

## THERMAL SPRAY COATINGS

Thermal spraying is a group of processes in which finely divided metallic or nonmetallic surfacing materials are deposited *in a molten or semimolten condition* on a *prepared substrate* to form a spray deposit (1). The surfacing material may be in the form of powder, rod, cord, or wire, and the different spraying processes are generally categorized into two groups according to the method of heat generation: combustion or electrical. This article is restricted to electrical processes: plasmas jets (nontransferred direct current arcs or induction discharges), wire arcs, and transferred arcs. Plasma jets utilize powdered materials whereas in the wire arc, the arc is struck between two consumable, automatically advanced wires. In these two processes, the substrate (e.g., metal, glass, ceramic, plastic, composite) is kept far below its melting temperature. This is not the case with the transferred arc process where the metallic substrate and the powdered surfacing material are molten, and the resulting coating is welded to its substrate. Now thermal spray is part of engineering technology for wear protection, thermal insulation or barriers, oxidation protection, corrosion or oxidation resistance, abradable seals, electrically conductive or insulating materials, dimensional restoration or manufacture, free-standing shapes, and medical implants (1–3). This market represented about \$1.2 billion US in 1995 (with 40% to 60% in plasma technology, depending on the sources) and is poised for substantial growth (4). This article presents

- the spraying processes with coating formation, plasma jet spraying, arc spraying, sprayed materials, and applications.

- the plasma transferred arc process with the plasma torch, the heat flux control for substrate and powders, and the coatings and their applications.

### COATING FORMATION

#### Key Parameters

The heat source (plasma or arc) is independent of the substrate which can be cooled independently and whose surface temperature can be as low as 50° to 70°C, for example, with cryogenic cooling for plasma spraying, and typically below 150° to 200°C with compressed air cooling. The plasma jet flow, or the propelling compressed gas for the wire arc, entrains the surrounding atmosphere. Therefore, spraying in air may result in surface oxidation of the hot particles in flight and the flattened particles and coatings, when substrate and coating are kept at temperatures over 200° to 500°C, depending on the materials. The only way to reduce oxidation drastically is to spray in a controlled atmosphere or preferably in a soft vacuum (~20 kPa to 30 kPa) which increases the cost of the industrial spray equipment by at least an order of magnitude. The use of nozzle shields to spray in air reduces oxidation problems, but they are not as effective as spraying in a soft vacuum.

The surfacing material must hit on the substrate or the previously deposited layers in a molten or plastic state. When it is in a plastic state, its velocity must be high, typically over 300 m/s to 350 m/s for particles in the 30  $\mu$ m range. Thus, only materials that melt at temperatures at least 300 K below their vaporization or decomposition temperatures can be

sprayed. The particles strike the surface, flatten, and form thin platelets (splats) that conform and adhere to the irregularities of the prepared surface and to each other with occasional diffusion or alloying. The splats cool down below their plastic state in a very short time ( $\sim 5 \mu\text{s}$  to  $30 \mu\text{s}$ ), and the next particles impinge on the same location in time of the order of tenths to hundreds of ms, that is, after the splats have solidified and cooled well below their melting point. Thus, the coating is built up, particle by particle, into a lamellar structure as shown in Fig. 1.

Except for oxide inclusions (for metals and alloys sprayed in air), the coating is generally porous and micro- and macro-cracked, as explained later. Thus, its properties differ from those of the bulk material. For example, its Young's modulus is one-third to one-quarter of that of the bulk material in most cases.

### Substrate Preparation

Coating adhesion is directly related to the cleanliness and the roughness of the substrate surface (1,2,4,5). Preparations of the surface is the most critical step in a thermal spraying operation. The first step in the preparation is to remove all surface contaminants, such as scale, oil, and paint, by different techniques: scraping, wire brushing, machining, vapor degreasing, vapor blasting, acid pickling, or oven backing. These must be adapted to the substrate material. After contaminants have been removed, the cleanliness must be maintained until spraying is completed: no finger prints, clean fixtures and materials, and no airborne debris especially during spraying. Thus, the air or gas flow close to the substrate must be carefully controlled, especially when the substrate is kept hot ( $T > 400^\circ\text{C}$ ) during spraying, to minimize, as much as possible, recirculation of submicron-sized debris or recondensed vapors.

After cleaning, the substrate surface has to be roughened to promote adhesion. In most cases this is achieved by grit blasting. Blasting parameters have to be controlled carefully to obtain reproducible surfaces, to reduce the embedded grit debris as much as possible, and to limit the induced compressive stresses (5) in a thin layer (tens of mm) below the grit-blasted substrate surface. Higher surface roughness, as measured by the root-mean-square average of surface roughness (often termed Ra) requires bigger grits which induce higher compressive stresses and more embedded debris. The embedded debris, which reduces coating adhesion proportionally to

the quantity, can be avoided by blasting with high pressure (100 MPa) water jets (6). The size of the peaks has to be adjusted to the size of the particles or more precisely to that of the resulting splats. If the peak height is  $100 \mu\text{m}$  ( $R_a \sim 12 \mu\text{m}$ ) splats with mean diameters below  $90 \mu\text{m}$  will have poor or even no mechanical adhesion. Roughening of composite or plastic-based materials is usually achieved by chemical methods.

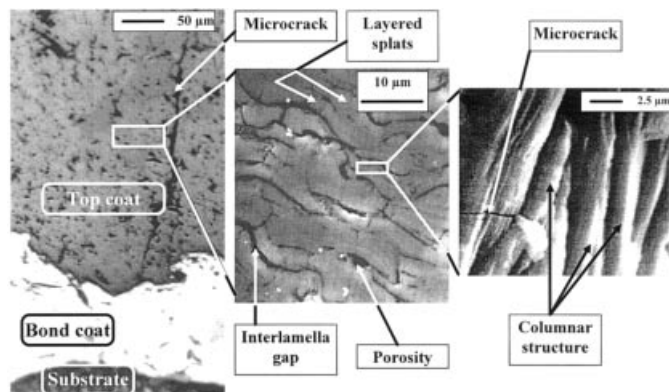
### Splat Formation

Splat formation has been extensively studied in the past decade, and work is continuing to get a better understanding of the involved phenomena. For example, in dc plasma spraying the short flattening ( $\sim 1 \mu\text{s}$ ) and solidification ( $\sim 10 \mu\text{s}$ ) times and solidification starting before flattening is completed make experiments and modeling very complex. The main conclusions of these studies are the following (7):

**Substrates Orthogonal to Particle Trajectory.** For a given particle material on smooth surfaces ( $R_a < 0.4 \mu\text{m}$ ), there is a critical temperature  $T_c$  for the substrate preheating temperature  $T_p$  above which the splat has a disk shape and excellent contact with the substrate (thermal contact resistance  $R_{th} < 10^{-7} \text{ m}^2 \cdot \text{K/W}$ ) corresponding to at least 70% to 80% of perfect contact. Below  $T_c$ , the splat is extensively fingered with  $R_{th} > 10^{-6} \text{ m}^2 \cdot \text{K/W}$  and has about 20% of good contact with the substrate. There is actually no clear explanation for  $T_c$ , which is not linked to the particle melting temperature. For example, for  $\text{Al}_2\text{O}_3$  or  $\text{ZrO}_2$ ,  $T_c \sim 200^\circ\text{C}$ . However, this phenomenon is linked to the fact that if the actual temperature of the substrate  $T_p < T_c$ , solidification starts before flattening is completed (7). In general, splat adhesion to the substrate increases with substrate temperature (over  $T_c$ ), provided that the metallic substrate is not too oxidized. The oxidation of metals or alloys depends on the original oxide layer thickness and composition. On oxidized surfaces, splats are "fingered" when the substrate temperature  $T_p$  is below  $T_c$ . For  $T_p < T_c$ , splats are very easily pulled off by the diamond tip of a perthometer even at very low load ( $< 0.1 \text{ N}$ ). The splat cooling rate, which controls their microstructure (size of columns or grains and phases), is strongly linked to  $R_{th}$  and splat thickness  $e$ . Very fast cooling rates (up to  $10^6$ – $10^8 \text{ K/s}$  for dc plasma-sprayed splats) may result in metastable phases or even amorphous structures. This is less likely when  $e$  and/or  $R_{th}$  increases.  $e$  depends on the particle impact velocity. For example, with  $30 \mu\text{m}$  alumina particles hit at  $v = 250 \text{ m/s}$ ,  $e \sim 1 \mu\text{m}$  (dc plasma spraying) and  $3 \mu\text{m}$  for  $v \sim 50 \text{ m/s}$  (RF plasma spraying).

The tensile stresses induced upon splat cooling (quenching stresses) can be very high, and they are partly relaxed by creep in metals and greatly relaxed by microcracking in ceramics (for more details about the other relaxation possibilities see Ref. 8). For alumina splats sprayed on a substrate at  $T_p > T_c$ , most of the splat surface exhibits microcracks. When  $T_p < T_c$ , only a small part, that is, in areas where the contact is good ( $< 20\%$ ), exhibits these cracks.

As the peaks and valleys perturb the liquid particle flow on rough surfaces, even when  $T_p > T_c$ , the splats are more extensively fingered and thicker. Their cooling rate is greater than that obtained on smooth surfaces, and the microcrack network with alumina, for example, is less dense. When  $T_p <$



**Figure 1.** Bilayer coating with a metal bond coat and a ceramic coat.

$T_c$ , the splats are extensively fingered, and their cooling rate is much slower (one order of magnitude) than when  $T_p > T_c$ .

**On Inclined Substrates.** For  $T_p > T_c$  and smooth substrates, splats have an elliptical shape, and their thickness increases in the direction of the liquid flow (due to substrate inclination). However, when this inclination is increased, the splats become fingered, and areas of poor contact appear. They can be distinguished easily by atomic force microscopy because crystalline growth in these areas is parallel to the substrate (9). The splats are more easily detached by the tip of a perthometer, especially when the substrate inclination is greater than  $30^\circ$ . For  $T < T_p$  on smooth surfaces, the splats are hardly collected on inclined surfaces. Thus if possible the torch and the coated surface have to be orthogonal.

### Bead and Pass Generation

When translating the torch relative to the substrate at a speed  $v_t$ , a bead is obtained (7). As a first approximation, its shape is Gaussian. Its thickness  $e_b$  depends on  $v_t$ , powder mass flow rate  $m_p^\circ$ , deposition efficiency  $\rho_d$ , and the substrate stand-off distance.  $e_b$  increases when  $m_p^\circ$  or  $\rho_d$  increase and  $v_t$  decreases. In fact, to coat simple (flat or cylindrical) or complex structures, additional handling equipment is required, for example, torch translation at  $v_t$  and cylindrical substrate rotation. In most complex structures, the torch is mounted on the arm of a computer-operated robot and the part to be coated is also moved by another unit. Such devices allow keeping the pass thickness constant and the torch orthogonal to the part of substrate it faces. The spray pattern results in overlapping beads. The thickness increase  $e_p$  of a pass depends on  $e_b$  and the rate of overlapping. Each pass thickness  $e_p$  varies generally from a few  $\mu\text{m}$  up to  $100 \mu\text{m}$ . The thinner the pass, the easier the coating and substrate cooling and thus the control of substrate and coating mean temperature  $\bar{T}_c$  between successive passes. The properties of the coatings are strongly linked to the substrate preheating temperature and to the control of  $\bar{T}_c$ . The adhesion/cohesion of coatings increases with preheating temperature  $T_p$ , provided that the substrate (if metallic) is not too oxidized. This means that, depending on the substrate material,  $T_p$  is limited to temperatures between  $300^\circ$  and  $600^\circ\text{C}$  in air. These temperatures are too low to improve adhesion/cohesion by diffusion, a phenomenon which is observed only when spraying in soft vacuum and when the substrate is hot enough (for example,  $\sim 950^\circ\text{C}$  for superalloy sprayed on superalloys). As is expected from the study of splats collected on inclined substrates, the adhesion/cohesion of coatings diminishes drastically when spraying on inclined substrates (10). Thus care has to be taken to keep the torch and the coated substrate orthogonal to each other during spraying.

When  $T_p$  and/or  $T_c$  increase, residual stresses increase also: quenching stress (due to the improvement of the contact between splats and substrate or previously deposited layers) and expansion mismatch stress. Too high a residual stress can result in coating peeling off, especially for thick coatings (11). These stresses result in microcracks within splats in ceramics and macrocracks parallel or perpendicular to the substrate (see Fig. 1). This can be handled in certain cases by using a bond coating, whose expansion coefficient is between that of the substrate and the coating, by macroroughening

(i.e., by machining or grinding in conjunction with bond coating and/or grit blasting), or by annealing the coating and substrate when a certain coating thickness has been deposited.

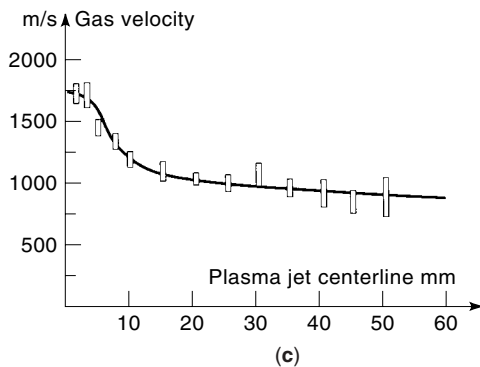
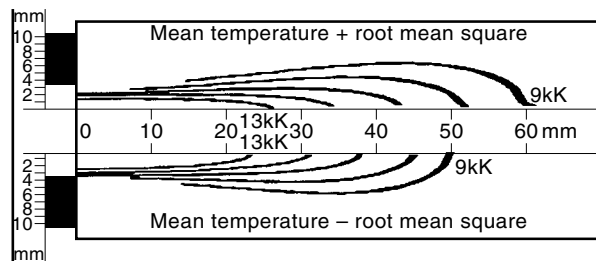
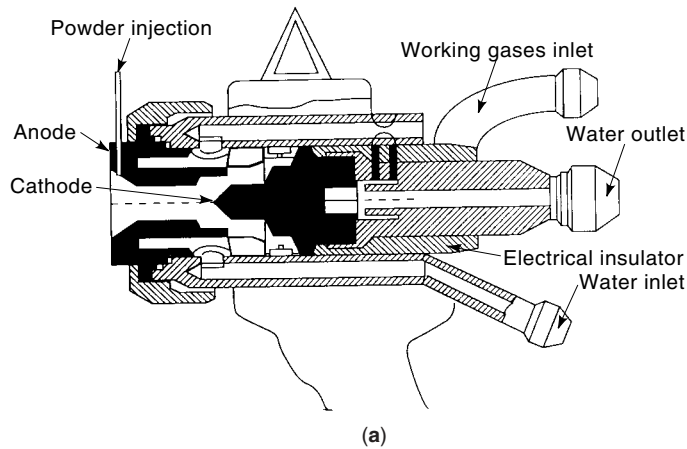
Coatings are not generally fully dense depending on the way they were sprayed, especially when sprayed in air, and porosity can affect the properties of thermally sprayed coatings significantly. The porosities generally observed are chamber-type pores a few micrometers in size because of shadow effects or poor accommodation of the gap between two splats, thin gaps between lamellae ( $\sim 0.1 \mu\text{m}$ ), and cracks. Thus, measured Young's moduli of metallic air plasma spray (APS) deposits are generally around one-third of bulk values and in ceramics they can be one-fifth (12). This heterogeneous structure also results in hardness values lower than those for equivalent materials in either cast or wrought form.

## PLASMA SPRAYING

### Plasma Torches

The following three types of plasma torches are used:

1. *Dc Plasma Torch with a Stick Type Cathode.* These torches represent about 95% of the torches used in industry. The plasma torch consists of a stick-type cathode (made of tungsten doped with 2 wt% of thoria to lower the electron extraction potential) and a water-cooled (at a pressure of 1.5 to 2 MPa) anode nozzle (Fig. 2) that has the same axis of symmetry. The arc strikes between the tip of the conical cathode and the anode. Because of the arc restrike mode at the anode, the arc-root lifetime at the same location is usually below  $100 \mu\text{s}$  (13). It drastically reduces anode erosion but induces voltage fluctuation and thus power fluctuation at frequencies in the range 3 to 20 kHz. The anode nozzle shape is usually very simple, a cone followed by a cylindrical duct. The nozzle may also have a divergent section to produce supersonic jets. In most cases, it is made of OFHP copper sometimes with a tungsten insert. The method of injecting the plasma forming gas plays an important role in developing the plasma jet at the nozzle exit (13). The most traditional method is to inject it as a vortex (creating a cold boundary layer at the anode wall and pushing the arc root further downstream), longitudinally along the anode axis or along the cathode conical tip which creates extra gas stabilization of the arc column. Within the arc column, temperatures in the range 10,000 K to 18,000 K are achieved, and the plasma-forming gas is dissociated (if molecular) and ionized. Downstream of the arc root, the ions, electrons, and atoms recombine releasing energy which maintains a plasma jet as it exits from the nozzle. This high velocity jet (from 1000 m/s to 2700 m/s for subsonic jets) creates vortical rings at the nozzle exit which coalesce and create large eddies that result in an engulfment process. Cold surrounding gas bubbles entrained by the large eddies mix with the plasma and cool it down while they are heated up, so that their density becomes close to that of the jet. At the nozzle exit, where temperatures of 13,000 K to 14,000 K are achieved, the plasma's specific mass is about one-fortieth of that of the cold gas. The most common plasma gases are mixtures of a pri-

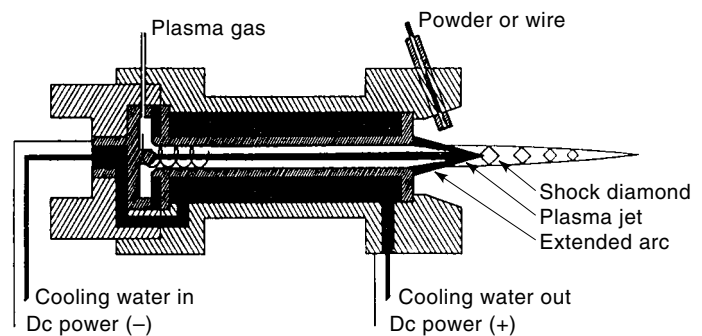


**Figure 2.** (a) Scheme of a dc plasma torch. (b) The upper and lower parts of the figure show the variation in the temperature fields of an Ar-H<sub>2</sub> plasma jet resulting from the arc root movement on the anode wall. (c) Evolution of plasma jet velocity along the jet center line (nozzle i.d. 7 mm, Ar 45 slm, H<sub>2</sub> 15 slm,  $I = 600$  A,  $V = 62$  V,  $r_{th} = 52\%$ ).

mary heavy gas Ar or N<sub>2</sub> with a secondary gas either hydrogen or helium which improves the gas thermal conductivity and thus the heat transfer (14). Helium increases plasma viscosity at  $T > 10,000$  K and delays mixing with the surrounding atmosphere. Ternary mixtures (Ar-He-H<sub>2</sub>) are sometimes used. Typical power levels are in the range of 40 kW, but some plasma torches operate at 80 kW especially in producing supersonic jets. Typical nozzle internal diameters are in the range 6 mm to 8 mm but generally the working parameters for a given nozzle are rather narrow. For example, with a 6 mm i.d. nozzle and a total gas flow rate of 40 slm (Ar + 25 vol% H<sub>2</sub>), the arc current can vary between 400 A and 700 A resulting in voltages between 80 and

65 V. Such torches are used to spray up to 6 kg/h to 8 kg/h of powder which is injected orthogonally to the jet axis inside (downstream of the arc root) or outside of the nozzle.

2. *Torches with Three Cathodes.* Recently torches with three stick-type cathodes set at 120° around the torch axis have become available. Their main advantage is the possibility of injecting the particles axially (between the cathodes). Thus, particles are accelerated and heated by the hot plasma column, and the heat and momentum transfer are far more efficient than with conventional torches.
3. *High-Power Torches.* Dc vortex plasma torches using a button type cathode and high gas flow rates have been developed to spray relatively large quantities of powder (up to 20 kg/h to 25 kg/h). Figure 3 shows a schematic diagram of such a plasma torch (15). The nozzle internal diameter is about 8 mm and typical working conditions are 200 slm to 300 slm N<sub>2</sub>, 100 slm to 150 slm H<sub>2</sub>, 500 A, and 400 V. The plasma jet maximum temperature is below 9000 K and has a rather flat distribution. Supersonic flows, if necessary, are achieved more easily (16) than with the stick-type cathodes where temperatures are as high as 14,000 K. Because of the higher plasma density, the particle acceleration is also more efficient than with the torches previously described.
4. *RF Plasma Torches.* A typical commercial torch is shown in Fig. 4. The ceramic chamber internal diameter is about 50 mm for a 50 kW torch, thus resulting in much lower flow velocities (about 100 m/s). The wall is protected by a strong vortex in which a few vol% of H<sub>2</sub> can be introduced. The plasma-forming gas is mainly argon to limit constricting it and requiring more dissipated energy. Because of the inductively coupled power, some sort of skin effect is observed, and the maximum temperature (below 9000 K) is off-axis. The central part of the plasma is heated mainly by conduction and convection. The gas flow may recirculate, especially at the top of the plasma. That is why particles are injected axially with a water-cooled probe at the level of the first loop of the coil. Larger particles (up to 150 μm) can be sprayed because of the lower gas velocity. This offers some advantages for easily oxidized materials, such as titanium-aluminum alloys, used to make the matrix of a carbon-carbon fiber reinforced material. Such torches



**Figure 3.** Schematic diagram of a dc vortex plasma torch (from Ref. 15).

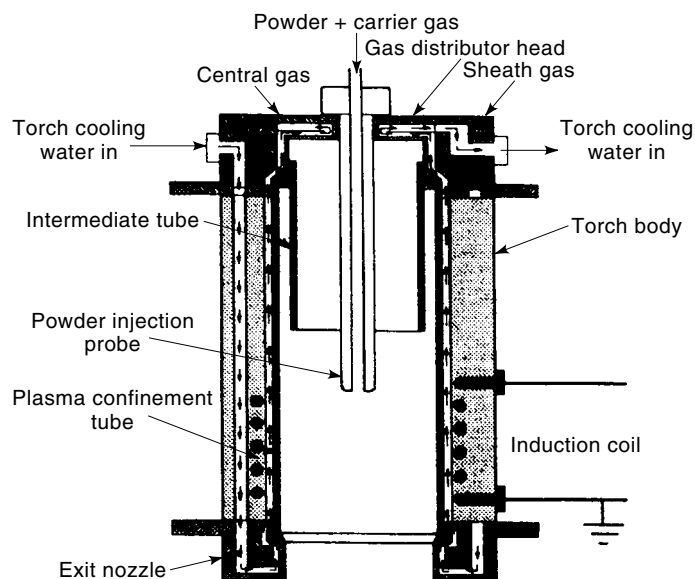


Figure 4. Schematic diagram of an RF plasma torch (from Ref. 17).

operate at pressures ranging from 10 kPa to 200 kPa (17).

- 5. Controlled Atmosphere or Soft Vacuum.** Controlled atmosphere (CA) or soft vacuum spraying (VPS) are used to confine hazardous materials (toxic beryllium or pyrophoric magnesium, titanium) and restrict forming oxides that would occur in air spraying. A controlled-atmosphere (CA) chamber includes a tight box, water-cooled if below a few  $m^3$ , the plasma gun and its mechanical equipment, a vacuum pumping system, and an inert gas backfill manifold. The chamber is pumped down to a low pressure (a few pascals) and then back-filled with high-purity, dry argon to maintain oxygen levels below 30 ppm. When the plasma jet flows in an argon atmosphere, it is longer and fatter than in air because there is no dissociation and ionization of the entrained gas, both of which consume a lot of energy. These CA chambers are used to spray carbides, borides, and similar materials. Thick coatings (up to a few cm) are achieved when the coating and substrate are cooled by liquid argon droplets during spraying. When the pressure of the chamber is maintained at 10 kPa to 30 kPa during spraying, long plasma jets (up to 60 cm) at lower temperatures ( $\sim 4000$  K to 5000 K) are obtained. The optimum spraying conditions, especially the chamber pressure, vary with the chemistry and particle size of each spray material. VPS leads to closer control of the composition and morphology of sprayed coatings, characterized by greater structural homogeneity, very low level of oxides, improved hardness, thickness capability, and deposition efficiency, and much better adhesion because of diffusion (for example a superalloy substrate can be kept at 950°C during spraying). However, the capital cost of such equipment increases considerably (by one to two orders of magnitude) depending on

the complexity of these systems for industrial production (see Fig. 5) (18).

- 6. Nozzle Shrouds.** To avoid the cost of CA chambers, water-cooled nozzle shields are located at the torch nozzle exit. Similar to Laval nozzles, they are especially designed to eliminate low pressures close to the nozzle shield wall to avoid a countercurrent flow that entrains air within the plasma jet. Although these devices consume 10 to 30% of torch energy, they reduce particle oxidation during their flight and are used commercially to spray superalloys (19).

#### Plasma Particle Heat and Momentum Transfer

Many models (20) and measurements (21) have been devoted to the study of plasma particle interactions. The heat and momentum transfer to a particle depend on its residence time within the hot zone of the plasma and the plasma-forming gas composition. The heat and momentum transfer is by far more complex (20) than in flames because of the high temperature gradients around the particle, its evaporation, and the Knudsen effect. This last noncontinuum effect is observed in plasmas at atmospheric pressure because the gas species mean free path  $\ell$  is already a few micrometers which is not very small compared to particles whose mean size is often around 20  $\mu m$  to 30  $\mu m$ . Of course, this effect is enhanced in VPS where  $\ell$  increases when the pressure chamber decreases in size. In spite of long jets, for example, at 10 kPa, melting particles, whose size is more than 40  $\mu m$  and melting temperature more than 1500°C, is almost impossible. In fact, the difficulty in melting a particle increases as the factor  $Q/\sqrt{\rho}$  where  $\rho$  is its specific mass and  $Q = (m \cdot C_p \cdot \Delta T + mL_m)$  where  $m$  is the mass of the particle,  $C_p$  its specific heat at constant pressure and  $L_m$  its latent heat of fusion.  $Q/\sqrt{\rho}$  for alumina is almost three times the value for molybdenum in spite of the higher melting temperature of the latter. When the particle has low thermal conductivity, compared to the mean thermal conductivity of the plasma, heat propagation occurs and the particle surface starts to evaporate when its center is still cold. This is the case for zirconia particles in an Ar + 25 vol%  $H_2$  plasma. Thus the stand-off distance has to be long enough

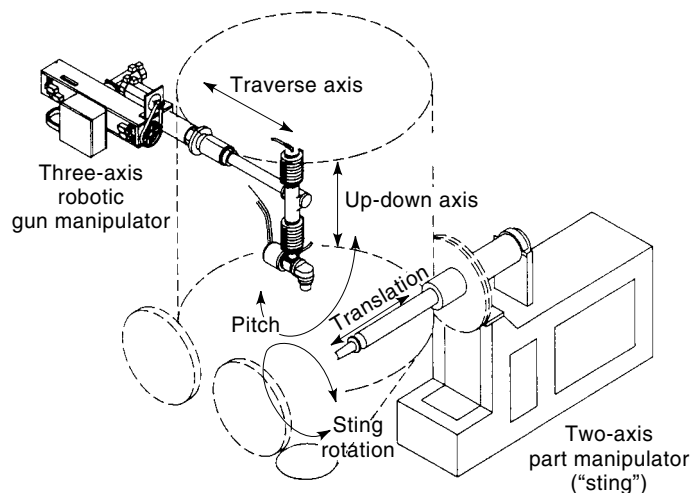


Figure 5. Schematic diagram of a soft vacuum plasma spraying chamber and its utilities (from Ref. 18).

for the particle to be fully molten. In general, better coatings are obtained with dense particles than with porous particles, such as agglomerated particles because thermal conductivity decreases for porous particles.

The key parameter for achieving fully molten particles is the method of injection into the plasma jet. With most dc torches, particles are injected radially to the plasma jet with the help of a carrier gas. However, it is a complex phenomenon (13). Particles have a size distribution and with the carrier gas they get a velocity distribution within the injector. Moreover, the particles collide with the injector wall, especially the finer ones, and with each other. Thus, at the injector exit they exhibit divergent trajectories, especially for those whose diameter  $< 20 \mu\text{m}$ . The optimum trajectory depends on the force balance between that imparted by the carrier gas and that resulting from the drag of the plasma. It is difficult to achieve an optimum trajectory for all of the particles and injection, in spite of its simplicity, has to be carefully checked. The position of the injector tip, injector tilting, and carrier gas flow rate may also perturb the plasma (22).

Finally, the stand-off distance  $d$  is a compromise between good particle melting, which is achieved for dc plasma torches at distances between 60 mm and 70 mm downstream of the nozzle exit, and good control of substrate and coating heating by the plasma heat flux, which varies as  $\exp(-d/d_0)$ .

### Process Control

Developing and using efficient controls for thermal spraying processes is absolutely necessary to produce coatings more consistently day after day. Most of the conventional systems control the arc current and voltage and the gas flow rates. For example, when the voltage decreases with time because of electrode erosion, a slightly higher percentage of  $\text{H}_2$  is introduced to keep it constant. In addition to the energy parameters, the spray pattern and the carrier gas flow rate are also controlled very often by computerized systems which adapt all of these parameters to preset values for a given coating.

Recently (7,23) more sophisticated systems have been developed for simultaneously monitoring a combination of particle parameters: velocity, trajectory, and mean surface temperature. These systems are adapted to a production environment and take advantage of hot particle radiation which makes it possible for them to react to the process and correct any drift detected. In the author's opinion, the most important operating parameters to control are the particle trajectories and the coating surface temperature. Different optical and noncontact techniques have also been developed for continuously measuring coating thickness. However, establishing a control strategy for a thermal spray process as a whole is very complex because the process involves many variables that concurrently influence the properties of the deposited coatings. A lot of work remains to be done in this field.

### Auxiliary Equipment

In addition to the cleaning and grit blasting systems, power supply, pressurized deionized water cooling system, and torch and robot control panel, plasma spraying requires

a specially designed, soundproof spray booth (a supersonic plasma gun can generate a noise up to 140 db), that is ventilated and allows keeping particles air borne (mini-

mum diameter, gas flow rate, and velocity) and a water wash efficient cleaning system;

an exhaust system that has ventilation equipment and adapted powder collectors which comply with safety regulatory requirements.

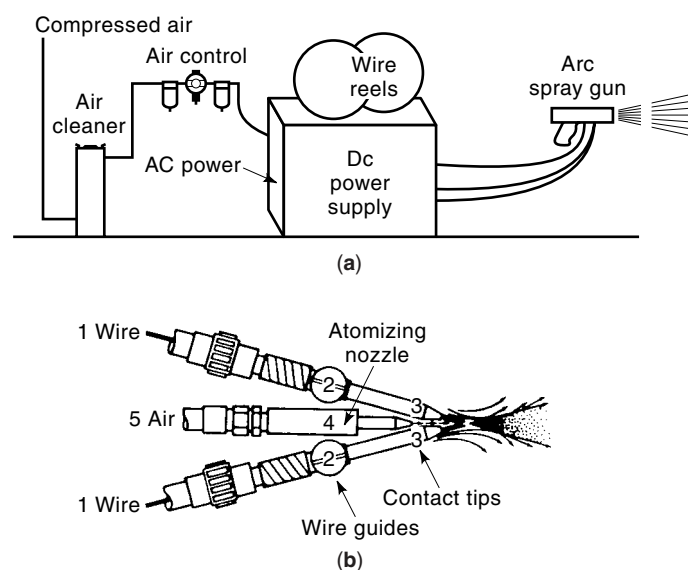
The torch and robot control equipment are located in a room close to the booth from which the operator observes and controls the operation through a window (with UV filters) or with cameras.

### ARC SPRAYING

In this process, illustrated in Fig. 6, two consumable wire electrodes automatically advance at a controlled rate to meet at a point and form an atomizing gas stream. A potential difference of 18 to 40 volts applied across the wires initiates an arc that melts the tips of the wires. The molten metal is atomized and propelled onto a prepared substrate by a stream of compressed gas, which is air in most cases. The design of the atomizing nozzle is very important (24). The arc source is at a constant potential, and usually arc current is limited to 400 A. The wire control unit is composed of two reel or coil holders, insulated from each other. Thus, this process is limited to relatively ductile, electrically conductive wire about 1.5 mm to 1.8 mm in diameter. In most instances this process is less expensive to operate than other processes discussed in this article, and the power consumption is low. Only fully molten particles are propelled to the substrate which is heated almost entirely by the impinging molten droplets (no flame touches the substrate). In general this process has high deposition rates, from 20 kg/h to a maximum of 55 kg/h, and rather high bond strengths (often  $>50 \text{ MPa}$ ).

### SPRAYED MATERIALS

As already noted, any material whose melting temperature is at least 300 K lower than its vaporization or decomposition



**Figure 6.** (a) Arc spray components. (b) Schematic cross section of an arc spray gun (from Ref. 1).



temperature can be sprayed. Sprayable materials include metals and alloys (including self fluxing alloys), oxides, cermets (such as carbides or graphite clad with Ni and Co), carbides and borides (sprayable only in a controlled atmosphere), and composites (e.g., superalloys agglomerated with polyimide).

The powders are prepared by different techniques, such as (2,25):

- gas or water atomization for metals and alloys (almost spherical particles)
- fusing or sintering for oxides, carbides, and cermets (blocky and irregular shapes)
- spray drying, a very versatile technique (nearly spherical shapes), but the mechanical resistance of powders is poor and they have to be sintered to reinforce them
- cladding where a core of one material is coated with a porous or dense layer of another material
- many other methods, such as the sol-gel technique, mechanofusion and so forth

All of these techniques allow preparing a wide variety of alloys, composites, and cermets tailored to the application and make spraying a unique technique for producing coatings suited to a wide range of service conditions. For example, spraying allows producing metallic coatings reinforced with homogeneously dispersed ceramic particles (in the micrometer range). The key parameters for a "good" powder are its flowability, low porosity, and size distribution. In most cases, particles range in size between 10  $\mu\text{m}$  and 45  $\mu\text{m}$  (below 10  $\mu\text{m}$  powder flowability is very poor) for ceramics. For metals and alloys, in general, the size range is between 45  $\mu\text{m}$  and 90  $\mu\text{m}$ . Of course, wider distributions (for example from 10  $\mu\text{m}$  to 106  $\mu\text{m}$ ) can be used to produce porous coatings.

In wire arc spraying the choice is more restricted because of the need for an electrically conductive and ductile wire.

## APPLICATIONS

Choosing a thermal spray material for an application is more complex than selecting a wrought or cast material for the same application because coating properties are not as predictable as those of conventional materials. However, now many applications are well established and new ones are being developed that allow pairing optimum base material and surface coating properties to obtain a combination of characteristics that would not be possible with homogenous materials. Because the aircraft and aerospace industries have provided an ideal proving ground for testing and integrating a few coating concepts, this technology has advanced steadily to the point where it has increased the credibility and reliability of coatings. The success in manufacturing aircraft components has led to applications in other markets, such as the paper, printing, steel, metal processing, textile, synthetic fibres, chemical, oil and gas, automotive, plastic, glass, pumps, pneumatic and hydraulic systems, mechanical engineering, shaped part, turbine, nuclear, electronic, and electrical industries (1-4,26). The most common applications today are the following:

- Minimization of wear, caused by fretting, sliding, impact, abrasion, erosion and other service conditions. Hard metal coatings, such as Cr-Ni-B-X alloys where X represents Nb, Ta Ti, self-fluxing alloys of Fe, Ni, Co, high carbon steels, NiCr alloys, and Mo, are used to improve the wear properties of low alloy steel and nonferrous metal surfaces.  $\text{Al}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3\text{-TiO}_2$  coatings are used in the textile industry.  $\text{Cr}_2\text{O}_3$  coatings are used in pumps and printing presses.  $\text{Cr}_2\text{O}_3\text{-SiO}_2$  coatings are used to absorb energy from impact loading. The carbide cermets are very popular for landing gear components, valves in oil drilling equipment, "Yankee" dryers in paper machines (coated on site), for large rollers in sheet steel production, grinding wheel mold rings, and cam followers.
- Wear resistant coatings often exhibit good resistance to heat and chemical attack. When using ceramic coatings this is achieved by using VPS bond coats.
- Corrosion protection coatings are used to protect iron and steel in a range of corrosive environments. The particular environment dictates the appropriate alloy selection. Sealed austenitic stainless steel, aluminum bronze, and Co and Ni base alloys are often used below 200°C. The sealant, for example, is Teflon or epoxy (below 150°C) or Cu or Zn deposited by electrolysis for higher temperature applications (<400°C). Zn and Al provide the broadest atmospheric protection and represent the biggest successful commercial application of wire arc spraying. Spraying is used to protect structural steel work, parts subjected to sulfurous atmospheres, offshore assemblies, pipelines, and ships.
- Oxidation protection: Ni and Co base, Ni, Cr and Co alloys and superalloy coatings are the most popular protection. Oxidation protection requires fully dense coatings and the superalloys are sprayed at high temperature (~950°C) under low vacuum.
- Liquid metal protection: Extrusion dies are coated with NiCr doped with  $\text{Al}_2\text{O}_3$  particles or with  $\text{CrO}_3$ ,  $\text{Cr}_2\text{O}_3$  + TiC.  $\text{MgO} + \text{ZrSiO}_4$  coatings are used for protection from liquid copper, stabilized zirconia against liquid zirconia, and so forth.
- Thermal barrier coatings are used in diesel engine power assemblies (piston dome heads and valves), gas turbines, and aircraft engines (not yet on turbine blades). The material used is  $\text{ZrO}_2$  stabilized with CaO or MgO for  $T_s < 800^\circ\text{C}$  and with  $\text{Y}_2\text{O}_3$  or  $\text{CeO}_2$  for higher temperatures.
- Heat transfer improvement can be achieved by using coatings with better thermal characteristics, such as Cu or Al or BeO for ceramics when electrical insulation is mandatory.
- Electrical properties:
  - Electrically insulating surfaces (mostly oxides and especially  $\text{Al}_2\text{O}_3$ ) are used for dielectrics (for example, ozonizers), high temperature strain gages, oxygen sensors (ionic conduction of zirconia), and insulation of induction heating coils.
  - Electrical contacts are produced with Al or Cu coatings. Resistors are made of NiCr, superalloys doped with  $\text{Al}_2\text{O}_3$  particles.
- Self-lubricating coatings containing free carbon or  $\text{MoSi}_2$  are plasma sprayed.

- Electromagnetic applications:

Electromagnetic or radio frequency interference which can damage electronic components or interfere with low level signals can be reduced by shielding. This is achieved by a metallic coating that is wire-arc sprayed on the inside surface of an instrumentation cabinet, which is usually made of plastic or a composite material.

Microwave integrated circuits (MIC) are made of plasma-sprayed Mg-Mn ferrite.

Al, Ta and Nb capacitor electrodes are plasma-sprayed in air.

Sputtering sources are also plasma-sprayed.

- Dimensional buildup for salvage of worn or overmachined parts. All thermal spraying processes are used for this salvage work and very often NiCr or NiAl are used.
- Clearance control: Abradable coatings wear preferentially when contact is made with the mating part, thus making possible to establish the necessary clearances automatically. High technology abradable coatings consists of two powders blended or agglomerated, for example, a metal matrix and a nonmetallic filler, such as graphite, polyester polyimide, boron nitride, or a friable mineral.
- Free standing shapes: Parts are fabricated from hard-to-machine materials by building up a coating on a removable form. This process is less costly than conventional processing methods, such as sintering or hot isostatic pressing. Ceramic tubes 1 m in diameter, 10 m long and with wall thickness of a few mm can be produced. Ceramic membranes, rocket nozzles, and ceramic crucibles are manufactured.
- Mold making is an important application of wire-arc spraying. A prototype part is coated with a mold release and then sprayed with tin-zinc, or NiAl, or similar suitable material to form the mold face. Backup is provided by a filled epoxy cast onto the mold face.
- Nuclear applications: In addition to the usual mechanical applications (however, with short lifetime elements, no Co, for example), coatings are used in Tokamak reactors and in magnetic fusion devices.
- Prostheses (orthopedic and dental): Alumina is used on the parts where friction occurs, and hydroxyapatite (of a composition similar to that of bone) is used to ensure a reliable contact between the implant surface and the living bone tissue to replace cement.
- Decoration: By changing the metal oxidation or the  $\text{TiO}_2$  stoichiometry, attractive colors are achieved.

This list is far from exhaustive but shows the wide applications of plasma sprayed coatings.

### PLASMA TRANSFERRED ARCS

The plasma transferred arc (PTA) process adds the capability of substrate surface heating and melting to plasma-arc spray. The advantages of this direct heating are metallurgical bonding, high density coatings, high deposition rates (up to 24 kg/h), and high thickness per pass (up to 14 mm).

### The Plasma Torch

Figure 7 shows a typical plasma torch used for PTA. It consists of a stick type thoriaed tungsten cathode (5 mm to 8 mm in diameter) with a conical tip, a nozzle which can be used as an anode to form a pilot blown arc, a powder injector at 30°, and a shroud gas (very often Ar + 5 to 10 vol%  $\text{H}_2$ , except when working with metals sensitive to  $\text{H}_2$ ) that is injected around the plasma. The arc is transferred to the substrate, which forms the anode, where a molten pool is created. The aim of the pilot arc is to allow better control of the transferred arc current. For a given anode-cathode distance, nozzle dimensions, and plasma-forming gas flow rate, there is a minimum transferred arc current to sustain it as a cathode jet-dominated (CJD) arc (27). The pilot arc, usually operating at a low power level, ionizes the gap between anode and cathode and heats the substrate allowing a CJD arc with much lower currents than those necessary without it. The control of heat transfer and size of the molten pool created at the arc root together with the plasma velocity close to the pool are the key parameters for achieving good coatings. In fact (27) when a CJD arc is obtained, the heat flux is distributed over a larger area and thus it can be one order of magnitude less than that obtained with an anode jet-dominated arc, thus limiting drastically the depth of the molten pool and its evaporation. CJD arcs are obtained when the anode is directly heated by the convective flux of the plasma. This convective effect is increased when the nozzle constricts the arc column, but it increases the plasma flow velocity and may result in turbulence of the molten pool, even blowing it out. That is why, in most cases, the nozzle diameter is larger than higher (a few millimeters) whereas the anode-cathode distance is below 10 mm. However, recently PTA torches with an important anode striction have been designed to achieve a higher density of energy, thus limiting the size of the heat-affected zone (28).

Such arcs work with pure argon, as the plasma-forming gas, at a low flow rate (for example 3 slm for 200 A). Sometimes, the plasma gas is pure helium which reduces its momentum at the anode pool but increases the gas temperature at the anode.

Three different types of torches are used depending on their melting capacity as shown in Table 1. Increasing the transferred arc current requires higher plasma-forming gas

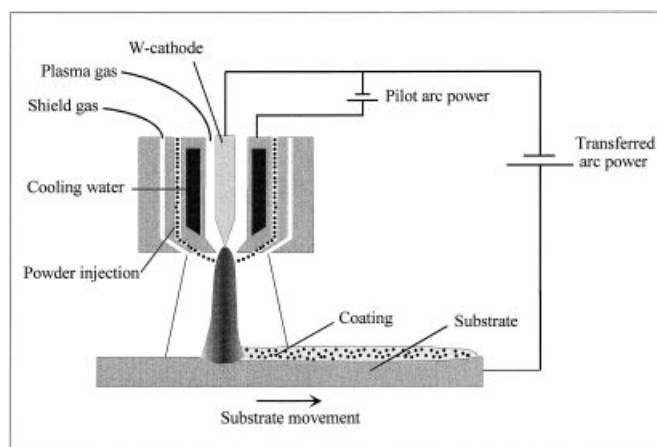


Figure 7. Schematic diagram of the PTA process.



**Table 1. Characteristics of Available PTA Torches**

Transferred arc current, A	<150	<200	<250
Pilot arc current, A	<200	<300	<500
Melting capacity, kg/h	6	10	24

flow rates and powder carrier gas to achieve a higher powder carrying capability.

### The Deposition Parameters

Plasma-forming gas flow and transferred arc current affect the quality of the deposit. When too high turbulence is generated (29), more pores and oxides are created. The evaporation of certain alloys also increases. Both of these two parameters must be adjusted to the powder flow rate.

The powders have to be injected so that the arc strikes mainly on the powders and not directly on the substrate. When increasing the powder feed rate, the dissipated powder must also be increased. A good size range for the particles is  $-180 \mu\text{m} + 53 \mu\text{m}$ . Complete melting is not achieved beyond  $200 \mu\text{m}$ , and below  $53 \mu\text{m}$  the dilution is drastically increased. Particle injection as close as possible to the tip of the cathode is also important. For a 10 mm anode to cathode distance, residence time is about 1 ms to 2 ms, insufficient time to melt particles completely but allowing them to melt partially and stick to the substrate.

Torch speed is a key parameter in reducing the dilution rate, that is, allowing melting of the base material to the smallest possible depth. This is achieved by adjusting the ratio of heat impact/torch speed. The torch speed  $v$  for given arc conditions can be calculated (28) by

$$v = d_p \frac{a}{5p^2}$$

where  $d$  is the diameter of the anode spot,  $a$  is the base material diffusivity, and  $p$  is the depth of the molten base material. It can be readily seen that  $p$  is reduced if  $v$  is increased. However, too high speed causes back fusion and also pores, and if  $v$  is too low, the plasma arc is directed on top of the molten pool and increases the porosity.

Finally the speed has to be adjusted so that the arc root is in front of the molten pool. The speed and the thickness of the pass also control the coating microstructure. A higher speed and thinner pass result in a finer microstructure.

Oscillation width is also an important parameter: If the energy input is too low for a given width, the molten pool is smaller than the width of the layer, and the layer has to be remelted at the next oscillations of the torch past the coated surface. This may cause incomplete melting between the base material and the deposited layer. If the energy is too high, the entire width of the layer is molten, and its protection against oxidation is no longer assured. In general, an oscillation width of 30 mm is a maximum. The oscillation must also be adjusted to give a satisfactory overlap. Small "ripples" are obtained with a feed in the surfacing direction shorter than 3 mm at each double oscillation of the torch. The overlapping also depends on the wettability of the surfacing material. To conclude, when deposition parameters are well adjusted, PTA results in low dilution of base material (10% for single pass coatings), a smooth surface finish, limited splat and clean pro-

cessing, fine microstructures, automated processing, a broad range of coating thickness in one pass (from 0.5 mm to 14 mm), and high deposition speed. The drawbacks are a limited range of alloys, compared to other spray techniques, and expensive, bulky equipment.

### Deposited Materials and Applications

The materials used in PTA spraying are mainly hard alloys that have good corrosion resistance at high temperatures. Most of them are Ni, Co, and Fe alloys, heat resistant steels, and Mn-hardened steels. However, recently new chromium base alloys (Cr-Ni-X such as Cr-Ni-Si-B with a chromium-rich primary crystal and eutectic) have been developed successfully. To increase the wear resistance without affecting other properties, composites are used that consist of a blend of matrix alloy and harder particles. For example, fine tungsten carbide (WC) particles are used against erosion or abrasion. Because their density is higher than that of the matrix, they sink in the coating during deposition without going through a liquid stage. Another route to improve wear resistance is to change the alloy system and rely on the precipitation of hard particles, for example, NiCrMo alloys. In all cases, however, the choice of the base material-deposited alloy couple is very important for avoiding cracks (not too high an expansion mismatch and reasonable quantity of hard phases).

Applications can be divided into two groups:

Reclamation of a worn, corroded, or overmachined part. By properly choosing the deposited alloy, the restored part can have wear and/or corrosion resistance higher than the initial part.

Reinforcement of a new part when special resistance to corrosion, oxidation, or wear is required. This is the case, for example, with valves in the automotive industry, guide rollers in rolling mills, rollers in continuous casting machines, teeth of brown coal dryers, cutting and stabilizer pads of thermal drilling equipment, roller-crushers in cermet plants, and heat exchangers in corrosive environment.

### FINISHING TREATMENTS

Thermal spray coatings or PTA deposits have common features: a sandpaper-like surface finish of a coating and a wavy shape for PTA deposits; and for coatings a porous structure (2 to 17 vol% depending on the process and sprayed material). In many cases, coatings or deposits must have a high surface finish and, when exposed to corrosive environment, the coatings must be sealed (PTA deposits are generally fully dense).

### Sealing

The pores (or cracks) of coatings must be filled to avoid infiltration by fluids or corrosive media that would contribute to premature failure. Sealing materials are petroleum-based wax, phenolic resins, polyester resins, vinyl, aluminum silicate, silicone, and electroplated metals. Most resins are limited to temperatures ranging from 90° to 250°C, but silicone can reach 400°C. For electrodeposited metals, the maximum operating temperature depends principally on the coating material.

## Surface Finishing

Machining can be used for most of the metals and alloys. Depending on their hardness, either high speed steel or carbide tools are used. Grinding can be used for metals and alloys and is mandatory for ceramics. In the latter case, care must be taken to avoid crack formation, and wet grinding is generally better than dry grinding.

Polishing, burnishing, grinding, honing, lapping, and superfinishing are used for surface finish. A roughness of  $R_a < 0.1 \mu\text{m}$  can be achieved with metal and alloys surfaces, but the best value for ceramics is a  $R_a \sim 0.4 \mu\text{m}$  to  $0.5 \mu\text{m}$ .

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P. FAUCHAIS  
A. VARDELLE  
University of Limoges