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A Perspective on Plasma Spray Technology

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Abstract Plasma spraying is often assumed to be a mature technology in which all the important phenomena have been observed and described adequately. However, the intricate interactions between the electrically conducting fluid and electromagnetic, thermal and acoustics phenomena that affect the operation of the plasma torch are not fully understood as yet. Also, variants of the plasma spray process are emerging and raise new scientific questions. These technologies include the spraying of liquid feedstock in the form of submicrometric particles or chemical precursors in a solvent and, coatings formed by vapor condensation onto the substrate. These relatively novel techniques make possible the production of thinner coatings than in air plasma spraying with a fine and even nanostructured microstructure. This paper attempts to define some of the current important issues and research priorities in the plasma spray field.

Keywords Surface engineering · Plasma spraying · Plasma spray torch · Splat formation · Suspension and solution plasma spraying · Very low pressure plasma spraying · Sustainable manufacturing

Introduction

Plasma spraying emerged as a surface finishing technology after the Second World War. It is now one of the leading technologies for applying a relatively thick coating (a few

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hundred of micrometers up to a few millimeters thick) on a substrate to protect its surface or improve its function. It is commonly used in many industrial sectors including aeronautics, industrial gas turbines, automotive, materials mining and processing, biomedical and electronics [1].

What distinguishes plasma spraying from other coating technologies is its applicability to a large range of materials including refractory materials like ceramics, high deposition rate (up to a few kilograms per hour) and rather simple operation. It is based on the injection of a powder into a plasma jet formed by electrical to thermal energy released in a plasma torch. The particles are accelerated and heated in the plasma jet and then impact onto the substrate where the sudden deceleration causes a pressure build-up at the particle–surface interface that forces liquid material to flow laterally. The liquid spreads outward from the point of impact, solidifies and forms a lamella; the coating is built by the piling of such lamellae. In air plasma spraying (APS), the size of the injected particles is generally between 10 and 100 μm and the resulting lamellae have a thickness of a few micrometers and a diameter ranging from a few tens to hundreds of micrometers. Thus, the main reference scale of the features of the coating microstructure (lamellae size, non-melted particles embedded in the coating, voids, cracks, etc.) is the micrometer even if the size of the columns or grains that grow within a lamella during the solidification process can range from a few tens to a few hundreds of nanometers. The minimum coating thickness for the formation of a consistent coating is about 50 μm.

The applications of this technology have changed considerably since its beginning in the fifties. The global pressures on prices force companies to face challenges in their manufacturing processes; they generally answer by an acceleration of production, increase in throughput and consistency in quality of the coating. Also, plasma-sprayed coatings have to cope with more demanding applications such as higher temperatures of operation, wear and corrosion under extreme conditions and longer life span of parts and devices.

A potential response for coatings with improved properties is the deposition of coatings with finer microstructure, i.e. finer lamellae and smaller voids and also coating with microstructure more compliant to mechanical and thermal stresses than the lamellar microstructure exhibited by conventional plasma-sprayed coatings. This requirement has led to the development of two innovative plasma coating processes for producing coatings with grain size in the nanometer range while keeping the high deposition rate and flexibility of plasma spraying. The first process uses the basic equipment of the conventional plasma spray process but the feedstock is a liquid suspension or a solution of chemical precursors instead of the conventional powder feedstock [2, 3]. The second technology takes advantage of the high enthalpy content of the plasma jet to evaporating the spray material and then forming a coating by fine droplets and/or condensation of the vaporized material on the substrate [4, 5]. Both techniques make possible the formation of thinner coatings than the usual plasma-sprayed coatings and thus broaden the range attainable by thermal spray processes.

Plasma spraying, as all other surface finishing technologies, is confronted with materials and products regulations, mostly from the European Union, as well as health and safety requirements. These trends and the two emerging plasma spray processes provide a rich source of topics for researchers in the plasma spraying field. This article discusses some important key challenges and opportunities in this field. It is partly based on the 2014 White Paper on Thermal Spray Technology of the ASM Thermal Spray Society [6]. It also discusses the environmental issues and research opportunities that the concept of sustainable manufacturing entails for the plasma spray technology This article does not delve into the science and traditional applications of plasma-sprayed coatings because there are several thorough reviews on these subjects in the literature, including the Fauchais articles [7] on the understanding of the process, Keshri and Agarwal [8] and Gardon and Guilemany [9] on functional coatings, Berndt et al. [10] on biomedical coatings, Hardwicke and Lau [11], Matějíček et al. [12] and Henne [13] on energy production applications, and Sampath [14] on applications in electronics and sensors. Also, several recent books cover the topic of plasma torches and plasma spraying, such as those by Zasypkin and Zhukov [15] and Fauchais et al. [16].

The Air Plasma Spray Technology

The properties of the coating can be considered to be a function of three inter-dependent sub-systems: (1) the formation of the plasma jet, (2) injection and processing of the powder material in the plasma jet issuing from the torch and mixing with the surrounding gas, (3) impact and solidification of the particles on the substrate. All of these sub-systems have been investigated in a large number of experimental and analytical works by universities and equipment suppliers and the results have advanced the plasma spraying process [16]. However, the full understanding of the phenomena controlling the arc dynamics in the plasma torch and the formation of a splat is still lagging behind. These topics are discussed in the following sections.

Arc Dynamics

In plasma spraying, the processing plasma medium is essentially the source of kinetic and thermal energy and generally is not the source of radicals and reactive species except in some specific developments such as reactive plasma spraying where the plasma-generated species interact with the processed material to synthesize a new material; e.g. AlN coating from aluminum powder sprayed with nitrogen or Ti coating containing carbides or nitrides, produced by injecting titanium powder in a methane and nitrogen jet.

The Conventional Plasma Torch

The plasma jet is predominantly produced by DC plasma torches of simple design, involving a rod-shaped doped-tungsten cathode with a conical tip and a concentric water-cooled copper anode. It generally uses a gas with a high atomic weight (Ar, N_2) mixed with a gas of higher thermal conductivity (H_2, He) or viscosity (He). The use of diatomic gases (N_2, H_2) results in the addition of dissociation energy to plasma enthalpy but also changes the operation mode of arc which is controlled by thermal, electromagnetic, acoustic and chemical phenomena whose interactions are not fully understood yet.

The conventional torch works at a low arc voltage (<70 V) but relatively high currents (400–1,000 A); it produces plasma jets with a specific enthalpy ranging between 5 and 35 MJ/kg. At the nozzle exit, the gas temperature is around 10,000–12,000 K and velocity between 400 and 2,600 m/s. Typically, the coating material is injected in the plasma jet radially to the torch axis a few millimeters upstream or downstream the nozzle exit.

While this type of plasma torch is widely used in industry, it suffers from three main drawbacks that have led researchers and manufacturers of plasma torches to develop new torch designs: arc instability, electrode erosion, especially the anode and radial injection of powder. The first two drawbacks are linked because the heat load to the anode wall, and thus its erosion, depends on the arc residence time and the current density at the arc attachment. Therefore, in a conventional plasma torch, continuous movement of the arc is necessary to limit anode erosion; the solution can be a high-frequency rotational motion of the arc in a plane perpendicular to the nozzle-anode axis but entails an axial movement of the arc attachment at the anode wall. This axial movement depends to a great extent on the balance of the forces exerted on the anode attachment column (essentially a pulling drag force by the cold gas in the boundary layer and Lorentz forces that may act in the same or opposite direction depending on the curvature of the attachment column) and surface roughness of anode wall resulting from erosion. The anode erosion can be limited by using a refractory but conductive material (e.g.; tungsten) to line it as in the F4 plasma torch of Sulzer Metco.

A large number of studies have been published on the operation mode of arc in a DC plasma torch (see for example the review paper [17]). Under plasma spray conditions, several modes have been identified [18] as a function of the torch operating parameters, the most common being the so-called restrike and takeover modes. These modes have been interpreted in term of the thickness of the cold boundary layer (CLB) that develops on the anode wall and behaves as an electrically insulating layer enveloping the arc. The restrike mode is characterized by large voltage fluctuation with steep voltage drops; it is favored by the use of diatomic gases and high gas flow rate that result in a rather thick CLBs. The takeover mode corresponds to a more random motion of arc and is favored by the use of monoatomic gases and high arc currents that yield thinner CLBs. It has also been shown by Krowka et al. [19] that the volume of the cathode cavity plays a role on arc instabilities as it may give rise to a resonant phenomenon because of compressibility effects of the plasma-forming gas in this cavity linked somehow to the anode arc attachment movement.

Arc instabilities have an effect on the enthalpy input to the plasma jet, its mixing with the cold surrounding gas and thus its deceleration and cooling; they also affect the injection and processing of the powder in the plasma flow making the process time-dependent.

Recent Designs of Commercial Plasma Torches

A high specific enthalpy is generally a precondition for spraying refractory materials; it helps to improve the deposition efficiency and spray rate and produce more homogeneous coatings on complex shape parts, because the coating microstructure is less sensitive to variation in spray parameters, in particular, spray distance and spray angle. Increasing the arc current and/or diatomic gas content both result in an increase in enthalpy but this is accompanied by a higher rate of anode erosion at the arc attachment point. A solution is to increase the voltage rather than the arc current and, generally, it can be done by means of cascaded anode consisting of a stack of copper rings insulated from each other (called neutrodes) and ending with an anode-ring on which the arc attaches. This solution improves arc stability as the movement of the arc is restricted to the anode-ring. To avoid the attachment of the arc on the copper ring at a floating potential, the thickness (d) of each ring must be such that $\int_0^d E dx < V_A + V_C$ where E is the electric field and V_A and V_C the anode and cathode fall respectively. A commercial plasma torch with a cascaded anode (APG torch from Sulzer) was proposed in the late 60s. Today, a few torches are available on the market that use cascaded anodes (e.g.; Oerlikon Metco Triplex Pro and Sinplex Pro[1] and C^+APS from TSD Inc, USA). A leap forward more stable commercial plasma torches with longer electrode life time has been taken in the late 90s with the Triplex Torch from

[1] http://www.oerlikon.com/metco/en/products-services/coating-equipment/thermal-spray/spray-guns/.

Oerlikon Metco. It combines the decrease of the local heat load to anode by using three collinear cathodes to produce three electric arcs and the stretching and anchoring of these arcs thanks to a cascaded anode. This plasma torch operates at voltage higher than 80 V with voltage fluctuations in the order of 0. 2 times the mean voltage and gas enthalpy around or higher than 30 MJ/kg. This design results in a longer plasma jet core (50–60 mm), as compared to that of the mono-cathode mono-anode plasma torch (typically 35–50 mm) and an increase in production rate thanks to the use of up to three powder injectors arranged symmetrically in a plane perpendicular to the torch axis. The three arcs emanating from the cathodes are forced towards each other by narrowing the nozzle diameter, but they do not combine because of the Lorentz forces and the plasma jet is made up of three lobes. The powder can, thus, be injected either within a lobe or between two lobes taking advantage of a cage effect. A further concept to stabilize the arc is to use a single cathode, a cascaded anode, and divide the last anode ring into three parts insulated from each other. This concept is implemented in the commercial Delta Gun from GTV GmbH.[2]

Another concern in plasma spraying applications is the efficient injection of the powder in the plasma jet in order to have the maximum number of particles injected in the gas flow, more homogenous treatment of particles and maximum deposition efficiency. To meet these requirements, the natural way would be the axial injection of the powder in the core of the plasma jet. Many studies have been done on the axial injection of the powder into the plasma jet and some have resulted in patents on the axial injection of the powder in a plasma spray torch. The solutions involved the use of a hollow cathode or several electrodes; to the best of the author's knowledge, no commercial plasma torch with a hollow cathode is on the market because of clogging and rapid erosion of the cathode by the particles fed through the cathode. The second solution generally involves either three cathodes with a single anode or three practically independent plasma torches. This second configuration is used in the commercial Mettech Axial III torch.[3] It combines three plasma torches whose plasma jets converge in a nozzle where the powder is injected along the line of symmetry of the three plasma torches; the nozzle is followed by an extension that delays the cooling and deceleration of the plasma flow by mixing with the surrounding gas and thus enables an increase in particle velocity. This configuration helps to reduce the two main drawbacks of multi-electrode torches: the difficulty to get the powder uniformly distributed in the plasma flow and avoiding build-up of particles in the nozzle. However, whatever the plasma torch design, its thermal efficiency is 50–60 % because of the necessity to have an efficient cooling of the torch electrodes.

Modeling of the Plasma Torch Operation

The expansion of plasma spraying into large-scale manufacturing (e.g., coatings for gas turbines) has driven improvement in process stability, deposition rate, deposition efficiency and economics. In addition, the development of process control using specialized software that control the process hardware (powder feeder, plasma torch, part handling, etc.) and sensors able to monitor the in-flight characteristics of particles (trajectories, velocity and temperature) and the substrate temperature have drastically improved the performance and consistency of plasma spraying. However, further steps are needed to address the more

[2] GTV Verschleißschutz GmbH website (August 2014) http://www.gtv-mbh.com/cms/upload/downloads/en/GTV_Delta_Plasmabrenner_en.pdf.

[3] Northwest Mettech Corp. (August 2014): http://www.mettech.com/.

stringent demands of the traditional applications of plasma spraying and also explore emerging markets, e.g. the electronics industry that will require further improved plasma torches.

For example, plasma torches with higher power (>90 kW) and deposition rates would be necessary in mass production as those used in the 80s and 90s to deposit coatings on

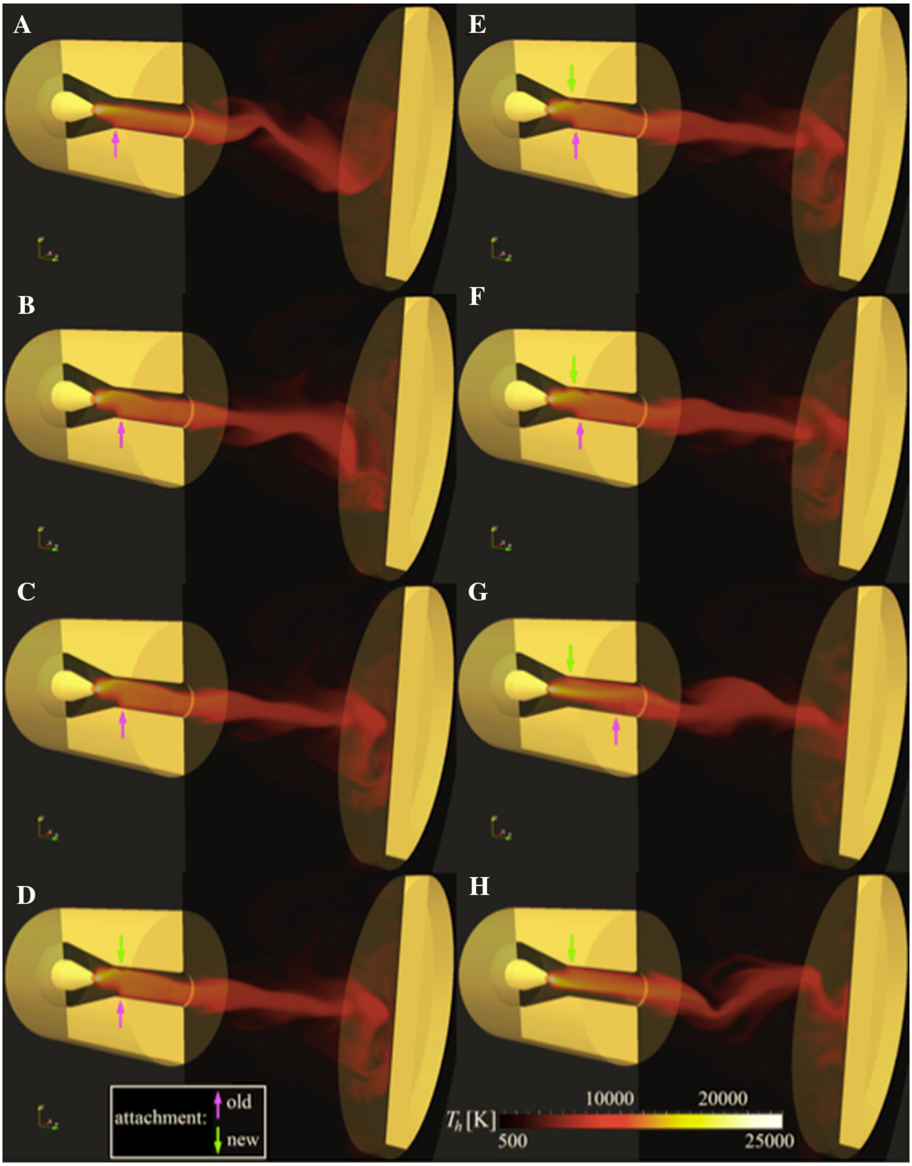

Fig. 1 Computation by Trelles [39] of the time-dependent and non- LTE gas flow of plasma jet inside and outside the plasma torch with inclusion of the substrate in the computation domain. The pictures show the flow dynamics during an arc reattachment event from the temperature distribution of heavy particles at different times; the *arrows* indicate the location of the initial (old) and formed (new) arc anode attachments

large rolls in papermaking machines; also plasma torches with a larger range of gas enthalpy and velocity than the existing torches and separate control of these parameters will allow better control of splat formation and, thus, of the coating microstructure (e.g., producing dense or porous coatings depending on the application); and also plasma torches with a focused spray spot.

A better understanding of the arc phenomena within the plasma torch and the relationship between torch operating parameters (arc current, gas flow rate and composition, inner geometry, gas injection design) and flow fields (enthalpy, temperature, velocity, chemical composition, turbulence) is also needed. As the measurements inside the torch are, at present, limited to time-variation of arc voltage, inner pressure, torch thermal efficiency and acoustic emission, mathematical modeling is essential for further development of plasma torches.

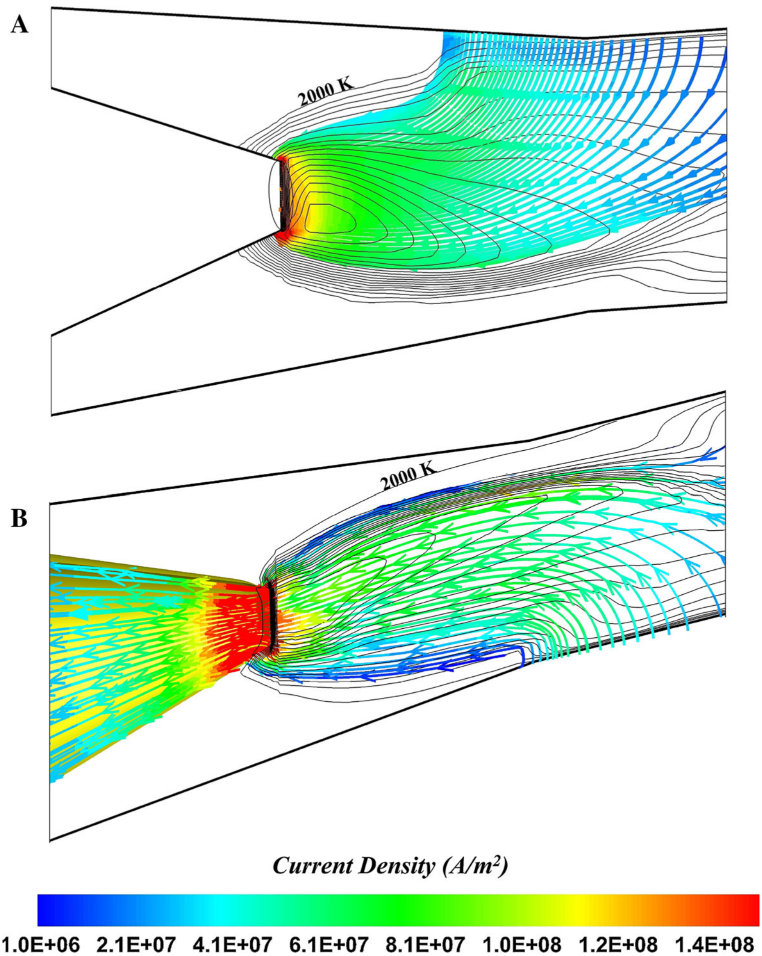

Fig. 2 Current density distribution (*vectors color scale*) close to the cathode tip of a DC mono cathode plasma torch and isotherms (*in black*). **a** with imposed current density profile at the cathode surface. **b** with arc–cathode coupling (computations by Alaya et al. [23]. Arc current of 600 A— plasma gas mixture of argon (45 slm) and hydrogen (15 slm)

Therefore, the question arises: Are the present plasma spray torch models adequate to simulate a process that involves multi-scale and multi-physics phenomena? These models simultaneously solve the Navier–Stokes equations (gas mass, momentum and species), energy conservation equation (gas temperature) and the Maxwell equations (electric and magnetic fields). The more advanced models make it possible to predict the three-dimensional and time-dependent operation mode of the arc within the plasma torch and gas flow fields inside the plasma torch and in the plasma jet; they can also take into account the thermal non-equilibrium (NLTE) that prevails close to the electrodes [20]. They use two energy equations, for electrons and heavy species respectively, to predict the temperature of the medium which generally is assumed to be in chemical equilibrium. However some questions remain: e.g.; the arc turbulence model that must account for the instabilities and may result from the rapid expansion and acceleration of the very hot gas and also the interaction between the flow and magnetic field (direct numerical simulations would be of great help to understand the development of turbulence and use the right model in practical applications but their very high computational cost still limit their use); proper calculation of the emission and absorption of the medium; for NLTE models, calculation of the medium composition and properties of the system; formulation of the NLTE energy equations and especially the formulation of the terms including the thermal conductivity and energy of ionization; importance of chemical non-equilibrium. These last points should be addressed to assess the importance of non-equilibrium effects in plasma jet generation and interaction with electrodes. A further step should the implementation of electrode sheath including space-charge sheath and ionization pre-sheath in the torch model. Sheath models are available in the literature [21, 22]. However, the implementation in a CDF model of a DC plasma torch has not been realized yet (Fig. 1).

Recently [23] the solid (electrodes) and fluid phases (plasma) have been included in the same computational domain and the electromagnetic and heat equation were simultaneously solved in both phases, thus making it possible to get rid of the artificial boundary conditions imposed at the cathode tip regarding the arc current density and magnetic field (Fig. 2).The coupling of the arc and electrodes with the implementation of phase change in the electrodes (melting production of vapor from molten spots) and the influence of metal vapors on the thermodynamic, transport and radiative properties of the medium are necessary steps in the reliable prediction of electrode erosion at specified operating parameters of the torch.

For the conventional plasma torch, other further investigation is also necessary of the conditions that result in arc break down and reattachment when the arc operates in the restrike mode and of the physical model to mimic these conditions. The combination of such models with the anode sheath model is a puzzling problem. Also, coupling of the arc dynamics with the propagation of the acoustic waves generated by the compressibility effect of the plasma-forming gas in the cathode cavity should allow for better control of the arc instabilities by designing an optimized inner geometry. This could be done by means of the geometric shape optimization theory. This approach represents an exciting challenge; it requires a model that makes it possible to evaluate the geometric structure effect, one criterion that has to be minimized and a set of optimization variables that take into account the constraints of the system.

Finally, to answer the earlier question, even if the present models do not fully address the physics that control the dynamics of the arc, they are useful tools for parametric studies and geometry improvement, if their use is underpinned by knowledge of torch operation and the model predictions are carefully validated against experimental data obtained under well-defined torch operating conditions and geometry. Also, the confidence in models would increase if they are validated experimentally and benchmarked with a test defined by the plasma spray community.

It is believed that the easier access to high performance and cloud computing resources has now open up the door to a comprehensive model of DC plasma torch operation that, in a reasonable time, will address fully the physics and help to improve the technology.

Splat and Coating Formation

Plasma sprayed coatings are built by the successive pile-up of lamellae formed by the spreading and solidification of the molten particles impinging on the substrate surface or already-deposited lamellae at a velocity ranging from one hundred to several hundred meters per second. Upon impact, the molten material spreads radially at high velocity for a few microseconds giving rise potentially to flow instabilities [24]. During spreading, the heat transfer from the liquid material to the underlying layer leads to rapid solidification (cooling rates in the range 10^7–10^8 K/s) that may interrupt the flow of liquid.

Dynamics of Splat Formation

The impact, spreading and solidification of a single molten particle impinging on a flat substrate has been the subject of numerous studies during the last two decades [24]. Experimental investigation of droplet impacts has been carried out by correlating the impinging droplet characteristics with resulting splat morphologies. The effect of parameters such as substrate material, surface roughness, oxidation state, cleanliness, temperature, ambient pressure etc. has been investigated. However, only the final shapes of splats can be observed, thus limiting the understanding of the transient behavior of the fluid flow during impact. To address this point, on-line optical monitoring systems were developed that made it possible to observe the fluid flow and measure the cooling rate of splat during and after impact on the substrate [24–26].

The substrate temperature was found to play a determining role on the spreading of the molten particles and final shape of the resulting lamellae. Typically, when the impact occurs on a hot substrate (above 300–400 °C), the droplets form a uniform disk whose diameter and thickness correspond to those predicted by analytical and numerical models [24]. These models assume that the initial kinetic energy of the impinging particle is transformed to thermal energy due to the finite viscosity of the molten material and surface energy of the liquid disk whose total surface is much larger than the surface of the impinging droplet. A none-slip condition is usually assumed at the interface of the fluid with the solid substrate surface. Three-D numerical models are used to model the flattening, solidification and splashing of the impinging droplets. They generally take into account the wetting behavior and thermal contact resistance at the fluid-substrate interface but neglect the undercooling of the liquid. They are based on a volume-of-fluid approach to track the evolution of the fluid surface during impact. Some models consider the influence of the gas surrounding the impact zone. Model predictions, although they do not take into account all physical phenomena involved during impact provide realistic representation of actual droplet impacts on hot substrates. They showed that solidification does not interrupt the liquid flow as it occurs mostly after the splat reached is maximum size.

When the impact occurs on a substrate at room temperature, the observed scenario changes considerably. The liquid flow parallel to the substrate evolves differently than that observed on the same substrate maintained at a higher temperature. On cold substrate, it is frequently observed that the liquid is in contact with the substrate only in a region slightly larger than the initial size of the impinging droplet. Outside this central region, the liquid is no more in contact with the substrate surface and continues spreading on a much larger distance forming a disk that is at least two times larger than that observed on a hot substrate. This is due to the fact that the velocity gradient through the thickness of the splat is reduced as the liquid does not touch anymore the substrate surface and slips over it. Thus, much less energy is dissipated due to the finite viscosity of the molten droplet permitting the splat to reach a much larger diameter. Also as there is little physical contact between the flowing liquid and the substrate, the heat transfer to the substrate is strongly

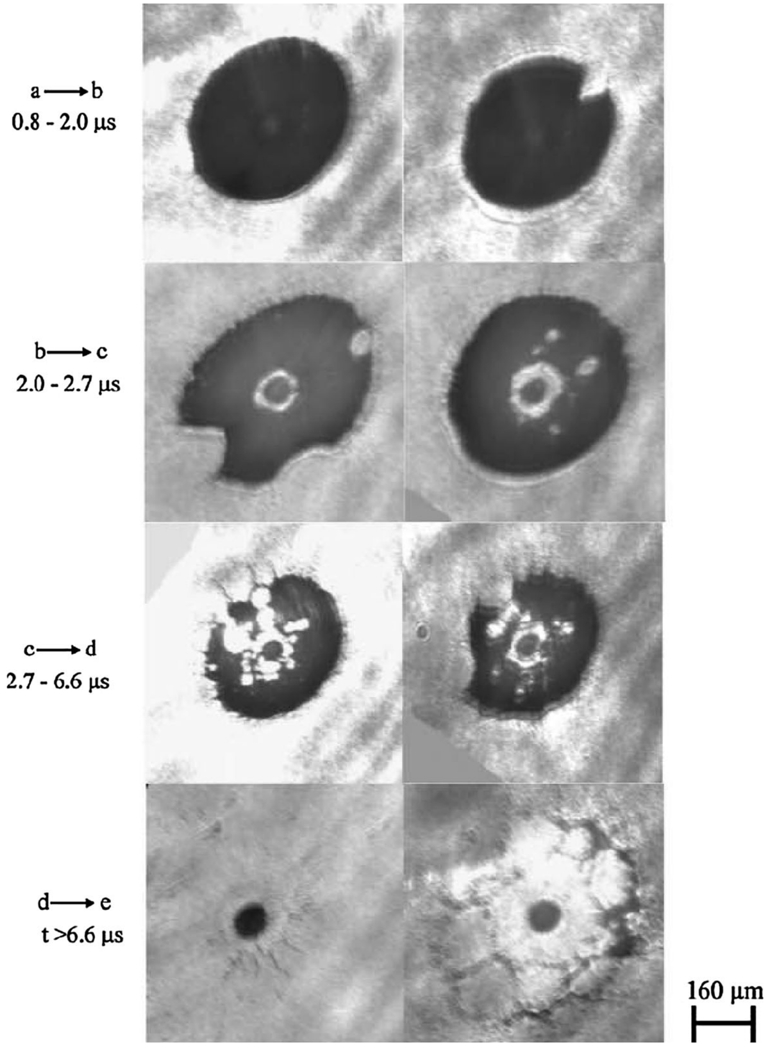

Fig. 3 High speed (5 ns exposure) images of plasma sprayed molybdenum particles taken by McDonald et al., a few microseconds after impact on a glass substrate held at room temperature [25]. The *top* images (0.8–2 μs after impact) show the splats close to their maximum extent. At later times (2 μs and more), holes start to form in the thin sheet of molten metal, holes that grow under the surface tension pull. After 6.6 μs, only the central portion of the splats with some debris is still visible

reduced compared to the case on hot substrate. This results in much lower cooling rates of the splat outside the central region where the liquid is in mechanical and thermal contact with the substrate. The liquid detachment and the reduced cooling rate are clearly seen in the high speed thermal images of plasma-sprayed zirconia droplets (50 µm diameter) acquired by Shinoda et al. [27]. On a cold substrate, the liquid film can reach 300 µm in diameter (flattening ratio of 7 and more) with a corresponding thickness of less than 1 µm. At its maximum extent or close to its maximum extent, the film can break following several patterns. Holes in the film are formed and grow rapidly due to the surface tension of liquid film; also the film may break around its periphery. Some debris of the broken film may stick and solidify on the substrate surface forming highly fragmented splats as often observed in scanning electron microscope images [24, 25]. Only a portion of the material of the initial droplet actually sticks on the substrate surface (around 10 % or less) (Fig. 3).

The temperature at which splat shapes changes from a highly fragmented shape to regular disk shape is called “transition temperature”, after the work of Fukumoto et al. [28]. The transition temperature was found to range between 300 and 400 °C for different combinations of substrate materials and spray particles impacting on a flat substrate. Explanations of splat fragmentation below the transition temperature include rapid solidification perturbing the liquid flow during impact, change of wettability with substrate temperature and presence of “adsorbates” on cold substrates. Also, low ambient pressure was found to reduce splat fragmentation. All these phenomena and their interplay are still under investigation.

It is worthwhile to note that detachment of liquid flow from the substrate surface during impact of droplets was also observed for millimeter size water/ethanol droplets impinging at low velocity (around 1 m/s) on a flat substrate at room temperature. Higher ambient pressure and droplet velocity were found to promote the detachment of the liquid flow along the substrate [29]. It is possible that the mechanisms of detachment intervening during the impacts of mm-droplets and plasma sprayed droplets be similar. In any case, more research is necessary to better understand the interaction of the plasma spray droplets with the substrate as the resulting lamellae are the building blocks of the spray coatings.

Coating Buildup

The substrate temperature affects also the interaction between the sprayed particles and already deposited lamellae whose surface is quite rough with a few ten of µm between pics and valleys. McPherson showed in the 80s that the actual contact zones between lamellae are relatively scarce and represent only a fraction of the lamellae interface (typically ranging from 10 to 50 %) [30] as elongated pores at the interface between lamellae form gaps of a few 100 nm thick. An increase in substrate temperature during spraying yields a significant decrease of these pores that significantly affect the coating properties: thermal and electrical conductivity, elastic and inelastic properties, adhesion, cohesion, wear resistance, etc.

The important effect of the substrate temperature during spraying on the interface quality between lamellae is still not well understood. Air or the plasma gas is entrapped between the impinging droplets and the already deposited lamellae. Under partial vacuum, the interface quality improves making vacuum plasma spray coatings denser with increased elastic moduli. Some of the remaining questions are: Do the absorbates play a role when coatings are sprayed on a substrate maintained at temperatures below 200 °C? In particular, what it the role of the ambient humidity in the coating buildup? What make possible the formation of an interlamellar gap when the molten droplets flatten on the rough coating surface that is exposed to ambient air and plasma gases? These questions are also of high practical importance as the interlamellar pores have an effect on actual coating properties that, in turn, determine the performance of the coatings in their targeted applications. Understanding of the mechanisms involved in the coating buildup and the variables that directly influence them will lead to high performance coatings that can be produced with a higher level of consistency.

Emerging Plasma Spray-Based Technologies

The plasma spray market is to a great extent driven by the gas turbine industry and, in particular, the manufacturing of the thermal barrier coatings (TBC) that protect the surfaces of metallic parts in the hottest zones of gas turbines used for the generation of electricity and propulsion of aircrafts. The world electricity delivered to end users is expected to rise by 2.2 percent per year from 2010 to 2040[4] and the airline passenger traffic to nearly double in the next 20 years.[5] These market developments come with the search for an increase in engine thermal efficiency and span time, and a reduction of greenhouse gas and high-altitude NO_x emission. Thermal barrier coatings are important in meeting the requirements for higher operating temperatures and longer span times. They have stimulated intensive research both on material compositions and alternative deposition technologies, in particular, in the plasma spray community. In addition to low thermal conductivity and phase stability during thermal cycling at high temperature, the ceramic topcoat of TBC systems must resist erosion by particulates and foreign objects and degradation by pollutants such as CMAS (calcium–magnesium–alumino–silicate).

While land-based turbines essentially use TBC ceramic topcoat deposited by air plasma spraying (APS), aircraft engines also use TBCs deposited by electron beam physical vapor deposition (EB-PVD) on the most demanding parts, such as blades and vanes. This capital intensive and line-of-sight process produces coatings with a columnar microstructure whereas the plasma-sprayed coatings exhibit a layered and porous microstructure with a lower thermal conductivity than the EB-PVD deposits and, also an inferior strain tolerance. Two technologies based on the use of DC plasma torches are now emerging: plasma spraying of suspensions and solutions and plasma spraying at "very low pressure"; they aim to reproduce somehow the microstructure of EB-PVD coatings. The former technology produces coatings with a finer microstructure than those produced by conventional plasma spraying. The latter is more akin to the vapor deposition techniques but with a deposition rate up to an order of magnitude higher. They both produce coatings with unique features; e.g., columnar microstructures, highly porous coatings and dense coatings.

Potential applications of these technologies include thermal barrier coatings with stress relieving structures and, also fuel cells, photocatalytic coatings, wear-resistant coatings and coatings for biomedical engineering.

The following sections of this article will focus on important R&D topics to promote the use of these technologies at an industrial scale; the scientific and application issues are addressed by Fauchais et al. in this issue and in the review articles by Fauchais [31, 32], Killinger et al. [33], Smith et al. [4], and von Niessen and Gindrat [5].

[4] International Energy Outlook Report 2013, US Energy Information Administration.

[5] Federal Aviation Administration, Press release, 12 March 2012.

Suspension and Solution Plasma Spraying

The idea at the heart of this technology is to form the coating by the piling up of molten particles with a size ranging from a few tens or so nanometers to a few micrometers at impact on the substrate. The coating material comes as a liquid consisting either of nano- or micro-sized particles in aqueous or organic solvent (called "suspension") or solutions made by dissolving metal salts or organometallic precursors, or liquid metal precursors, in a solvent (called "solution"). In the case of suspension, particles are present in the liquid prior to its injection in the plasma jet whereas in the case of solution, they are formed in flight in the plasma jet and eventually deposit onto the substrate; therefore do not require the handling of nanoparticles (Figs. 4, 5).

Specific Features of Liquid Plasma Spraying

The injection and processing of a liquid in the plasma jet instead of a powder requires reconsideration of the mechanisms that control coating formation and also adaptation of the plasma torch and feedstock feeder, and operating parameters.

The specific features of plasma spraying liquids are:

- The low specific density of the liquid injected in the plasma jet and small inertia of the fine particles makes them very sensitive to space- and time-variations in plasma flow fields,
- The sequence of processing steps of liquid and then particles or agglomerates in the plasma jet. In the case of suspension, they encompass liquid primary and secondary breakup depending on the liquid form (continuous jet or droplets), p lasma and liquid properties (relative velocity, gas density and liquid surface tension and viscosity), solvent evaporation, release of the solid content in the form of individual particles or agglomerates with possible fragmentation of agglomerates, particle and agglomerate melting, evaporation and eventually re-solidification before impact on the substrate. In the case of solutions, in addition to the above phenomena, the solute precipitates inside the droplets as the solvent is vaporized and a series of chemical reactions (e.g. pyrolysis) lead to the synthesis of the coating material from the chemical precursors.
- Non-continuum effect and slip conditions for the heat and momentum transfers between the fine particles and the plasma gas,

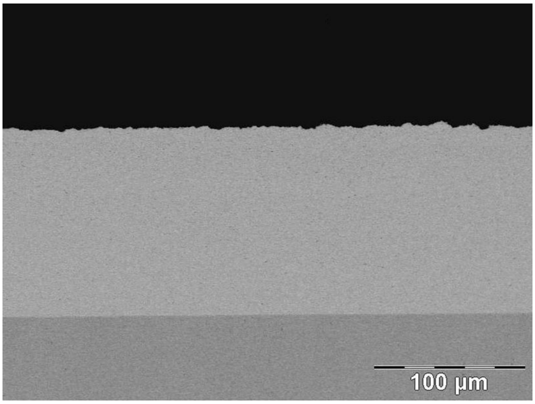

Fig. 4 Suspension plasma spraying coating (yttria-stabilized zirconia) prepared by Joulia et al. [40]. The coating exhibits a rather dense and homogeneous fine structure

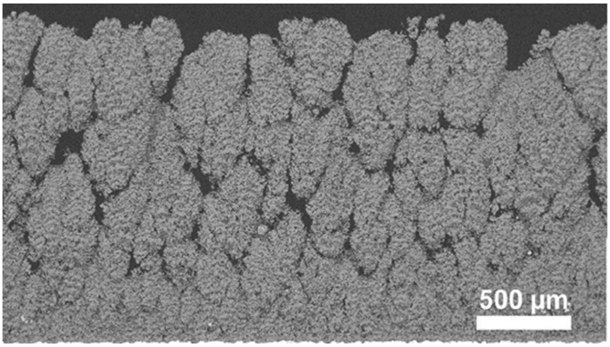

Fig. 5 Suspension plasma spraying coating (Mg–Al-spinel) prepared by Schlegel et al. [41]. The coating exhibits a columnar structure with a cauliflower-like appearance of the surface

- Fast deceleration of the fine particles that impose shorter spray distances that come with higher heat flux to substrate,
- During the impact phase, the particles with low inertia may be advected by the flow and thus follow trajectories almost parallel to the substrate surface,
- After impact, possible further processing of particles and droplets because of high substrate temperature and heat flux to substrate,

After nearly 15 years of intensive studies, suspension and solution plasma spraying are not sufficiently developed to meet industrial standards, i.e. reliable and robust cost-effective processes easy to adopt within an industrial environment; especially the stability of the process, deposition efficiency and deposition rate have to be increased. Further advances in science and technology are required to meet these challenges and increase technology readiness. However the industrial demands for stable plasma torches should not prevent researchers from exploring novel ideas, as the pulsed plasma jets with a timely injection of the liquid in the plasma puffs, proposed by Krowka et al. [19].

R&D Opportunities to Embrace

Addressing these challenges requires more basic research studies to unravel the complex interactions between the liquid feedstock and plasma gas and between impacting particles/droplets and substrate. They should address the following questions: proper and stable injection of the liquid feedstock into the plasma flow; choice of suspension particle size; choice of solvent; proper composition of solution; stability and homogeneity of plasma jets; plasma enthalpy and velocity fields; ensemble of mechanisms responsible of columnar growth.

Efforts in the development of physics-based models must be pursued. They entail the time-dependent modeling of the liquid feedstock injection and fragmentation, droplet and particle phase change, eventual agglomeration and coupling between liquid evaporation and plasma flow, fine particle trajectories in the substrate vicinity and their impact and flattening on substrate.

It is also essential to develop dedicated diagnostics for observing the liquid and particles processing and measuring their velocity, size, temperature and evaporation from the injection point to the substrate. However, measurements on entities with size below 5 μm in a very luminous medium are difficult to carry out. In addition, the medium evolves from a dense region close to the injection point to a dilute region where distances between droplets are much larger than droplet sizes. Under such conditions, the results from a single technique can be ambiguous; various techniques, as those already used for the observation of sprays and soot in combustion engines (e.g.; particle image velocimetry, interferometric particle imaging, planar laser-induced fluorescence, shadowgraphy, Raman scattering, laser diffraction particle sizing, optical pyrometry) should be used in parallel.

The use of optical diagnostics in combination with reliable models of plasma torch and liquid treatment in the plasma jet could significantly advance the field by helping to design adapted plasma spray torches and liquid feeding systems and also sensors to control the process.

Very Low Pressure Plasma Spray (VLPPS)

This process, proposed by E. Muehlberger of Sulzer Metco in the 90s [34] uses a high-power plasma torch operated in a lower pressure chamber (<1,000 Pa) than in traditional low-pressure plasma spraying (5,000–20,000 Pa). Usually, fine powders, and also liquid suspension, solutions and even gaseous precursors are injected into the plasma to deposit metal or ceramic coatings. When the feedstock is a liquid or gas precursor, coating material is synthesize in the plasma jet in a series of chemical reactions similar to CVD process.

Deposition may be in the form of vapor condensation or very fine molten particles or mixed mode; the coatings can consist of splats, as in the case of air plasma and low-pressure plasma spraying or, of dense or columnar structures as in the case of PVD or CVD coatings or mixed structures. The advantages of VLPPS are a higher flux of radicals and deposition rate than in PVD/CVD techniques and the capacity to apply uniform coatings on large substrates [5, 6, 35] (Fig. 6).

Specific Features of Very Low Pressure Plasma Spraying

Very low pressure plasma spraying results in the formation of a low-density elongated plasma jet issuing from the plasma torch. The plasma density, velocity and temperature are related to the operation pressure and have a significant effect on the coating microstructure.

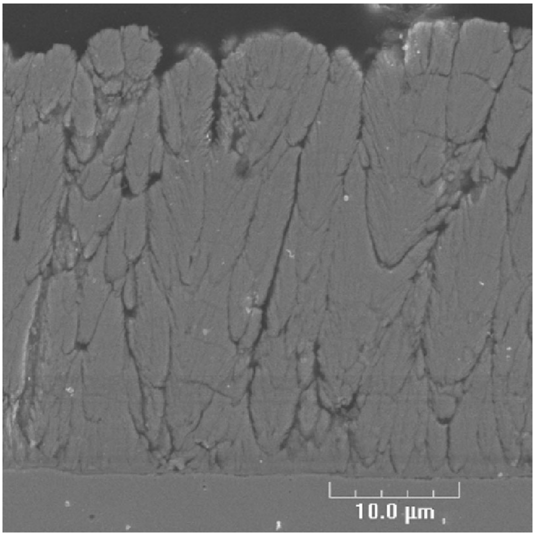

Fig. 6 Very low pressure plasma spraying coating (yttria-stabilized zirconia) prepared by Smith et al. [4]. The coating, about 40-μm thick, exhibits a columnar structure similar to vapor deposited coatings

The specific features of VLPPS are:

- The length (1 m and more) and width (a few tens centimeters) of the plasma jet and long spray distances. They make it possible (1) to deposit uniform coatings on large substrates with a thickness typically ranging from 1 to 100 μ and (2) to evaporate a significant portion of the feed material.
- The dependence of the plasma characteristics on both the operation pressure and plasma operating parameters. For example, Dorier et al. [36] found that the velocity and temperature of an Ar-H_2 plasma jet increased from 700 to 3,000 m/s and from 5,000–12,000 K, respectively, when the pressure decreased from 1,000–200 Pa at an axial distance of one meter from the plasma torch exit. The flow is still subsonic at 1,000 Pa but supersonic at lower pressures.
- The variation of concentration of the different species of plasma gas and evaporated coating material along the plasma jet length and width.
- The formation of coating from vapor condensation either directly or via a chemical reaction. Its microstructure depends to a great extent on substrate temperature and vapor concentration close to the substrate and its growth may involve steps close to those observed in thin films formation, i.e., condensation on substrate, physisorption and chemisorption, surface diffusion, nucleation, island growth, coalescence, continued growth.

The VLPPS technology has been studied and developed in the last two decades in industrial and academic laboratories but its industrial applications are still limited. As coatings may have a microstructure similar to that of coating deposited by EB-PVD, the most promising application is the substitution of yttria-stabilized zirconia (YSZ) EB-PVD coatings used as TBC in gas turbines where it offers the advantages of a higher deposition rate, larger spray patterns, non-line-of-sight deposition process and lower costs of investment and maintenance.

Up to now, most studies deal with ceramic coatings, especially YSZ coatings, and use high power plasma torches (about 180–200 kW). However, further study of VLPPS metal coating could result in a variety of applications, such as wear resistant metal-ceramic composite coatings and alternatives to electroplated coatings.

R&D Opportunities to Embrace

To exploit the possibilities of VLPPS and transfer the technology from laboratories to industry, more research efforts are necessary to understand the various steps of the process: plasma generation and flow in a very low pressure environment, interactions between plasma and particles, liquid or gaseous feedstock material, physical and chemical transformation of coating material, deposition mode on the substrate and development of coating microstructure. The study of the VLPPS process should benefit from the experience gained in the experimental observation and modeling both in air plasma spraying and vacuum film deposition techniques. In particular, the transport phenomena between the rarefied plasma and the solid, liquid or gas precursors must be properly modeled as well as the coating growth mechanisms [37].

To meet the industry requirements the process must be reliable, robust, easy to implement and economically interesting. This requires improving the components of the process (useful life of plasma torch operated at high power, injection of coating material, etc.) and control of the coating microstructure. Also, the VLPPS processes should be benchmarked against other thin film deposition technologies: PVD, CVD, suspension and solution plasma spraying, in particular the deposition of TBCs in aeronautics and land gas turbines.

Plasma Spraying in the Context of Sustainable Manufacturing

Coating techniques help considerably in the conservation of natural resources, e.g. protection of parts against wear and corrosion, refurbishment of worn parts, reduction of vehicle consumption and emission through improved engine management, higher operating temperature and mass reduction. Also, plasma spraying allows the design of components from widely available raw materials, and adaptation of the component surface to service conditions by applying only a thin layer with the required properties. However, all coating processes use energy, materials and chemicals and have certain impacts on human health, ecosystems, and resource conservation.

The societal responses to negative impacts of technology are the implementation of laws and regulations about public and occupational health, pollution prevention, ecosystems protection and resource conservation. Societal needs require the manufacture of products with full consideration of their environmental, health, and economic impacts over their entire life cycle from the extraction of raw materials to ultimate disposal of used products. Sustainable manufacturing focuses on both how the product is made and the product's attributes (e.g. recyclability, lower energy use); it rests on clean technologies to produce green products.

Societal needs together with industry-driven technology advances (e.g. growth of the use of composites in the automotive and aerospace industry) and global price competition are forcing the whole surface finishing industry to evolve. This is a challenge but also an opportunity for current and emerging plasma spraying processes if they are environmentally friendly and sustainable in comparison to other deposition techniques. This requires the development of measures of technology cleanness and resource conservation.

Life cycle assessment (LCA) is a structured, comprehensive and internationally standardized method (ISO 14040 and 14044) that provides a methodology for identifying, comparing and improving "cradle-to-grave" environmental impacts associated with a product or a process. It should become a routine for the thermal spray community to address not just the technical and economic questions but also the environmental issues with which the process or product must comply [38] (Fig. 7). LCA typically requires (1) quantifying resources used and emissions at all stages of the products/processes supply chain and life cycle and (2) converting the data of the inventory to impact scores along

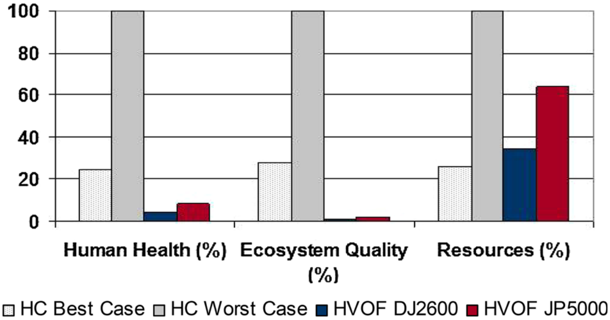

Fig. 7 Comparison of environmental impacts of hard Chrome and thermal sprayed coatings (WC–Co) manufacturing. *HC* hard chrome; *HVOF* high velocity oxyfuel; DJ2600 and JP5000 refer to different HVOF spray guns. Best case and worse case refer to two scenarios based on a set of best and worst case assumptions for hard chrome plating (computations by Krishnan et al. [38])

different environmental dimensions. The ISO 14040 and 14044 standards provide the indispensable framework for LCA but leaves the individual practitioner with a range of choices, which can affect the credibility of the results of the LCA results. A useful guidance for consistent and quality-assured LCA data and studies is provided in the International Reference Life Cycle Data System (ILCD).[6]

Concluding Remarks

Air plasma spraying is now a mature technology implemented in many industrial fields and the challenges generally consist in applying scientific knowledge to the solution of engineering problems. The development of plasma spray techniques using liquids as feedstock or operated at very low pressure has opened an exciting field of research for the plasma spray community. Their applications are promising but the production of a coating with a microstructure adapted to its service conditions requires a fundamental understanding of the interactions between the plasma and the processed material, its physical and chemical transformations and the mechanisms controlling the deposition onto the substrate and coating growth. These emerging technologies have proven to be more complex than APS and impose to work at smaller length and time scales. Their control requires developing or adapting experimental techniques and models able to observe or predict more detailed physical and chemical processes in the gas and liquid phase and also on the substrate. Finally, both older and newer plasma spray techniques should be subjected to life cycle analysis in order to improve material, energy and economic efficiency and, stand out for their environmental benefits in addition to their technical and economic merits.

References

1. Tucker RC (ed) (2013) ASM handbook, volume 5A: thermal spray technology. ASM International
2. Karthikeyan J, Berndt CC, Tikkanen J, Reddy S, Herman H (1997) Mater Sci Eng A 238:275
3. Gitzhofer F, Bouyer E, Boulos MI (1994) Suspension plasma spraying, US patent 8,296,674
4. Smith MF, Hall AC, Fleetwood JD, Meyer P (2011) Coatings 1:117
5. Von Niessen K, Gindrat M (2011) J Therm Spray Technol 20:736
6. White Paper on Thermal Spray Technology of ASM Thermal Spray Society, (Addendum 5: Key Research Challenges in Thermal Spray Science and Technology (2014)
7. Fauchais P (2004) J Phys D Appl Phys 37:R86
8. Keshri AK, Agarwal A (2012) Nanosci Nanotechnol Lett 4:228
9. Gardon M, Guilemany JM (2014) J Therm Spray Technol 23:577
10. Sun L, Berndt CC, Gross KA, Kucuk A (2001) J Biomed Mater Res 58:570
11. Hardwicke CU, Lau Y-C (2013) J Therm Spray Technol 22:564
12. Matějíček J, Chráska P, Linke J (2007) J Therm Spray Technol 16:64
13. Henne R (2007) J Therm Spray Technol 16:381
14. Sampath S (2010) J Therm Spray Technol 19:9281
15. Zasypkin IV, Zhukov MF (2006) Thermal plasma torches: design, characteristics, application. Cambridge International Sciences Publishing, Cambridge
16. Fauchais P, Heberlein J, Boulos M (2014) Thermal spray fundamentals. Springer, New York
17. Trelles JP, Chazelas C, Vardelle A, Heberlein J (2009) J Therm Spray Technol 18:728
18. Duan Z, Heberlein J (2002) J Therm Spray Technol 11:44
19. Krowka J, Rat V, Coudert JF (2013) J Phys D Appl Phys 46:505206
20. Trelles P, Pfender E, Heberlein J (2007) J Phys D Appl Phys 40:5937
21. Gonzalez JJ, Cayla F, Freton P, Teulet P (2009) J Phys D Appl Phys 42:145204

[6] ILCD Handbook, General guide for Life Cycle Assessment, © European Union.

22. Benilov MS (2008) J Phys D Appl Phys 41:144001
23. Alaya M, Chazelas C, Mariaux G, Vardelle A (2014) J Thermal Spray Technol 24
24. Chandra S, Fauchais P (2008) J Therm Spray Technol 18:148
25. McDonald A, Moreau C, Chandra S (2010) Surf Coat Technol 204:2323
26. Cedelle J, Vardelle M, Pateyron B, Fauchais P (2005) IEEE Trans Plasma Sci 33:414
27. Shinoda K, Murakami H, Kuroda S, Oki S, Takehara K, Etoh TG (2007) Appl Phys Lett 90:194103
28. Fukumoto M, Huang Y (1999) J Therm Spray Technol 8:427
29. Xu L, Zhang WW, Nagel SR (2005) Phys Rev Lett 94:184505
30. McPherson R (1981) Thin Solid Films 83:297
31. Fauchais P, Vardelle A (2011) J Phys D Appl Phys 44:194011
32. Fauchais P, Montavon G (2010) J Therm Spray Technol 19:226
33. Killinger A, Gadow R, Mauer G, Guignard A, Vaßen R, Stöver D (2011) J Therm Spray Technol 20:677
34. Muehlberger E (1998) Method of forming uniform thin coatings on large substrates, US Patent 5853815 A
35. Vautherin B, Planche MP, Bolot R, Quet A, Bianchi L, Montavon G (2014) J Therm Spray Technol 23:596
36. Dorier J-L, Gindrat M, Hollenstein C, Loch M, Retke A, Salito A, Barbezat G (2001) Plasma jet properties in a new spraying process at low pressure for large area thin film deposition. In: Proc. Inter. Thermal Spray Conference, Singapore, 28–30 May 2001, pp 1–6
37. Mauer G (2014) Plasma Chem Plasma Process 34:1171
38. Krishnan N, Vardelle A, Legoux JG (2008) A life cycle comparison of hard chrome and thermal sprayed coatings: case example of aircraft landing gears. In: Proc. of International Thermal Spray Conference 2008: ''Crossing Borders'', DVS-ASM, Hamburg, p 212
39. Trelles JP (2013) J Phys D Appl Phys 46:255201
40. Joulia A, Bolelli G, Gualtieri E, Lusvarghi L, Valeri S, Vardelle M, Vardelle A (2014) J Eur Ceram Soc 34:3925
41. Schlegel N, Ebert S, Mauer G, Vaßen R (2014) J Thermal Spray Technol 24