

Thermal Spraying of Ceramics

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Invited Review Paper

In the last few years, the number of publications dealing with ceramic coatings has increased very rapidly. To present an overview of this field, a bibliographic review of the thermal sprayed ceramics is performed. Investigated and studied successively are the thermal spraying techniques (flame, plasma and detonation), the sprayed ceramics and the applications of these coatings. It appears that plasma spraying is the most common technique, that ceramic coatings are most often made of the metal oxides and their main application is for wear resistance.

1 - INTRODUCTION

Men have always tried to improve the qualities of their materials, either to combat all kinds of aggression, to improve their confort, or to increase the life time and/or performance of tools. Actually, for reasons of efficiency and cost, mechanical devices must sustain higher mechanical stresses and work at much higher temperatures than the classical materials (essentially metals) can sustain. That is why one turns towards ceramics. Unfortunately, it is difficult to realize bulk ceramic castings and moreover, aside from hardness, ceramics have poor mechanical properties. So ceramic coatings on metallic substrates are being applied more widely for a variety of reasons including economics, material conservation, unique properties and design flexibility which can be obtained by separating the surface and the bulk properties.

The processes to produce coatings are numerous: physical vapor deposition including evaporation, ion plating and sputtering, chemical vapor deposition, electro-deposition and electro-less deposition, thermal spraying including flame, arc and plasma spraying as well as detonation gun, polymeric coating, etc... The number of materials currently used in coating is very large and the coatings obtained may be classified into thin or thick films. A general bibliography about coatings, even when restricted to only ceramic coatings, is then beyond the scope of this paper which will be restricted to thick films of ceramics. Of course, if, at the beginning, only the physical dimension of the film's thickness was used to make the distinction between thin and thick films, a «Confucian» definition has been advanced. It states that if a coating is used for its surface properties (electronic emission, catalytic activity...) it is a thin film, whereas, if it is used for its bulk properties (corrosion resistance, thermal barrier...) it is a thick coating. Then the fact that the film is thin or thick depends mainly on its application. Choosing thick films restricts this study to the thermal spraying of ceramics that is flame, plasma spraying and detonation gun coatings which are used mainly for wear, corrosion, oxidation resistance, as thermal barriers, or for electric insulation, in nuclear technology, in medical applications, for their friction and wear properties, as substrates for high power electronic circuits or even for decorative purposes.

Thermal spraying is a particulate deposition process where solid ceramic particles are injected into a high temperature gas where they are heated, eventually melted, then accelerated and sprayed at relatively high velocity onto a substrate where they impact and form a coating consisting of many layers of overlapping thin lenticular particles, or splats.

The properties of the coating depend on the starting materials, on the microstructures obtained, on the residual stresses induced while spraying, and on the porosity of the coating (open or closed). However the coating/substrate being a composite material its properties also depend on the interaction between the two, i.e. the structure and properties of the coating-substrate interface, which is paramount to the very important factor of adhesion of coatings.

This paper will first comment briefly on the sprayed coatings and the way they are generated with the resulting properties such as microstructure, chemical changes, porosity and adhesion, before describing the three techniques studied (flame, plasma spraying, detonation gun) and their limitations controlled by the heat and momentum transfer to the particles. It will then present the different materials sprayed with these techniques before summarizing the uses of the different ceramic coatings. This bibliography will end with comments about the actual limitations of these methods, their future developments and the needs for new research.

The quantitative criterion applied in this bibliographic review is the number of papers compiled since 1958 on the subject. As arbitrary this type of classification can appear, it is one which is easily applied. Moreover, as the list of bibliographic references is not exhaustive, for it is impossible to find every article about any given subject, it is not judged useful to look for a more sophisticated classification¹. Nevertheless, to find the maximum of information about ceramic coatings, 20 data bases have been questioned which yielded about 2000 references among which were selected 500 that seemed clearly related to the subject. Unfortunately, some of these references were uninteresting or inaccessible so that finally only 150 references have been compiled. As it appears in Figure 1, which represent the number of publications on ceramic coatings, thermal spraying is the widest used technique.

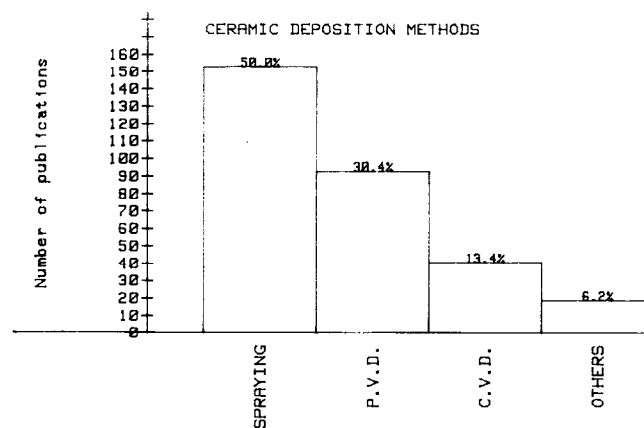


FIGURE 1 - Number of publications dealing with the ceramic deposition methods in the last twenty years.

2 - THERMAL SPRAYED COATINGS

2.1 - General introduction

Within the last decade, the thermal spraying of protective coatings has assumed a growing importance in mechanics² and the number of possible applications is increasing continuously.

Thermal spraying consists of introducing particles in a thermal device where they are heated, melted, accelerated, and then projected onto the substrate. Thermal spraying can realize ceramic or metallic coatings which do have not the same properties as the substrate. The technic is different from other surface treatments by the following typical features³:

(i) It is a cold process. The energy source is separated from the substrate so that it is possible to realize refractory coatings on low melting point materials.

(ii) The particles of the injected powder undergo physical changes such as melting and then freezing and sometimes even chemical modifications during the spraying process.

(iii) The coatings are built up particle by particle and have a lamellar structure.

(iv) When impacting and crushing onto substrate surface, the particles are quenched rapidly (up to 10^6 K/s). The resulting coatings may consist of metastable phases or even amorphous ones.

2.2 - Macroscopic properties of coatings

2.2.1 - Structure

A thermal sprayed deposit consists of successive layers of material built up by the impact of molten or solid droplets, projected at a very high velocity, which flatten against the substrate and solidify very rapidly. Many powders can be sprayed, but it is necessary that the temperature of their melting point is separated at least of 200 or 300 K from the decomposition or evaporation temperature. Even with high powder feed rates the particles are deposited on already solidified layers^{2,3}. Heat transfer calculations indicate that freezing of the particles occurs in a few microsecond and that the complete cooling cycle amounts to perhaps only 100 μ sec. The zone of thermal effects in the underlying materials is therefore quite small, so that the temperature gradients reach 10^5 Kcm⁻¹. These coatings have a sandwich like structure whose properties result from the deformation and solidification processes of individual particles, and/or their interaction on contact. The wetting and flow properties of the liquid droplets are of primary importance, since they will influence the porosity within the coating and the substrate interface.

Neglecting the influence of surface tension³, and assuming that the particles flatten before solidification occurs, yields the degree of flattening (ratio of the diameter of flattened disc (D) to the diameter of the initial particle (d))

$$D/d = 1.29 \left(\frac{\rho v d}{\mu} \right)^{0.2} \quad [1]$$

where ρ is the liquid density, μ is the liquid viscosity and v is the droplet impact velocity. This ratio will be high either if the particle is above its melting point with a reasonable velocity (a few tens of m/s) or if it is below its melting point, but already in the plastic deformation temperature area with a very high velocity (1000 m/s, or more). It may be seen that the structure of a coating depends upon the velocity, temperature (function of the process used) and the size of the particles at the moment of impact.

2.2.2 - Coating adhesion

The adhesion of a coating to a substrate is one of the most important properties of a thermal sprayed deposit, but

the factors controlling adhesion are not well understood and there is considerable controversy concerning the mechanisms involved^{2,3,12}. One point of view suggests that adhesion is controlled purely by mechanical factors, that is, the interlocking of the coating with the rough substrate surface while, another viewpoint is that chemical interaction occurs between the particles and substrate.

However it seems unlikely that very extensive interaction layers could be formed between a metal substrate and a ceramic coating and most of the authors agree that for ceramics, mechanical adhesion is by far the most important phenomenon depending of course on the surface treatment, often one of sand blasting, just prior to spraying.

2.2.3 - Internal stresses in coating

The residual stresses which develop in coatings may be subdivided into microstresses within the individual particles and the macrostresses within the coating as a whole. Microstresses arise because of the restraints due to the thermal contraction of individual particles as they cool in the solid state and are bonded to the underlying material which remains at a relatively constant temperature. These stresses will therefore depend largely upon the thermal expansion coefficients of the coating material and the elastic constants of the coating and the substrate, as well of their temperature dependancies. They would also be expected to be influenced at the interface by the yield strength of the substrate, the plastic deformation of which could allow for stress relaxation, and also the effectiveness of the particle to substrate bonds.

Macroscopic residual stresses will arise, during cooling of the coated structure to ambient temperature because of the differences in thermal expansion between the coating and substrate and the presence of temperature gradients during coating formation. High interfacial stresses may lead to the peeling of the coating, particularly on smooth substrates. High tensile stresses in the coating may lead to its cracking. A residual compressive stress in ceramic coating could, however be desirable as a method of increasing their strength. To minimize residual stresses it is obviously necessary to reduce thermal gradients as much as possible and to keep the complete assembly at a low temperature by cooling the surface with an air blast while spraying.

The thickness of the coatings is often dependent upon the stresses generated while spraying. With ceramic coatings for which the thermal conductivity is usually low, very high temperature gradients may be achieved while spraying if the substrate is cooled on the opposite side of the coating. With such gradients the stresses may reach such high values that thicknesses of 0.2-0.3 mm are the maximum for a high quality coating. However, if the coating is cooled by a gas jet blown continuously on the surface of the coating during spraying, the temperature gradients are not so severe and thicknesses of a few mm can be achieved. However, with these high cooling rates (up to 10^7 K/s), the microstructure of the deposit may correspond to amorphous or metastable phases.

2.2.4 - Porosity

Although high porosity is desirable for some thermally protective coatings, porosity greatly reduces the strength of the coatings. Interconnected porosity is undesirable in coatings for oxidation or corrosion resistance and porosity at the substrate interface can greatly reduce the coating adhesion. The nature of coating formation by impact and solidification of separate particles, either solid or melted, necessarily results in some porosity which generally lies in the range 3-20% and depends both on the spraying conditions and the material being sprayed. The porosity will then depend upon the trajectories of the particles into the hot gas used for spraying, of their heat treatment and of their final velocities, very high velocities being necessary when the particles are not melted and lower velocities when they are well melted, for they have to flatten and not explode when they are liquid.

2.2.5 - Chemical changes in sprayed particles

Chemical changes may occur in particles in a plasma jet by reactions with the hot gas. The chemical reactions are governed by diffusion of the hot gas towards the condensed phase and by the inverse diffusion of gaseous products. This diffusion occurs at a low rate (10^{-2} - 10^{-1} s) compared with the melting time (10^{-4} - 10^{-2} s) when high thermal conductivity gases are used. Oxides being very stable, spraying with reducing gases will not be a problem, but surface reactions may occur with carbides, nitrides or borides if oxygen has diffused into the sprayed jet from the ambient atmosphere.

2.2.6 - Crystal structure

An extremely rapid cooling rate from the liquid state is characteristic of flame or plasma sprayed material when the substrate is cooled while spraying and this may result in the suppression of crystallisation, or the formation of metastable phases as observed under conditions similar to splat quenching. A classical example of this effect is provided by alumina coatings which consist predominantly of one or more of the many metastable forms (η , γ , δ , θ) rather than the corundum α - Al_2O_3 stable structure. The formation of metastable phases may be explained on the basis of a lower activation energy for nucleation of the spinel type structure from the liquid when it is undercooled well below the equilibrium melting point as a result of rapid cooling⁵¹. The phase which is finally observed depends upon the rate of transformation from one metastable form to another and to α - Al_2O_3 , as well as the cooling rate of the solid after solidification. This explains the observations that different metastable phases are observed depending upon the spraying conditions, size and shape of particles and the temperature of the substrate⁵¹.

2.3 - Spraying processes for ceramics

2.3.1 - Detonation gun

a) Principle

The principle⁴ of the detonation gun is based on the controlled use of the explosion of an oxygen-acetylene mixture in a special chamber (Figure 2). This chamber generally consists of a water cooled barrel about 1 to 1.5 m long with an inside diameter of about 2 to 3 cm closed at one extremity and the associated gas and powder equipment. If particles of the powder to be deposited are suspended in the gas mixture before the explosion, the hot gas flux which follows the detonation wave accelerates, heats (eventually melts), and then projects the powder particles onto the substrate with a high velocity (up to 800 m/s). The cycle is repeated about four to eight times per second.

b) Detonation process

When the explosive gas mixture in the detonation gun (for example O_2 and C_2H_2) is ignited, a short period of combustion occurs. The flame front accelerates, compresses, and heats the gas which is immediately in front of it. During this compression, the gas mixture reaches a critical temperature and auto-ignition produces a detonation wave or shock wave. Further compressing the gas and increasing its temperature (between 3200 and 4100°C depending upon the initial conditions). So a fast dilatation of gaseous products of the reaction accelerates the powder particles to velocities of about 800 m/s and also heat them to their melting point, if it is not too high.

c) Coating

Each pulse of powder results in the deposition of a circle of coating about 25 mm in diameter and a few microns thick. The circular coating is composed of many overlapping thin lenticular particles, or splats corresponding to the individual powder particles. The total coating is, in turn, produced by

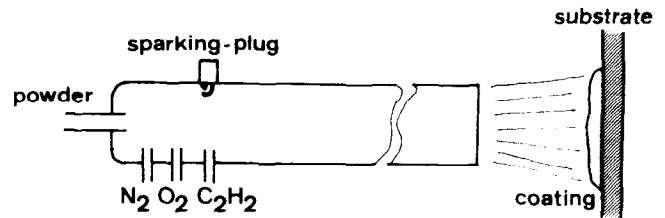


FIGURE 2 - Schematic principle of a detonation gun.

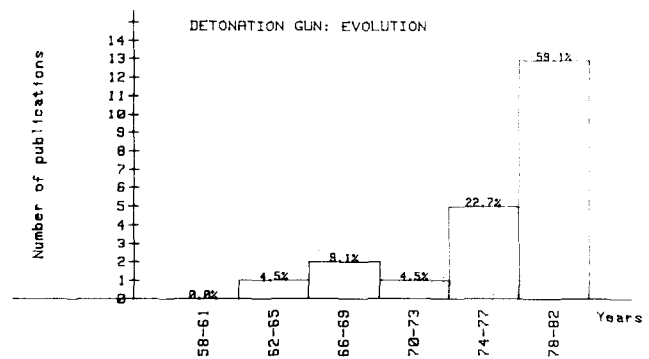


FIGURE 3 - Evolution of detonation gun spraying in the last twenty years.

many overlapping circles of coating, a pattern which is closely controlled to produce a smooth coating and minimize the substrate treating and residual stresses.

2.3.2 - Flame spraying

Flame spraying was used for the first time by Dr. Schoop to realize metallic coatings. He named this method the Schoop process.

a) Principle

The material is introduced as powders or sticks in the flame of a burner²⁵ where it is melted and sprayed onto the substrate. The powder systems are similar to Verneuil's burner which is used in the manufacture of synthetic gems. The gases which are commonly used are the mixtures O_2 - H_2 and O_2 - C_2H_2 which give maximum flame temperature of 2600°C and 3000°C respectively. Another possibility is to use the oxygenocyanogen mixture which gives a flame temperature of 4700°C.

The stick burner (Figure 4)

The combustible-combustible mixture is fed into a circular burner whose apertures are disposed in crown around the pipe containing the stick. This one, continuously advanced by a variable speed engine, is melted a few millimeters after the exit of the pipe. Then a droplet of liquid material is dragged out as well by the flame as by the compressed air flow which is used to avoid back-flash.

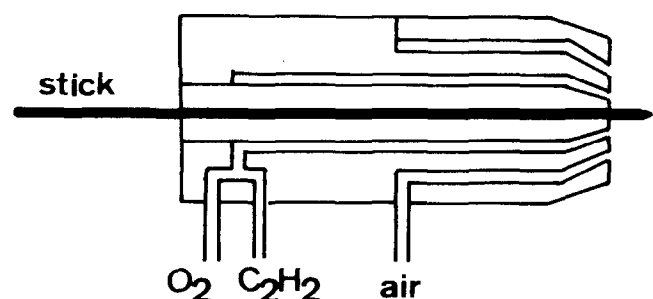


FIGURE 4 - Schematic diagram of a stick burner.

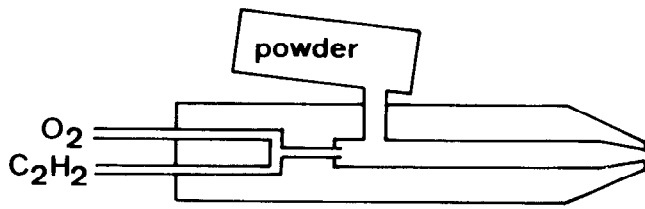


FIGURE 5 - Schematic diagram of a powder burner.

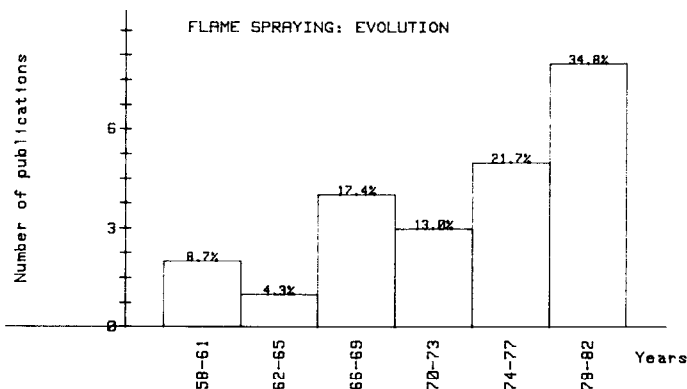


FIGURE 6 - Evolution of flame spraying in the last twenty years.

The powder burner (Figure 5)

Three methods are commonly used to introduce the coating powder into the flame:

- a fluidized bed using additional air flow,
- gravity,
- a fluidized bed using one of the gases of the burner.

The first method must be reserved for easily melted materials because of the cooling effect of the flame by the air flow. Figure 5 shows a burner with a gravitic powder feeder of a very simple construction. As to the third method which is simple, it requires of course a powder feeder with a variable mass flow of powder controlled by an Archimedean screw, feeding a vibrating bowl. The stick burner has the best spraying efficiency because the material is sprayed only when it is melted. However, as it is rather difficult to obtain sticks of ceramics, the sticks consist of agglomerated powders with an organic binder. In this case, the material may not necessarily be melted because the bonding burns long before melting.

b) Coatings

If the flame and the substrate are both maintained at rest the resulting coating have a bell shape corresponding to the fact that for a good coating most of the powder has to travel through the central part of the flame to achieve the best heat transfer. However, it is unavoidable that a few particles travel at the periphery of the jet with their temperature and velocity upon impact on the substrate lower than that of the particles travelling in the central part of the jet. So the structure and porosity of the coating, when the flame and substrate are at rest, is not uniform. The substrate or the flame must be moved with a closely controlled pattern to produce a smooth and uniform coating.

2.3.3 - Plasma spraying

a) Principle

The principle of plasma spraying is the same as that of flame spraying, but the heat production system is different, the energy being supplied to a non-chemically reactive gas by an electrically blown arc. In this case the enthalpy of the

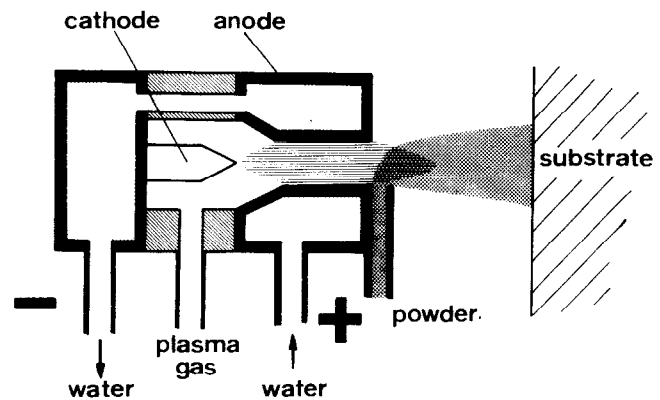


FIGURE 7 - Schematic diagram of a plasma torch.

gas is quite independent of the combustion processes and can reach values of 10^9 kJ/kg compared with 10^7 kJ/kg for flames. The powder of the material to be sprayed is introduced into the plasma where it is melted and projected with a high velocity on the substrate where it spreads.

b) The plasma torch

The plasma torch, shown diagrammatically in Figure 7, is very simple. However, in the reality, when one wants to realize a plasma torch, many problems are not solved. The plasma spraying equipment requires a high power source of direct current which can typically deliver up to 1000 A under 100 V. The main parts of the plasma torch are the electrodes. The geometry of the electrodes depends on the plasma gases⁵¹. The cathode is usually a bar of thoriated tungsten and the anode nozzle is usually made of electrolytic copper that is water cooled. The cooling water has two aims. It removes the heat dissipated at the anode where the thermal flux can reach 10^4 W/cm² and thus avoids its destruction. Moreover, it stabilizes the arc and the hot gases in the nozzle because all excursion of the arc towards the anode wall cools it and then, the electrical conductivity decreasing, the arc returns to its initial position along the nozzle axis.

When the gas crosses the strong electric field prevailing between the electrodes, it is dissociated and ionized. The atom-atom and electron-ion recombinations produce the plasma jet blown out of the nozzle anode with lengths varying between 30 and 150 mm (this length is a function of the power input, of the nature, flow rate and pressure of the plasma gases, and of the dimensions and shapes of the electrodes...). Related to the gas mixture used (generally Ar-H₂ or N₂-H₂) and at atmospheric pressure, the ejection velocity of the gases can vary from a few hundred of meters per second to almost 1000 m/s.

Although the temperature of the plasma is very high (up to 15000 K on the axis), as the gases are ejected very quickly, the particles may experience too short of a residence time to be completely melted. So the most refractory materials must be introduced as far as possible into the nozzle, however, without perturbing the arc. In all the cases, the injection velocity of the particles must be perfectly adapted, because, as the plasma is very viscous, if the injection velocity is too low, the powders tend to rebound on the jet and pass at its periphery in the cold zone where they are not melted. On the contrary, if the injection velocity is too high, the particles may cross the jet and again travel in a cold zone of its periphery. This difficulty of introducing the particles in the viscous plasma with its thermophoresis forces (due to the thermal gradients of up to 4000 K/mm - tending to reject the particles out of the flame) is certainly one of the main problems of this technique where the injection velocity and thus the pressure of the carrier gas must be adjusted for each type and granulometry of the sprayed powders.

c) Coatings

The shape of the coatings when the plasma torch and the substrate are at rest is similar to that obtained with flames

(bell shape), but because of the high radial gradients of temperature (up to 4000 K/mm) and of velocity (up to 200 m/s/mm) the physical properties of the wings of the bell may be very different. For example when spraying alumina particles⁵¹ on a target at rest 50 mm far from the nozzle exit of the plasma gun, the porosity of the deposit was observed to increase from only 10% on the axis of the jet to 22% at a 15 mm radius. On the axis the particle velocity is 150 m/s higher than at the 15 mm radius and the percentage of melted particles (given by the ratio $(\frac{\gamma}{\alpha+\gamma})$ because when melted the particles, initially in α phase, crystallise in γ phase due to their rapid cooling after their impact onto the substrate) is 95% on the axis against only 75% at the 15 mm radius. Then, as for flame spraying, the relative displacement of the substrate and of the plasma torch is absolutely crucial for the quality of the sprayed layers.

2.4 - Auxiliary equipment and related coating limitations

In addition to the flame, plasma or detonation gun, gas controls should meet several general criteria such as:

- an excellent control,
- a uniform distribution of powders at a constant rate. The powder feeder is at least as important as the gun to produce the hot gases. Conversely, a pulsed flow of powder is required for a detonation gun with again a uniform distribution of the powder in the barrel together with the constancy of the amount of powder in each pulse,
- automated or semi-automated torch and substrate handling, because hand held torches lead to varying stand-off, poor thermal control (residence time is very dependent upon the distance between the gun and the substrate) and non-uniform coating thicknesses.

Flame and plasma deposition are line of sight processes in which the structure of the coating is a function of the angle of deposition i.e. the angle between the axis of the gun and the plane tangent to the surface to be coated. Coatings with the highest density and adhesive strength are achieved with a 90 degree angle of deposition. The possibilities to reduce this angle of deposition are a function of the type of the gun and of the operating parameters. If the particles are well melted and the velocities not too high (less than 150 m/s), but not too low (more than 20 m/s), angles as low as 60° can be tolerated. However with a plasma gun, angles of less than 75° may cause significant deterioration. The detonation gun, with its higher particle velocity, can tolerate angles as low as 45°. These angular limitations may cause problems in coating complex shapes, especially when narrow grooves or sharp angles are present.

Another limitation is related to the size of the torch and the required distance between the nozzle exit and the substrate. This is particularly important in the case of plasma spraying where a difference of 5 mm may lead to a very poor coating and when an inside diameter is to be coated. For example ceramic coating can hardly be achieved if the inside diameter is smaller than 8 cm. Of course the detonation-gun cannot fit into a cylinder or other cavity, but it can be used for inside diameters to a depth about equal to the diameter (deposition angle of 45°).

2.5 - Heat transfer between hot gases and particles

If radiative losses are neglected, the energy received by a particle during spraying can be approximated as:

$$E = \int_0^{\tau} h (T_p - T) dt \quad [2]$$

where T_p and T_s are respectively the temperature of the gas of the spraying system and the particle surface temperature, and where τ is the residence time of the particle in the flame. The key point is the calculation of the heat transfer coefficient, h , of the gas. This is due to both the convective and conductive heat transfer. The convective coefficient, a function of the Reynolds and Prandtl numbers, has a value (for a given particle) which is generally lower than one third of the conductive term so, to first approximation, it is possible to neglect convection. Then, one uses the conductive Nusselt number which is, in permanent heat transfer, equal to 2 and is related to h by the relationship:

$$Nu = \frac{h d}{\lambda} = 2 \quad [3]$$

in which d is the diameter of the particle and λ is the mean thermal conductivity of the flame (mean integrated thermal conductivity taking into account, especially in the case of plasmas, the drastic temperature variation in the boundary layer around the particle - in the case of a plasma, for example: from 10000 K far away from the particle to 2000 K at the particle surface with transport properties that do not vary linearly with temperature). The heat transfer coefficient is then approximately equal to:

$$h = 2 \lambda / d \quad [4]$$

Using this equation, Table I summarizes the mean heat transfer characteristics of the three different thermal spraying techniques reviewed. Flame spraying and plasma spraying have very similar features, but detonation gun spraying is quite different.

The main difference between plasma and flame spraying is that the flame spraying process is limited to about 2400°C for the highest melting temperature, while plasma spraying is not limited at all, provided first that plasma is of sufficient length to provide a long enough residence time, and secondly that the particles really penetrate in the plasma jet overcoming its high viscosity and the thermophoresis forces from the high radial temperature gradient (up to 4000 K/mm). Moreover in plasma flames using diatomic or polyatomic gases, when the temperature is higher than the dissociation temperature, the mean thermal conductivity λ increases rapidly, (up to 10 times), enhancing the heat transfer as compared to a classical combustion flame. In a detonation gun the ceramic particles are very seldom melted (alumina is the upper limit) and hence, when crushing on the substrate, their deformation, characterized by the ratio of the diameter D of the splattered particle to the one of the impinging particle does not exceed 2 as compared with 7 for plasma spraying, where the particles impact on the substrate at much lower velocities, but at much higher temperatures than the melting

TABLE I - Main characteristics of the different thermal spraying technics.

	Gas temperature (°C)	Particle velocity before impact (m/s)	Treatment length of particles (m)	Treatment time of particles (ms)	Energy received by one particle*	
					thermal (J)	kinetic (J)
Detonation	2800	800	2	2.5	5.10^{-5}	2.10^{-5}
Flame	2800	15	0.15	10	2.10^{-4}	6.10^{-9}
Plasma	12000	100	0.05	0.5	2.10^{-4}	6.10^{-7}

* For a 30 μ m diameter melted alumina particle.

TABLE II - Main characteristics of the different thermal sprayed coatings.

	Detonation	Flame	Plasma
Thickness of coating or coating speed	0.01 to 2 mm	0.01 to 2 mm	0.01 to 2 mm
Porosity	< 1% even 0,5%	can be rather important	few %
Adhesion	very good	good	good
Covering power	middle (simple shapes)	middle (simple shapes)	middle (simple shapes)
Sprayed materials	all melting material	all melting material ($T_m < 2700^\circ\text{C}$)	all melting material
Covered materials	very diverse (metals, plastics...)	very diverse (metals, plastics...)	very diverse (metals, plastics...)
Coating environment	air, neutral	air, neutral	air, neutral
Treatment temperature of the substrate	< 100°C in the mass	< 100°C in the mass	< 100°C in the mass

point. Hence with a detonation gun, high melting point ceramic particles impacting on the substrate will no cover as well as with flame and plasma spraying where the particles have much lower viscosities (when the temperature is higher than the melting point) and the porosity will be higher. In fact, one can obtain low porosity detonation sprayed coatings with very strong adhesion because of the high ratio of kinetic energy to thermal energy.

3 - CERAMIC COATINGS

3.1 - Characteristic of the coatings depending upon the spraying process

Summarized in Table II are the main characteristics of sprayed coatings.

3.1.1 - Detonation gun spraying

Detonation sprayed coatings are very homogeneous and have a low porosity when they are metallic. Their very strong adhesion to the substrate is mainly due to the kinetic energy (Table I) of the particles. In the case of metals, the particles splash into thin lamella and can produce, by release of their kinetic energy, a metallurgical bond with the substrate or the previously deposited particles. The substrate itself does not require any previous treatment⁶. One must note that the force of the explosions, repeated several times a second, requires a specially arranged room for the detonation gun.

In 1955 this spraying method was patented by Union Carbide¹⁴⁵. In 1963, Ballard⁷ mentioned the realization of detonation sprayed alumina coatings but, at that time, the process was very long and expensive. Pollock⁸, in 1968, considered that it was the best method for preparing very dense coatings. During the seventies, this method developed more and more⁹⁻²⁰ and yielded very good quality coatings, particularly with a very strong adhesion and a very low porosity (less than 5% in certain cases). Figure 3 shows the evolution of this method, as reflected by the publications of the last twenty years.

3.1.2 - Flame spraying

A critical point is that materials whose melting points are higher than the flame temperature cannot be sprayed with a burner. In practice, however, this condition is more restrictive, because, for example, with an $\text{O}_2\text{-C}_2\text{H}_2$ burner (3000°C maximum), it is not possible, due to the heat problems, to spray materials more refractory than zirconia with a melting point of 2715°C²⁶. Even if particles are well melted in the flame, the coating porosity is higher than with the detonation gun process or plasma spraying. This is because the gas velocity of the burner (a few tens of m/s) is much lower than that of the plasma (a few hundreds of m/s) and that of the detonation gun (800 to 1200 m/s). The flame sprayed particles have a smaller kinetic energy and, unless they are perfectly

melted at a temperature higher than T_m , they cannot cover the roughness of the substrate or the particles previously sprayed and solidified. In fact, the main advantages of the flame spraying process compared to the two others methods are its low cost and its easy utilization.

It was in the beginning of the 1960's that ceramic thermal spraying increased^{7, 25-31}. Following years have seen a growing evolution in the study of the involved phenomena, as in the various applications^{21, 32-39} as visible in Figure 6. However this evolution does not appear to be as fast as that for the detonation process. This is probably because this second method, although more expensive and requiring heavier equipment, has more possibilities and yields better coatings.

3.1.3 - Plasma spraying

All materials for which the melting point is separated from the boiling point, or from their decomposition temperature by a few hundred degrees can be plasma-sprayed. The melting point is not a problem because the temperatures reached in the plasma are very high (up to 10000 to 15000°C). However the thermal properties of the material to be sprayed are critical. For example, chromium oxide whose melting point is 600°C higher than alumina is easier to melt. Indeed, the dark color of chromium oxide reflects less heat than the white alumina, its heat of fusion is smaller (190 cal/g for Cr_2O_3 and 240 cal/g for Al_2O_3 ⁵²) and its thermal conductivity is better.

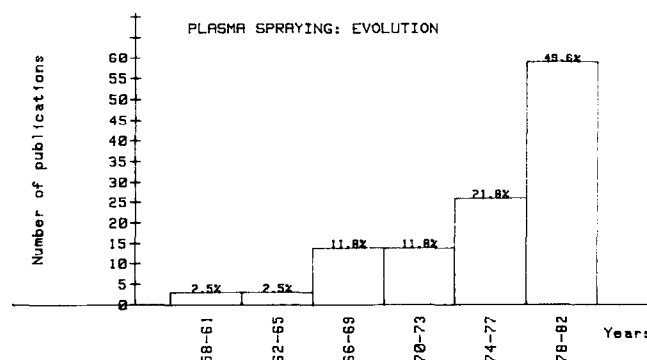


FIGURE 8 - Evolution of plasma spraying in the last twenty years.

The adhesion of plasma-sprayed coatings is essentially mechanical for ceramics and it is fairly good, provided that the substrate has been sand blasted a few minutes (less than 30 min) before spraying. However, in the particular cases of metallic coatings (Al-Ni mixture which gives an exothermic reaction after melting) or using transferred arcs (under controlled atmosphere if possible), the adhesion can also be diffusional. In all of the cases, the surface to be coated must be clean and roughened.

One can coat almost every material by plasma spraying when cooling sufficiently the substrate. For example, alumina plasma sprayed coatings have been realized on paper, without burning it. In this case, the adhesion seems to be stronger than the paper's own mechanical resistance. Of course, during the spraying, the coating surface was strongly cooled by a compressed air flow and a second air flow, normal to the flame and just before the substrate, was used to interrupt the heat flux from the plasma.

By optimisation of the spray parameters and using well defined powders (granulometry), one can obtain coatings with very low porosity levels (less than 2%)⁵¹. When the substrate is maintained cold (less than 100°C) during spraying, the particles are drastically quenched (up to 19° K/s) and one can obtain coatings of metastable phases (for example, Al_2O_3) or amorphous ones (like glass of nickel). However, these phases are not always desirable.

To avoid oxidation or decomposition of some materials and to improve certain particular properties of the coatings, it can be desirable to control the spraying atmosphere. In this case, the plasma torch and the substrate are maintained in a chamber with a low pressure (about 50 torr) of inert gas. Then, the plasma jet becomes expanded and much longer than for case of atmospheric spraying, the gas velocity is more important (up to Mach 3), but the heat transfer is reduced owing to the lack of equilibrium in such plasmas with an electron temperature two or three times greater than the heavy particle temperatures usually lower than 3000 K). Such equipment is heavier, because of the vacuum installation with a powerful pump and the large stainless steel chamber with its walls water cooled. Moreover, substrates cannot be too large for reasons of the dimension and of volume of the chamber. The price of such a vacuum device compared to the atmospheric one is about six times greater, independent of the automation of the torch displacement.

The first publication dealing with plasma spraying was in 1958⁵³. This technic was not much used to the beginning of the seventies^{7, 8, 10, 15, 29 to 31, 33, 34, 54 to 78}. This is probably because it was not a well known method, presented serious problems, and was very expensive. Within the last few years, however, plasma spraying is becoming more popular^{4, 5, 11, 12, 14, 16 to 21, 23, 24, 32, 37 to 40, 42, 43, 47 to 49, 79 to 136}.

If the biggest part of coatings is made by arc plasma spraying, Urban⁵⁶ recommends spraying with a H.F. plasma torch, however, the velocity of the particles is often not sufficient and the trajectories are too divergent, so the coating sometimes has bad properties. In 1980, Gafri¹²⁵ used a H.F. plasma under low pressure to prepare BN coatings by the reaction of NH_3 and BCl_3 . Reardon¹³⁴ used the vacuum projection and Reale¹¹¹ mentions the transferred arc plasma process for coatings, but especially for thickening. Such transferred arc deposits can have a very good adhesion because the substrate surface is melted and there develops a diffusional bond with the coating. Figure 8 shows the exponential evolution of use of plasma spraying.

3.2 - Thermal sprayed materials

Any material that melts can be sprayed by arc, flame or detonation methods. Indeed, plasma spraying has no temperature limit, but one must be concerned with the atmosphere, particularly with flame spraying and plasma spraying. Figure 9 shows the percentages of different types of thermal sprayed ceramics. It is evident that the oxides are the most important thermal sprayed ceramic. Indeed, very often, borides, carbides and nitrides do not melt, so it is not possible to thermal spray coatings of those materials. Nevertheless it is possible to cover the compound with a metal which will protect it from decomposition and will assume the bond between the ceramic particles, but of course with poorer mechanical properties, because it results of a coating that consists of unmelted ceramic particles in a metallic matrix. Table III list the references of publications dealing with ceramic coatings with the three methods of thermal spraying. Given the importance of oxides and, at a lower level, of carbides a few comments about these two categories of ceramics are appropriate.

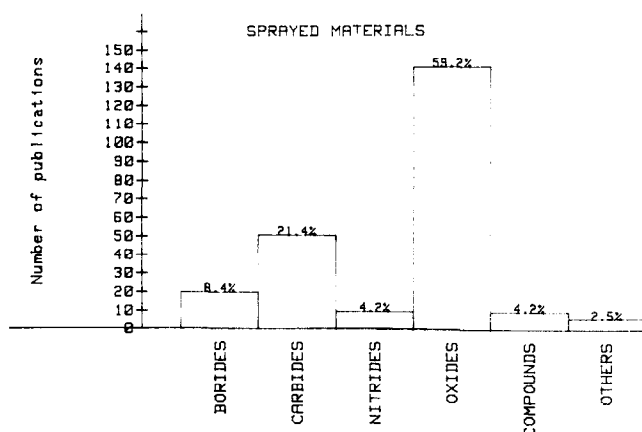


FIGURE 9 - Number of publications dealing with different sprayed materials.

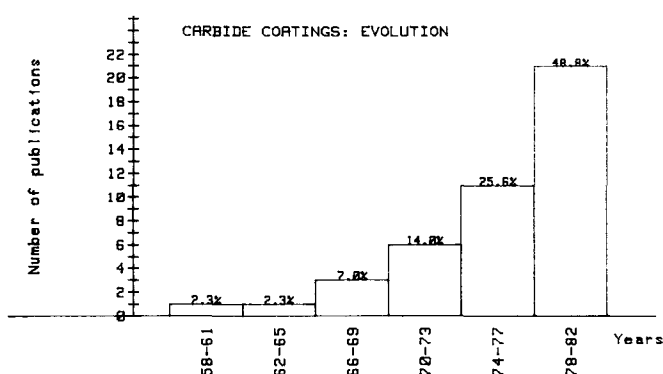


FIGURE 10 - Evolution of carbides sprayed coatings in the last twenty years.

3.2.1 - Carbides

As some carbides do not easily melt, it is often imperative to make the coatings by the techniques of physical or chemical vapor deposition processes. It is however possible to realize carbide coatings (melted particles, basic deformed particles) with the detonation gun process^{4-6, 9-12, 14, 16-18, 24}, by flame spraying melted particles^{35, 38, 39, 44, 47}, and plasma spraying melted particles^{54, 56, 60, 61, 67, 68, 72, 78, 80, 81, 89, 91, 93, 101, 102, 109, 110, 114, 116, 122, 132, 134, 135, 137-139}. The most thermally sprayed carbide is tungsten carbide, WC, although sometimes W_2C and chromium carbide are also sprayed. Thermal spraying and more particularly plasma spraying is the most common method. Indeed, rather few carbides are decomposed if they are not in contact with oxygen when they are at high temperatures. So most of the carbides must be under vacuum or in controlled atmospheres with no oxygen present and an excess of carbon, often using CH_4 in the

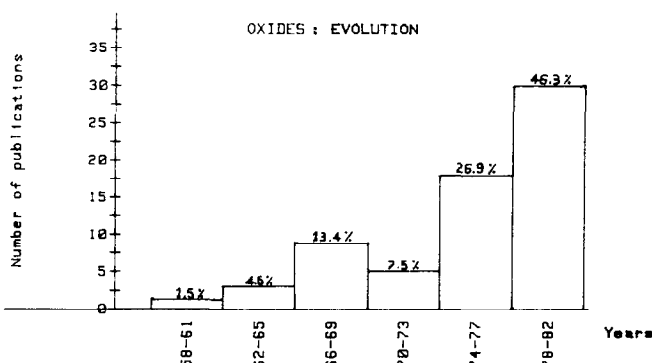


FIGURE 11 - Evolution of oxides sprayed coatings in the last twenty years.

TABLE III - References for each thermal sprayed ceramic.

		Detonation	Flame	Plasma
	MoS ₂			64, 73, 75
<i>Borides</i>	TiB ₂			62, 63, 116, 135
	ZrB ₂			62, 63
	TaB ₂			62, 63
	HfB			62, 63
	CrB			62, 63
	LaB ₆			62, 63
	NbB			62, 63
	SiB			62
	MoB			62, 63
<i>Nitrides</i>	TiN			62, 63, 91
	ZrN			62, 63, 75
	Ta ₂ N			62, 63
	BN		43	43
	ZrO ₂ CaO			37
<i>Carbides</i>	TiC			93, 116, 135
	WC	4, 6, 9, 11, 12, 14, 32	32, 44	4, 11, 12, 20, 32, 38, 39, 42, 60, 61, 67, 69, 71, 76, 78, 80, 91, 93, 101, 103
	Cr ₃ C ₂	14, 16, 18		16 to 18, 76, 78, 81, 93, 101, 134
	VC			135
	UC			68
	Mo ₂ C		44	
	(W, Ti)C	11, 24		11
<i>Oxides</i>	Al ₂ O ₃	4, 6, 11 to 14, 20, 24	20, 30, 37, 42, 144	4, 11, 12, 20, 24, 37, 42, 56 to 60, 65, 70, 71, 73, 74, 88, 94, 98, 100 to 103, 105, 107, 124, 130
	ZrO ₂	4, 11, 12, 20	20, 27, 30, 31, 36, 43	4, 11, 20, 31, 43, 55, 57, 58, 60, 87, 97, 100, 101, 103, 112, 117, 119, 126, 128 to 130
	Cr ₂ O ₃	4, 11, 14, 15, 20, 22	20, 30, 40	4, 11, 20, 24, 39, 40, 42, 60, 71, 73, 83, 84, 90, 92, 93, 101 to 103, 105, 111, 120
	Al ₂ O ₃ + TiO ₂	4, 6, 11, 14, 24	42, 48	4, 11, 24, 38, 39, 42, 57, 60, 66, 71, 101, 103, 105, 106, 130
	TiO ₂		30	60, 104
	MgO			56, 130
	HfO ₂	12		
	BeO			59
	NiO			79
	Y ₂ O ₃			108, 127, 129
<i>Compounds</i>	MgAlO ₄			74, 103
	BaTiO ₃			28
	CaTiO ₃			129
	ZrSiO ₄			57, 74, 103
	Ca ₂ SiO ₄			129
	Ferrite			82
	BaF ₂			85
	CaF ₂			75, 79, 85, 115
	BaF ₂ + CaF ₂			85

plasma gases. Figure 10 presents the evolution of carbide coatings in the last twenty years and shows the increasing interest for these types of coatings.

3.2.2 - Oxides

Because of the importance of oxides as compared to

Zirconia (ZrO_2) also has very interesting properties (for example, its low thermal conductivity). It has been used to protect metals from high temperatures since the beginning of ceramic coatings. Zirconia has been applied by all of the spraying techniques: detonation process^{4, 10-12, 20, 23} flame spraying^{25, 28, 30, 31, 35-37, 43, 45-47} although coatings are not very dense, and particularly plasma spraying^{53-57, 60, 72, 86, 87, 89, 97, 100-102, 108, 112, 114, 117-119, 122, 123, 127, 129-131, 133}. Zirconia sprayed coatings are growing in popularity since about 1975. Before, zirconia coatings were not used often because its melting point is very high (2710°C) and the plasma techniques were not yet well developed.



Chromium oxide is a green stoichiometric oxide (Cr_2O_3), but one can find it in the hypostoechiometric form $\text{Cr}_2\text{O}_{3-x}$. Hypostoechiometric layers have a metallic character and poor corrosion resistance. However, chromium oxide coatings are very hard, have an excellent wear resistance and their porosity can be very low. One does not encounter metastable phases of chromium oxide after spraying. Historically, chromium oxide coatings are new compared to those of alumina the first realization date being the middle sixties. However, they are growing almost exponentially.

[illegible]

3.3 - Use for thermal sprayed coatings

Coatings deposited on mechanical parts or on other pieces may have two objectives; a protection against aggression and/or to confer particular properties to the substrate. Of course, the first question is why to use coatings instead of bulk materials which can be machined directly without further treatment. The answers to this are numerous: the impossibility to have some bulk materials, the high price of the bulk material, the impossibility of obtaining good properties for the bulk materials, etc. These are why one uses coatings more and more often, their use being quite automatic as soon as one needs surfaces with particular properties. One can see in Figure 12 that the most common objective of ceramic coatings is wear protection and at a lower level, protection against corrosion and for thermal barriers. Table IV summarizes the references of articles which deal with the different applications of sprayed coatings.

3.3.1 - Wear resistant coatings

It has been a very long time since man first became interested in wear phenomena. For example, in 55 B.C., Lucretius¹⁴⁰ noted that water could wear a stone and that travellers paving stones. Given the importance of wear phenomena, it is natural that many technicians and scientists have worked on the problem. They have remarked that with hard surfaces wear is considerably reduced. Generally, ceramics rather well answer to this criterion, but as it is often difficult to make ceramic bulk materials, therefore one realizes wear coating by detonation^{4, 9, 11-13, 15-17, 19, 21-24}, by flame spraying^{25, 30, 35, 38, 40, 43-45, 47-49}, and by plasma spraying^{53-56, 58, 60, 61, 66, 67, 71, 72, 74-76, 78-81, 84, 85, 89-91, 93-95, 99-102, 104, 105, 114, 115, 121, 122, 124, 130, 131, 134, 136, 139}.

3.3.2 - Corrosion resistant coatings

Corrosion is the result¹⁴¹ of the action of a reactive fluid on a metal or an alloy. Its well known form is the rust of iron exposed to moist air. Regarding its results on diversified human activities, it is of a very great importance. It has been estimated that 20% of steel production is used for changing equipment destroyed by corrosion, which explains the great interest in corrosion resistant coatings^{4, 12, 16, 17, 19, 21, 23, 25, 35, 37, 40, 41, 45, 49, 54, 56, 58, 66, 68, 72, 74, 76, 89, 93-95, 97, 99, 101, 102, 105, 114, 122, 124, 126, 127, 130, 131}. These coatings must be inert to the opposing atmosphere in which they must work, so they must also have as low a porosity as possible. Particularly, the coating must be impervious to the corroding agent.

3.3.3 - Oxidation resistant coatings

Oxidation is a particular case of dry corrosion of metals and alloys at elevated temperatures except for noble metals (gold, platinum...). When a metal is in a gaseous atmosphere¹⁴¹, there is some absorption of the gas in working conditions. To avoid oxidation of metals one realizes by spraying oxidation resistant coatings^{4, 17, 19, 21, 23, 45, 56, 74, 89, 100, 114, 125} which must be impervious to oxygen. In fact, the oxidation resistant coating must be a diffusion barrier for oxygen and for the protected metal.

3.3.4 - Thermal barrier coatings

As indicated by the name, a thermal barrier must limit or stop the heat flux received by the wall of a piece in order to protect it from possible damage from the thermal flux. Thermal barriers should be particularly interesting in the case of heat engines because one knows that the theoretical yield increases with the difference between the temperatures of the ambient and of the combustion gases, the latter being limited

by the walls resistance. Thermal barrier coatings have been made by all of the different thermal spraying technics: detonation^{4, 16, 19, 23}, flame spraying^{25, 31, 35, 36, 43} and plasma spraying^{54, 56, 58, 60, 72, 74, 78, 85-87, 89, 91, 93, 100-102, 105, 108, 112, 114, 117, 120, 123-133}.

3.3.5 - Coatings for friction applications

Friction corresponds¹⁴³ to the phenomena which occur at the surfaces of two bodies in moving contact. Friction leads to an ageing of the surfaces, to cold-hammering by the application of stresses and to the creation of heat, which leads to relaxing the residual stresses. The main parts of usual construction materials rub correctly thanks to their superficial oxide layers. Technical problems are very difficult when this oxide layer does not exist. That is what happens in a vac-

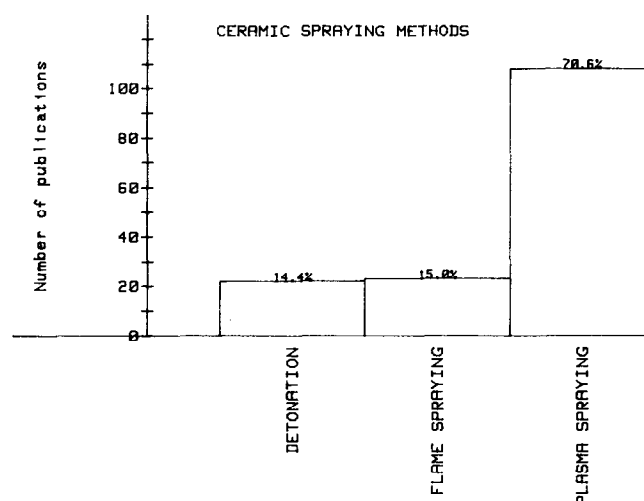


FIGURE 13 - Number of publications dealing with the ceramic spraying methods.

uum. The problem of friction in a high vacuum is at the origin of the reason for friction studies. Another impulse comes from the new needs of the atomic and aeronautic industries and chemical engineering. Numerous friction surfaces have been made by thermal spraying^{13, 16, 35, 49, 60, 64, 75, 76, 79, 83, 85, 90, 98, 99, 114, 115, 138}.

4 - CONCLUSIONS

Thermal spraying of ceramic coatings is growing very rapidly in industry. For example the use of plasma spraying is almost doubling each year in the United States as the papers published on the subject show (see Figure 13).

The bibliographic study emphasizes particularly the development of the plasma spraying techniques and to lesser extent the use of detonation gun methods. Obviously this increasing interest for the spraying techniques in general and for plasma in particular is due to the fact that such processes with the rapid solidification of the sprayed particles and of the obtained coatings combine melting, quenching and consolidation into a single operation and lead to unique properties and features of the materials produced by spraying techniques. These include:

- extreme versatility or range and variety of deposited materials.
- coatings with properties independent of the thermodynamic compositional constraints.
- ability to vary defect concentrations over wide limits.
- high quench rates available to deposit amorphous or metastable phase materials.
- generation of microstructures different from conven-

tionally processed materials, especially with submicron grain sizes.

vi) fabrication of self standing shapes or bodies from brittle materials.

However, the retention of dense high-strength deposits requires that:

a) a large fraction of the injected powder particles are heated to the molten state before they impinge on the substrate, or previously deposited particle.

b) besides being in a molten state the particles must also have sufficient velocity so as to spread out and flow into the irregularities of the previously deposited layers.

c) strong interparticle or particle/substrate bonds must be formed.

These requirements, are partly met by plasma spraying, which explains the development of this last technique. Anyhow a lot of research has yet to be done to improve the understanding as well as the physical and mechanical characteristics of the sprayed coatings, as well as the hot gases and their particle interactions.

The areas where an understanding of the basic processes is clearly lacking include the following.

(A) For the coatings:

i) microstructure and properties in the submicron range.

ii) residual stresses with the influence of the process parameters.

iii) particle adhesion on the surface with the effects of substrate surface conditions (oxidation, contamination..., roughness and preparation such as sand blasting...) and of the deformation and solidification of the particles upon contact (phenomena taking place is a few μs ...).

(B) For the interaction hot gases/particles:

iv) the momentum and heat transfer between solid particles and gases especially in detonations and plasma gases with the Drag and Nusselt coefficients, the influence of the particle sizes (Knudsen numbers), and the forces acting on the particles (thermophoresis, Basset history term, turbulences...)

v) the knowledge of the gas parameters: velocity, temperature or temperatures when plasmas are considered when spraying under vacuum (10-50 Torr) or when a cold gas is injected (particles carrier gas).

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