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A REVIEW- STUDY OF THERMAL SPRAY COATINGS FOR CORROSIVE WEAR

Prajapati Amit Kumar
M.Tech Research Scholar
LPU, Phagwara
Prajapatiamit23@gmail.com

Vaibhav Khurana
ASSISTANT PROFESSOR
LPU, Phagwara
vaibhav.17867@lpu.co.in

Abstract— Thermal spray coating process is a surface modification technique in which a coating material like cermet's, metallic, ceramic and some other materials in form powder are feed into a torch or a gun, the powder inserted into torch will be melted by high temperature developed by torch. Coating thickness can achieve by applying multiple layer of melted coated material. This papers aims at the review of various coating techniques used for the corrosive wear applications. Thermal sprayed thick (from 50 to 3000 μm) coatings, including cold spray coatings are more and more used in industry for the following reasons: (i) They provide specific properties onto substrates which properties are very different from those of the sprayed coating; (ii) They can be applied with rather low or no heat input to substrates (allowing for example spraying ceramics onto polymer substrates); (iii) Virtually any material that melts without decomposing or vaporizing can be sprayed including cermets or very complex metal or ceramic mixtures, allowing tailoring coatings to the wished service property; (iv) Sprayed coatings can be strip off and the worn or damaged coatings recoated without changing part properties and dimensions; (v) Some spray processes can be moved on site, allowing spraying rapidly big parts, which displacement would otherwise be rather long and expensive.

Keywords— Corrosive wear, Corrosion, Thermal spray, Wear.

I. INTRODUCTION

Coatings have historically been developed to provide protection against corrosion and erosion that is to protect the material from chemical and physical interaction with its environment. Corrosion and wear problems are still of great relevance in a wide range of industrial applications and products as they result in the degradation and eventual failure of components and systems both in the processing and manufacturing industries and in the service life of many components. Various technologies can be used to deposit the appropriate surface protection that can resist under specific conditions. They are usually distinguished by coating thickness: deposition of thin films (below 10 to 20 μm according to authors) and deposition of thick films. The latter, mostly produced at atmospheric pressure have a thickness over 30 μm , up to several millimetres and are used when the functional performance and life of component depend on the protective layer thickness. Both coating technology can also be divided into two distinct categories: "wet" and "dry" coating methods, the crucial difference being the medium in which the deposited material is processed. The former group mainly involves electroplating, electro less plating and hot-dip galvanizing while the second includes, among others methods, vapour deposition, thermal spray techniques, brazing, or weld overlays. This chapter deals with coatings deposited by thermal spraying. It is defined by Hermanek (2001) as follows, "Thermal spraying comprises a group of coating processes in which finely divided metallic

or non-metallic materials are deposited in a molten or semi-molten condition to form a coating”. The processes comprise: direct current (d.c.) arcs or radio frequency (r.f.) discharges-generated plasmas, plasma transferred arcs (PTA), wire arcs, flames, high velocity oxy-fuel flames (HVOF), high velocity air-fuel flames (HVAF), detonation guns (D-gun). Another spray technology has emerged recently; it is called cold gas-dynamic spray technology, or Cold Spray (CS). It is not really a thermal spray technology as the high energy gas flow is

Produced by a compressed relatively cold gas ($T < 800^{\circ}\text{C}$) expanding in a nozzle and will not be included in this presentation. Most processes are used at atmospheric pressure in air, except r.f. plasma spraying, necessarily operated in soft vacuum. Also, d.c. plasma spraying can be carried out in inert atmosphere or vacuum and Cold Spray is generally performed at atmospheric pressure but in a controlled atmosphere chamber to collect and recycle the spray gas (nitrogen or helium) because of the huge gas flow rates used (up to $5 \text{ m}^3.\text{min}^{-1}$). In the following only processes operated in air at atmospheric pressure will be considered, except when the coating material is very expensive, such as platinum that must be sprayed in a chamber to recover the overspray. The coating material may be in the form of powder, ceramic rod, wire or molten materials. The central part of the system is a torch converting the supplied energy (chemical energy for combustion or electrical energy for plasma- and arc-based processes), into a stream of hot gases. The coating material is heated, eventually melted, and accelerated by this high temperature, high-velocity gas stream towards a substrate. It impacts on the substrate in the form of a stream of droplets that are generated by the melting of powders or of the tips of wires or rods in the high-energy gas stream. The droplets flatten or deform on the substrate and generate lamellae called “splats”. The piling up of multiple layered splats forms the coating.

Thermal spray processes are now widely used to spray coatings against, wear and corrosion but also against heat (thermal barrier coating) and for functional purposes. The choice of the deposition process depends strongly on the expected coating properties for the application and coating deposition cost. Coating properties are determined by the coating material, the form in which it is provided, and by the set of parameters used to operate the deposition process. Thermal spray coatings are generally characterized by a lamellar structure and the real contact between the splats and the substrate or the previously deposited layers determine to a large extent the coating properties, such as thermal conductivity, Young’s modulus, etc. The real contact area ranges generally between 20 to 60 % of the coating surface parallel to the substrate. It increases with impact velocities of particles provided that the latter are not either too much superheated or below their melting temperature. That is why roughly the density of coatings increases from flame, wire arc, plasma, HVOF or HVAF and finally D-gun spraying and self-fluxing alloys flame sprayed and then re-fused. Also thermal spray coatings contain some defects as pores, often globular, formed during their generation, un-molten or partially melted particles that create the worst defects, exploded particles, and cracks formed during residual stress relaxation. The cracks appear as micro-cracks within splats and macro-cracks running through layered splats especially at their interfaces and tending to initiate inter-connected porosities. Moreover, when the spraying process is operated in air, oxidation of hot or fully melted particles can occur in flight as well as that of splats and successive passes during coating formation. Thus, depending on the spray conditions and materials sprayed, the coatings are more or less porous and for certain applications must be sealed by appropriate means

II. COATINGS AND CORROSION

The different types of corrosive attack, especially for coatings can be classified as (i) general corrosion, corresponding to about 30% of failure, where the average rate of corrosion on the surface is uniform and as (ii) localized corrosion, corresponding to about 70% of failures. The latter comprises: (i) galvanic corrosion occurring when two dissimilar metals are in contact with each other in a conductive solution (electrolyte), the more anodic metal being corroded, while the more cathodic one is unaffected. The electrolyte plays a key role, as well as the relative surface contact area; the smaller the anodic to cathodic area ratio is, the more severe is the anodic metal corrosion. For example the protection of low-carbon iron part from atmospheric corrosion by a coating may use either an anodic coating (nickel) or cathodic one (aluminium or zinc). In the first case no discontinuity in the coating can be tolerated, while it has no importance with cathodic coating, as illustrated in Figure 1, (ii) inter-granular corrosion, occurring when a chemical element is depleted during the coating or bulk material manufacturing, e.g. during heat treatment, (iii) pitting, which is a localized corrosion characterized by depression or pit formation on the surface. It occurs for example when stainless steel is corroded by chloride-containing solutions, (iv) trans granular corrosion is mainly due to high static tensile stress in the presence of a corrosive environment. It can be intergranular but also trans granular when cracking occurs. The coating material and its microstructure play an important role in this type of corrosion.

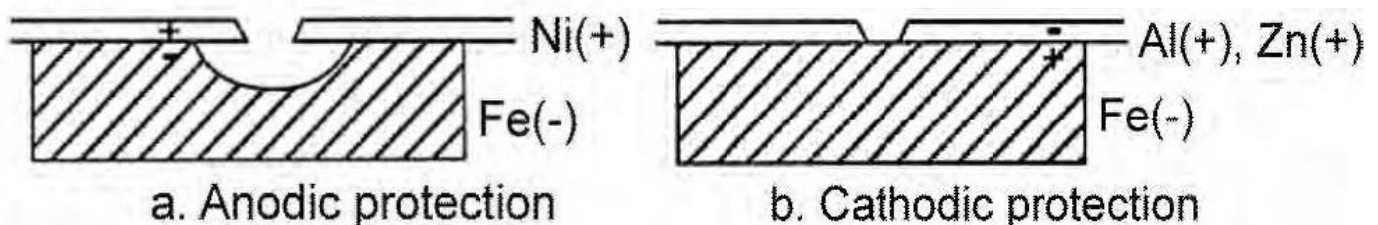


Fig. 1. Examples of protective coatings: a). Anodic (no discontinuity possible in the coating),

b). Cathodic (discontinuity possible in the coating, resulting in no corrosion of iron).

Thus coatings can be used against corrosion: (i) As sacrificial coatings (cathodic behaviour relatively to ions, for example Zn or Al on steel): the thicker they will be the longer will be the protection (typical thickness varies between 50 and 500 μm , the most frequent one being around 230 μm), (ii) As dense as possible (even sealed) if they have an anodic behaviour and used against either atmospheric or marine corrosion, and high temperature corrosion: oxidation, carburization, nitriding, sulfidation, molten salt, molten glass... Corrosive wear occurs when the effects of corrosion and wear are combined, resulting in a more rapid degradation of the material surface. A surface that is corroded or oxidized may be mechanically weakened and more likely wear out at an increased rate. Furthermore, corrosion products, including oxide particles, which are dislodged from the material surface can subsequently act as abrasive particles. Stress corrosion failure results from the combined effects of stress and corrosion. At high temperatures reactions with oxygen, carbon, nitrogen, sulfur or flux result in the formation of oxidized, carburized, nitride, sulfidized, or slag layer on the surface. Temperature and time are, then, the key factors controlling the rate and severity of high temperature corrosive attack *Chattopadhyay (2001)*.

III. COATINGS AGAINST CORROSIVE WEAR

Corrosive wear occurs when the effects of corrosion and wear are combined, resulting in a more rapid degradation of the material's surface. A surface that is corroded or oxidized may be mechanically weakened and more likely to wear at an increased rate. Furthermore, corrosion products including oxide particles that are dislodged from the material's surface can subsequently act as abrasive particles. Stress corrosion failure results from the combined effects of stress and corrosion. At high temperatures reactions with oxygen, carbon, nitrogen, sulfur or flux result in the formation of oxidized, carburized, nitrided, sulfidized, or slag layer on the surface. Temperature and time are the key factors controlling the rate and severity of high temperature corrosive attack *Chattopadhyay (2001)*.

A few examples are presented below. An important concern in the oil and gas production industry is the behavior of materials in an aggressive environment with the presence of suspended sand particles, which contribute to corrosion, erosion and overall wear of the surface. *Al-Fadhli et al (2006)* have HVOF-sprayed Inconel-625 onto stainless steel components used in oil/gas industry. Coatings were applied on three different metallic surfaces: (a) plain stainless steel (SS), (b) spot-welded stainless steel (SW-SS), and (c) a composite surface of stainless steel and carbon steel welded together (C-SS-CS). These coated surfaces were tested in a jet impingement rig under two fluid conditions: (i) free from added solids, (ii) containing 1% silica sand. The coating was found to be highly sensitive to the presence of sand particles in the impinging fluid. As the period of coating exposure to the flow of slurry fluid increased, weight loss increased significantly. This increment was dependent on the type of substrate material.

WC-Co HVOF-sprayed coatings present poor resistance to corrosive wear: the tungsten carbide in HVOF coatings dissolves as well as the cobalt-chromium matrix, leading to cobalt in solution. WC and Co go through an oxidation process before dissolution, the oxidation of WC to WO_3 makes the pH drop, accelerating the dissolution of cobalt and corrosion of hard phase leading to its removal. So, there are serious implications when coatings are used in corrosive-erosive environments *Souza and Neuville (2006)*. These authors have tested WC-Co- Cr HVOF-sprayed coatings. They have shown that the corrosion of these coatings is very complex and corrosion rate increases with temperature. However, chromium forms an oxide layer, which protects from dissolution and retards the corrosion. *Toma et al (2001)* found similar results, concluding that due to its low erosion-corrosion rate the HVOF sprayed Cr₃C₂-NiCr coating can be considered to be an excellent replacement for the thermal sprayed Cr₂O₃ coatings. *Espallargas et al (2008)* found that both WC-Ni and Cr₃C₂- NiCr coatings are promising alternatives to hard chromium from the point of view of erosion-corrosion resistance. Plasma-sprayed aluminium oxide and chromium oxide coatings are widely used to improve the resistance of metallic components against various types of wear and corrosion. However their corrosion resistance depends strongly on their porosity, especially open pores. *Leivo et*

al (1997) used aluminium phosphates to seal the structures of Al₂O₃ and Cr₂O₃ coatings. The abrasive wear resistance of sealed coatings did not decrease after immersion tests of 30 days in liquids of pH 0 to 10, except for the Al₂O₃ coating, which corroded in pH 0 and pH 14 solutions. No corrosion was found with aluminium phosphates in very acidic solutions. Aluminium phosphate is a good candidate to seal oxide coatings that are exposed in corrosive environments, excluding high basic environments of approximately pH 14. In diesel engines, sulfur in the fuel induces corrosive attack possibility. *Uusitalo et al (2005)* have tested the newly developed ferrous powder (Fe-C-Ni-Cr-Cu-V-B alloy) plasma sprayed with the Rota-Plasma_ of Sultz-Metco on Al-13Si cylinder wall. It presented excellent corrosion and wear resistances, compared with currently used bulk casting materials such as Fe - C - Si - B alloy and Fe - C - Si - Mo - B alloy for cylinder liners.

Basak et al (2006) have tested the corrosion and corrosion-wear behaviour of thermal sprayed nanostructured FeCu/WC-Co coating in Hank's solution and compared the results with that of stainless steel AISI 304 and nanostructured WC-Co coatings. The multiphase structure of the FeCu/WC-Co coating induces a complex corrosion behaviour. Under corrosion-wear conditions, the nanostructured FeCu/WC-Co coating exhibited a

DE passivation/repassivation behaviour comparable to that of stainless steel AISI 304 and nanostructured WC-Co coatings. Generally speaking, thermal sprayed coatings behave better when their density is improved. For example *Liu et al (2007)* have investigated the effects of laser surface treatment on the corrosion and wear performance of Inconel 625, and Inconel 625-based WC HVOF-sprayed metal matrix composite coatings. Significant improvement of corrosion and wear resistance were achieved after laser treatment as a

result of the elimination of discrete splat-structure, micro-crevice and porosity, and also the reduction of micro-galvanic driving force between the WC and the metal matrix. In addition, the formation of faceted dendritic structure of the WC phase was considered to be beneficial for the wear performance.

IV. CONCLUSIONS

Thermal sprayed thick (from 50 to 3000 μm) coatings, including cold spray coatings are more and more used in industry for the following reasons: (i) They provide specific properties onto substrates which properties are very different from those of the sprayed coating; (ii) They can be applied with rather low or no heat input to substrates (allowing for example spraying ceramics onto polymer substrates); (iii) Virtually any material that melts without decomposing or vaporizing can be sprayed including cermets or very complex metal or ceramic mixtures, allowing tailoring coatings to the wished service property; (iv) Sprayed coatings can be strip off and the worn or damaged coatings recoated without changing part properties and dimensions; (v) Some spray processes can be moved on site, allowing spraying rapidly big parts, which displacement would otherwise be rather long and expensive. The main thermal-sprayed coatings drawbacks are the following: (i) They are a line-of-sight technology, e.g. making it impossible to coat small and deep cavities; (ii) Most coatings have lamellar structures with contacts between layered splats that represent between 15 and 60 % of the splat surfaces depending on spray conditions; (iii) They have pores, cracks... that can be connected, depending on the spray process and spray conditions, and that must be sealed for certain applications. Most bulk materials used in corrosion conditions can be sprayed, however splat boundaries and cracks (for ceramics coatings) often dominate the corrosion properties of coatings. Sacrificial coatings (cathodic behaviour relatively to ions, for example Zn or Al on steel) are extensively used for the protection of large steel structures such as bridges, pipelines, oil tanks, towers, radio and television masts, overhead walkways and large manufacturing facilities, as well as for structures exposed to moist atmospheres and seawater such as ships, offshore platforms and seaports. Their porosity does not affect the anodic material protection, except when the whole cathodic coating structure is completely corroded. Painting as sealing or densification by shot peening are often used to extend their lifetime. No-sacrificial coatings, against corrosion or corrosive wear are extensively used in many industries: aerospace, land-based turbines, automotive, ceramic and glass manufacturing, printing industry, pulp and paper, metal processing, chemical, nuclear, cement, waste treatment. However, in almost all cases these coatings must be retreated to get rid of their porosity. This is achieved by using self-fluxing alloys that are fused after spraying, heat treating or annealing, laser glazing, austempering, sealing with organic, inorganic, metal peening densification, diffusion. Such post-treatments increase the cost of coatings. However, in many cases the cost of retreated coatings is lower than the use of bulk materials and this is especially the case for the repair of parts.

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