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ABSTRACT

With the attainment of high temperatures it becomes possible to process any kind of materials (particularly ceramics) in their liquid state. In the plasma spraying process, the material to be sprayed is rapidly heated until it is molten and is propelled by high velocity gases onto a surface where it adheres to give protective coatings for a wide range of applications. The method could be considered as one of the most versatile and rapid to build up thick deposits (of plastics, metals, ceramics, cermets) and also free-standing artefacts for particular requirements without resorting to lengthy forming and sintering studies. Although plasma spraying is at production stage in industry, advanced processes have been also developed for producing economically a wide range of new materials. This paper intends to show the benefits of the process and evaluate the challenges it represents.

1. INTRODUCTION

Shaping of materials is greatly restricted because most of them cannot be efficiently melted. Low melting point alloys are easily cast to nearly net shape with high productivity die- or investment casting. Higher melting point materials such as steel require non-flexible and disciplined mass production. Refractory alloys and ceramics are formed by lengthy and energy consuming processes of powder metallurgy technology.

Coating methodologies are also laborious and need large amount of raw materials. Hard and refractory coatings require more sophisticated technology and do not proceed usually through the liquid state. Most of the coating processes are limited to the coating compositions for which they are designed and cannot be easily adapted to coat various kinds of base material.

With the attainment of high temperatures, more particularly with the plasma technology, it becomes possible to process any kind of materials in their molten state. Plasma spraying can be considered as one of the most versatile method for depositing coatings and also forming parts. It is not intended to compare this technology with others but rather to look at it as a complementary forming process, to show its benefits and evaluate the challenges it represents.

2. PLASMA SPRAYING PROCESS

As shown in figure 1, the plasma spraying process consists of introducing a material in its powder form into a hot gas stream and propelling it onto the

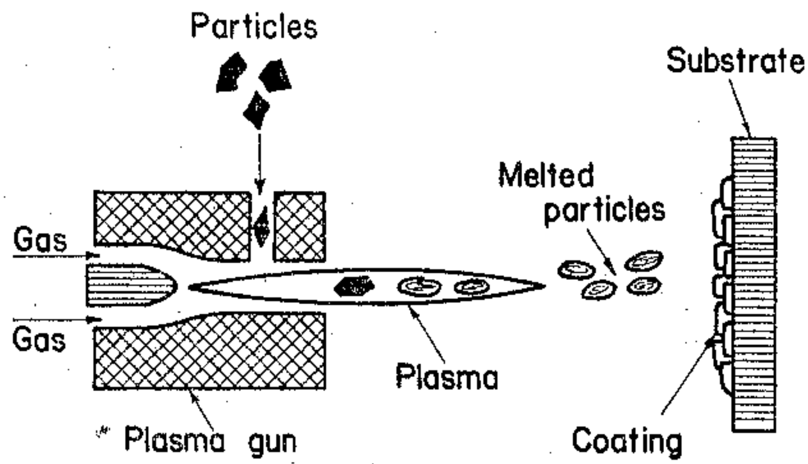

Figure 1 - Schematic view of the plasma spraying process.

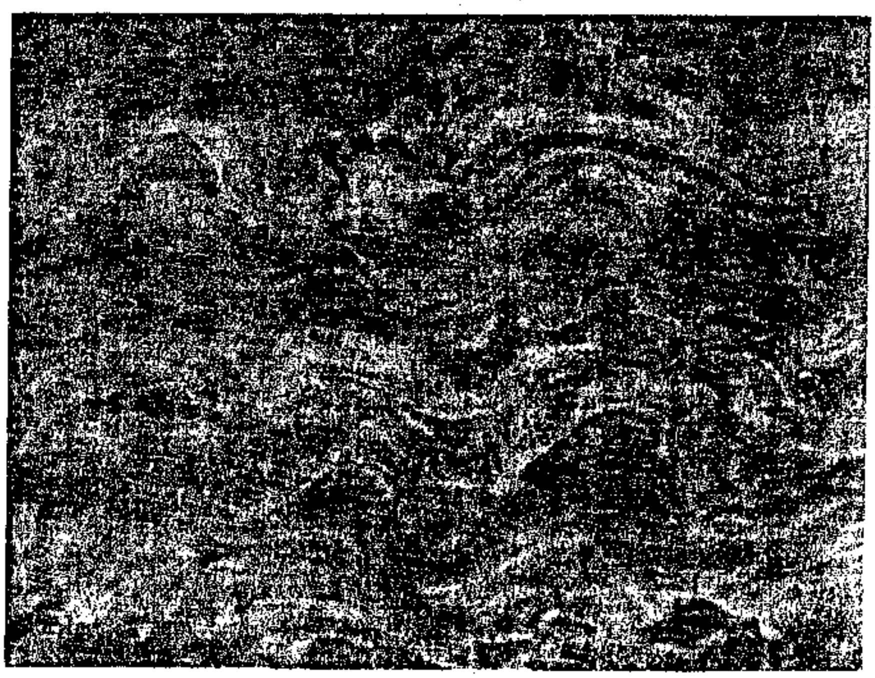

Figure 2 - Microstructure of a deposit.

surface of substrate (1). The high-enthalpy, high-velocity effluent is produced when an ionizable gas generally inert (argon, helium, nitrogen, hydrogen) goes through the arc formed between two concentric electrodes. Whenever sufficient energy is imparted to a gas to cause its partial ionization, a plasma is generated (2). The temperatures within the plasma emerging from the anode vary from 7,000 to 10,000°C, far beyond the melting point of any material.

The particles that have been introduced into the plasma are heated and melted. As soon as they enter, they are accelerated to the speed of the surrounding gas stream forming a cone of high speed particles oriented in the direction of the substrate. The particle speed which depends on the properties of powder and on the operating parameters can be as high as 600 m s^{-1}. Then, these particles impact on the surface where, after losing their kinetic energy, they are rapidly cooled and solidified. They flatten in the form of flat disks, interlock and overlap one another, securely bond together and form a coherent deposit.

The structure of the deposit is not common. As shown in figure 2, it consists of lamellar, randomly-oriented particles, of a multitude of splats overlying one another. The flattened solidified droplets are almost always parallel to the substrate. They are composed of fine columnar grains or microcrystals whose boundaries are perpendicular to the substrate, or more particularly oriented toward the source of cooling (3). When the droplets are adequately sprayed, the layers are packed so closely together that it becomes difficult to discern the boundaries between them. Most of the porosity is, in this case, located within the lamellae (3,4). However, depending on the physico-chemical characteristics of sprayed material and on the spraying parameters, the deposit may contain porosity and also small spherical particles which have been solidified before reaching the substrate. With highly refractory or difficult to melt materials, for instance TiC, some particles can be entraped in the deposit and may also remain totally or partly unmelted as confirmed by transmission electron microscopy (5). Overmelting can cause material alterations (6).

3. SPRAYED COATINGS

When the particles impact a well-prepared surface, an adherent bond is created and a coating is formed by the subsequent stacking of platelets that adhere to each other.

3.1 ADHERENCE OF SPRAYED COATINGS

The adherence of this coating to substrate is of considerable concern and most of the spraying parameters must be viewed in this perspective. When the molten particles impact a roughened surface and conform to the surface topography a mechanical interlocking of coating and substrate is provided. This interlocking is termed mechanical adherence and believed to be the predominant mechanism of adherence. However, localized diffusion between the substrate and the impacting particle and localized fusion of the substrate can be possible (2). Recent studies have shown that a very thin layer could be melted when particles impact the substrate. Thus, when the conditions for incipient melting of the substrate by the impinging particles are favourable and when the two materials are soluble a metallurgical bond is formed (7).

3.2 ADVANTAGES

Because the high temperatures generated by the plasma arc are far beyond the melting point of any known material, any material that has a distinct range over which it remains in the liquid state can be sprayed (ceramics, metals and some plastics). Although the temperature of the plasma may exceed 10,000°C, the substrate temperature can be kept low (below 125°C) avoiding the risk of work piece distortion. Because there is no maximum dimensional limit on which coatings can be applied, the spray technique can be easily implemented in industry. The flexibility of the technique is illustrated in figure 3 where a composite multilayered coating has been sprayed onto a graphite electrode (7 feet long, 20 inches diameter) to protect it against oxidation during the steel melting process.

3.3 APPLICATIONS

These undeniable advantages have enabled plasma-sprayed coatings to find a wide range of utilizations as protective coatings (1). The majority of applications fall under one of the broad classification defined below.

3.3.1 Tribological Applications

Wear-resistant surfaces can be provided by plasma spraying on components subjected to lubricated or unlubricated operation. For the first type of service, the plasma spray technique offers compositional flexibility and controlled porosity. The coating material is selected to withstand the wear

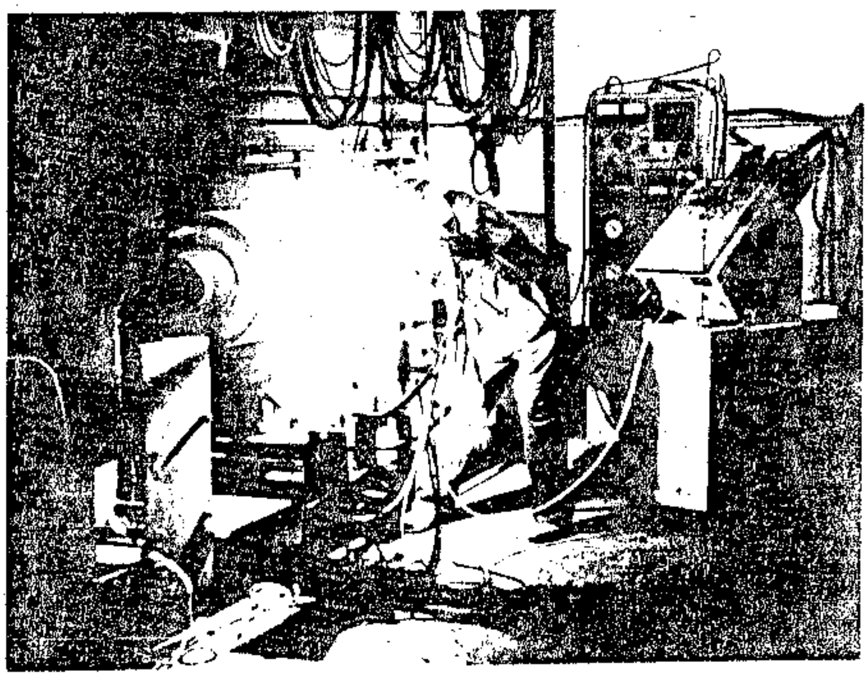

Figure 3 - Coating of a graphite electrode.

mechanism while porosity promotes oil retention. Coatings required to resist abrasive and adhesive wear are largely composed of ceramics. Successful wear-resistant coatings have been developed using cobalt- and nickel-based alloys containing carbide of chromium and tungsten as abrasion-resistant particles. Self-lubrication can be provided by incorporating low-friction materials or dry lubricants, such as PFTE, the aromatic polyester "Eknonol" (8), graphite and molydenum disulfide, for example. Wear barriers may be considered as the biggest utilization of plasma-sprayed coatings on a commercial basis, despite the fact that parts subjected to high impact, as encountered with mining equipment, are not adequately protected by this technique.

3.3.2 Chemical Corrosion-Resistant Coatings

A wide range of materials have been plasma sprayed for corrosion and oxidation protection. Aluminum, zinc and their alloys are used to protect industrial equipment and structures subject to corrosion such as bridges, tanks and marine ware. However, plasma spray deposits are not ideal for corrosion protection: the infiltration of fluids may not be entirely prevented, since coatings have some porosity and permeability. Adequate protection can be obtained when the surface tension of the corrosive fluid is such that there is no capillary transfer through the pores. For other applications, the pores are sealed by wax or a phenolic or silicone sealer. Plasma sprayed coatings are extensively used for corrosion protection, despite the fact that care must be exercised to avoid galvanic corrosion.

3.3.3 Thermal-Barrier Coatings

Metallic and non-metallic parts exposed to high temperature must be protected by coatings. Thermal and antioxidant thermal barriers are multi-layered and graded coatings of metals and ceramics which have high-temperature capability and low thermal conductivity. They consist of an insulating ceramic layer applied over an oxidation-resistant metallic bond coat. They are extensively used for protecting the surfaces of metal components, gas turbines and other heated engine parts which are also exposed to fuels contaminated with tallic impurities. In order to reduce metal temperatures, heat flux and lution, these coatings can be employed for piston heads, valves and exhaust parts of reciprocating engines, particularly diesel engines, parts of the space shuttle, in rapid-earth-drilling schemes, on turbine shrouds and seal surfaces (9).

3.3.4 Reclamation

Another very important application of the plasma spraying technique is reclamation, where it is used to repair worn or badly machined components. For example, a compressor housing which has suffered damage from rotor impingement may be reclaimed by plasma spraying. Cases are machined out to below the identation and plasma sprayed with a coating thick enough to allow the original dimensions to be restored after machining. This type of coating is used to built up worn surfaces of brake drums, grinders, spindles, etc. and also to repair blow holes in castings.

4. FORMING SHAPES AND PARTS

What is left out of account by many design and material engineers is the potential of plasma spraying as a fabrication technique (10). The spray technique can produce discrete parts having shapes and properties that cannot be made by any other way.

Basically, as shown in figure 4, the forming process is identical to the coating process except that the material is deposited onto an appropriate pattern or mandrel which is removed or machined away after deposition. It leaves discrete or free standing shape that reflects the shape of the mandrel surface.

The principal attraction of the process lies in the fact that it can produce parts in high-temperature materials that cannot be cast or easily formed by any other process. Materials that are difficult or impossible to machine, such as refractory metals or ceramics are formed easily by plasma spraying. Many configurations difficult to obtain by powder metal compacting may be readily produced. Plasma spray forming can be used to elaborate configurations prohibited in powder compacting such as internal undercuts, re-entering internal angles, re-entering external angles, sharp internal corners (10,11). The technique is also particularly suited for producing thin-walled and large length-to-diameter ratios parts such as thermocouple sheaths (12). Tungsten tubes (2-inch diameter, 12-inch long) with only 0.007-inch wall thickness have been built (11). Thin-walled ceramic artefacts (crucibles, crucible liners, containers for sintering operations, conduits) with wall thicknesses less than 0.05 inch have not yet been formed with some success by slip casting, pressing, extruding and sintering, hot pressing techniques (13,14). Finally, toxic or pyrophoric materials can be also spray formed

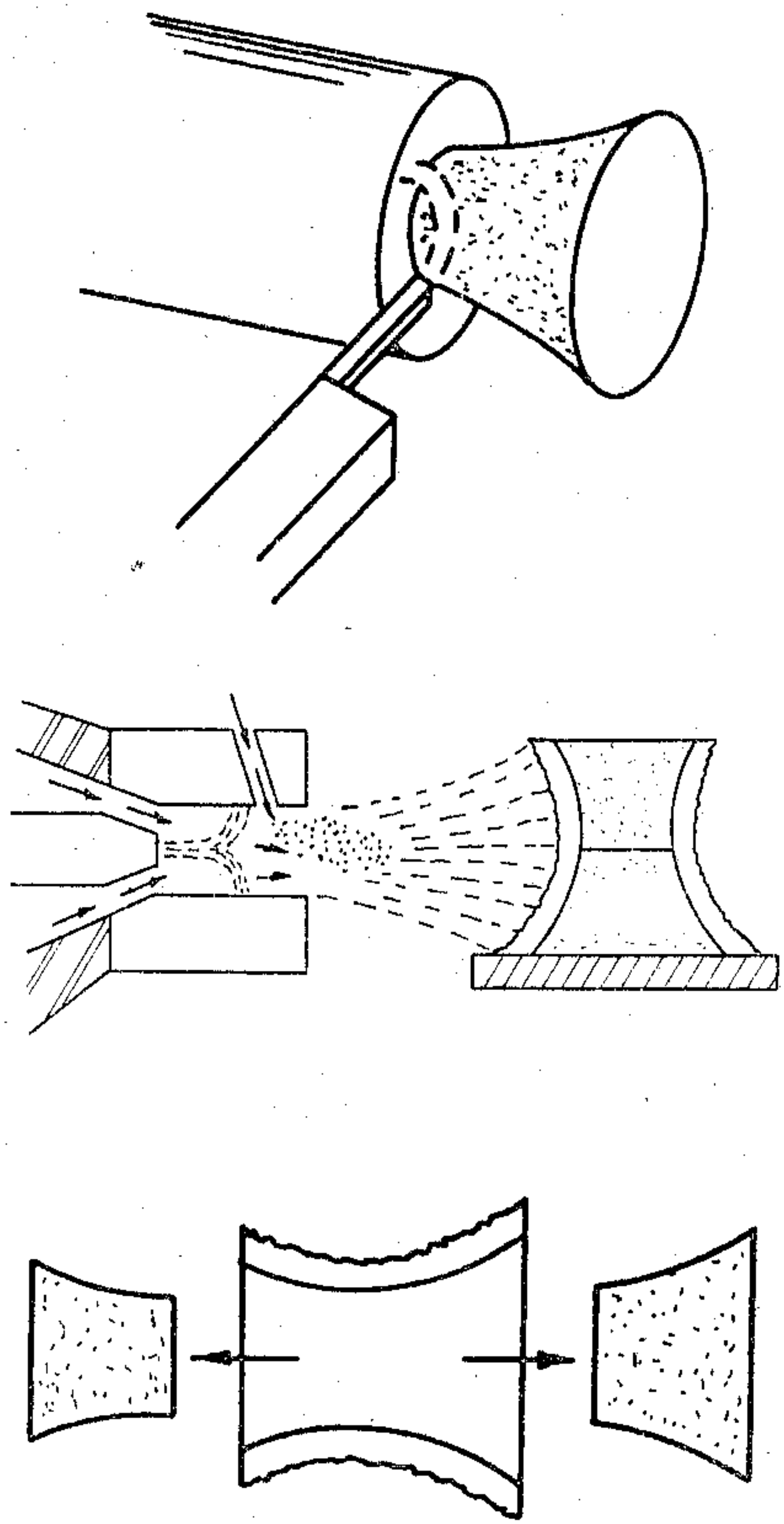

Figure 4 - Schematic view of the fabrication of a free-standing shape, Top figure: Machining the mandrel; Middle figure: Spray forming; Bottom figure: Removing the mandrel.

without difficulty, thereby not requiring to be machined by cryogenic or glove-box techniques (11). Table 1 shows materials that have been spray formed for aerospace, electronic and other advanced applications.

This method has distinct advantages for prototype or small volume applications. Cost comparisons between plasma spray forming and other fabrication processes are not attempted because each forming method has its own merits which may be more important than the cost alone.

5. ADVANCED PROCESSES IN PLASMA SPRAYING

Although plasma spraying is at production stage in industry, its potential for producing economically a wide range of new materials has not been fully exploited. The concept of graded coating has already reached the stage of industrial production while others are now being investigated and developed to produce new materials at economic prices.

5.1 GRADED COATING

The use of ceramic coatings in applications requiring cyclic excursions to high temperatures has proved to be difficult due to the problem involved in bonding the ceramic to metallic components. Metallic-ceramic attachments are however required in applications where the temperatures are beyond the limits of metallic alloys.

Ceramic to metal attachment is impaired by the significant difference in coefficients of thermal expansion (α) between the ceramic and metal.

TABLE I Materials used for plasma sprayed free-standing shapes

METALS	OXIDES	CERMETS	CARBIDES
Be	Al_2O_3	$Cr-Al_2O_3$	Cr_2C_3
Cu	BeO	$Ni-Al_2O_3$	TaC
Hf	Cr_2O_3	$Mo-Al_2O_3$	TiC
Mo	Y_2O_3	$Al-Cr_2O_3$	WC
Ni	ZrO_2	$Cr-Cr_2O_3$	ZrC
Steel	$\beta-Al_2TiO_5$	$NiCr-Al_2O_3$	
Ta	$MgZrO_3$	$Mg-Al_2O_3$	
Ti	$ZrTiO_4$	Co-WC	
W			
Zr			

The expansivity differences impose substantial stress at the baseline during thermal cycling which leads to fracture and failure by spalling of the ceramic coating (15).

For instance, exposing isothermally materials which have different coefficients of thermal expansion to high temperature will cause the metal to expand more than the ceramic. If the metal is restricted from movement as a result of a bond at the ceramic-metal interface, a stress would be present. In a high temperature environment, this stress greatly exceeds the shear strength of the bond or the allowable tensile strength of ceramics and delamination occurs. When a thermal gradient exists through the thickness of ceramic, it will cause the hotter surface to expand more than the colder one.

The mismatch of thermal expansion coefficients between the ceramic and metal can be minimized by placing a number of layers between the metal and ceramic (16,17). The difference of coefficient of thermal expansion between each layer should be minimized to minimize the interfacial stress. The concept of graded coating, as schematically illustrated in figure 5, reduces the α mismatch by incorporating layers of different compositions and matched values of α.

The graded coating seems to be impracticable by using conventional technology but can be successfully done by plasma spraying. Figure 6 shows the metallographic cross-section of a graded coating based on a single compliant layer while figure 7 shows a "gradually" graded coating (18).

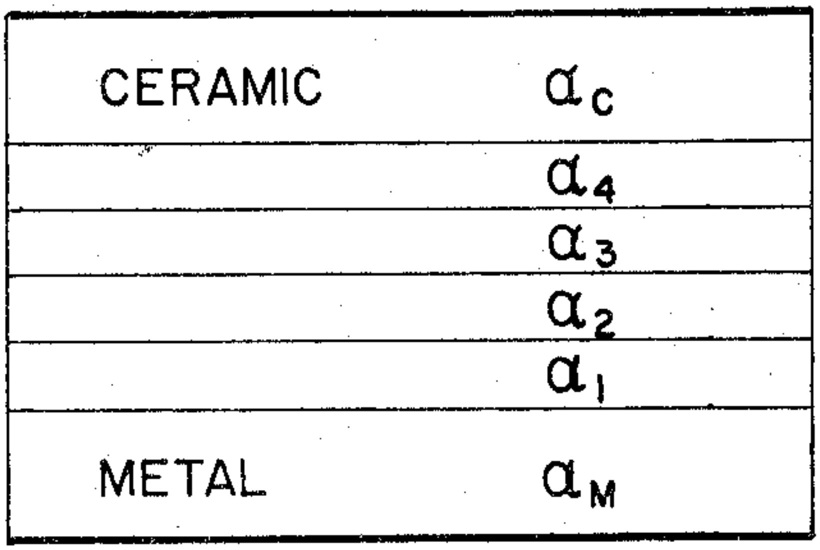

Figure 5 - Schematic view of a graded coating.

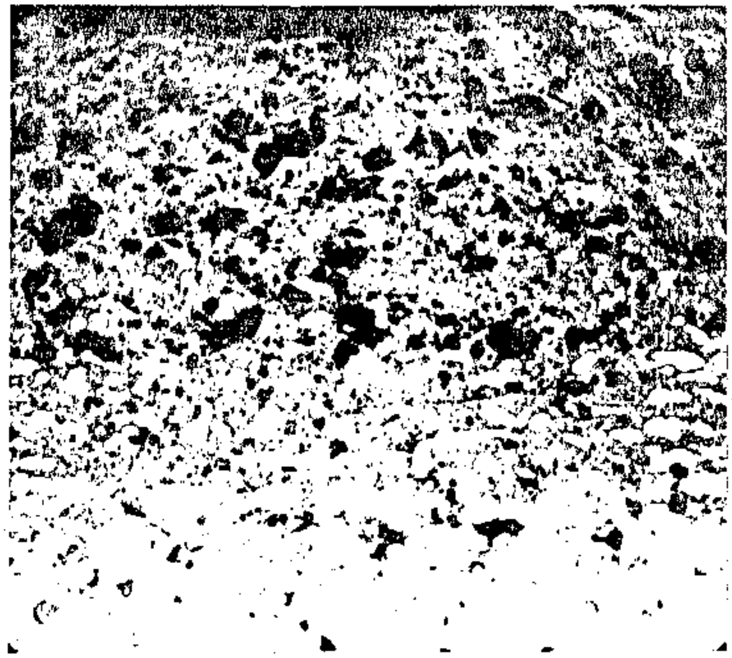

Figure 6 - Graded coating with only a compliant layer.

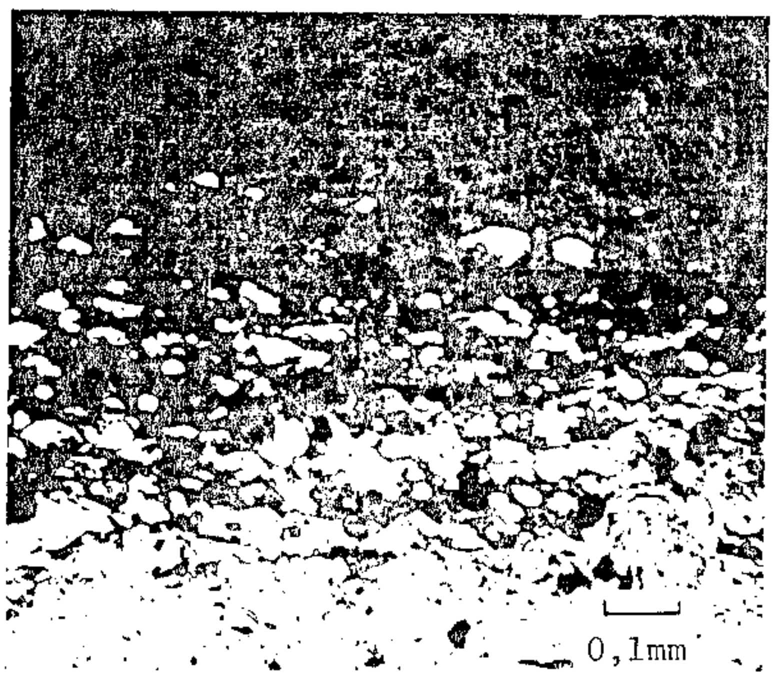

Figure 7 - Gradually graded coating.

5.2 PLASMA SPRAY SYNTHESIS OF TiB_2-Fe COATINGS

To overcome the brittleness of borides and to take advantage of their high hardness, it has been demonstrated that amounts of metals must be added to them to produce wear-resistant materials. However, materials constituted of a ceramic phase and metallic binder like those based on TiB_2 and iron can be used in wear-resistant applications only if a good dispersion of the components is insured by the use of an appropriate forming technology (19).

The better way to ensure a good dispersion of the ceramic phase (TiB_2) into the matrix (Fe) and a perfect bond between the metal and the boride was thought to consist in synthesizing TiB_2-Fe materials themselves through a reaction instead of blending boride and iron powders (20,21).

It has been found that TiB_2-Fe cermets can be obtained when a ferrotitanium alloy reacts with elemental boron (20). When the chemical composition is adjusted so that the boron-to-titanium atomic ratio is 2.0 these elements react exothermically according to the following reaction:

$$FeTi + Ti + 4B \rightarrow 2\ TiB_2 + Fe \qquad (1)$$

Hot-isostatically pressed (HIPed) parts made from TiB_2-Fe powders possess good mechanical strength and abrasion resistance (20,22). The microstructure of a dense part is shown in figure 8.

The synthesis of TiB_2 can be also done by means of the auxiliary metal bath process (23,24). In this case, ferrotitanium and ferroboron alloys are

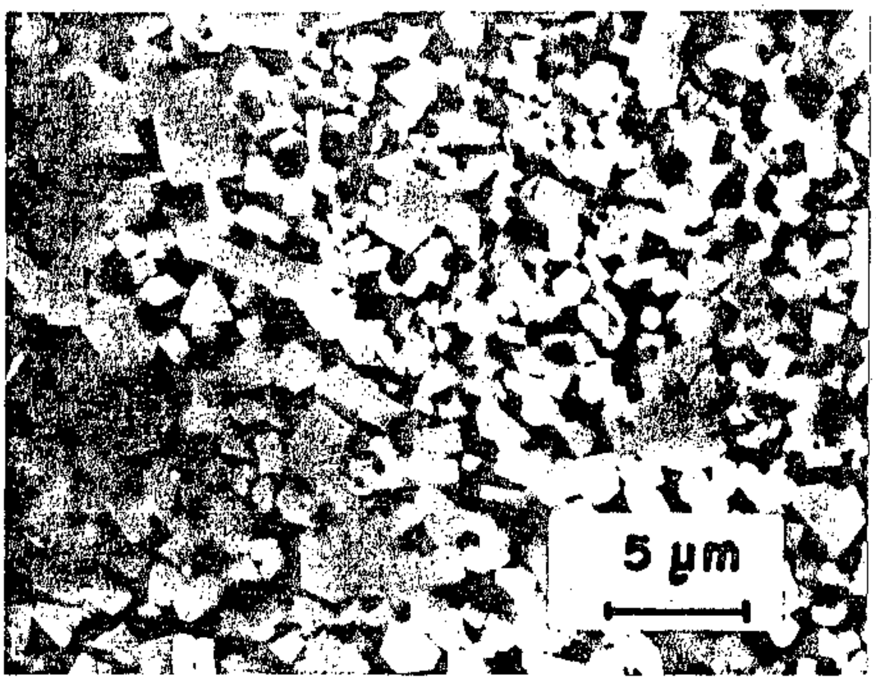

Figure 8 - Typical microstructure of TiB_2-based materials HIPed at 1300°C - 48MPa - 3600s (deeply etched).

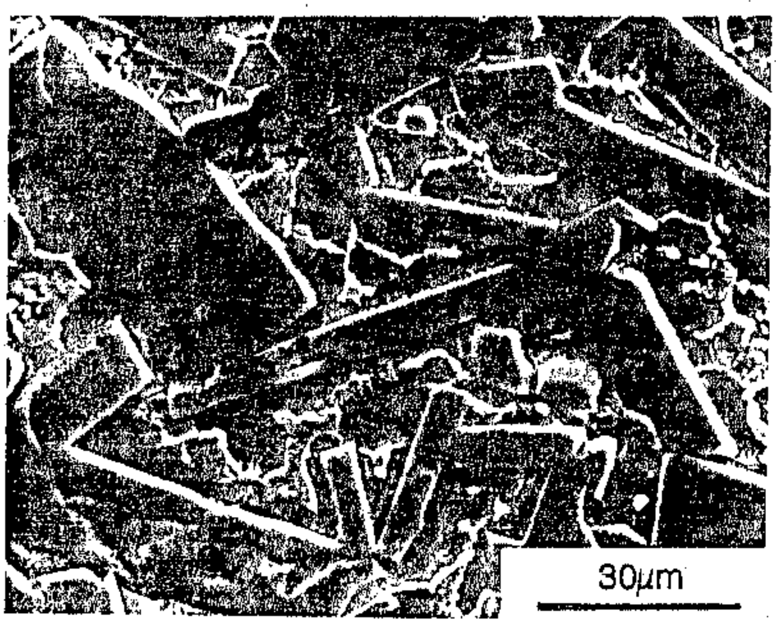

Figure 9 - Scanning electron micrograph of an arc-melted bath wherein the B/Ti atomic ratio is 1.8.

used as reagents and the reaction can be represented by the following equation:

$$FeTi + Ti + 4\ FeB \rightarrow 2\ TiB_2 + 5\ Fe \qquad (2)$$

Figure 9 shows a typical as-cast microstructure of a metallic bath melted by an electric arc (23).

The plasma spraying process has then been extended to combine in a one-step process both the synthesis of boride materials and their deposition to form wear-resistant coatings (21,25-27). The so-called plasma spray synthesis (PSS) process is schematically represented in figure 10. After micropellets comprising the reagents have been injected into the plasma, the reaction (1 or takes place. The reaction products containing TiB_2 and iron are propelled the plasma onto a substrate to form a cermet coating.

The synthesized TiB_2-Fe coating whose microstructure appears in figure 11 has a hardness higher than 1400 kgf mm^{-2} and exhibits, as shown in Table II, an abrasive wear resistance comparable to the expensive Mach II WC-Co coating, one of the most performing material now on the market.

5.3 NON-STRUCTURAL APPLICATIONS

Plasma spraying can also be considered as a novel approach to the fabrication of high-surface-area bodies such as electrodes in electrochemical or photoelectrochemical cells.

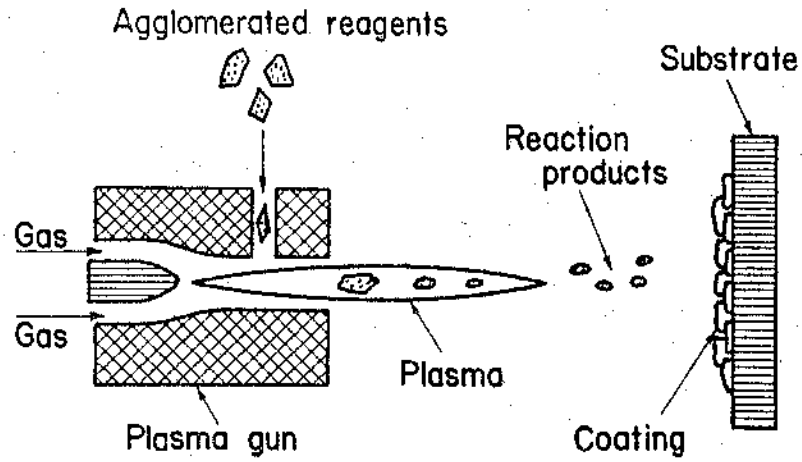

Figure 10 - Schematic view of the plasma spray synthesis.

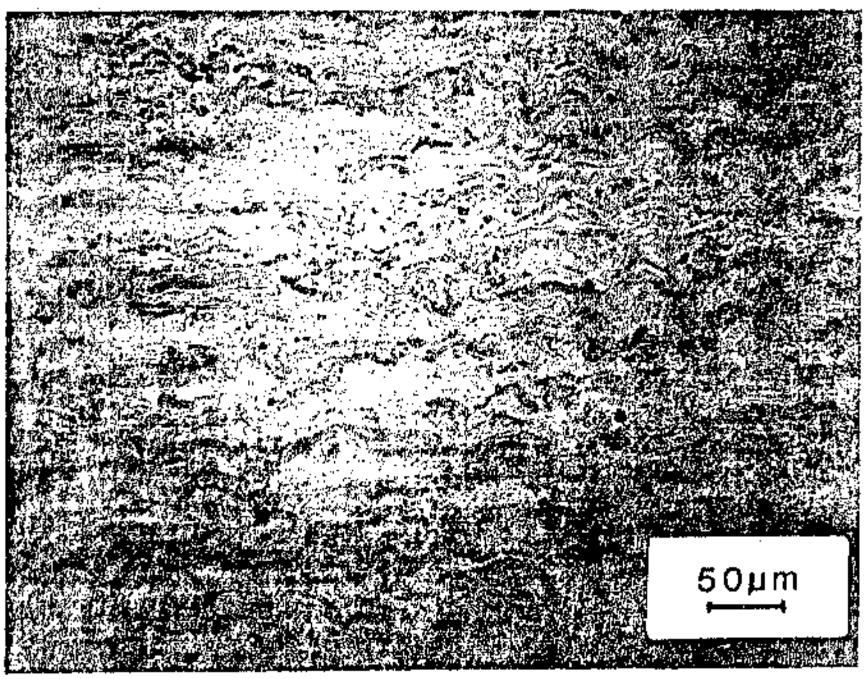

Figure 11 - Optical micrograph of a plasma spray synthesized TiB_2-Fe coating.

TABLE II Abrasive wear resistance of TiB_2-Fe coatings

Abrasion resistance of TiB_2-Fe materials

Material	Volume losses (mm^3)	
	High stress abrasion	Low stress abrasion
SAE 1018 steel	214.4	294.0
WC-6.8% wt Co	2.3	4.2
HIPped TiB_2-Fe	18.8	14.8
TiB_2-Fe coating (exothermic)		16.0
TiB_2-Fe " (endothermic)		21.0
WC-Co " (Mach II)		13.0

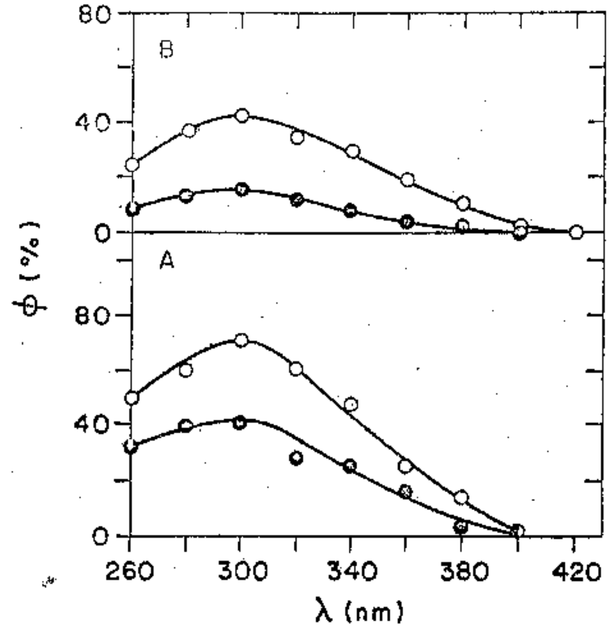

Figure 12 - Quantum yield, Ø, for Ar-treated (open symbols) and and untreated (dark symbols) TiO_2 sprayed on titanium (A) and on alumina (B), as a function of the wavelength.

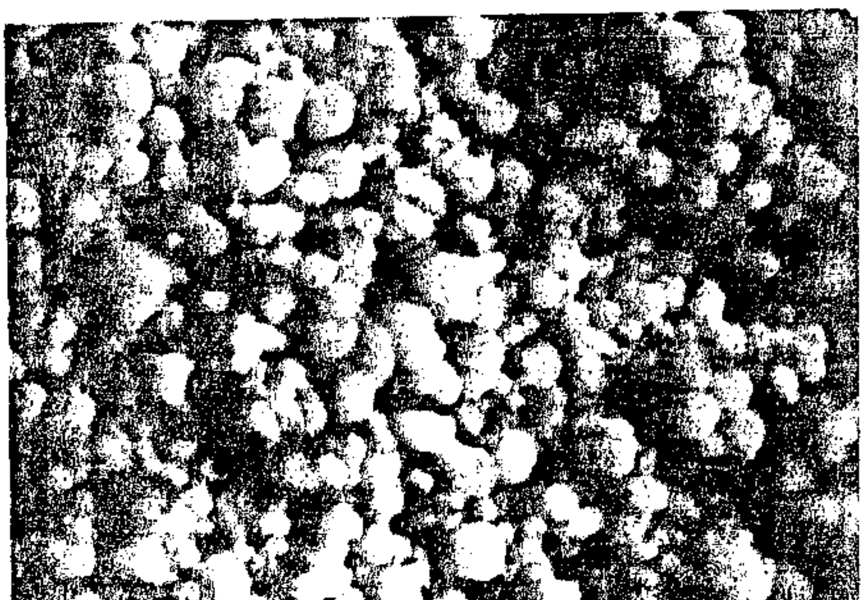

Figure 13 - Surface texture of a PbO ZrO_2-TiO_2 coating after heat treatment.

Several techniques for the preparation of these surfaces have been used, namely thermal oxidation, anodic oxidation, chemical vapor deposition, plasma-enhanced chemical vapor deposition, sputtering, powder pressing and sintering and screen printing (28). None of these techniques is well adapted for low cost and large scale production. Plasma spraying has been successfully used to produce polycrystalline electrodes from TiO_2 and Fe_2O_3 (28,29). Photoanodes with a highly textured surface display photoelectrochemical properties comparable to those measured on TiO_2 monocrystals (28,30). For instance, the quantum yield reaches a value as high as 0.80 at 300 nm as shown in figure 12 3,30). Plasma-sprayed electrodes consisting of Fe_2O_3 adequately dispersed in $_3O_4$ may generate NH_3 when immersed in aqueous solution without external potential (29).

In the area of sensors fabrication, the technique seems also promising. A $PbO-ZrO_2-TiO_2$ coating with the adequate PZT structure has been obtained recently (31). Its unusual surface texture as shown in figure 13 could enhance PZT properties and make the spraying process more attractive than expected.

CONCLUSION

An attempt has been made to indicate how a high temperature technology can be used for fabricating coatings and parts by processing materials in their liquid state. Plasma spraying is not an entirely new technology at the early stage of development. It has already achieved success in certain specific areas but its virtues should not be over-emphasized. It is a technology still in its infancy. Therefore, more pioneering work is necessary to take full advantage of its flexibility.

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FIGURE CAPTIONS

Fig. 1. Schematic view of the plasma spraying process.

Fig. 2. Microstructure of a deposit.

Fig. 3. Coating of a graphite electrode.

Fig. 4. Schematic view of the fabrication of a free-standing shape.

- Top figure : Machining the mandrel.
- Middle figure: Spray forming.
- Bottom figure: Removing the mandrel.

Fig. 5. Schematic view of a graded coating.

Fig. 6. Graded coating with only a compliant layer.

Fig. 7. Gradually graded coating.

Fig. 8. Typical microstructure of TiB_2-based materials HIPed at 1300°C - 48MPa - 3600s (deeply etched).

Fig. 9. Scanning electron micrograph of an arc-melted bath wherein the B/Ti atomic ratio is 1.8.

Fig. 10. Schematic view of the plasma spray synthesis.

Fig. 11. Optical micrograph of a plasma spray synthesized TiB_2-Fe coating.

Fig. 12. Quantum yield, Ø, for Ar-treated (open symbols) and untreated (dark symbols) TiO_2 sprayed on titanium (A) and on alumina (B), as a function of the wavelength.

Fig. 13. Surface texture of a PbO ZrO_2-TiO_2 coating after heat treatment.