different distances R from the plasma jet axis. Spraying conditions as in Fig. 10

3.5 Reaction of the Particles with Their Environment

As already emphasized in Section 3.1, when an unconfined high-velocity jet issues from a nozzle into the surrounding atmosphere, it entrains the cold ambient gas. For example, the entrainment of ambient air in a plasma or HVOF jet may increase the mass flux of the jet by a factor of more than 10.^[154,155] The entrained surrounding gas can react with the hot particles or the vapor originating from particles. This will create either defects (oxidation or microparticle trapping) or interesting processing opportunities such as reactive plasma spraying.

3.5.1 Particle Evaporation Condensation. Vaporization can be easily achieved with d.c. plasma jets either with relatively low-boiling temperature materials or refractory materials with low thermal conductivity, where the heat propagation phenomenon will dramatically increase the particle surface temperature.^[84] The vaporization is strongly linked to particle size, as

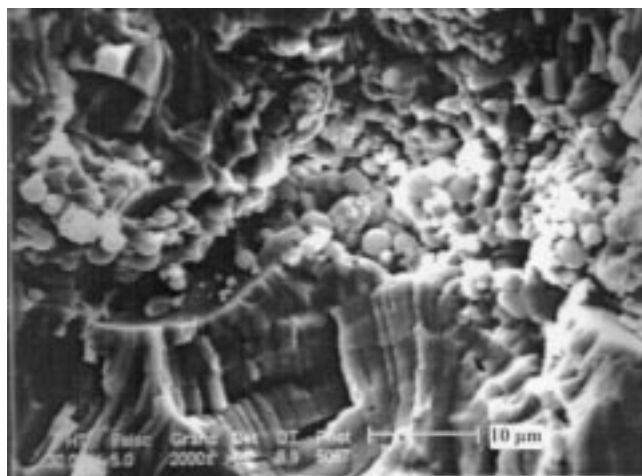


Fig. 12 Interface between two successive passes of zirconia coating ($\text{ZrO}_2 + 8 \text{ wt.}\% \text{ Y}_2\text{O}_3 - 45 + 15 \mu\text{m}$), kept at 500°C during spraying (conditions as in Fig.)

illustrated in Fig. 10,^[156] for iron particles with different diameters injected in an Ar-H₂ plasma jet.

The vaporized mass fraction for iron particles ($-55 + 14 \mu\text{m}$) increases dramatically with arc current and H₂ vol.% in the plasma jet. Metal vapors are oxidized by the entrained air and condense in the cold zone of the jet. This also occurs with the vapors of refractory materials, *e.g.*, ZrO₂, as has been demonstrated by using an electrical low-pressure impactor at various radial and axial distances (Fig. 11)^[157] Such vapors often appear as smoke.

The small condensed particles ($d < 1 \mu\text{m}$) may stick between successive passes, especially when the substrate is maintained over 500°C , and create defects, as illustrated in Fig. 12.^[158] These fine particle layers reduce the coating A/C (15 MPa compared to 50 MPa without them). Such particles can be eliminated to a great extent by using air barriers blowing orthogonally to the jet close to the substrate.

Of course, their recirculation in the spray booth must also be avoided with an efficient dust collection system.^[159]

3.5.2 Particle Oxidation. When spraying in air, particle oxidation takes place in-flight, at the splat surface and between passes. As already emphasized, the quantity of air entrained in HVOF or plasma jets depends strongly upon the jet velocity^[160-163,155] and, for plasma process, upon its velocity and viscosity.^[98,164] The oxidation effect is discussed in terms of (1) in-flight processes, (2) during coating formation at the substrate surface, and (3) the influence of shrouding systems to control oxidation.

In-Flight. Other than the quantity of entrained air, oxidation depends strongly upon the particle temperature and whether the molten droplets or solid particles can react.

Oxidation of Molten Droplets. If it is over the melting temperature, the convection within the molten droplet will ease the formation of internal oxides, especially if the suboxide formed has a low melting temperature. Oxidation is then no longer controlled by diffusion because fresh metal at the particle surface is continuously renewed while the formed oxide is entrained within the particle by the convective movement of the liquid. This phenomenon is observed with low-carbon steel particles,

which can contain more than 10 wt.% of FeO when sprayed in air.^[165]

With d.c. plasma jets working with Ar-H₂, this phenomenon is enhanced by the piston flow induced by the arc root fluctuations (restrike mode). This results in air entrainment in the plasma core as close as 20 mm downstream of the nozzle exit.^[166] The oxygen of the air entrained in the plasma core is almost instantaneously converted in atomic oxygen of higher reactivity.

Oxidation of Solid Particles. If the particle temperature is below the melting temperature, oxide shells will be formed around the particle. For example, with low-carbon steel, the shell is mainly made of Fe₃O₄ and not Fe₂O₃.^[167] Thus, oxidation conditions will be very different in (1) HVOF with particles usually below their melting temperature and with velocities between 300 and 500 m/s, resulting in residence times of the order of 1 ms; and (2) in plasma jets with fully molten particles, with about the same residence time, but with surrounding oxygen mostly in the atomic form.

With HVOF, when increasing the oxygen to combustion gas ratio, the gas temperature decreases and the volume fraction of molten phase (VMP) decreases. Therefore, the oxygen content of coatings decreases. On the contrary, if the combustion pressure increases, the VMP also increases, as does the oxygen content of coatings.^[155,168] It seems also that well molten particles can burst when impinging on the substrate surface, forming oxidized subparticles. Thus, the oxide content of coatings rises due to an increased oxidized specific surface area.

The particles react also with the surrounding air entrained in the flow,^[154] as shown by the decrease in particle stream luminescence when the jet flows in an inert atmosphere. For example, in the experiment of Hackett and Settles,^[154] the coating oxygen content when spraying under a controlled atmosphere or air varied from 0.9 to 3.4 wt.%.

Splat Oxidation and Oxidation during Spraying. Splats exposed to the oxygen of the jet for a very short time (a few tens of microseconds) are probably not oxidized very much. On the contrary, sprayed layers, which may be exposed a few seconds to the hot jet containing sometimes more than 90 vol.% air, are more sensitive to oxidation, especially if they remain at high temperature (*e.g.*, over 400°C for steel) and if the jet temperature close to the substrate is over 3000 K and results in the presence of atomic oxygen in a plasma jet plume.^[162-164]

With HVOF, for example, the substrate temperature and oxide content of aluminum coatings sprayed solely on the centerline of the jet both decrease with an increasing stand-off distance.^[155] It is, thus, of primary importance to control the substrate and coating surface temperature, for example, by using air jets^[169] or liquid CO₂.^[170]

Influence of Shrouding on Oxidation. Determination of the oxide content of coatings is not necessarily simple.^[171,172] The effect of the metal oxidation on the coating properties is severe. For example, the tensile strength of 316L stainless steel decreases with the oxide content and its elongation drops from 40% with 2 wt.% oxide to 3% with 23 wt.%.^[168] Therefore, solutions have been searched with gas or nozzle shrouding to limit oxidation as much as possible, without using controlled atmosphere spraying, for HVOF,^[168,173] plasma torches,^[174-177] or wire-arc spray.^[178] When the mass flow rate of the shrouding inert gas increases, the oxygen content in the coating decreases.^[168] For HVOF, the shrouding gas-flow rate is important (≈ 0.3 to 0.4

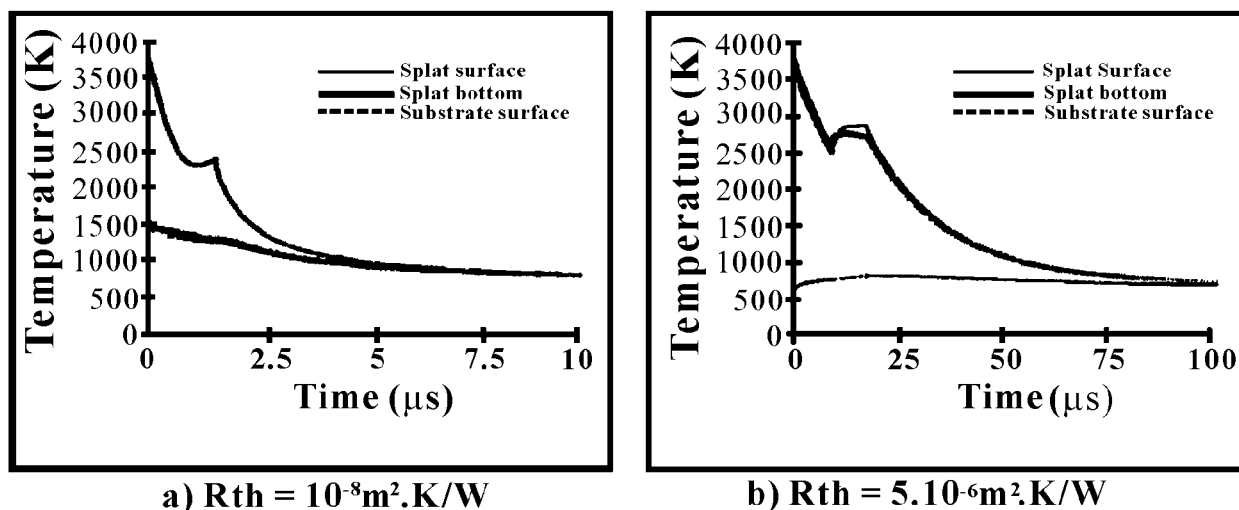


Fig. 13 A 1 μm thick zirconia splat on a smooth stainless steel substrate preheated at 600 K: evolution with time of the splat surface and interface temperatures for two values of R_{th} (particle impact temperature: 3800 K)

kg/s) since it slows down the particles and reduces their temperature, which may also help to decrease their oxidation.

With plasmas, shroud nozzles are used with shroud gas injection at the nozzle exit to avoid air entrainment along the nozzle wall, owing to the fact that the nozzle divergence has to be sufficient to avoid molten particle sticking.^[174]

3.5.3 Reactive Plasma Spraying. Wear-resistant carbide-, silicide-, or nitride-reinforced coatings have been produced by reactive plasma spraying.^[179–184] A nozzle made of refractory material and kept at about 2000 K is positioned downstream of the plasma torch anode nozzle, which works in a controlled atmosphere chamber. Gases containing carbon (*e.g.*, from CH_4), nitrogen (from NH_3 . . .), and Si (from SiH_4 . . .) are introduced within this nozzle. These gases are heated, dissociated, and ionized by the plasma jet to form C, N, and Si species, which react with the molten metal particles. The result is the formation of dispersed ceramics (TiC , Si_3N_4 , and MoSi_2) within the sprayed metallic matrix. As the coating is formed in a controlled atmosphere chamber, it can be kept at 800 to 1000 °C during spraying and the deposited layers can also react with the active atoms. Much work has been devoted to the technique. However, even if very promising, this new method still requires more studies to control the ceramic particle size and distribution within the coating. Moreover, as it requires a controlled atmosphere, it is rather expensive.

This method has also been used for the in-flight carburizing of MoSi_2 powders in $\text{Ar-H}_2\text{-CH}_4$ induction plasma. Up to 8 wt.% C was incorporated into the MoSi_2 particles.^[185]

4. Coating Formation

A coating is built by successive impacts of particles in a molten or plastic state on the substrate or previously deposited layers, the next particle impacting on an already completely solidified one. Thus, coating thermomechanical properties depends not only on the way particles flatten and the resulting splats solidify and cool down, but also on the thermal history of the par-

ticles layering at the same location. These facts were detailed by McPherson,^[110] in 1981, long before measuring devices to study splat formation and their layering were developed.

4.1 Splat Story

In practical situations, particles impact on rough surfaces, which are more or less oxidized for metals and alloys; but most measurements deal with smooth surfaces, while models, besides the smooth surface, assume there is no intermediate oxide layer between the substrate and first splats.

4.1.1 Models. The first analytical models^[186–192] found a relationship between the flattening degree ξ and the Reynolds number of the particle. The former is defined as $\xi = D/d$, where D is the diameter of the splat, assumed to have a disk shape, and d is the impacting droplet diameter; and the latter is defined as

$$\text{Re} = \frac{\rho_p \cdot v_p \cdot d}{\mu_p} \quad (\text{Eq 1})$$

where ρ_p , v_p , and μ_p , are, respectively, the specific mass, velocity, and viscosity of the particle.

The simplest expressions were of the type

$$\xi = K \cdot \text{Re}^a \quad (\text{Eq 2})$$

with different values of K (from 0.8 to 1.294) and a (from 0.125 to 0.2).

Some more complex expressions involving the Weber number We^2 and contact angle θ were also established. Only two models dealt with a rough surface.^[193,194]

Numerical models are all related to smooth surfaces. A few of them take into account the shock waves developing at the beginning of the flattening,^[195–197] but they assume incompressible flow. Early authors^[198–203] have partially or totally neglected the material solidification, while more recent studies^[204–212] have in-

² $We = \rho \cdot v \cdot d / \sigma$, where σ_p is the surface tension of the droplet.

cluded solidification, which starts before flattening is completed. All these models assume that the thermal contact resistance between the splat and substrate or previously deposited layers is very low (10^{-7} to 10^{-8} m²·K/W), which is probably the case at the beginning of the flattening but which might not be the case at the end of it. One-dimensional calculations of splat cooling have shown the drastic influence of the value of the thermal contact resistance R_{th} ³ on splat cooling.^[213] This is illustrated in Fig. 13, which shows the time evolution of the splat surface and interface temperatures as well as the surface temperature of the substrate.^[214] When R_{th} is low, the cooling of the splat bottom is faster than that of its top, while the heating of the substrate surface is very fast and the temperature attained is high (Fig. 13a). When R_{th} is high, the splat cooling is slow; thus, its top and bottom have almost the same temperature, and the heating of the substrate surface is also slow with a maximum temperature half that of the preceding case (Fig. 13b).

These 1-D calculations were achieved by assuming that nucleation took place at the material melting temperature, but the results can be greatly modified if the nucleation process is included in the model.^[215–217] The microstructure development of the deposit depends on the solidification details and the resulting microstructures of the splats.^[218] The latter depends on the molten state of the impinging particle, its velocity, and the thermal contact resistance between the resulting splat and the substrate.^[213] However, the microstructure is also linked to the particle and substrate oxidation, as shown for Ni splats sprayed under APS and vacuum plasma spraying^[218] conditions.

In fact, a “good” model should be a numerical one, which takes into account (1) the particle flattening, (2) its solidification starting when the hypercooling temperature is reached, (3) the nucleation phenomenon and the evolution of the contact between the flattening particle and the substrate or the previously deposited layers.

4.1.2 Experiments: Measuring Devices. Techniques allow the collection on a smooth surface, the temperature of which can be controlled, either of a few splats related to particles with a given trajectory^[219–221] or of thousands of them related to particles within the whole spray cone.^[222–224] Splats are analyzed by image analysis, giving their shape and mean diameter.

The particle flattening behavior and related cooling of a single droplet impinging on the substrate are investigated from the droplet’s thermal radiation with high speed ($\tau < 100$ ns) pyrometers, either monochromatic or bichromatic.^[225–228] To achieve good measurement precision of the velocity and diameter of the impacting particle, a laser phase doppler particle analyzer (PDPA) can be used.^[228] When spraying on a glass substrate, it is even possible to measure the splat diameter evolution during its cooling.^[230]

Results

On smooth substrates, the five main results are as follows.

1. There exists a critical preheating temperature T_c of the substrate, over which the splats have an almost perfect disk shape and below which they are extensively fingered.

³ The thermal contact resistance, R_{th} , represents the temperature gap ΔT at the interface of two materials: $\Delta T = R_{th} \times q$, where q is the heat flux (W/m²); $R_{th} = 0$ for a perfect contact.

The value of T_c seems to be linked mainly to the splat material and not very much to that of the substrate.^[231,232] For alumina and zirconia, T_c is in the range 200 to 250 °C^[151,223,224,233] for splats collected on low-carbon steel, stainless steel, aluminum alloys, zirconia, and alumina. For Ni particles, $T_c \approx 500$ to 600 °C;^[231] for Cu, $T_c \approx 400$ °C; and for Mo, $T_c \approx 500$ °C.^[218] At the moment, however, there is no clear explanation about this critical temperature; it can be linked to some critical value of the Weber number^[231] or the Sommerfeld number,⁴^[232] to some combination of properties of substrate and particle,^[234,235] or to the fact that nucleation starts regardless of whether flattening is completed.^[236] The most sound and reliable explanation seems to be that T_c is the temperature at which adsorbates and condensates at the substrate surface are eliminated.^[237] Anyhow, the measurements performed all over the spray cone^[234] for zirconia particles show that, when the substrate temperature is higher than T_c , all the splats are disk shaped for particles whose velocities range between 100 and 250 m/s and whose temperatures range between 3000 and 4000 K. The value of T_c plays an important role in the cooling rate of the splats, as illustrated in Fig. 14 for zirconia splats sprayed on 304L stainless steel, kept either below or over T_c .

2. The splat contact with the substrate or previously deposited layer depends strongly on their crystalline structure^[238,239] for ceramics and on the oxide formed at the surface^[240,241] for metals. This oxide layer depends, when preheating the substrate with the plasma jet in air, on the heating rate, preheating temperature, and preheating time. For example, zirconia splats are fingered when the 304 L stainless steel substrate is preheated at 500 °C during 300 s, while they have a perfect disk shape when preheating lasts only 90 s.
3. Splats sprayed on organic covered cold substrates (xylene, glycol, and glycerol) are extensively fingered.^[242]
4. When the impact angle decreases from 90 to 30°, the splats are disk shaped at 90°, exhibit an elliptical shape between 90 and 60°, and became fingered for low angles (<45°).
5. Extensively fingered splats exhibit a poor adhesion and can be easily removed by the tip of a perthometer.^[234,236]

Very few results have been published on the splat interaction with rough surfaces. For example, when spraying ceramics on rough substrates, it seems that phenomena similar to those observed on smooth surfaces can be observed. With faster cooling rates, when $T > T_c$, a more important microcrack network is observed at the splat surface and it corresponds to a better contact with the substrate,^[236] as confirmed by coating adhesion values more than twice those obtained when the substrate is kept below T_c .

⁴ The Sommerfeld number $K = \sqrt{We} \sqrt{Re}$ where We is the Weber number and Re the Reynolds number. It has been established^[233] for liquid droplets impacting on a smooth surface ($Ra < 0.05$ μm) with no solidification taking place. In this case $K < 3$ corresponds to rebounding particles, $3 < K < 58$ to deposited particles and $K > 58$ to splashing. It is worth to note that in plasma spraying K is almost always higher than 58 and can reach value up to 1200.

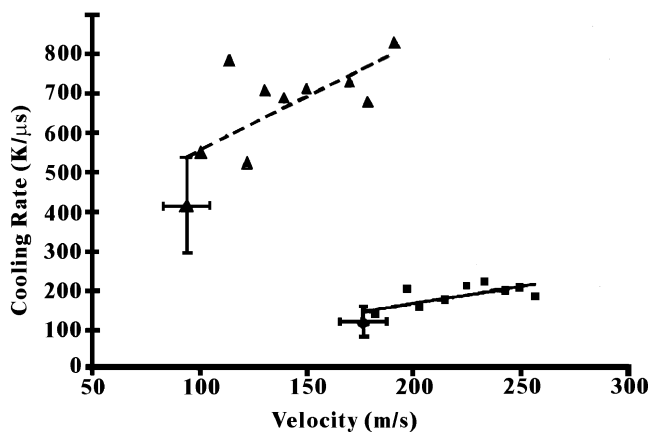


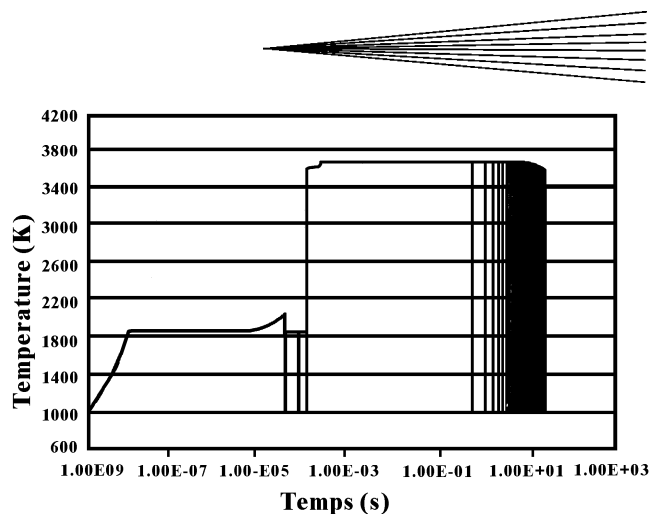
Fig. 14 Evolution of the splat cooling rate (CR) with particle velocity^[229] under the same spraying conditions as those depicted in Fig. ($T_s > T_c$, $T_s < T_c$)

4.2 Splat Layering: Coating Formation

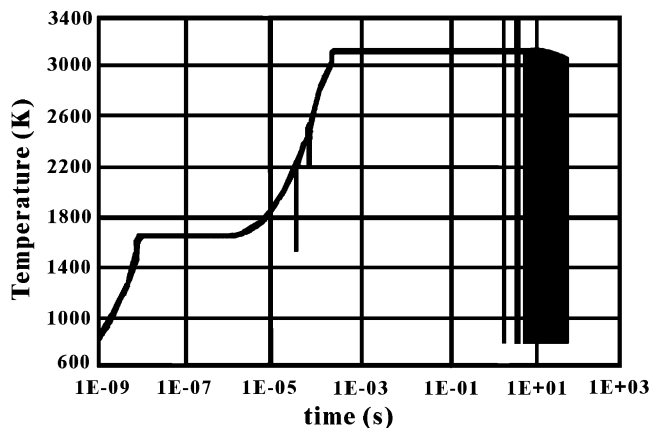
4.2.1 Temperature Time History. The temperature-time history of layering splats is governed by very different timescales.^[243] For d.c. plasma spraying, for example, particle flattening lasts 1 to 2 μs , particle solidification 2 to 10 μs , next particle impacts 12 to 80 μs later, and the layering of a pass takes a few milliseconds, while the next pass occurs a few seconds later.^[244] A particle undergoes very rapid cooling (a few microseconds), followed by impulsive reheating by the incoming particles thereafter. The heat impact diminishes quickly as the layers of splats are formed on the top.^[243]

The simple 1-D models of Haddadi^[244] and Fauchais *et al.*^[214] allow calculation of the temperature-time history of a splat. This is illustrated in Fig. 15 for the first splat of the sixtieth pass, each of them being made of three 1 μm thick splats. Figure 15 (a) for alumina indicates poor reheating from the next impacting splats compared to what happens with zirconia (Fig. 15b). The difference is essentially owing to the difference in material diffusivities. It can be noted in both figures that once the three splats are layered, during the time gap between two successive passes, the temperature of the coating drops to a mean temperature. This mean temperature depends on the substrate preheating, cooling devices used to reduce the heat flux from the plasma jet,^[169] and pass thickness. When layering thick passes (50 to 200 μm depending on the sprayed material), it is possible to achieve a columnar growth through the entire pass,^[156,244,245] resulting in coatings similar to those obtained in electron beam PVD. This behavior is possible because the entire pass remains in a liquid state before it starts solidifying from the pass bottom.

The achievement of thick passes depends on the torch/substrate relative velocity, which must be slow (a few tens of mm/s) and the powder feed rate (which must be high, >3 kg/h). Of course, the mean temperature achieved at the end of one pass must be sufficiently low to limit the residual stresses (next section).^[246,247] This can be done by using air cooling^[169] or a liquid CO_2 device.^[170] For example, the cooling air flow rate can be monitored by an infrared (IR) pyrometer^[224] or an IR camera.^[245]



(a)



(b)

Fig. 15 Temperature-time history of the first splat of the sixtieth pass, each pass being made of three splats 1 μm thick each: (a) alumina splats and (b) zirconia splats

4.2.2 Residual Stresses. Residual stresses are important because of the role they play in determining various coating properties, such as resistance to spallation. A much better understanding was achieved when experiments were developed to measure residual stresses continuously during spraying,^[248–251] together with simple analytical models that took into account the progressive deposition.^[252] According to the review of Clyne and Gill,^[253] the main stresses in the coated substrate are due to (1) grit blasting, during which the value of the compressive stress peak below the substrate surface increases with the grit size, the grit blasting pressure, and the blasting time;^[254] and (2) splat cooling inducing a quenching stress, which depends on the characteristics of the impinging particles and the substrate temperature, especially when the latter is over the critical temperature corresponding to good splat contact.^[255,256]

The quenching stress is rather low (<50 MPa) for plasma-sprayed ceramics because of its relaxation by microcracks. The stress is below 100 MPa for soft metals such as Ni and Al, due to the relaxation by plastic yielding, creep, and interfacial sliding; and it is high (over 300 MPa in certain cases) for alloys with excellent high-temperature strength. When spraying particles in a plastic state such as in HVOF, besides the quenching stress,

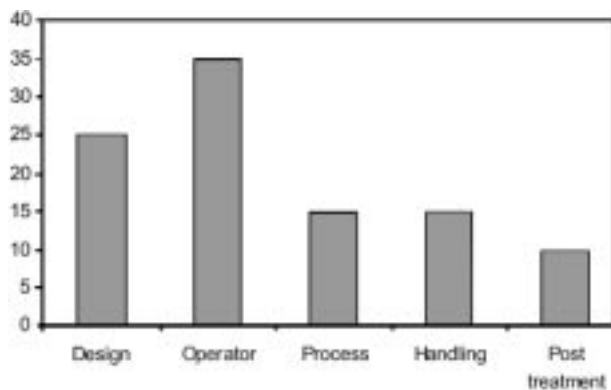


Fig. 16 Distribution in percent of errors made related to thermal spraying^[273]

which is not very high, the peening action of the high-velocity particles introduces significant compression stress within and beneath the deposited layer.^[257]

A third mechanism that may give rise to residual stresses arises from expansion mismatch due to the difference in expansion coefficients of coating and substrate and with the temperature difference between the mean spraying temperature and room temperature.^[253] As for splat layering, mean spraying temperature is again one of the key parameters. A too low temperature (below the critical temperature T_c) of the substrate results in splats having poor adhesion but low residual stresses due to quenching and expansion mismatch. If the temperature is significantly over T_c , the adhesion is improved but the residual stresses may become too high.

4.2.3 Coating Properties. Models related to the piling up of splats to form coatings^[258–263] aim to represent the coating microstructure by making predictions about the relationship between porosity and process parameters. However, all of these models require complex rules of deposition to be defined.^[263]

First, a description of the particle on arrival is needed, with the description of each particle flattening to produce a splat that is allowed to curl up during cooling. Porosity is produced if the gap between the curled splat is not filled by subsequent splats.

Second, a set of physically based rules is required, for combining the flattening events and the splat layering. In principle, such models predict microstructures and try to correlate them to porosity and deposition efficiency, the values of which depend strongly on the rules and assumptions. In ceramic coatings, for example, the porosity produced by cracking is not taken into account. The angle of particle impact also plays an important role on deposition efficiency and porosity, as shown by measurements,^[263–265] but this is not included in the models. The angle of impact effect might be the increase in splashing of the impacting droplets, resulting in redeposition over large areas on the target surface^[264] and/or the creation of oriented cracks for ceramic coatings.^[265,266]

Many experiments to link coating properties to particle velocity, temperature, and diameter of particles on impact^[116,167,267–270] are still necessary before reliable models can be defined. This is especially true for the relative values^[271] of coating adhesion/cohesion (A/C), which are closely linked to the flattening of particles through their resulting splat effective contacts

with the substrate or the previously deposited layers^[110] and also the residual stresses at the coating substrate or bond coat interface.^[253]

For plasma spraying, the results presented in the previous subsection with the critical temperature T_c and the oxidation state of the metallic substrates are well correlated to the A/C values of the coatings.^[224] Measurements performed with HVOF coatings have not yet shown such a dependence on substrate preheating, but in all cases, A/C increases with particle impact velocity.

The A/C values of zirconia coatings on 316L stainless steel substrate can be multiplied by 3 with an optimum preheating temperature compared to those obtained with no preheating. However, if the preheating with the plasma plume lasts 300 s instead of 90 s, the A/C value is only 1.5 times higher.^[224] Similar results have been obtained with alumina coatings for which the influence of substrate roughness has also been studied. For example, if the best A/C values are obtained with $Ra \approx 10$ to $12 \mu\text{m}$ for a cold steel substrate, when it is preheated at 400°C , the best values correspond to $Ra \approx 4$ to $5 \mu\text{m}$.^[272]

5. Coating Reliability and Reproducibility

Pejryd *et al.*^[273] have underlined that reproducibility problems in current thermal spraying can be divided into five parts: (1) design errors, (2) operator errors, (3) process instability, (4) handling (transportation) errors, and (5) post-treatment errors.

Their respective contributions to the total errors are as shown in Fig. 16.

The following sections point out, through our present knowledge, actions that can be implemented to address these problems.

5.1 Education

The education of the designers and operators is certainly one of the keys to the problem. The question is, however, “what education”? In our opinion, besides good knowledge of the different coating types according to service conditions and the spray process used, education should also be focused on the following areas.

- The different processes, with their limitations and drawbacks. This should include the influence of the following key parameters: the plasma or combustion mass flow rates (and *not* gas flow rates); the power dissipated; the erosion of the electrodes or nozzle wear with their consequences and the different possibilities to compensate for them; the particle injection, which, in spite of its importance, is generally not one of the main concerns; and the stand-off distance.
- The importance of powder morphology on coating properties.
- The need to have particle impacts, as close as possible to the normal of the part at the spray spot location and the way to achieve this condition with computerized robots, provided the part design has an appropriate geometry.
- The influence of the mean coating temperature before spraying (preheating), during spraying, and after spraying (cooling), on coating properties especially A/C and residual

stresses. Methods of controlling this mean temperature according to the part thickness, pass thickness, and used cooling devices also need to be examined.

- The importance of surface preparation: cleaning and roughening, as well as the time elapsed between grit blasting and spraying. It seems that the influence of the grit blasting procedure is not sufficiently understood, especially for the influence of the grit residues.^[254,272]
- The necessity to control fumes and small particles or dust that are sucked into the plasma jet and to create defects between each pass, especially when the coating mean temperature is over 400 to 500 °C. It is important to underline how to eliminate these small particles with carefully designed aspiration systems close to the spray cone and/or air barriers moved with the torch and positioned close to the substrate.

5.2 On-Line Control

Existing Systems. As emphasized by Moreau,^[17] the following three parameters are currently monitored.

1. The torch working parameters with more or less accurate devices (*e.g.*, flow rates measured with mass flow meters instead of rotometers) and systems are increasingly being computerized. The main question with these systems is, “Which action must be done when a drift is observed?” For example, if the torch voltage diminishes owing to electrode erosion, “How is it compensated?” In most cases, it is done by increasing the hydrogen flow rate, but the powder carrier gas flow rate is not necessarily re-adjusted. The continuous measurement of the transient voltage in a d.c. plasma torch and/or the noise emitted by the plasma jet can provide information on the erosion state of the electrodes, especially that of the anode,^[44,45] but which action is necessary to compensate for this change?
2. The substrate and coating temperature is measured with IR pyrometers,^[274,275] with, for the most sophisticated equipment, a close loop to control the cooling gas flow to achieve a given preheating temperature and maintain it constant during spraying.
3. The robot trajectory should be monitored to achieve passes with a constant thickness and keep the nozzle axis as close as possible to the normal of the part^[276–279] at the sprayed spot location.

New Devices for On-Line Control. The development of new equipment to control on-line the particles in-flight^[91,111–124] opens new possibilities. However, at the moment, this equipment is mainly used to monitor the process, instead of controlling it^[273] (refer also to Section 3.2). Fincke *et al.*^[16,280,281] have built a system model, accurately representing the spraying system characteristics. It has been built by randomly varying the process input parameters (arc current, plasma-forming gas flow rate, carrier gas flow rate, *etc.*) and observing the outputs of particle mean temperature and velocity. This allows particle temperature and velocity ramps to be monitored, but the main question is still pending: “What is the influence on a given coating property?” Moreau^[17] has pointed out, however, that, coupled with a better control of the substrate temperature, the implementation of this control approach should lead to better consistency in the coating properties. It should also permit the

transport of spray parameters among different booths and from one torch to another.

5.3 Standardization

As emphasized by Reiners *et al.*,^[282] “The increasing importance of Quality Management (QM) in all industrial sectors calls heavily for reliable destructive and especially non-destructive characterization techniques of coatings.” Successful QM needs contributions and engagement of all the employees of a company. The basis is described in ISO 9000. Besides the costs, reliable and standardized, if possible, methods should be used to evaluate (1) the quality of the used powders (Section 3.3); (2) the preparation, spraying, and machining procedures (Section 5.1); (3) the evaluation of coatings including the microstructure, phase composition, porosity, residual stress distribution, interface characterization, A/C, hardness, mechanical, and thermal properties, *etc.*; and (4) the tests for given service conditions (wear resistance, thermal shock, *etc.*) These tests should be defined to take account of the working costs, the education level of the employees, and the investments costs.

However, for coating evaluation, as already shown,^[271,283,284] the different tests for a given property, *e.g.*, porosity, A/C, and residual stress, result in different values. They are not comparable because they are often based on different physical and/or mechanical phenomena. Moreover, the results depend strongly on the substrate and coating preparations (*e.g.*, cutting and polishing procedures), especially for ceramic or cermet coatings. What’s more, very few tests are nondestructive.^[284] Standards are “rules of technology” and there is a strong demand to develop them. Up-to-date information on those that are accepted in surface technologies are available from the Internet.^[285]

6. Conclusions

Compared to the 1980s, thermal spraying has dramatically evolved from an art to a science. At the moment, it is possible to achieve coatings tailored to specific service conditions, and thermal spraying is now an integral part of the industrial commodity-making process. However, besides new marketing issues of the thermal spray market, the development is linked to a better reproducibility and reliability of substrate surface preparation, spraying, and post-treatment of coatings.

A consistent effort has to be made in the following areas.

- Achieve better control of surface preparation with a grit residue level as low as possible and a roughness adapted to sprayed particles, and a desired grit blasting residual stress level. This is strongly linked to the choice of the grit material, its size, the blasting pressure, and time. But new techniques, inducing no grit residue at all, seem very promising with high-pressure water-jet roughening, ice-particle blasting, or pulsed-laser surface treatment.^[286]
- More effort is necessary to develop cheap and robust sensors to follow the key parameters of coating manufacturing, *i.e.*, trajectory distribution of hot particles linked to their injection conditions, particle impact velocity and temperature coating and substrate temperature and coating thickness during spraying. At the moment, reliable but sophisticated (and, therefore, expensive) devices are available and have

been tested with success in booths to follow particle trajectories, velocities, and temperatures in-flight. Their cost does not allow each booth to be equipped with a single device. New sensors studied in laboratories, which are much less expensive, are now being tested in booths. They are based on photo-diode arrays or CCD cameras. However, the question which arises is as follows: "Is it necessary to control all these parameters, or just one or two of them?" For coating and substrate temperature, rather cheap IR and small pyrometers are now available.

- It is vital to find reliable correlations between coating properties and particle impact parameters as well as coating and substrate temperature, pass thickness, *etc.*, in order to establish feedback control. At the moment, it is probably the weakest point of our scientific knowledge with no clear theory backed by measurements that establish correlations between particle parameters on impact, substrate, and coating temperature, pass thickness, *etc.*, and coating specific properties. An important research effort should be devoted to this problem. However, it is now possible to establish empirical correlations for given spraying conditions and particle parameters at impact, which could be used to keep, with the help of sensors previously described, the measured parameters in a "window," resulting in an acceptable coating property.
- It is important to control the dust (especially fine particles resulting from the condensation of vaporized material) in the booth and close to the sprayed part. The development of flow modeling close to the substrate should help to design suction devices to limit seriously the dust level around the spray spot. Such knowledge and equipment would not only improve the quality of the thermal spray product but enhance the environmental controls of these processes.
- It is necessary to achieve standardization of coating characterization methods. It has been started but it is far from being finished. It should be emphasized that a better on-line control would probably reduce the number of characterization methods needed for quality assurance but not suppress them entirely.
- Finally, education at all levels should be developed and expert systems need to be created that can help operators and designers.

Regarding equipment, knowledge of the plasma spray and HVOF processes has made much progress, and, probably in the near future, new equipment will be marketed. For example, plasma torches working with lower temperatures (8000 K as opposed to 13,000 K) enable a better particle acceleration and limit the surrounding air entrainment (higher viscosity), as well as fluctuations of the anodic arc root. New shrouding systems should also be designed to limit oxidation when spraying metals or alloys in air. For HVOF or HVAF processes, the trend is to increase the particle velocities and reduce their temperatures below their melting point. The design of D-Guns should be improved according to the much better knowledge of the involved phenomena. For the wire-arc process, the design of the atomizing nozzle is still poor. Finally, research work should be devoted to flame spraying, which has not been studied much but is responsible for probably about 25% of the spray market.

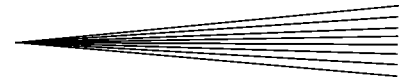
Another topic of importance concerns new designs of feed stocks. New powders formed by, for example, mecanofusion, SHS, and fiber reinforcement, are increasingly used and are opening new possibilities. Recently introduced suspension spraying is also very promising, both for classical and nanoscale coatings. Nanoscale materials deposited by thermally activated processes such as HVOF, plasma spray, and plasma-assisted CVD open new possibilities with the possibility of great technological impact.^[287]

Finally, the coating market is still wide open: (1) to produce parts by plasma or HVOF spraying and manufacture forms and volumes that are difficult or even impossible to obtain using conventional processes;^[288–291] and (2) to manufacture parts with complex shapes and material gradients, with associated protection against wear, heat, and other advances challenging operating conditions, and (3) to replace hard chrome plating.^[292–295]

These equipment controls, new processes, and novel feedbacks will have long-term impact on consumer industries. For example, the automotive industry reveals a wide market with more automated, more reproducible, and less expensive coatings. As well, TBCs will also enable potential applications that have to be tailored to the particular loads they will see.^[296]

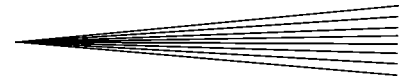
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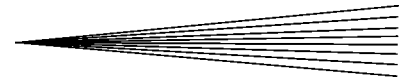
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