

Recently Patented Work on Thermally Sprayed Coatings for Protection Against Wear and Corrosion of Engineered Structures

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Abstract: Advanced ceramic and metallic coatings for wear and corrosion protection of engineered structures applied by thermal spraying techniques have become a mainstay of surface engineering. Estimated global sales of thermally sprayed coatings are in the US\$5 billion range per year, 50% of which are achieved by atmospheric plasma spraying. The development of suitable deposition equipment, sophisticated on-line process control, ease of application to complex surfaces, availability of a broad range of tailored feedstock materials, and sensitive characterization and quality assurance methods make novel surface coatings and their improved deposition techniques increasingly attractive. This review will cover patented progress in the field of wear- and corrosion-resistant coatings achieved during the past few years.

Keywords: Wear resistant coatings, corrosion resistant coatings, plasma spraying, HVOF, thermal spraying.

INTRODUCTION

Wear and corrosion destroy national wealth in the multi-billion dollar range annually. Modern high performance machinery, subject to extremes of temperature and mechanical stress, requires surface protection against high temperature corrosive media, and mechanical wear and tear. To apply protective coatings a highly versatile, low cost technique must be selected that can be performed with a minimum in equipment investment and maintenance, and that does not require overly sophisticated training for the operator. Such a technique has been found in thermal spraying [1]. It uses partial or complete melting of wire, rod or powder feeds passing through a high temperature regime generated either electrically by a gas plasma as in atmospheric plasma spraying (APS) or by a combustion gas flame as in high-velocity oxyfuel (HVOF) deposition [2]. The molten droplets impinge on the substrate surface to form the coating layer by layer. This technique is being used widely to repair and resurface metallic surfaces but also, in recent years, to build up protective coatings against wear, corrosion, and environmental and thermal attack to provide ever increasing fields of service to a broad range of industry.

Wear- and corrosion-resistant coatings are most frequently based on transition metal carbides (WC, TiC, Mo₂C, TaC, NbC, Cr₃C₂) and also some hard oxides (Al₂O₃, TiO₂, Cr₂O₃), metals (W, Mo, Ti, Ta) and their alloys (NiCoCr AlY), and also diamond. While the former are being applied by thermal spray deposition, for example atmospheric plasma spraying (APS), low pressure plasma spraying (LPPS) or high velocity oxyfuel (HVOF) deposition, diamond coatings require more subtle techniques such as microwave-assisted chemical vapor deposition (CVD).

Since the melting temperatures of the transition metal carbides are extremely high, and oxidation/decarburization and thermal decomposition generally occur at such high

temperatures, pure carbide powders cannot be properly melted and deposited even in high enthalpy plasma jets. Instead, carbide particles are embedded into easily melted binder metals with high ductility such as Ni, Co, Cr and their mixtures and alloys, respectively. Such composite coatings are frequently called cemented carbides or cermets. While their original use was to produce cutting tools they now enjoy wide application as surface layers to protect an extraordinarily wide range of machinery and tools from wear, erosion and corrosion. The coating techniques being applied comprise conventional flame spraying, high velocity oxyfuel (HVOF) techniques and their variants (D-GunTM, Gator GardTM, Jet KoteTM), arc spraying, atmospheric (APS) and low pressure (LPPS) plasma spraying, reactive plasma spraying, underwater plasma spraying (UPS), laser spraying, suspension plasma spraying (SPS), thermal plasma chemical vapor deposition (TPCVD), and more.

However, in many applications cemented carbides do not stand up well to chemical degradation at high temperature, in particular in a steam environment, due to decarburization, oxidation and matrix-alloying under formation of η -carbides. In these cases, the material of choice may be an oxide ceramic coating, most frequently alumina and chromia, and their modifications and composite formulations. However, the advantage of considerable increase in chemical and thermal resistance is counterbalanced by the disadvantage of generally low values of the coefficients of thermal expansions, and thermal conductivity, as well as in particular, mechanical strength and fracture toughness. Also, the adhesion of such oxide coatings to a metallic substrate is compromised by the non-metallic bonding character of oxides. Hence suitable bond coats may be required as well as carefully engineered and increasingly sophisticated graded and duplex structures (see, for example [1]).

Metallic coatings are, in general, easy to apply to other base metal surfaces usually by flame spraying, wire arc spraying, or HVOF deposition. However, high melting refractory metals such as W, Mo, Ti, Cr, Nb or Ta require APS or LPPS techniques. While superalloys such as Inconel, Hastelloy and NiCoCrAlY-type alloys can easily be sprayed

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by HVOF, utilization of low pressure plasma spraying (LPPS) is recommended for the latter to avoid undue oxidation.

The patent review presented below does not consider the rapidly growing field of cold gas dynamic spraying (CGDS) as well as diamond and diamond-like carbon (DLC) films and coatings. Moreover, a review of an extremely quickly developing field such as that of surface engineering by thermally sprayed coatings can by no means be exhaustive: many hundreds of novel patents emerge every year of which a substantial portion are concerned with the subject matter dealt with in this contribution. Attempting to consider all novel findings is akin to shooting at a moving target. Hence, the review presented below is just a snapshot of the vast landscape of evolving thermal spray technologies applied to surface protection against wear and corrosion.

THERMAL SPRAYING - THE PHYSICS BEHIND

Thermal spraying is a rapid solidification technology during which material introduced into a combustion flame or a plasma jet is melted and propelled against a surface to be coated. The technology is versatile: any thermally reasonably stable metallic, ceramic or even polymeric material with a well-defined melting point can be coated onto nearly any surface. However, in praxis many limitations persist related to high coating porosity, insufficient melting of particles, impaired development of splats, insufficient adhesion to the substrate, occurrence of residual coating stresses, and line-of-sight technology.

In the following paragraphs only the two most popular thermal spraying techniques will be considered: high-velocity flame spraying (HVFS) and atmospheric plasma spraying (APS). Its limitation to electrically conducting wire feedstock notwithstanding, electric wire arc deposition can still be found in low-tech industrial applications as an economic, fast and safe coating process.

High Velocity Flame Spraying

In the HVFS process, a fuel gas (propylene, acetylene, kerosene *etc.*), and oxygen (HVOF) or air (HVOF) are mixed under pressure and ignited in a combustion chamber. Powder particles are injected either radially or axially into the center of the combustion chamber by a stream of pressurized carrier gas, in most cases nitrogen. Ensuring stoichiometric combustion the flame temperature is around 3,000°C. The high-temperature gas stream is directed through a deLaval-type nozzle and, according to Bernoulli's principle, the constriction of this converging-diverging nozzle profile leads to an acceleration of the gas stream up to velocities in the neighborhood of 7 Mach. The physics behind this process is exactly the same as encountered in the gas turbine of a supersonic aircraft. Hence research and design of aerospace gas turbines have profoundly affected the construction and recent improvement of HVOF equipment.

The Mach number M is defined as the ratio of the actual gas velocity (v_g) to its sonic velocity (c): $M = v_g/c$ whereby $M < 1$ is referred to as subsonic flow, $M = 1$ as sonic (critical) flow, $1 < M < 5$ as supersonic flow, and $M > 5$ as hypersonic flow. The speed of sound c is given by $c = \sqrt{\gamma \cdot RT}$, where γ is the ratio of the specific heats, C_p/C_v . On

exit from the deLaval nozzle the gas stream expands during release of the high static pressure inside the nozzle. Hence expansion (rarefaction) and compression (shock) waves interact in a complex pattern, yielding wave forms akin to so-called N-type shock waves, commonly called 'shock diamonds' [3]. While the shock front is characterized by a decrease of the Mach number M , an increase in the static pressure, and a loss of the total gas pressure, the areas of the shock diamonds show an increase of M , a decrease of the static pressure and a constancy of the total pressure [2]. Hence the shock diamonds are isentropic expansion fans governed by Prandtl-Meyer flow [4]. They continue in an abated fashion along the gas jet until damped out by viscous action.

The condition under which the gas velocity v_g equals the sonic velocity c ($M = 1$) is called the critical state. HVOF gun nozzles are designed in such a way that maximum gas speeds and maximum gas mass flow rates can be achieved. The critical gas mass flow rate m_c at $M = 1$ is associated with likewise critical gas density ρ_c , critical gas velocity v_c , and critical orifice area A_c as well as critical gas pressure, P_0 and critical gas temperature T_0 . Then

$$m_c = \sqrt{(\gamma/R)[2/\gamma+1]^{(\gamma+1/\gamma-1)} \cdot [P_0 A_c / \sqrt{T_0}]}$$

From this equation, it is evident that an increase in the pressure decreases the temperature and vice versa [2,3]. Hence, a balance has to be attained between pressure and temperature to yield the maximum gas mass flow rate.

The HVOF spray equipment comes in two variants: the HVOF Diamond Jet (DJ) gun whose name is being derived from the readily observable shock diamond pattern in the exiting gas stream, and the HVOF Continuous Detonation Spraying (CDS) configuration.

Atmospheric Plasma Spraying

Plasma spraying can be conveniently described as a connected energy transfer process, starting with the transfer of electrical energy from an electric d.c. potential field to a suitable gas forming a plasma by ionization, proceeding with the transfer of thermal energy and impulse (heat and momentum transfer) from the plasma to the injected powder particles, and concluding with the transfer of thermal and kinetic energy from the particles to the substrate to be coated [1].

The plasma originates from ionization in an electric potential field of a suitable gas, preferentially argon or nitrogen. Hence plasmas by definition consist of positively charged ions and electrons but also neutral gas atoms, and photons. Moving charges within the plasma column induce a magnetic field B perpendicular to the direction of the electric field characterized by the current j . The vector cross-product of the current, $[j \times B]$ is the magneto-hydrodynamic Lorentz force whose vector is mutually perpendicular to j and B . Hence an inward moving force is created that constricts the plasma jet by the so-called magnetic or z -pinch [5]. In addition to the magnetic pinch, there is a thermal pinch that stems from reduction of the conductivity of the plasma gas at the cooled inner wall of the anode nozzle leading to an increase in current density at the center of the jet. Hence the charged plasma tends to concentrate along the central axis of

the plasmatron thereby confining the jet. As the result of these two effects, the pressure in the plasma core increases drastically and as a consequence the jet is blown out of the anode nozzle of the plasmatron with supersonic velocity.

A portion of this supersonic velocity will be transferred to the injected powder particles, i.e. the powder particles will gain acceleration from the plasma jet by momentum transfer. Also, a large part of the (electric) energy spent on ionization of the plasma gas will be recovered by recombination in the form of heat. Hence the powder particles accelerated by momentum transfer along a trajectory in the jet will be heated by the hot plasma.

The more or less liquid droplet will impact the surface to be coated, and splash across the already deposited and frozen splats. The roughness of the surface determines to a large extent the solidification kinetics as the size and morphology of the newly arriving particles do.

The selection of the proper intrinsic (plasma power, argon gas flow rate, auxiliary gas flow rate, powder carrier gas flow rate *etc.*) and extrinsic (spray distance, powder feed rate, powder grain size, particle morphology, surface roughness *etc.*) plasma parameters is crucial for sufficient powder particle heating, flow and surface wetting on impact, and hence development of the desired coating porosity and adhesion to the substrate.

The heat transfer from the molten particle to the solid substrate follows the generalized heat transfer relation expressed by the simplified Fourier equation

$$\text{div grad } \Theta - (1/a) (\partial\Theta/\partial t) = 0$$

where Θ = temperature, a = thermal diffusivity, and t = time. The kinetic energy acquired by the particle will cause the splat to deform on impact hereby creating a shock wave moving with supersonic speed into the solid substrate. The ratio of deformation $\xi = D/d$ (D = splat diameter, d = original particle diameter during flight) depends on many parameters. Under simplifying assumptions the flattening ratio can be estimated using the semi-quantitative Madejski splat-quench solidification model $\xi = D/d = A \cdot (\rho \cdot v / \mu)^2 \approx Re^2$, with Re = Reynolds number, ρ = density, v = impact velocity, and μ = viscosity of the melt [6].

While in a dilute situation, *i.e.* low-plasma loading conditions particle movement, and momentum and heat transfer can be considered a ballistic process without particle interaction, dense loading conditions appear to change drastically both the flow and temperature fields in a plasma jet. As such dense loading conditions are being realistically selected for economic reasons during industrial plasma spraying, the impact of high powder feed rates on melting and spreading behavior of the particles has to be considered. With increasing powder feed rates both momentum and temperature of the plasma will decrease

Larger particles or the solidified part of an impacting particle can shatter on collision with the substrate surface owing to differential pressures across the particle as the leading and the trailing faces are subject to different dynamic pressures. When the dynamic pressure exceeds the yield strength of the solid material fragmentation occurs. However, fragmentation is not confined to particle impact. Using

fractal analysis it has been observed that fragmentation may already occur in-flight along the particle trajectory when large thermal stresses develop owing to limited thermal conductivity within the particle [7].

FEEDSTOCK MATERIALS

Today many feedstock compositions are already commercially available for a broad range of applications. They can be utilized as powders, solid wires, rods or filled wires. Novel compositions emerge tailored to respond to the shifting emphasis from purely structural coatings devoted to protection against mechanical wear, and chemical and electrochemical corrosion towards sophisticated functional coatings serving as thermal and chemical barrier coatings, electro- and photocatalytically active coatings, and bio-medical coatings for human implants.

Powder Feedstock Materials

Metals and Alloys

Films of high temperature resistant chromium oxide were produced on alloy powders of composition MCrAlX ($M = \text{Co, Ni, Fe; } X = \text{Y, Hf, Ta...}$) by treating them with an aqueous solution of phosphoric acid and chromic acid [8]. HVOF thermal spray powders useful as overlay coatings and bond coats for zirconia-based thermal barrier coatings were developed within the compositional system MCrAlY-X ($M = \text{Ni, Co, Fe; } X = \text{Hf, Re, La, Ta; } Y > 1 \text{ wt } \%$) to improve the formation and adhesion of protective oxides scale [9]. Metallic spray powder for high corrosion resistance, in particular to produce APS, LPPS and HVOF coatings against attack by sulfur, vanadium and sodium contained in heavy oil and released during combustion in gas turbines were produced by gas atomization to consists of 45-60 wt% chromium, 5-15 wt% aluminum, 0.5-10 wt% zirconium, balance cobalt or iron, or both [10].

Co-Fe-based alloy powders containing carbon were designed for wear-resistant HVOF coatings whereby the mass ratio carbon/cobalt + iron is 2% or higher [11]. Powders for highly resistant coatings containing either Mo, B, Co and Cr, or Mo, B, Ni and Cr (typical composition: 30-70 wt% Mo, 5-12 wt% B, 10-40 wt% Co, 15-25 wt% Cr, < 1wt% C) were manufactured by a multistep process involving wet mixing of powders, spray drying or granulation, sintering, and classifying [12]. Ni-Al powders with minor additions of rare earth elements, chromium or zirconium with outstanding resistance against thermal barrier coating spallation were invented for application in gas turbine engines [13].

Metal powders comprising pre-alloyed iron-base powder particles diffusion-alloyed with Mo were developed for coatings on aluminum substrates. These powders show less segregation than previously used ones and also require less Mo to attain the desired properties [14].

Hard films were developed by nitriding of iron powder to create thermal spray powders with improved properties. The iron powder was charged into a thermal plasma while contacting the strongly luminant part of the plasma containing nitrogen with the substrate [15,16].

Carbides and Cemented Carbides

Corrosion resistant cemented carbide spray powders were formulated consisting of 30-60 wt% tungsten, 27-60 wt% chromium, 1.5-6 wt% carbon, and 10-40 wt% nickel + cobalt and manufactured by inert gas (Ar) atomization at a typical temperature of 1600°C. Higher carbon contents beyond 6 wt% lead to increased processing temperatures and thus difficulties during atomization [17]. A method to produce WC-based powders with baseball shape was developed involving mixing of WC, Co or mixtures of Co and Cr with hexane and paraffine wax, wet grinding, spray drying, sintering and classifying [18].

Powders to deposit coatings with extremely high toughness and impact resistance were formulated consisting of 75-95 wt% of WC and at least one of several chromium carbides (Cr₃C₂, Cr₇C₃, Cr₂₃C₆) and 5-25 wt% of a metal phase made of Ni or Ni alloy powder [19].

Powders for HVOF and detonation spray coatings with high cavitation erosion and slurry erosion resistance were developed containing WC, chromium, nickel and chromium carbide that show high compression strength in the range of 400 to 900 MPa [20]. Similarly, cermet powders consisting of ≤ 92 wt% WC, ≥ 8 wt% Co, Ni or Cr were tested for wear protection application [21]. However, the metal contents given as 8 wt% in WC-based cermets [21] as well as 5 wt% in Cr₃C₂-based cermets reported in Ref. [19] are just claims-related lower cutoff values. Indeed, powders with such low metal contents are difficult to spray by HVOF and result in brittle coatings with inadequate values of wear resistance, fracture toughness, and adhesion. Better performing coatings should have at least 10 wt% metal content.

High temperature wear protection can be provided by coatings produced from powders consisting of high-rhenium containing materials, for example carbides of the 5th and 6th group of the PSE as well as Al₄C₃, B₄C, SiC and carbonitrides cemented with either Ni or Re (> 25 wt%). The mixed precursor powders were sintered in two steps including consolidation by hot isostatic pressing [22].

Thermal spray powders for high temperature wear and erosion protection were developed based on SiC with addition of Zr-, Ti- or Hf borides. Such powders can be deposited without decomposition on metallic or nonmetallic substrates using a plasma power of 80 kW [23].

Ni- or Co-based selffluxing alloy powders containing precipitated chromium carbide (30-42 wt% Cr, 2-4 wt% Si, 1.5-4 wt% B, 0.5-2 wt% Mo, 2.5-4.5 wt% C; Ni, Co bal.) were developed by an atomizing process. Coatings deposited with these powders show excellent high temperature hardness, wear resistance, and corrosion resistance, and are also resistant against thermal cycling [24,25].

Ni alloy/chromium carbide thermal spray powders with a high crushing strength of 150-250 MPa were invented whose grain size distribution was $d \leq 10 \mu\text{m}$: < 1 wt%; $d \leq 38 \mu\text{m}$: < 7 wt%. Coating deposited with this powder show adequate abrasion wear resistance [26].

Ni-Cr alloy + Mo powders containing chromium carbide or oxide with a solid lubricant added (at least one of CaF₂,

MnS, MoS₂) and a composition of 10-40 wt% Ni-Cr alloy, 30-70 wt% Mo, 3-40 wt% ceramic were designed for wear-resistant sliding members of various machinery [27].

Thermal spray powders consisting of a Cr-Fe-based alloy including ≥ 2 wt% carbon were found to be suitable for HVFS coatings [28].

Oxides

Abrasive particles of Al₂O₃-SiO₂ composition were produced by injecting precursor powders of alumina and silica into a flame or a plasma jet and quenching the droplets produced [29]. Yttria-alumina composite powders with crushing strength of at least 15 MPa and an average particle size of 0.2 to 3.0 μm for plasma spray application were developed using granulation and sintering techniques [30, 31]. Powders containing granulated and sintered yttria particles or deposition of coatings with excellent plasma etching resistance were produced in air or oxygen. Processing in inert gas (Ar, N₂) generates lattice defects in the crystal lattice of yttria [32].

A method has been invented to produce very pure alumina powder for large-sized members of semiconductor manufacturing apparatus by thermal spraying. The method consists of fusing the precursor material, crushing, and removing impurity particles by acid cleaning, magnetic separation and calcining to burn out carbon contamination. The alumina powder has a purity of ≥ 99.9% with a Na content of ≤ 0.04% [33]. Similar spherical alumina powders with excellent moisture resistance, thermal conductivity, wear resistance, and packing properties were designed and provided with a silicon coating layer [34].

A thermal spray powder composed of zirconia stabilized with oxides of Ca, Y, Mg, Ce or Hf, zirconium silicate, and other oxides was developed that appears to be ideally suited to form a refractory oxide coating on hearth rolls for annealing steel [35,36]. Yttria-stabilized zirconia powder doped with 0.5-1 wt% Al₂O₃ was developed as a ceramic abradable seal material for clearance control of turbine blade tips and the shroud or casing in gas turbine engines [37].

Spray powders for wear resistant coatings with an essentially single phase crystalline structure consisting of 45-100 wt% chromia and 0-55 wt% α-alumina were manufactured by mixing powders of alumina and chromia, and firing the mixture at 1300-1500°C [38]. A quite similar patent was issued to the same authors later [39]. An improved powder composition was also formulated in which the volume proportion of the smaller particles (< 10 μm) was reduced [40]. Also, mixed chromia-NiO powders (Ni-Cr spinel, Ni picotite) with addition of oxides of Ti, Nb, Fe, Mn, Si, Zr as well as TiN or TiB₂ were designed for IR radiation active ceramic coatings [41]. Coatings show thermal stability up to 700°C, high thermal shock resistance, and low IR radiation attenuation in long-term use.

Yttrium oxide powders of 0.3 - 1.5 μm [42] and 2-10 μm [43] grain size and crushing strengths of 25-250 MPa and 10-40 MPa, respectively were formulated by granulating and sintering of small, primary particles.

Composite Powder Materials

Methods were invented to manufacture composite powders containing solid lubricants such as hexagonal boron nitride, calcium fluoride, graphite, molybdenum disulfide and others, inorganic binder such as bentonite, fillers such as albite, illite, quartz, alumina-silica, and metal matrix components such as Ni, Co, Cu, Fe, Al. Application of these powders include coatings for abradable seals for gas turbine engines [44-47].

TiC-based composite powders were developed that consist of two cubic hard phases constituting a core-rim structure. The hard core contains Ti and C and the rim contains an additional metal and C. These grains are embedded in a binder phase containing Ni, Co or Fe. At least one of the additional alloying elements exist either in the hard material phase, in the binder phase, or in both [48].

Composite oxide-carbide-boride powders for utilization in the aerospace industry consist of oxides of Si, Al, Al-Ti, Zr, YSZ, borides of Ti, Zr, Hf, and carbides of Si, Cr, B. The composition of the powders is tailored in such a way that it comprises an oxide matrix and at least 15 wt% of borides or carbides [49]. Mixtures of borides of Mo and Cr, and carbides of Cr and W are used to form powders whose application yields coatings with high abrasion resistance, resistance against molten metals and in particular with enhanced dross adhesion resistance [50].

Powders for production of lubricating coatings by high velocity flame spraying (HVFS) are produced in which molybdenum disulfide will be coated by an electroless plating method with metal such as Cu. The metal coating will prevent thermal decomposition of the solid lubricant [51].

To prevent corrosion of steel coatings are being proposed produced from composite spray powders consisting of a thermoset polymer such as 20-50 wt% epoxy resin and a thermoplastic material such as 10-30 wt% co-polyamide with 30-50 wt% zinc powder added. The preferred deposition method is a low temperature flame into which the composite powder is being introduced axially or tangentially [52]. Luminous glass powders can be sprayed at low temperature [53]. Also, spray powders of solid microspheres containing needle-like potassium hexatitanate has been developed for special applications [54].

Wire Feedstock Materials

A workpiece system has been invented for thermal coating or build-up welding, and for production of filler wires consisting of 10-80 wt% mixed carbides of Ti, V or W and 20-90 wt% metal matrix powder based on Fe, Co and/or Ni [55]. Composite wires for wear and corrosion resisting coatings comprising a metallic outer sheath (Cr-bearing Ni-base alloy) and an inner core composed of boron carbide and chromium carbide (1:4 to 4:1) are manufactured by conventional techniques wherein the specially formulated powder core is encapsulated by the outer sheath [56].

PROCESSING APPARATUS AND TECHNOLOGIES, AND PROCESS CONTROL

While devices and apparatus to deposit thermally sprayed coatings have enjoyed continuous development over the last

decades [1] modifications are being introduced to adapt existing apparatus to specific requirements of feedstock materials, processing technologies, and coating applications. Also requirements of statistical process control by providing on-line feedback monitoring devices are being addressed.

Processing Apparatus

An APS unit for coating deposition in the aerospace industry has been developed replacing the conventional plasma ignition by a high frequency electric spark by an electrode-less microwave ignition device [57]. To assist on-line feedback control during thermal spraying a design has been introduced in such a way that the relative position between the heating and feeder zone can be changed in the operating state (Fig. (1)) [58,59]. A different design solution is described in [60]. A detachable coupling unit connects the supply line adapter section and the base section, and includes an eccentric closure device, bayonet connector or screw. The gun modified in this way is designed for flame spraying, arc spraying or HVOF, and may also be used in detonation flame spraying [61].

To improve the operating efficiency of wire arc spraying the wire feedstock will be preheated [62].

To deliver liquid feedstock solution to the plasma jet a special device has been invented as shown in Fig. (2) [63].

Spraying powder can be supplied continuously by a deLaval nozzle characterized in that metal particles atomized by a supersonic gas stream or a laser device are cooled to a solidified or semi-solidified state [64,65].

A thermal spraying device (Fig. (3)) has been described comprising an endpiece (1) housing the cathode (3), the anode (4), the annular space (5) separating the electrodes, and a gas injection opening (12). A frame element (6) attached to the endpiece carries an outlet (7) of which the jet is directed towards a substrate (11). The frame element projects in the jet ejection direction from the endpiece (1) that at least partly surrounds a jet zone extending from the endpiece, and that presents an inner circumference that is larger than the inner circumference of the outlet (7). The powder port (10) is arranged on the inner periphery of the frame element (6) at a distance from the outlet (7) of the endpiece (1) as seen in the jet ejection direction. There also exists an additional port for introducing pressurized gas (15) into the plasma jet attached to a gas channel (13) and a through hole (14) [66].

A method was developed to inject micro- to nano-sized particles suspended in a liquid preferentially axially into a thermal spray apparatus. The method allows complete entrainment of the droplets in a high temperature gas stream, while the injection orifice remains potentially blockage-free for long periods of operation [67].

A HVOF gun was invented by Rusch *et al.* [68] that generates a means for turbulent atomization and that uses one or more jets as injection ports for liquid fuel and oxygen to improve the combustion, using preheated oxygen or air to improve vaporization prior to combustion of the fuel.

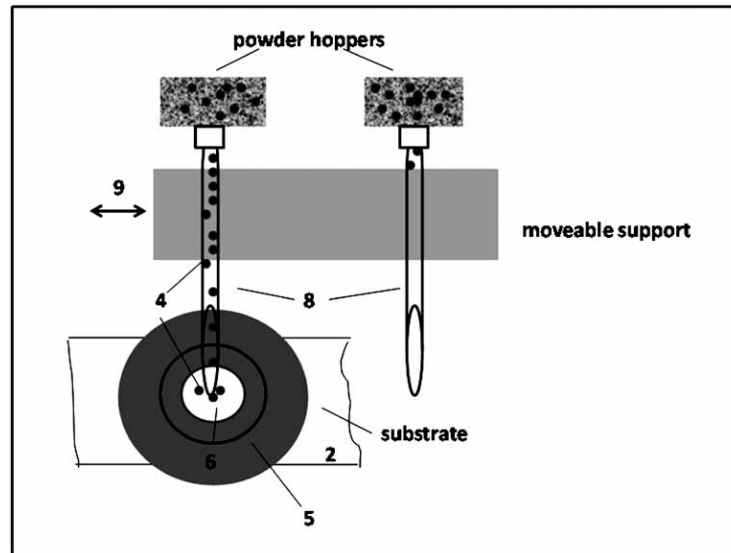


Fig. (1). Thermal spray device for continuous alteration of the relative position between target and powder feeder during operation (2 substrate surface, 4 coating powder, 5 spray gun, 6 heating zone, 8 powder feeder, 9 relative position) [59].

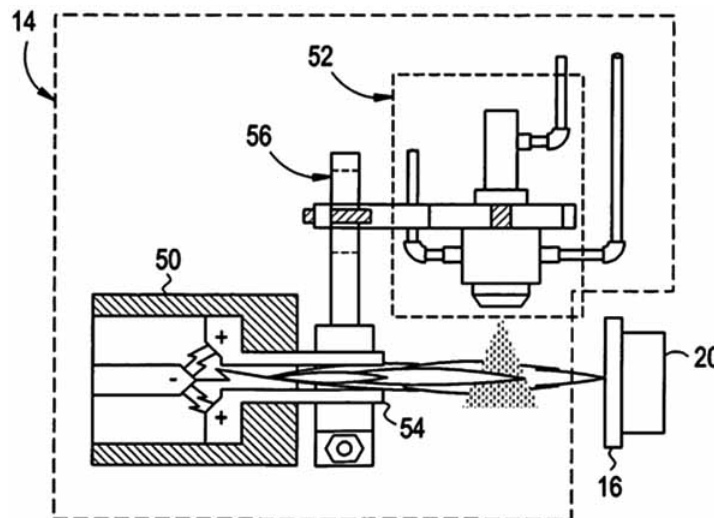


Fig. (2). Apparatus for delivery of a precursor solution to a plasma spray operating unit (14 application system, 16 substrate, 20 substrate holder and heat sink, 50 plasmatron, 52 liquid injector, 54 anode nozzle, 56 support) [63].

PROCESSING TECHNOLOGIES

A gas shroud-HVOF (GS-HVOF) technique was developed to deposit corrosion resistant austenitic metallic coatings on Mo-bearing stainless steels [69]. Duplex coatings of Al- and Ti oxide, and Cr- and Ti oxide were developed to result in two contiguous micro- and nano-structural states. Deposition techniques include plasma spraying whose parameters were adjusted in such a way that the resulting coatings have at least a nano-structured state and a larger scale state [70].

High velocity air fuel spraying (HVOF) was found to be superior to conventional HVOF spraying to produce erosion resistant WC-CoCr coatings as HVOF reduces carburization and yields coatings with limited dissolution of the WC grains in the metallic matrix thus promoting higher erosion resistance (Fig. 4) [71].

A technology was invented to embed hard metals and/or ceramics by thermal spraying into a carbon layer produced by pyrolysis of organic materials including recycled waste materials to yield coatings for high performance compounds [72].

Substrates to be coated by thermal spraying have to be roughened routinely for the deposited splats to adhere tightly to the surface asperities. This is normally being done by grit blasting. A novel way to roughen a surface prior to spraying was invented by which simple cutting or grinding tools are being used to produce an average surface roughness of 2-10 μm . Optimum splat size was found to be between 10,000 and 100,000 μm^2 [73].

A technology to improve the rapid prototyping process was described by [74] to yield metallic or ceramic coatings

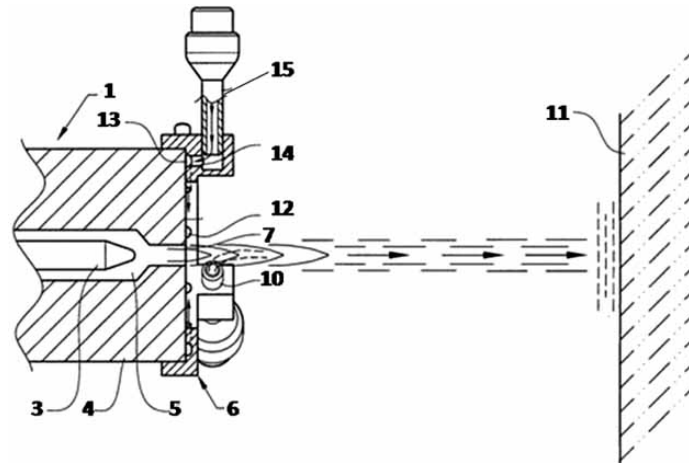


Fig. (3). Plasma spray nozzle and feeder arrangement as proposed by [66]. For explanation of numbers see text.

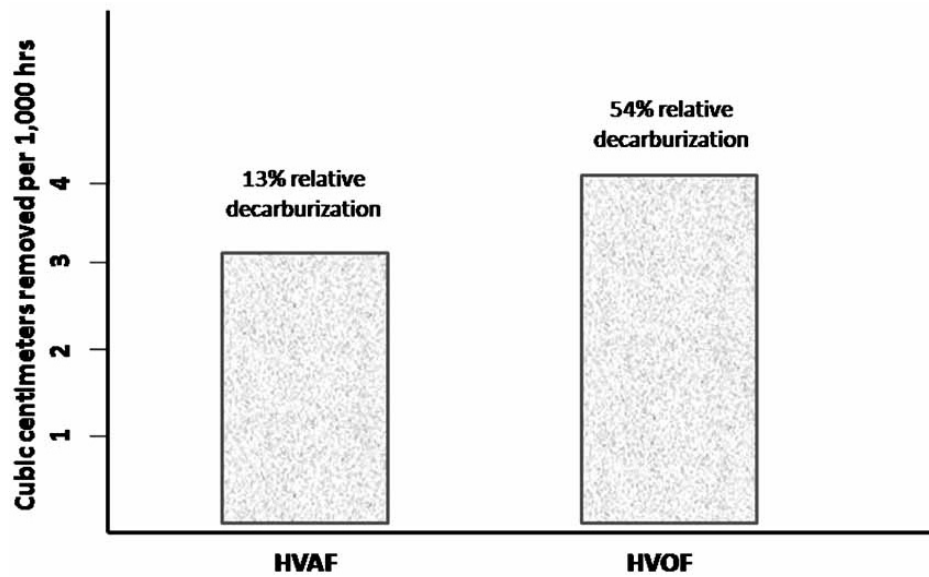


Fig. (4). WC-CoCr coatings deposited by HVOF shows higher erosion resistance compared to coatings produced by HVOF [71].

deposited by thermal spraying onto an intermediate layer of Cu or Ni produced by CVD, PVD or laser technique.

Wear resistant coatings containing Fe, Mo and B are being deposited by conventional thermal coating methods onto workpieces to be protected and subsequently fused by an arc lamp [75].

Hard coatings of carbides, borides, and nitrides have been deposited by high frequency inductive plasma spraying on fiber reinforced composite materials such C/C or C/C-SiC materials to counteract the corrosive and erosive action of hot gasses and to produce radiation guides. Useful working gasses are Ar and mixtures of Ar with He or H₂. The advantage of the proposed thermal spraying method is that the lower particle velocities obtained will minimize the damage inflicted on the substrate. Figure (5) shows a schematic rendering of the apparatus used to achieve the proposed advantages [76]. Powders (A) as well as liquid suspensions (B) can be fed into the r.f. plasma column to adopt the thermal plasma chemical vapor deposition (A) or suspension plasma spray (B) modes [77].

To repair and resurface worn machinery parts a method has been proposed that involves application of high density coatings of the same composition as that of the damaged substrate by HVOF or detonation gun techniques [78].

Additional information on process devices and thermal spraying equipment can be found in patents listed in [79-88]. Recent patents on processing technologies and specific inventions are collected in [89-97]. As these patents describe very special and generally only incrementally improved inventions they will not be elaborated on further.

Process Control Devices

To monitor on-line the thermal spray process, the radiation produced by the plasma is recorded by a glass fiber waveguide and fed into the receiving unit of a particle flux counter or a spectrometer as shown in Fig. (6) [98].

Quality assurance during thermal spraying is being provided by means of computer processing or encoding of digital images. The process involves recording, controlling

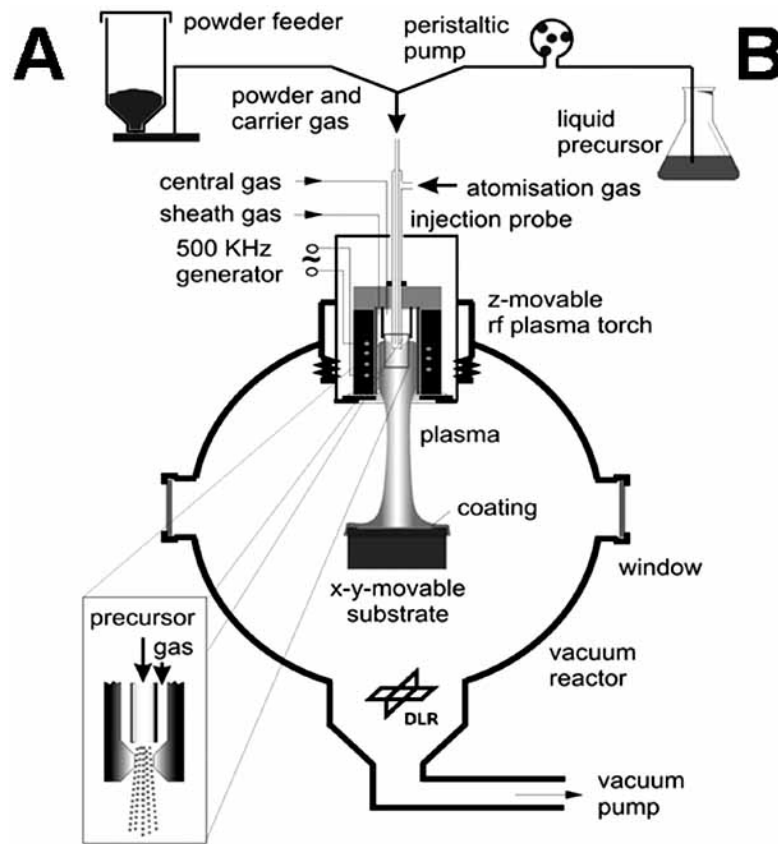


Fig. (5). HF induction plasma spray chamber and precursor feed configurations A (for TPCVD mode) and B (for SPS mode). Adapted from [76].

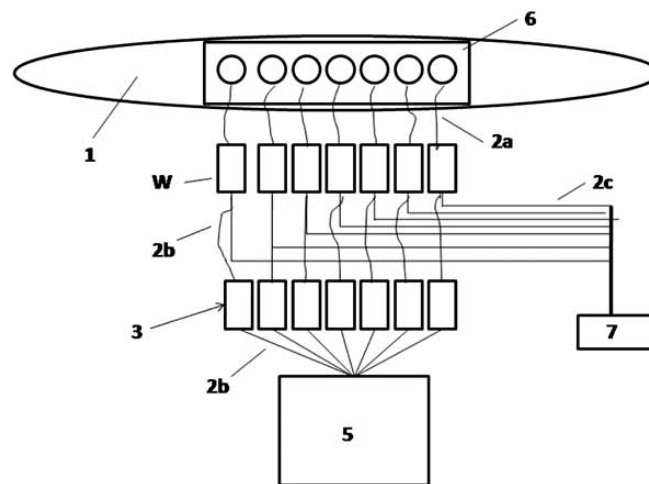


Fig. (6). Arrangement for monitoring the thermal spray process (1 plasma, 2 optical waveguides, 3 spectrometers, 5 processors to record the current state of the systems, 7 particle flux counter, W optical splitters) [98].

and monitoring through a digital camera whose images are analyzed and characterized for connecting regions of similar intensities with symmetrical flat geometric shapes [99].

A process and device for determining the quality of thermally sprayed coatings by spectral analytical means (Echelle spectrometer) has been invented that determines the degree of mixing of the deposited coating materials with the base material. This can be determined by the analysis of the

radiation/illumination given off during the process or also by a specially produced plasma, on the surface of the applied material [100].

Non-destructive measurement of adhesion of coatings thermally sprayed by APS, HVOF, LPPS, electric wire arc spraying and other techniques was reported through detecting and recording adhesion fault regions along the bonding interface by an eddy current probe. The test object was a

stationary seal of a gas turbine coated with a thermal barrier coating consisting, for example of NiCrAl. A pulsed eddy current of 500 kHz was used [101].

On-line feedback control is provided by a device invented by Vardelle and Boussoutrot consisting of a sensor designed to measure the characteristics of the plasma jet by a camera and a pyrometer. The data gathered are being analyzed by a computer and a signal is transmitted to a control box to correct and reset the operating parameters of the plasmatrone [102].

COATING COMPOSITIONS FOR WEAR PROTECTION

Metals and Alloys

Wear resistant coatings for work machines were invented consisting of fusion coats including combinations of Fe, Mo and B that are being applied by thermal spraying techniques or chemical or physical processes to surfaces of high-, medium- or low carbon steels. The powder or wire feedstock may be melted by an electric arc (two-wire electric arc spraying) or a non-transferred or transferred plasma spraying process or a high velocity oxyfuel (HVOF) combustion process [75].

Wear and erosion protection coatings for components of steam turbines, gas turbines and hydroelectric generating turbines comprising α - β Ti alloys, near β -Ti alloys or β -Ti alloys were deposited by plating, ion plasma deposition or plasma spraying onto Fe-, Ni-, Co- or Ti-based alloy substrates [103].

Caterpillar Motoren GmbH, Kiel, Germany invented a process to manufacture valve components by coating valve elements with a partially melted mixture of Ni, Cr, B and Si as well as Mo known to be a component of solid lubricating materials [104].

Bearings, bushings, coupling and rollers subject to abrasive wear in contact with molten Al and Zn can be coated with high density refractory metals such as group Vb, VIb and VIIb transition metals, preferably Mo, W and their alloys [105].

To combat wear and corrosion of vehicle wheels made of forged Al, coatings of Ni-based superalloys or stainless steel were deposited using thermal spraying processes [106].

Wear and seizure resistant coatings for sliding portions of engines such as faces of the cylinder bore were formulated consisting of an APS polyphase mixed structure with an Fe-type portion, a Mo-type portion and a soft graphite phase. Alternately, a hard phase such as chromium oxide or chromium carbide can be included in the metallic portions of the multiphase coating [107].

Thick metal films can be deposited by low pressure plasma spraying (LPPS) onto carbon-based composite materials to impart heat resistance and excellent welding properties. The carbon composites can be manufactured by impregnating PAN fibers by pitch or phenolic resins, carbonization and high temperature baking. Then a thin (5-20 μm) Ni or Ag-Ti alloy brazing material will be applied to the carbon composite base materials. The top layer consists of a thick Nb, Ta or Re metal coating (100-1,000 μm) [108].

Carbides

Sliding components such as piston rings of internally combustion engines can be protected from excessive wear by composite coatings consisting of chromium carbide particles ($\leq 5 \mu\text{m}$) dispersed in a Ni-base matrix such as NiCr alloy or NiCr/Ni metal. Such protective coatings show excellent resistance against abrasion and peeling as well as anti-seize properties [109].

Coatings were developed to counteract impact peeling by creating a laminated arrangement of base materials with specific Vickers indentation hardness, bond or undercoating with adjusted microhardness, and a hard top coat consisting of WC cermet [110].

For durable walls of plasma reactors for dry etching with, for example BCl_3 , a plasma-sprayed coating consisting of boron carbide, in particular B_4C was developed on Al metal [111].

A high velocity air fuel (HVOF) thermal spray process was used to deposit erosion resistant coatings for hydroelectric turbine components. The coatings consisted of WC grains ($< 2 \mu\text{m}$) embedded in a matrix of CoCr (4-12 wt% Co, 2-5 wt% Cr, bal. WC) [112].

Excellent cavitation erosion protection is being provided by WC+Cr grains embedded in a Co-based matrix or WC+chromium carbide grains in a Ni-based matrix. The useful grain size of WC was given as 3-9 μm , that of chromium and chromium carbide as 2-50 μm [16].

Wear and corrosion resistant hard coatings were applied to vehicle wheels made of Al. The coatings consisted preferably of WC/Co- or WC/Cr cermets, or Al and Si carbides [106].

To improve the performance and longevity of piston rings coatings comprising chromium carbide particles ($< 5 \mu\text{m}$) in a Ni or NiCr alloy matrix were deposited by HVOF/HVOF technique. Piston rings coated in this manner showed excellent wear-, scuffing- and peeling resistance during service in internal combustion engines [113].

The wear resistance of blades for cutting and slicing paper in fast moving printing rolls or similar applications is being improved by an intermediate edge deposit that underlies a hard top coating of carbide, cermets or a combination thereof. The intermediate layer consists of NiCr with or without embedded stabilized zirconia particles and functions to alleviate stresses introduced by different thermal expansion coefficients between the blade base material and the wear resistant carbide top coating [114].

Duplex coatings consisting of a first layer of Ni- or Co-base alloy and a second layer of hard materials containing cemented carbide were invented for wear and corrosion protection of pump vanes. The functions of the first layer include those of a barrier layer against diffusion of carbon from the second layer into the substrate material. An example is given in that the first layer consisting of a NiCrMo alloy is being applied by a plasma transferred arc welding process and a second layer consisting of a Co-cemented hard carbide coating by the same technique [115].

Oxides

Wear resistant ceramic composite coatings comprising oxides of Si, Al, Ti, Zr and Y were developed for application in the aerospace industry, frequently in combination with borides of Ti, Zr and Hf as well as carbides of Si, Cr and B [36].

Coatings containing yttrium oxides as main component for application in plasma etching devices used in semiconductor industry were invented by Kitamura *et al.* [116] and the etch rates of such coating in contact with a CF₄ plasma described.

Mitsubishi Heavy Industries Ltd. invented a process in which rotor couplings of generators and steam turbines for power generation equipment requiring wear protection and electrical insulation were flame-spray coated with alumina over a NiCr bond coat likewise applied by flame spraying. To further reduce sliding resistance the alumina coating can be coated with a silicone resin [117].

Composite Coatings

Thermally sprayed coatings comprising specific boride, nitride and oxide ceramics in conjunction with matrix metals show excellent wear-, build-up- and thermal impact resistances when applied to hearth rolls for conveying steel plate arranged inside a continuous heat treatment furnace [118].

Composite chromium nitride, carbide and silicide coatings were deposited by HVOF and plasma powder spraying onto wear-prone parts such as piston rings whereby the ratio of the hard ceramics and the NiCr alloy matrix varied between 1:1 and 9:1 for CrN/NiCr coatings and between 1:1 and 99:1 for CrC/CrSi (75-95% Cr, 2-15% Si, 1-10% C) - NiCr alloy composite coatings [119].

COATING COMPOSITIONS FOR CORROSION PROTECTION

Metals and Alloys

Corrosion by chloride-containing agents of reinforcing metal bar and wire in concrete building material constitutes a serious problem. A patent has been filed by Eltech Systems Corp. to address this problem by thermally coating the concrete with corrosion-resistant metals such as titanium and a subsequent anodical activation. The thickness of the coating is between 10 and 100 μm and its porosity adjusted to 5-30%. Under such conditions the corrosion rate was found to be below 0.05 mils/year (1.3 μm/year) [120].

Coatings of Al-Mg alloy (1-80 wt% Mg, preferentially 3-30 wt% Mg) of 100 to 1,000 μm thickness were deposited on aluminum heat transfer tubes of liquid natural gas (LNG) vaporizers to provide a sacrificial coating for corrosion protection against sea water of said tubes produced by Kobe Steel Ltd., Japan [121].

Rotor and stator blades of gas turbines composed of Ni-based superalloys such as Inconel and subjected to corrosion can be suitably protected by duplex diffusion barrier coatings consisting of a stress relief layer of Re alloy and a layer of σ-phase ternary ReCrNi alloy. Such layers can be deposited by various techniques including thermal spraying, chemical

vapor deposition, physical vapor deposition or magnetron sputtering [122].

The corrosion resistance of iron or steel can be improved by a duplex coating consisting of a layer of second metal such Ni or Cr, and a layer of an aluminide of the second metal. The first layer can be applied by electrolytic plating, electroless plating or thermal spraying, the second layer can be applied by pack aluminization or thermal spraying. The coating performance includes long-term oxidation protection and corrosion resistance for steel parts operating in a high temperature environment [123].

Thermally sprayed coatings for thermal exchange equipment such as rolled steel plates may consist of niobium (columbium) oxide and alloys such as Ni-Nb, Al-Nb and others. In particular, the coatings will provide protection against corrosive gasses such as H₂S and CO₂, and corrosive fumes of solvents and acids [124].

Corrosion-resistant coatings of water-cooled stator bar clips for electric power generators (Fig. 7) were invented consisting preferentially of Sc, Ti, Cr, Zr, Nb, Mo, Hf, Ta, W, Ni or Al and their alloys and/or oxides. The essential problem consists of corrosion owing to cooling water trapped in the concave brazing joints as shown in Fig. (7), items 46 and 50. Application of, for example a Ti coating to the sensitive areas prior to assembling the device or in

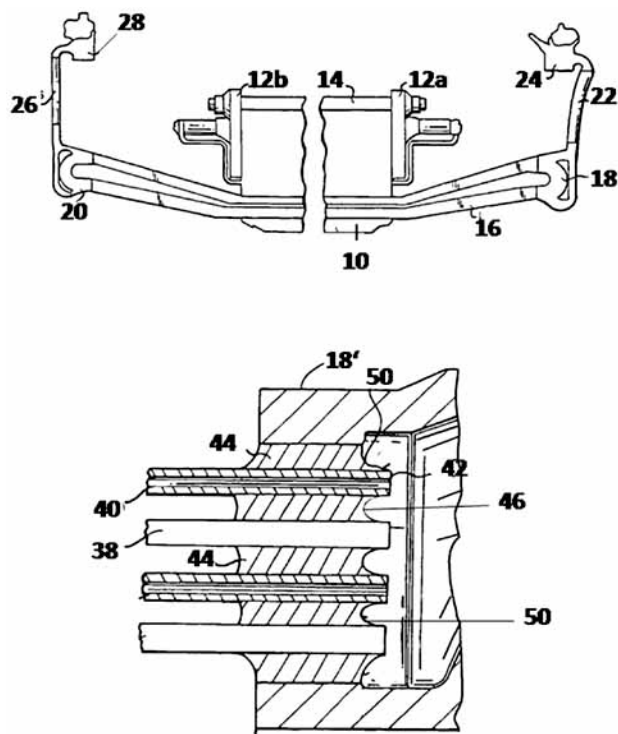


Fig. (7). Schematic view of a conventional liquid cooled stator winding arrangement (top: 10 stator core, 12a, b stators core flanges, 14 core ribs, 16 stator bars, 18 and 20 inlet and outlet end fittings, 22 inlet cooling hoses, 24 inlet coolant header, 26 outlet coolant orifice) and a conventional brace joint between stator bar strands and a hydraulic fitting (bottom: 38 solid and 40 hollow ends of the copper strands, 42 end edges, 44 braze alloy material, 46 and 50 concave pockets formed by flowing alloy) [125].

service by a specially designed pencil-type coating nozzle will provide sufficient corrosion protection to the bar clips. The application technology is not critical as a very wide array of coating methods can be utilized ranging from ion plasma deposition, sputtering or wire arc deposition to HVOF and d.c. plasma arc deposition to electroplating and electroless plating [125].

Metallic coatings for high corrosion resistance produced by APS, LPPS and HVOF processes will provide corrosion protection against attack by sulfur, vanadium and sodium contained in heavy oil and released during combustion in gas turbines. Such coatings may consist of 45-60 wt% chromium, 5-15 aluminum, 0.5-10 wt% zirconium, balance cobalt or iron, or both [10].

Carbides

The steel body of aircraft wheels (Fig. 8) can be protected from corrosion by applying HVOF technique a wear- and corrosion resistant cemented (78-90)WC(10-22)Co coating to the side portion of the wheels, and a sacrificial corrosion-resistant metallic-ceramic coating with a composition as described in [126, 127] to the body portion of the wheel [128].

Excellent corrosion protection is provided to structural machine components by thermally sprayed tungsten carbide coatings with Ni-group binder metal alloys applied to the metal base material surface [129]. However, since pure Ni does not stand up well to highly corrosive environments containing, for example chlorides in such case the metallic binder should additionally contain chemically more stable elements like Cr and Mo.

Coatings consisting of Re- or Ni-based superalloy binder metals with embedded ceramic hard particles of WC, TiC or HfC, or carbides of group IVb, Vb and Vlb, transition metal carbides, nitrides, borides or silicides were fabricated in a two step sintering process whereby the percentage of the hard phase was less than 75%. Such coatings show enhanced performance at high operating temperature in terms of hardness and strengths as well as superior corrosion and oxidation resistance [130].

Oxides

Superior corrosion protection coatings consist customarily of HVOF or plasma-sprayed chromium oxide. They are being applied when corrosion resistance is required in addition to abrasion resistance, *i.e.* in the case of strongly synergistic corabrusion. Such coatings adhere very well to most metal substrate surfaces and show exceptional hardness of 2300 HV_{0.05}. Applications abound in chemical industry as

coatings of joints in movable parts, in water pumps, steel rollers for ore classification, and smooth top coats for printing rolls. Chromia coatings are also potentially gastight as shown by the occurrence of protective oxide films against sulfidation and carburization on high chromium steel and alloys at high temperatures [7]. However, at high pressure sealing of such coatings can possibly be achieved by infiltration, for example with aluminum phosphate [131]. While during APS operations only the ditrigonal α -modification with corundum structure occurs, at reduced pressure Cr₂O₃ decomposes forming metallic chromium as well as a metastable Cr₃O₄ phase.

Chromium oxide coatings perform particularly well in ship and stationary diesel engines where a corrosive environment is being created due to the use of less expensive but lower quality diesel fuel. Serious corrosion occurs through the impurities of the fuel such as sulfur, vanadium, sodium *etc.* Erosion is also of concern because due to catalytic cracking of fuel precursors Al₂O₃-SiO₂ particles are being introduced into the diesel fuel. Thus chromia coatings are required, for example to protect valve stems of diesel engines from wear and corrosion. Such coatings must be optimized for good adherence (> 40 MPa) and maximum fracture toughness. Better coating quality can be obtained by HVOF spraying. Here micro-hardness can be routinely achieved exceeding 2,000 HV and a porosity of less than 1%, an essential requirement of anti-corrosion coatings. The hardness and the coefficient of friction can be improved by adding other components such as MoO₃. Friction coatings on braking units of transportation machines have been suggested that consist of very rough plasma-sprayed 60Cr₂O₃40 TiO₂ coatings with a very high friction coefficient of 0.8 and a porosity < 3.5%. Similar surfaces have been developed based on refractory metal carbides of Si, W, Mo, Cr, Ta, Nb, V, Ti, Zr or B to serve as gripping surfaces [132].

Given the amount of research and development performed on chromium oxide coatings it is not surprising that very few if any novel patents have emerged in the period of observation covered by this review. In contrast to this, a variety of alternative compositions have been proposed.

Rare earth (RE) oxide and rare earth-based compositions of type RE_mAl_nO_p, RE_mSi_nO_p or RE_mZr_nO_p have been deposited by low pressure plasma spraying (LPPS) to metal, alloy and ceramic surfaces without particular limitation to provide very uniform and dense highly heat-, abrasion- and corrosion-resistant coatings for a variety of industrial applications [133].

Components used as jigs made from carbon, silicon nitride, refractory metals and carbides and utilized for sinter-

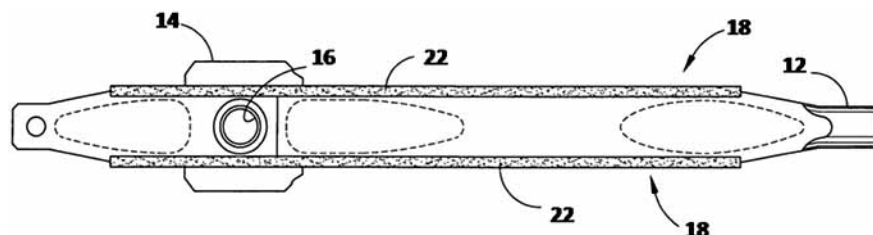


Fig. (8). Aircraft wheel rotor drive (12 end extension, 14 outboard engagement portion, 16 bolt hole opening, 18 side areas, 22 WC-Co composition) [128].

ring parts made from powder metallurgy metals, cemented carbides or ceramics in vacuum or in oxidizing atmosphere were coated with Al-, Zr- or preferably rare earth oxides having a textured surface with an embossed or slit pattern. The coatings were found to be HT-corrosion resistant and hence durable under the high temperature regime provided by this particular application [134].

Cerium (III) or (IV) oxide-containing corrosion resistant coatings were invented for application in semiconductor processing equipment [135]. The sidewalls of plasma chambers for semiconductor processing equipment were protected by a corrosion resistant coating consisting of alumina but also carbide and nitride ceramics that were deposited by thermal spraying over a Ni bond coat applied by electroless plating technique [136].

Protection against high temperature corrosion in the presence of gasses such as H₂S, SO₂, CO₂, and vapors of inorganic and organic acids can be provided by niobium oxide-based coatings or Nb alloy coatings such as Ni-Nb or Fe-Nb. The coatings will be applied by HVOF with O₂ pressure of 2.0 -4.0 kg/cm² and acetylene pressure of 0.5-1.0 kg/cm² [137].

A process has been invented by Nagara *et al.* to protect turbine components by a ceramic layer consisting of zirconium or hafnium oxide (60-98 mol%) containing 2-40 mol% structurally stabilizing oxides of Y, Ca, Sc, Mg and others. While these coatings are highly effective as thermal barrier coatings they also provide effective corrosion protection against corrosive gasses [138].

Complex yttria-alumina oxide coatings with resistance against corrosion by halogen-based gasses and their plasmas (ClF₃, NF₃, CF₄, WF₆, Cl₂, CCl₃ and others) were developed to obtain coating with high peel resistance [139].

CURRENT & FUTURE DEVELOPMENTS

Comparison of performance and properties of APS and HVOF coatings shows that the latter frequently outperform the former in terms of lower overall porosity, improved interlamellar cohesion, microhardness, and fracture toughness. Since the particles acquire comparatively more kinetic than thermal energy the amount of residual stresses in thick coatings is noticeably lower than in APS coatings or such stresses may be compressive thus being beneficial to the life time of coatings under dynamic loading. This has recently been confirmed for wear- and corrosion-resistant coatings composed of alumina and chromia [140] as well as WC-based cermets [141]. However, despite these advantages, for many applications atmospheric plasma spraying is still the technique of choice to deposit wear- and corrosion-resistant coatings in a plethora of industrial segments owing to its versatility. Indeed, the APS process develops sufficient thermal energy to melt any coating material, even the most refractory ones. For example, as reported by Ilavsky *et al.* [142] the wear resistance of 80Ni20Cr coatings deposited by APS and WPS (water-stabilized plasma spraying) was much higher than those deposited by HVOF, despite the higher porosity and substantial amount of oxides in plasma-sprayed coatings compared to the dense HVOF coatings. Presumably oxide particles act as reinforcement of the coating microstructure by creating a composite cermet structure.

Hence, both processes have their advantages and disadvantages so that the option is clearly not “APS or HVOF” but rather “APS and HVOF”, depending on the material’s selection, coating performance requirements, and economic viability.

Current and future developments, undoubtedly highlighted by a further increase in the rate of technological innovation, will likely include improved on-line real-time feedback control with close-loop strategies, intelligent statistical process control (iSPC), increased application of artificial intelligence (AI) tools and sophisticated expert systems, design of new equipment and spray powders as well as 3D-process modeling and improved understanding of the complex non-linear physics underlying the high velocity flame and plasma spray processes.

A recent account on the development of d.c. plasma spraying given by Fauchais *et al.* [143] indicates four main focus points of current and future developments:

- Process on-line control requiring correlation of particle in-flight characteristic as well as substrate and coating temperatures to thermo-mechanical and other in-service coating properties,
- Study of arc root fluctuations and their causes by experiments and 3D modeling, and relating them to structure and properties of coatings,
- Study of splat formation and layering mechanisms and their effect on the properties of splat-substrate and splat-splat interfaces, and
- Development of novel spray techniques to produce nano-structured coatings, in particular using suspension and solution plasma spraying.

These future activities will include the development of expert systems that integrate exhaustive databases with expert knowledge and practical experiences. For example, powerful software has been developed that allows the engineer to determine the best coatings for a given part or application, as well as information on how and where the coatings are being used. Process simulation including process mapping [144] plays an increasingly important role to estimate the interdependence of spraying parameters and desired coating properties as well as ever more complex modeling and numerical simulation of the generation of plasma and its interaction with materials immersed in the plasma jet. Process control, including modeling of complex plasma-particle-substrate interactions, on-line process diagnostics, and development of novel coatings with improved wear and corrosion performance are areas rich in research needs and opportunities.

In the area of high velocity flame spraying (HVFS) current developments and future trends have been identified as follows [141]:

- Development of novel high-pressure high-velocity oxyfuel (HP-HVOF) spraying equipment operating at increased combustion chamber pressure. Such equipment allows to deposit less ductile metal powders such as iron- and nickel-based alloys (AISI 446, AISI 316L) and highly oxygen-sensitive materials such as titanium

and MCrAlY with increased deposition efficiency exceeding 85% at high powder feed rates.

- Development of powder feed systems with ultrasonic assistance to establish constant and reliably controllable flow of powders with ultrafine (< 10 μm) grain size distributions. Such powders generate coatings with excellent sliding wear resistance but, unfortunately, poor abrasive wear resistance. Owing to their low surface roughness such coatings can be economically finished by belt grinding. However, the viability of the option to reduce coating costs using ultrafine powders depends on the specific tribological mechanisms of the component surfaces involved. Hence the benefits gained in terms of lowered production cost of coated parts may be outweighed by a significant decrease of component life.
- Extension of HVOF coatings to realms hitherto not achievable by this technology. For example, HVOF-sprayed cermet coatings such as 75Cr₃C₂25(Ni20Cr) can now be applied to protect lightweight aluminum components against wear without compromising their fatigue strength. Such coatings may be designed to meet today's environmental requirements for non-ferrous engine blocks, hybrid solutions for aluminum automotive engines, and coatings for engine cylinder bores for both gasoline and diesel engines [145].
- Development and implementation of test and characterization methods specifically adapted to provide increased reliability of coatings for heavy duty equipment and industrial tools.

Areas of application of plasma- and high velocity flame-sprayed coatings can be predicted by application technology mapping. Marketers look for applications of materials, and then determine the performance needs for particular applications. These data are mapped against the value-in-use estimate and the perceived customer's ability to pay as shown in Fig. (9). The military have clearly a high ability to pay for sophisticated materials and coatings, or products with a high value-in-use, for example piezoelectric and

superconducting coatings for range finders and surveillance systems. These materials also include ferroics, i.e. crystalline materials with distinct twin domain states that are reversibly orientable under appropriate driving fields, such as ferro-magnetics, ferroelectrics, or ferroelastics [146].

Titanium nitride, titanium carbide, and diamond coatings for ceramic cutting tools are high-value-added but nevertheless cost-competitive because of their superior wear performance in numerically controlled high-speed machining of tough and hard steels, and superalloys. On the other hand, heat engine components such as ceramic turbochargers, thermal barrier coatings (TBC's) and a variety of automotive sensors based on functional ceramic coatings and thin films have a low value, and the ability to pay for it by the car manufacturer is also low in order to maximize profit. New developments are presently being considered such as thick thermal barrier coatings (TTBC's) for diesel engines to replace water cooling by air cooling systems. The middle ground of Fig. (9) is occupied by wear-and corrosion resistant parts for non-automotive markets, i.e. process equipment and machinery tools. In this area a new strong driving force is evolving that is geared towards first-generation materials to improve process efficiency and overall productivity in the manufacturing and resource industries [147].

New energy systems including solid oxide fuel cells (SOFC) are high on the R&D agenda and may be close to a breakthrough to replace generation of electrical energy by conventional burning of fossil fuel. Wear and corrosion resistant coatings will be required in this field. For example, interconnects (bipolar plates) made of 94Cr5Fe1Y₂O₃ for SOFCs need to be coated with a protective layer of (La,Sr) CrO₃ that ought to prevent high-temperature corrosion by vaporization of Cr oxide from the interconnect. Future power generation by nuclear fusion will require a host of wear and corrosion resistant coatings including coatings based on B₄C for biological shielding.

Calcium phosphate-based biomedical coatings for implants [148] have a very high value-in-use as they provide

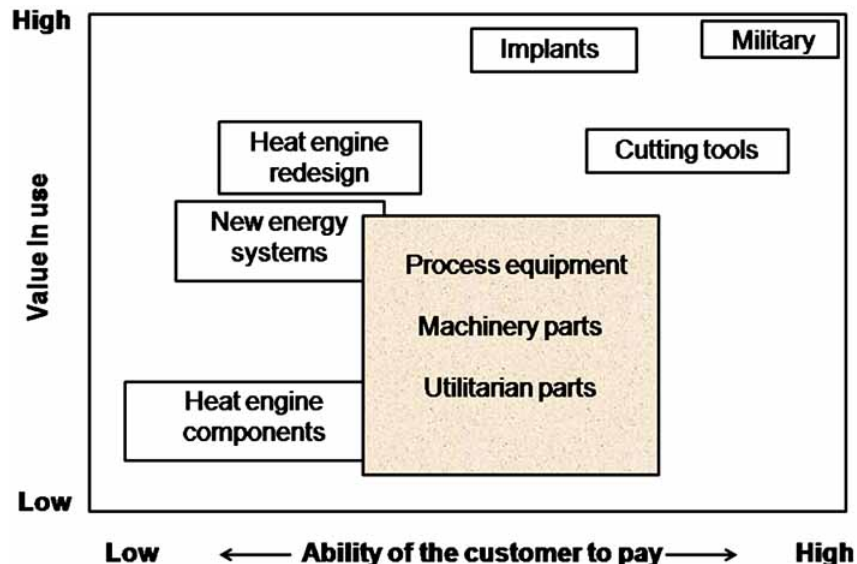


Fig. (9). Application technology mapping for coatings (adapted from [1]).

improved ability of movement and freedom from pain to patients receiving hip or knee joint implants even though the ability to pay is in many countries limited by deficiencies in the national health care systems.

In conclusion, the future of advanced materials coatings for wear and corrosion protection applied by thermal spray technologies looks very bright. However, there are still many problems to be solved, and strategic alliances of universities, research organizations, and industry worldwide are busy to address many of these areas that require improvement.

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