INDUSTRIAL THERMAL SPRAY COATINGS FOR TRIBOLOGICAL APPLICATIONS. INFLUENCE OF NANOSTRUCTURE ON WEAR PROPERTIES

Michail Vardavoulias
PyroGenesis SA

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INDUSTRIAL THERMAL SPRAY COATINGS FOR TRIBOLOGICAL APPLICATIONS. INFLUENCE OF NANOSTRUCTURE ON WEAR PROPERTIES

Michail VARDAVOULIAS

PyroGenesis SA, Technological Park of Lavrion, 195 00 Lavrion, Greece
*Corresponding author: mvardavoulias@pyrogenesis-sa.gr

Abstract: *The paper presents the applications of thermal spray (TS) coatings, when a high tribological performance (wear resistance, friction, lubrication) is necessary. For many decades Cr plating was applied when high wear resistance was requested. However this technique is characterized by the hazardous emission of Cr6+ ions, and the need of management of a large amount of toxic wastes. Several coating techniques are proposed as alternative to hard Cr. Among them, thermal spray seems to be the most appropriate, since it combines cost effectiveness, short production time and a large flexibility in the choice of coating material. In addition, the use of nanostructured materials in TS adds a new dimension.*

Keywords: *Coatings, Thermal spray, Tribological performance, Cr replacement, Industrial applications*

1. Introduction

The degradation of industrial components by wear is a severe problem in many industrial sectors. Material losses, and finally damage of components may cause health and environmental hazards. As a result, the operating and maintenance costs in industry increase. Material losses due to wear and corrosion represent in developed countries 4% of their gross internal product (GIP). Wear of tools and industrial/mechanical components in USA results in a cost for spare parts of 22 billion Euros per year [1]. One has to add an equal amount for indirect costs related to production stops, scrap creation and management, and maintenance personal. On the other hand, high friction between parts results in high energy losses. Thirty per cent of the energy produced in industrial countries is consumed by friction and wear phenomena [2]. To solve those tribological problems, the demand for engineering coatings is becoming more and more stringent. Environmental concerns are also being considered as an integral part of the design process. To generate future economic competitiveness and lower environmental impact, researchers' attention must be focused onto processes that consume a minimum of resources.

Protective coatings can impart superior properties on a substrate and are used in a large number of engineering applications. Table 1 lists the principal coating processes, the typical coating thicknesses attainable, common coating materials, and some applications [3–8]. Not all processes are suitable for all coating materials and not all coating thicknesses are attainable with all methods. Beyond that, the equipment necessary for some processes can be quite complex and, therefore, costly, especially for plasma spraying. Cost analysis can determine whether a coating is a practical solution for a particular application. Present regulations [6] require that ecological criteria of the respective coating processes must also be examined, as not all methods are environmentally equivalent.

Table 1. Principal coating processes and their characteristics [6]

Coating Process	Typical Coating Thickness	Coating Material	Characteristics	Examples
PVD	1-5 µm	Ti(C,N)	Wear resistance	Machine tools
CVD	1-50 µm	SiC	Wear resistance	Fibre coatings
Thermal Spray coating	0.04-3 mm	Ceramic & Metallic alloys	Wear resistance, corrosion resistance	Bearings, axles
Hard Chromium Plating	10-100 µm	Chrome	Wear resistance	Rolls
Weld Overlay	0.5-5mm	Steel, Stellite	Wear resistance	Valves

Galvanisation	1-5 µm	Zinc	Corrosion resistance	Steel sheet
Braze Overlay	10-100 µm	Ni-Cr-B-Si alloys	Very hard, dense surface	Shafts

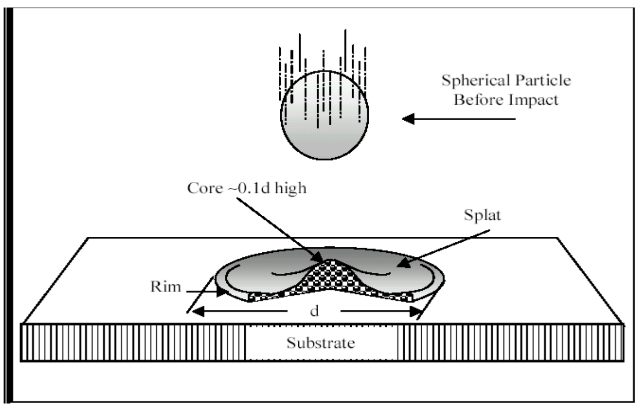
For many decades Cr plating was applied when high wear resistance was requested. However this technique is characterized by the hazardous emission of Cr6+ ions, and the need of management of a large amount of toxic wastes. The recent changes in the European legislation impose strict limitations associated with handling, storage and disposal of chromium ions that have been proved to be very harmful. Thus, despite the fact that such high quality Cr electrodeposits are obtained mainly from trivalent chromium aquatic baths, the large amount of slurry to be managed after the depletion of the solution and the non-negligible probability of the trivalent chromium (Cr^{3+}) to be oxidized to hexavalent (Cr^{6+}), have shifted recently the scientific interest to the investigation of potential alternatives that could have similar anti-wear efficiency and high “environmental-friendly character”.

Thermally sprayed hard coatings are extremely effective at increasing a metallic component’s life and value. Many researchers and people from the market consider them as the ideal candidates to replace electroplating, in one hand due to the very slight amount of materials’ spoil during deposition and in the other hand due to the minute amount of waste produced during such processes [9-10]. In the case of oxide coatings, alumina (Al_2O_3) ones are the most widely investigated with respect to both the quality of the feedstock powders used, as well as their wear resistance under various tribo-pairs configurations [11-15] whilst the most suitable thermal spraying technique to obtain oxide coatings is Atmospheric Plasma Spraying (APS). In the case of carbide coatings, feedstock powders of tungsten carbide (WC) with a metal binder fraction of ~10% are used to elaborate extremely wear-resistant and ultra-hard coatings, via High Velocity Oxy-Fuel (HVOF) spraying [16-21], a process that controls the in-flight carbide decomposition phenomena. Although these coating types can provide excellent anti-wear protection of metallic components, their deposition processes require large, stationary installation facilities, a fact that limits their industrial applications to parts of relevant small dimensions and does not allow in-situ deposition on non-removable metallic systems. Moreover, in the case of WC-based HVOF coatings, their extremely wear resistance, which is highly attractive during operation, renders them rather “non-machinable” with conventional tools, a main drawback for the majority of engineering applications, since post-deposition grinding of the coatings to low surface roughness is a requirement.

A main breakthrough in wear resistant coatings is the development of materials where hardness increases dramatically by a nanosized composite structure. Nanocrystalline materials were found to possess unique properties such as being exceptionally strong, hard, wear resistant, erosion resistant, corrosion resistant and chemically very active. This is mainly due to the fact that 30–50% of the atoms reside in the grain boundaries [22].

2. Thermal Spray Technology and Equipment

Thermal spraying is applicable to a large range of coating materials, coating thicknesses and coating characteristics. Thermal spraying methods are grouped into three main categories: flame spraying, electric arc spraying and plasma arc spraying, referring to the energy sources producing the flame to heat the coating material to a molten or semi-molten state. The heated molten particles are accelerated and propelled towards a prepared surface by either the process gases or atomization jets. Upon impact [4], a bond forms with the substrate and the subsequent particles form a lamellar structure. Droplet size and injection velocity [5] are the most important parameters, whereas the injection angle is of lesser importance. Thermal Spray principle is schematically represented in Figure 1.



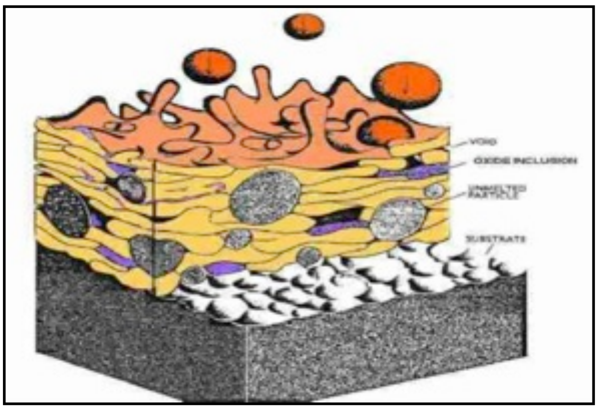


Figure 1. Schematic diagram of spherical particle impinging onto a flat substrate (left) and 3D view of deposited coating (right)

2.1. Plasma Spray (PS)

Plasma is produced by generating an electric arc between two electrodes and passing a stream of gases through the arc. The plasma energy is used for melting and accelerating the feedstock material, which is in powder form. Argon, hydrogen, helium, nitrogen are the common gases used for the plasma generation. Flame temperature can exceed 10000°C in the core of the plasma jet, while spraying velocities range between 350 — 700 m/s. Nevertheless, the substrate temperature during spraying is low (< 200°C), thus it is not affected from severe temperature variations.

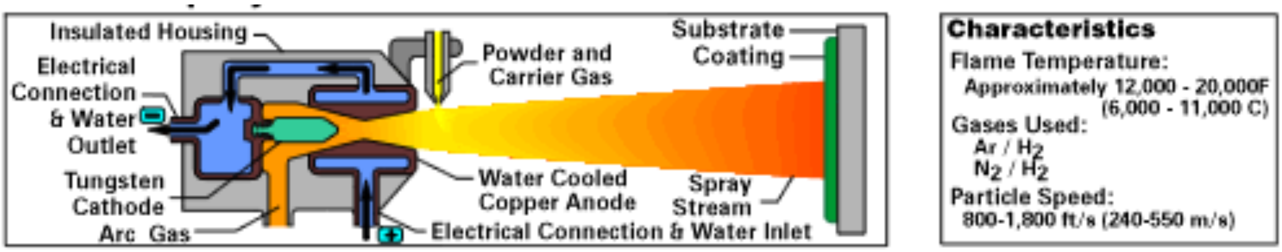


Figure 2. Plasma Spray process

2.2. High Velocity Oxygen-Fuel (HVOF) Spray

The high internal pressure combustion of a fuel, such as hydrogen, propylene or propane with oxygen, is the energy source in the HVOF spray process. The temperature is lower than in the case of plasma (3000ºC instead of 10000ºC), but particles velocity, when they meet the substrate is much higher (1100 m/s). HVOF coatings are very dense, hard and adhere very well to the substrate.

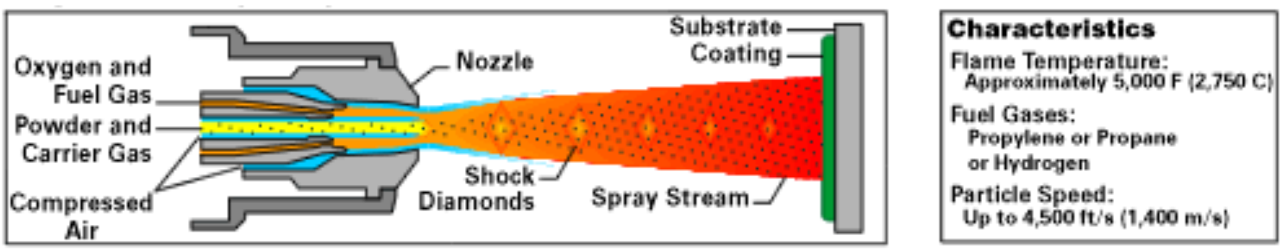


Figure 3. HVOF Spray process

2.3. Flame Spray (FS)

The material, in wire or in powder form, is melted in a flame (usually oxy—acetylene flame). The molten particles are propelled to the substrate with compressed air. Flame temperature is lower compared to the other spraying techniques (about 2000 — 2500°C) and so is the particle velocity during spraying. It is a relatively easy to use method, simple in operation and with high deposition rates, that can be used in wear and corrosion applications.

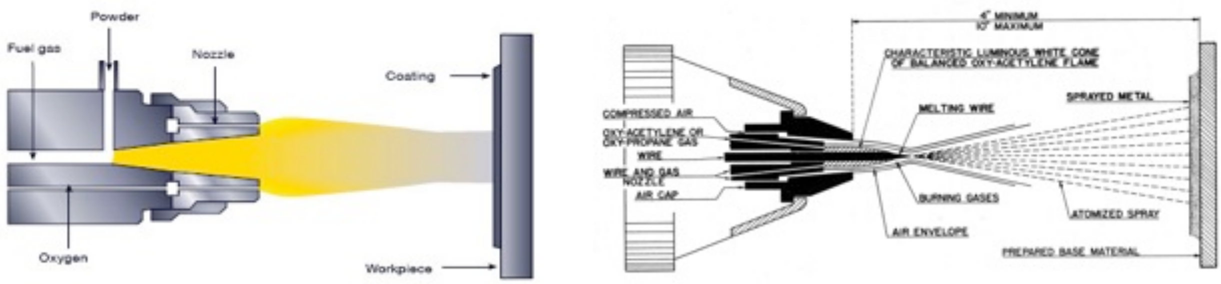


Figure 4. Flame Spray process: (a) powders,   (b) wire

2.4. Wire Arc Spray (WAS)

In this process, an electric arc melts two electrically opposite charged wires as they touch. As the wires touch, an electric arc is formed melting the wire feed stock. The molten particles are sprayed in a high-velocity air stream. Flame temperature can exceed 5000°C. It is a particularly efficient and productive technique. WA coatings are applied against wear and corrosion, as well as for the restoration of worn parts.

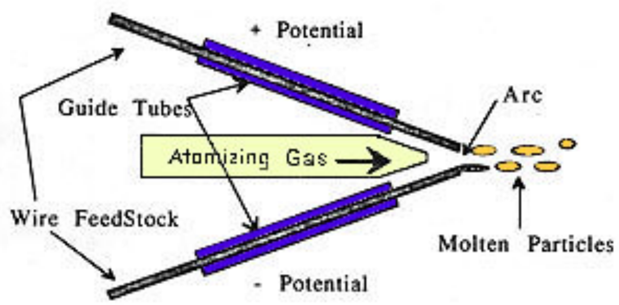


Figure 5. Wire Arc Spray process:

2.5. Cold Spray (CS)

Cold spraying is an emerging coating process that is classified as a thermal spray process. Figure 6 shows a schematic of typical cold gas spray principle. The process gas is compressed and heated. The gas expands in a de Laval type nozzle and reaches supersonic velocities at the nozzle exit. The feedstock material, which is in powder form, is injected in the convergent section of the nozzle. The particles are then accelerated to high velocities and heated by the process gas, but their temperature always remains lower than the melting temperature of the material. The distinguishing feature of the cold spray process compared with conventional thermal spray processes is its ability to produce coatings with preheated gas temperatures in the range of 0 to 700 C, a range that is generally lower than the melting temperature of the coating particle materials. Deleterious effects of high-temperature oxidation, evaporation, melting, recrystallization, phase transformations, residual stresses, debonding and other concerns associated with thermal spray methods can be minimized or eliminated [23-24].

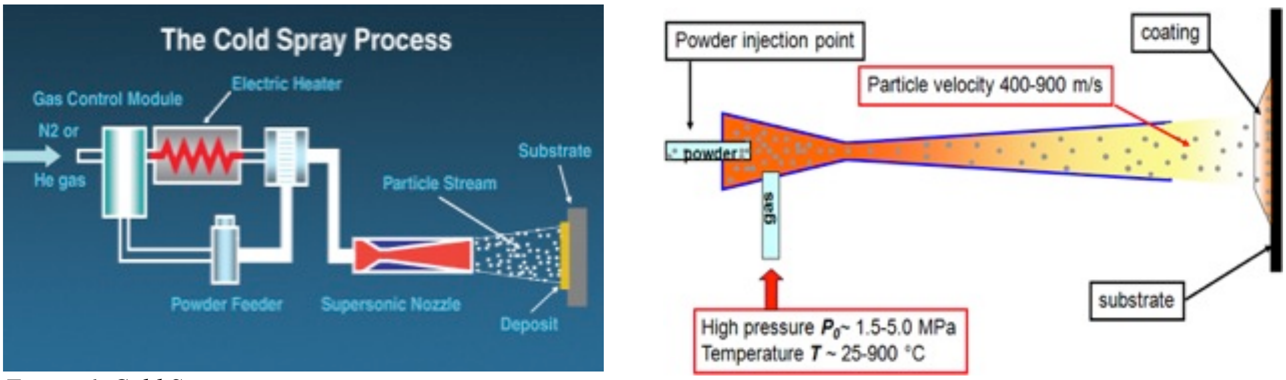


Figure 6. Cold Spray process:

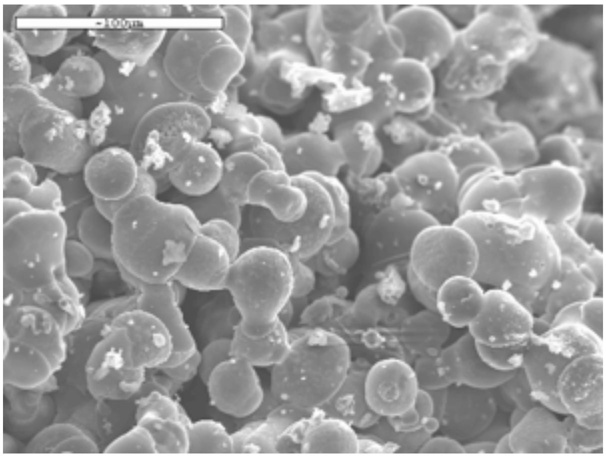
3. Specific Tribological Features of TS Coatings. Influence of Nanostructure on Wear Properties

A characteristic image of the microstructure of thermal spray coatings is presented in Figure 1. Some specific microstructural characteristics may play a remarkable role in the tribological behavior of the coatings. The most important between them are the porosity and the degree of oxidation of metallic coatings.

3.1. Porosity

By adjusting properly the thermal spray parameters, the porosity of the coatings can be controlled, concerning the % percentage and the pore size. Coatings may have almost 0% porosity (cold spray, HVOF), but also 20-30% porosity (flame spray, plasma spray of ceramics). Low porosity may be valuable for high wear resistance, while high porosity is very helpful in cases where liquid lubrication is necessary, since the lubricant can be retained inside the pores. A flame sprayed microstructure with very high porosity is shown in Figure 7.

Figure 7. Flame spray ceramic with high porosity



3.2. Degree of oxidation during thermal spraying

The amount of oxygen or air, which is used during thermal spray, can result in a certain degree of oxidation. Oxidation of Fe-based coatings is preferable in several cases, since the final microstructure can be a "metallic matrix composite" with superior sliding wear resistance. Similarly pure nitrogen can be used instead of air for the atomization of metallic droplets in wire arc thermal spray, resulting in the presence of nitrides in the sprayed microstructure. An oxidized Fe-based microstructure is shown in Figure 8, with 20-25% oxides and 2-3% porosity, which presents very good wear characteristics.

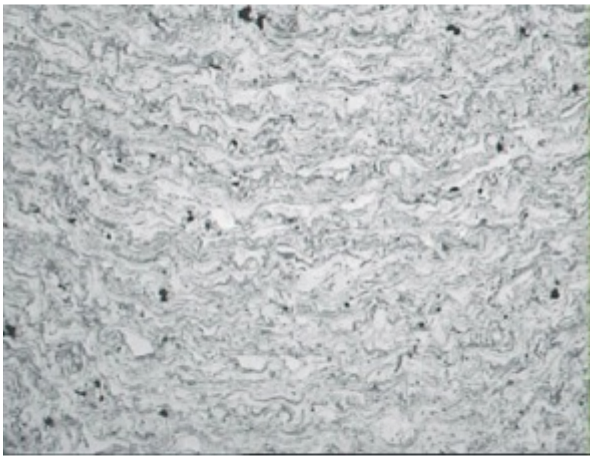


Figure 8. Flame spray Fe-based coating with 20-25% oxide content

3.3. Influence of nanostructure on wear properties

In PyroGenesis we have participated in several RTD projects on the development of nanostructured coatings for superior wear performance. Thermal sprayed nanostructured cermet coatings are attracting attention due to their enhanced tribological properties. So far, main attention has been given on the synthesis of nanostructured powder and processing of thermal sprayed nanostructured coatings [25-27] together with some investigations on the mechanical and tribological properties [28-29]. Recently, we have reported [28-29] on the superior tribological and mechanical behavior of such nanostructured cermet coatings consisting of a relatively soft nanostructured FeCuAl-matrix and dispersed nanostructured alumina particles, as wear resistant ones, in applications where hardness as well as toughness are essential. The metallic phase in the coating provides toughness, while the ceramic phase increases hardness. Though the starting powders for plasma spraying consisted of metallic and ceramic nanostructured powders, the resulting coating structure exhibited four different phases of different compositions and hardness. In a preceding investigation on this type of coatings [29], the focus was on their overall response in tribological behavior with minor attention on its origin.

The nanostructured powders were produced by High Energy Ball Milling˙ These nanostructured powders were then agglomerated by using an organic binder (commercially available) to obtain an agglomeration of about 50 lm in diameter. That binder did not induce any physical changes rather than holding the nano-sized powders together as verified by detail characterization of the powder and coating with the help of XRD and TEM. During spraying, the binder phase evaporated (decomposed) due to high processing temperature. In Figure 9 agglomerated nanostructured particles before thermal spray are presented.

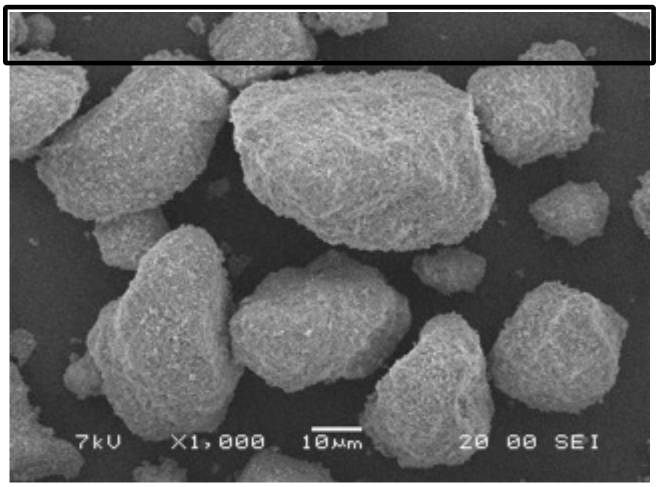


Figure 9. Agglomerated nanostructured particles before thermal spray

Nanostructured WC–Co and WC–Co–Al coatings, with about 300-µm as-deposited coating thickness, were deposited by high velocity oxy-fuel (HVOF) spraying. Agglomerated nanostructured cermet powders produced by High Energy Ball Milling, was used for HVOF spraying. Dense and well-adherent coatings with crystal sizes below 30 nm were deposited on stainless steel 304 substrate. Porosity was less than 5% and the bond strength with the substrate was around 60 MPa. Experimental data on friction, wear, and abrasion resistance revealed that nanostructured WC–Co based coatings containing some Al as alloying element, exhibit improved tribological characteristics in comparison to nanostructured and micron-sized WC–Co coatings. This was attributed to a carbide particle distribution within the coating revealed by SEM, the absence of brittle W_2C-like phases revealed by XRD, and the presence of Al at particle/matrix boundaries revealed by TEM [30-31].

4. Tribological Applications of Thermal Spray Coatings in Industry

Many Coatings are developed and produced in PyroGenesis for industrial tribological applications. A selection of some of them is presented in the next figures.

Figure 10. Restoration and Wear Coating of Valve Ball - Flame Spray, Hard Steel Coating

Figure 11. Restoration and Wear Coating of Army Tank Al Wheels - Wire Arc Spray, Hard Steel Coating

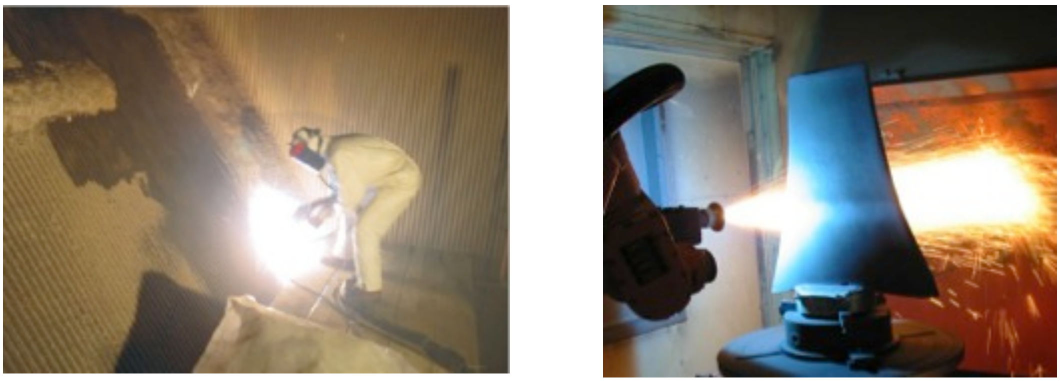


Figure 12. Particle Erosion Coating on Boiler Walls and on Aluminum FDF fans (Energy Production) - Wire Arc Spray, Hard Alloy Coating

Figure 13. Friction-Wear Coatings on Piston Rings - HVOF, Carbide Coating

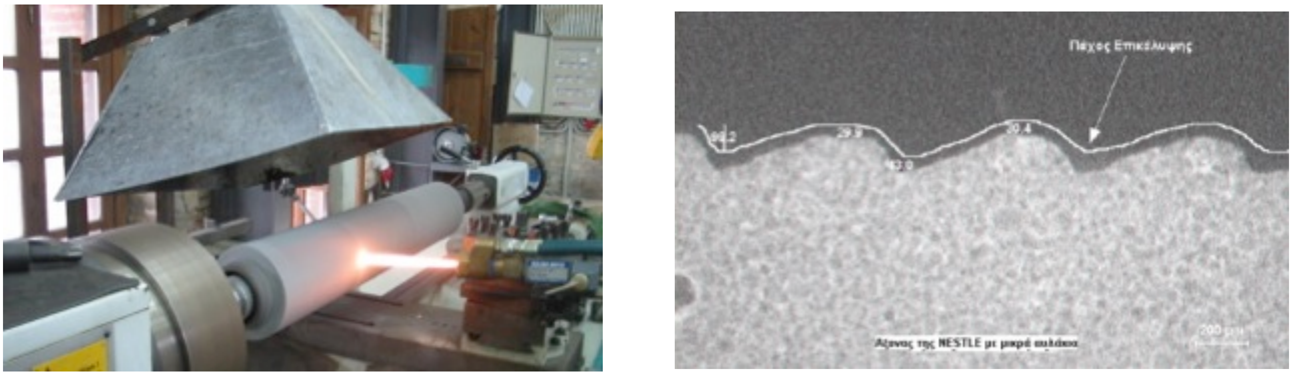


Figure 14. Wear Coatings on Coffee Mill Rolls - HVOF, Carbide Coating

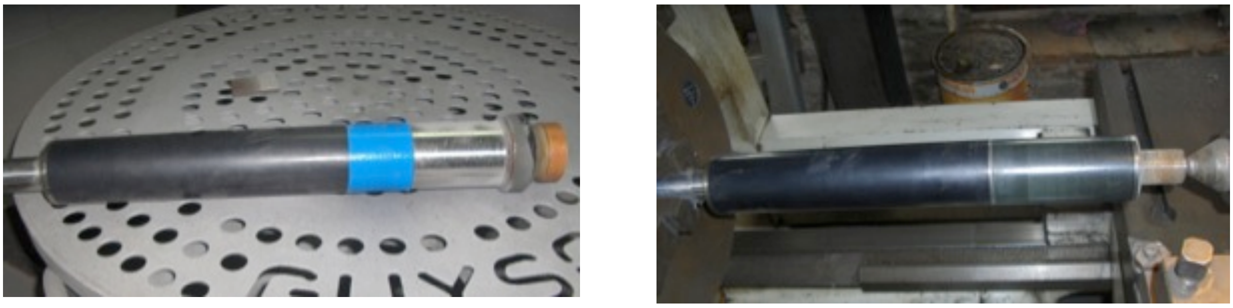


Figure 15. Wear Coating and Restoration of Hydraulic Systems - Plasma Spray, Ceramic Chrome Oxide

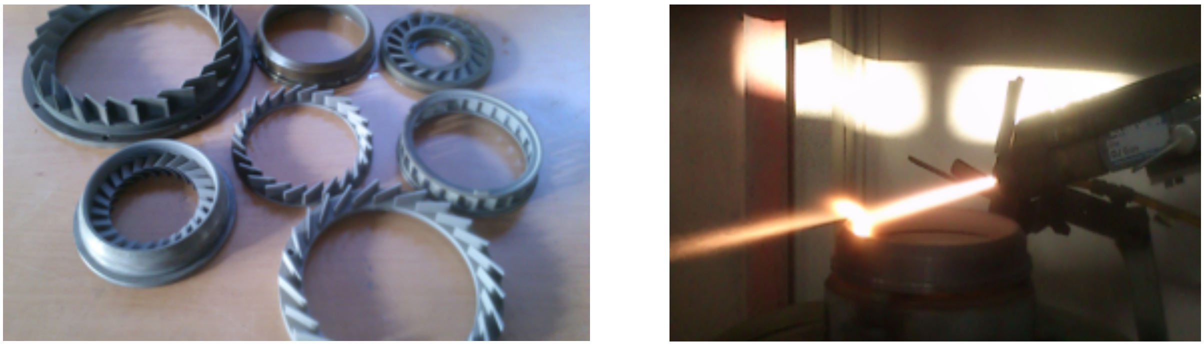


Figure 16. Wear Resistant Coating on Turbocharger Nozzles - HVOF, Carbide Coating

5. Conclusions

Thermal spraying is an attractive surface modification technique. It offers a wide choice of materials and processes that have a reduced impact on the environment. Benefits include higher hardness and strength resulting from a reduced grain size and slip distance respectively. In ceramics, higher hardness and toughness may be achieved with reduced defect size and enhanced grain boundary stress relaxation, even at ambient temperature. In nanostructured coatings, diffusivity is greatly increased, associated to a larger amount of grain boundaries.

Thermal spraying such as APS and HVOF appears as a flexible method to deposit nanostructured coatings, and allows building up thick coatings. Hard nanostructured coatings based on WC–Co were successfully spray deposited from engineered nanosized powders. The HVOF spraying was found to be most suitable for depositing nanostructured WC–Co based coatings with good coating quality and without brittle phases. On the other hand, APS is not that suitable for depositing WC–Co since it leads to the predominant formation of brittle phases in the coatings. It is important to avoid brittle phases in sprayed coatings to achieve a good tribological performance.

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