ADVANCED TECHNIQUES FOR SURFACE ENGINEERING OF INDUSTRIAL MATERIALS

S. K. Mishra

National Metallurgical Laboratory Jamshedpur

ABSTRACT

This paper deals with the various advanced surface modification techniques. It has been pointed out that each techniques has its own merits and demerits and a proper choice has to made depending upon the properties and quality expected from for specific applications.

INTRODUCTION

Surface engineering provides unique ways to alter the surface and near surface regions of materials, resulting in significantly improved surface sensitive properties. Surface composition and microstructure play major roles in improving and extending the usefulness of materials. The mechanical interaction with its environment such as friction and resulting wear, chemical effects such as oxidation and corrosion, are all governed by the properties of a thin layer at the surface, properties that may differ from the bulk ,which can be modified in terms of chemistry and microstructure. A variety of surface alloying and coating techniques exists ranging from simple application of paints to the relatively sophisticated electroplating, nitriding, boronising and surface diffusion treatments. Unfortunately these conventional surface treatments have limitations due to equilibrium solid solubility limits, low solid state diffusivity and grain growth of the bulk material. Newer techniques have emerged to overcome these limitations and to meet the stringent requirements in different applications. Some of the advanced techniques are: physical vapour Deposition (PVD), spraying, chemical Vapour Deposition (CVD), electrolysis and Surface modification by surface melting, heat treatment and ion beam implantation which are discussed in this paper.

Surface engineering can be defined as the design of a composite system (substrate and the modified surface) having superior performance compared to either the modified surface or the substrate . The different properties which can be controlled within limits for the engineering requirement from the different parts of such composite are shown in table 1.

Table 1 : properties of the coating-substrate composite system which can be controlled for optimum performance in any given application.

Part of the composite	Properties get affected	Improvement/alteration
Coating just top surface few A layers	Roughness Erosion Corrosion/oxidation	Electronic properties Frictional Characteristics Porosity
Coating	Residual Stress Cohesion Cracking/defects	Multilayers Graded composition Adhesion
C/S interface	Adhesion Substrate properties Expansion mismatch	Interdiffusion Diffusion barrier Cleanliness/roughness
Substrate	Mechanical properties Thermal properties	

Out of the many advanced surface engineering technologies, recently there has been a substantial interest in the new hybrid technology plasma immersion ion implantation (PI**3), laser surface alloying and modification, deposition of coatings by thermal spray (HVOF) processing to tailor surface properties. In the PI**3 technology, ion implantation as well as plasma nitriding can be achieved. In addition, due to high energetic ion bombardment, thermal diffusion can be used to obtain thicker layers than in the conventional ion implantation. The process can be further used in an ion beam enhanced deposition mode to obtain various kinds of coating. The economic aspects make PI**3 an interesting technique to modify a wide range of material. Laser technology can provide a unique tool for high quality surface modification. Normally high powder CW-CO_2 lasers are used for surface modification. Laser is used for surface melting to alter the surface microstructure or for alloying to alter the composition of the surface. The thermal spraying specially high velocity oxy-acetylene fuel (HVOF) thermal spray coatings have shown a very promising technique to deposit a good adherent wear and corrosion resistant coatings. Different techniques under all these processes are tabulated in table-2.

THERMAL & ELECTRON BEAM EVAPORATION:

In this process the material is evaporated using a heating source. The process is carried out in a vacuum chamber where the material in the form of wire, powder and lump is evaporated from the filament or boat by electrically heating or by focussing the electron beam on to the materials which evaporates and deposits on the substrate/ working piece. A schematic is shown in the Figure 1 for thermal and electron beam evaporation. Thermal evaporation is useful for the evaporation of metals up to melting point 1500-1600°C whereas the electron beam evaporation is used for high melting point metals, ceramics and alloys. It can be used to deposit any type of layer such as hard coatings of metal, metal alloys and ceramics.

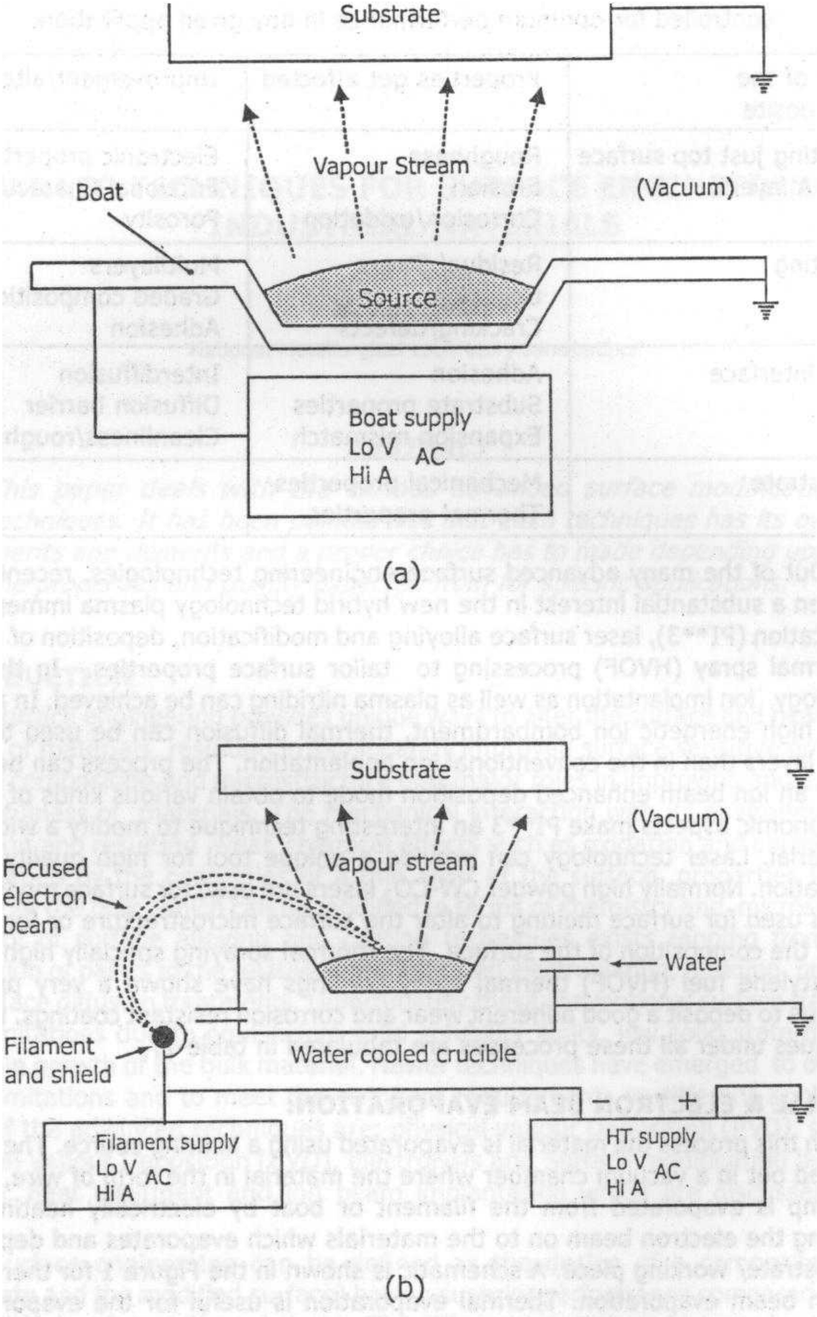


Fig. 1 : Schematic of (a) thermal and (b) electron bean evaporation

Table 2 : Different processes of surface modification

Physical Vapour deposition	Chemical Vapour deposition	Spraying	Surface melting/ change in microstructure/ surface chemistry	Electrolysis
Thermal evaporation	Chemical vapour deposition	Thermal spraying	Laser surface beam modification	Anodising
Electron Beam evaporation	Plasma Enhanced chemical vapour deposition	High velocity oxy fuel (HVOF) Spraying	Heat treatment	Plasma immersion anodising
Sputtering RF/ DC diode RF/DC Magnetron Ion beam sputtering		Plasma Spraying	Ion beam implantation	
Plasma Ion immersion coating		Cold spraying	Plasma ion beam immersion and implantation	

SPUTTERING

Sputtering is an atomistic process which uses glow discharge plasma to generate flux of ions incident on the target surface to produce thin coatings. When a gas plasma is created by application of electric field ionisation of gas takes place where ions, electrons and other species are also generated. The process is shown in Fig. 2a. The accelerated ions due to electric field bombard the target surface and surface reaction takes place with the upper and inner layers of the target material . Atoms from target are ejected from the surface. The sputtering phenomenon is shown schematically in Fig. 2b. The sputtered atoms from the target are deposited on the substrates. The whole process is carried out in a vacuum chamber which is first evacuated to 10^{-6} mtorr and then is brought back to the order of 10^{-2}or 10^{-3} mtorr pressure by argon or deposition gas. When electric field is applied between the electrodes plasma is created. The schematic of a sputtering unit is shown in Fig.2c. The quality of deposition in terms of adhesion, uniformity and reproducibility is excellent. Different modifications have been made in sputtering technology such as RF/DC magnetron sputtering, ion beam sputtering. RF source is used for the deposition on insulators and high resistive materials. In magnetron sputtering a magnetic field is applied across the plasma, which confines the plasma by interacting with the electron motion of the plasma. Due the magnetic field the electron path

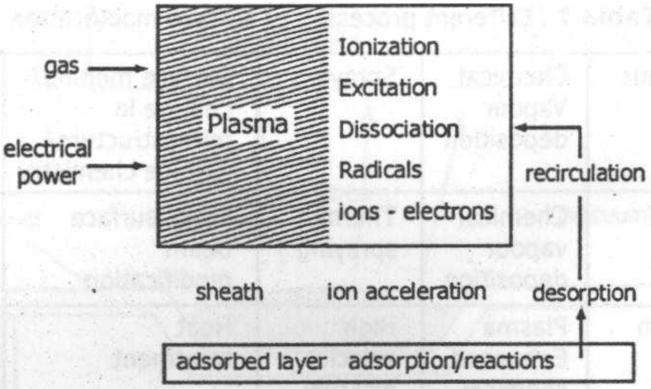


Fig. 2a : Different processes in plasma in a glow discharge

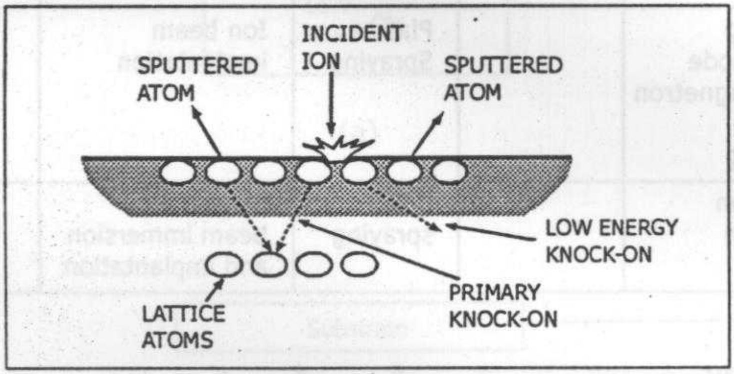


Fig. 2b : Schematic of sputtering process

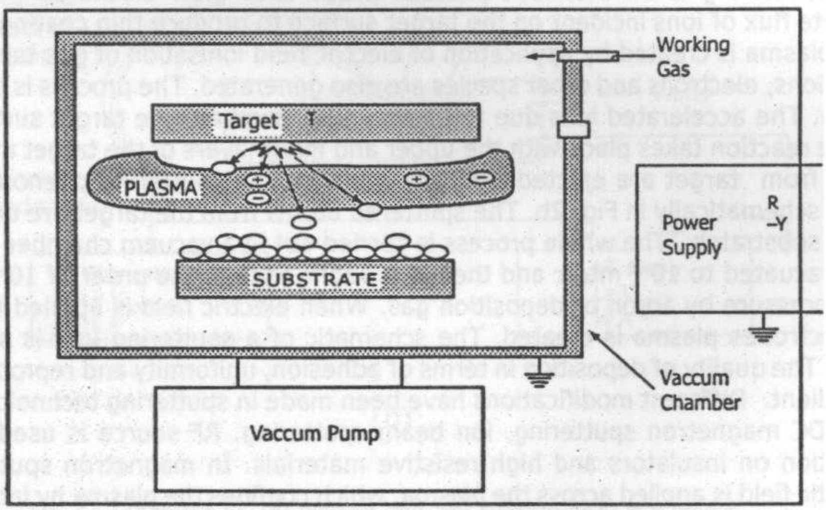


Fig. 2c : Schematic of a sputtering unit becomes a spiral, which helps in confining the plasma and in increasing the number of ions available for deposition. The large collision taking place during spiral path helps in increasing the deposition rate and adhesion of the coatings. In the ion beam sputtering, ions are extracted from the plasma and accelerated towards the target kept in an isolated chamber by suitable application of magnetic and electric fields. The ions bombard on the target and target atoms get sputtered and deposited on the ground surface and the substrate. Coatings can be deposited at lower pressures (10^{-4} mtorr) with better quality of deposition .

Sputtering is one of the most viable processes although the initial capital cost is high. The quality of coatings and properties that can be obtained by this process is unparalleled. Figure 3 shows an example of magnetron sputtered coated film of transition metal doped diamond like nitrides on aluminium and steel. The erosion properties have been improved drastically.

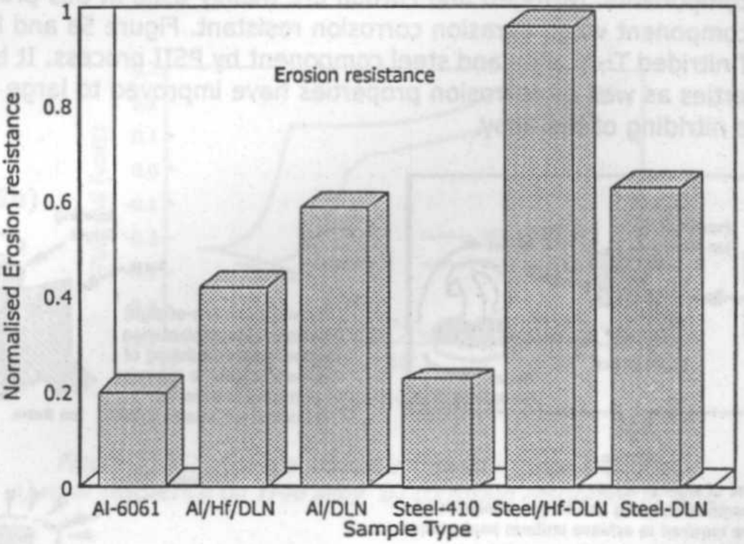


Fig. 3 : Erosion resistance enhancement due to magnetron sputtered transition metal doped DLN on Al alloy and steel.

ION BEAM IMPLANTATION

Ion implantation does not produce a coating but is used to change the surface chemistry. In this process an intense beam of very high energy ions (much higher than sputtering) penetrates into the substrate surface and modifies the chemistry. Normally Boron, carbon, nitrogen are used to harden the surface layer. Implantation is used for selective doping in semiconductor electronics. The process operates in vacuum and the area which is to be implanted are exposed to ion beam by suitable masking of the work piece. The implanted ions are scattered beneath the surface, some of them get trapped in dislocations and other defects effectively pinning them, others form metastable nitrides or borides or carbides which give the hardening effect on the surface.

PLASMA SOURCE IMMERSION ION IMPLANTATION

Plasma source ion implantation (PSII) is an efficient surface modification process where high doses of ion implantation can be done into non-planar work piece in a simple, efficient and cost-effective way. The work piece is immersed into the plasma of the species to be implanted or deposited and a series of high, negative voltage pulses are applied to the work piece. The ions of the plasma are accelerated by the electrical potential, and impinge normal to the work piece surface resulting in uniform surface modification. It has a significant departure from conventional ion beam implantation process, where ions are extracted from an ion source, accelerated as a direct beam to high energy and then raster scanned across the target. The work piece need manipulation in vacuum, whereas in PSII no such manipulations are required. Figure 4 shows the schematic of both conventional ion implantation and PSII process. This process can be utilised in surface modification of very large industrial components. Nitrogen and carbon are mainly used in this process which make the component wear, abrasion corrosion resistant. Figure 5a and b shows an example of nitrided Ti-Al alloy and steel component by PSII process. It is clear that wear properties as well as corrosion properties have improved to large extent due the surface nitriding of the alloy.

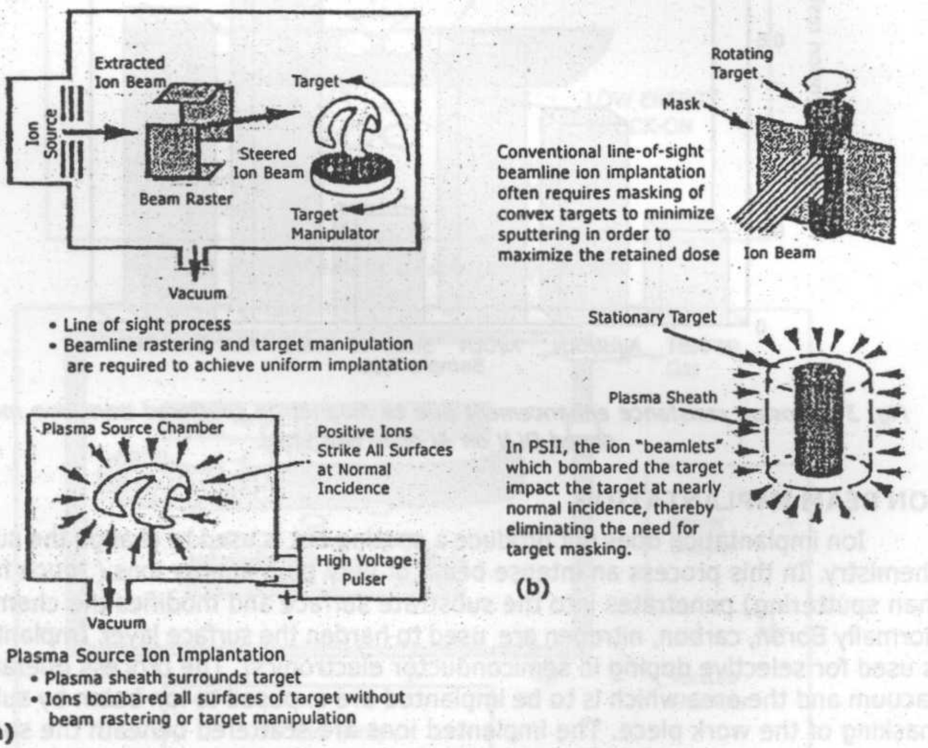


Fig. 4 : schematic of ion beam implantation and plasma ion immersion implantation process.

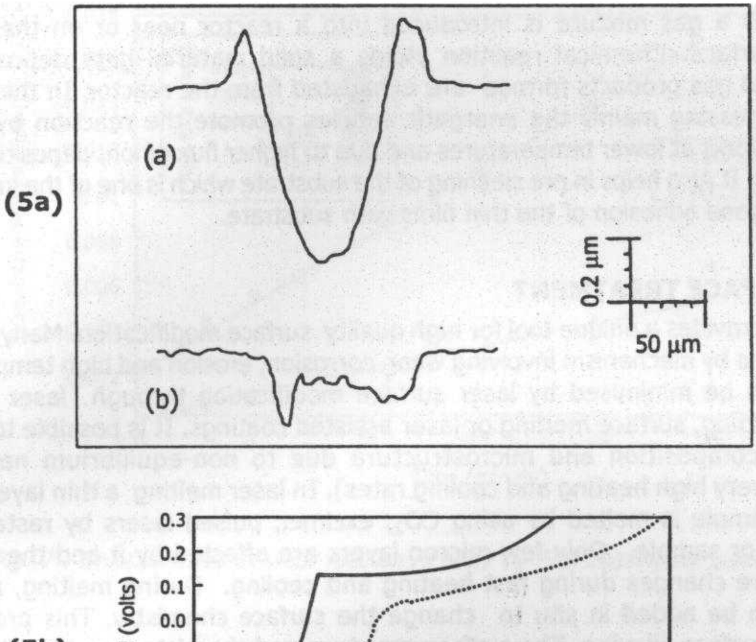


Figure 5: PSII surface nitridation resulting into improved a) wear resistance on Ti-Al alloy b) corrosion resistance in steel.

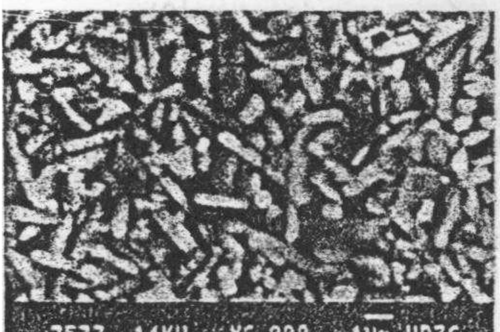
CHEMICAL VAPOUR DEPOSITION

In chemical vapour deposition (CVD) of heterogeneous gas/ solid reactions are used to produce coating. The deposition reactions are usually induced and maintained by heating the substrate. Solid material coating is obtained from gaseous precursors. There are different activation techniques of reaction and accordingly the processes have been named after such as TACVD, thermal assisted CVD, PECVD plasma enhanced CVD, LCVD laser assisted CVD, EBCVD electron beam CVD, IBCVD ion beam CVD. Sometime the names have been also given on the basis of precursor used or the pressure used during he deposition such as LPCVD low pressure CVD, APCVD atmospheric pressure CVD, UHVCVD ultra high Vacuum CVD, MOCVD metallorganic CVD. The conventional CVD process is thermally activated and most used CVD is PECVD. Principally PECVD is closely related to activated reactive evaporation and reactive sputtering.

In CVD a gas mixture is introduced into a reactor near or on the heated substrate surface. Chemical reaction yields a solid material gets deposited on substrate and gas products formed are exhausted from the reactor. In the plasma assisted processing mainly the energetic species promote the reaction by kinetic effect. This works at lower temperatures and due to higher flux of ion, deposition rates are increased. It Also helps in pre cleaning of the substrate which is one of the important criterion for good adhesion of the thin films with substrate.

LASER SURFACE TREATMENT

Laser provides a unique tool for high quality surface modification. Many surface related failures by mechanism involving wear, corrosion, erosion and high temperature oxidation can be minimised by laser surface modification through laser surface alloying, cladding, surface melting or laser assisted coatings. It is possible to freeze metastable composition and microstructure due to non-equilibrium nature of processing (very high heating and cooling rates). In laser melting a thin layer at the surface of sample is melted by using CO_2, excimer, pulsed lasers by rastering of laser source or sample. Only few micron layers are affected by it and the surface microstructure changes during fast heating and cooling. During melting, alloying elements can be added in situ to change the surface chemistry. This process is called laser surface alloying. The surface structure and chemistry can be tailored by choosing correct power and alloying conditions. Laser is also used to deposit coatings on the substrate from a target material. Figure 6a and 6b show an example of laser surface melting of superconductor. It is clear that microstructure has been refined to a great extent. The laser melted sample showed acicular growth on the surface. The current density could be increased to the magnitude of two orders to change the surface microstructure. Fig. 7 shows the enhancement of wear properties of laser surface treated/deposited Fe-Al alloy used in automotives.



(a)

(b)

Fig. 6 : Surface microstructure modification of YBCO superconductors by Laser meting (a) 0 watt and (b) 100 Watt.

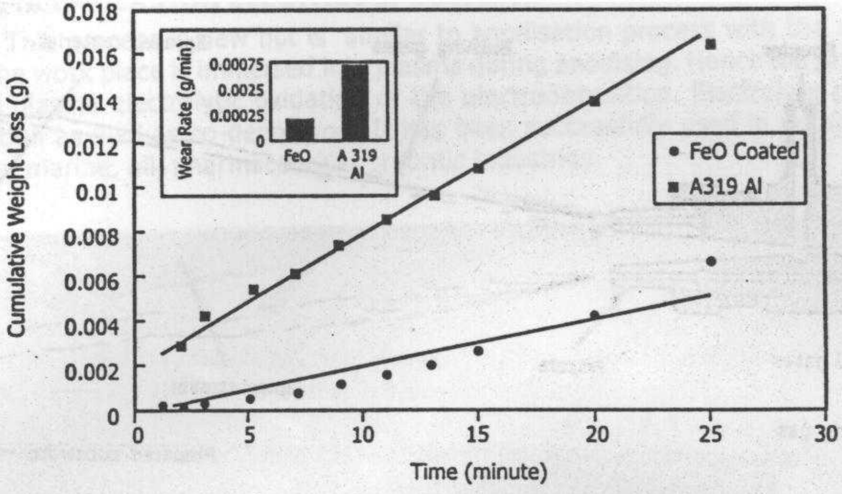


Fig. 7 : Enhancement of wear rate on Al alloy by FeO coating by laser melting

THERMAL SPRAYING

Thermal spray processing is a well established means to get coating thickness of greater than 25 micrometers. It is a competitive processes having high throughput, significantly improved process control and lower cost of production. Thermal spray processing is basically melting of material feed stock (wire or powder) and allowing to solidify on the substrate. A schematic view is shown in the Figure 8. The high temperature for melting is achieved chemically through combustion or plasma. These melting methods also facilitate penetration of molten particle to the substrate material, forming a deposit. The deposit is built up by successive impingement of these individual flattened particle or splats. The various thermal spray processes are distinguished on the basis of the feedstock characteristics (wire/powder) and the heat source employed for melting. The different processes are combustion flame spraying, high velocity oxyfuel spraying, plasma spraying, cold spraying

Combustion flame spraying employs compressed air or oxygen, mixed with acetylene, propylene, propane or hydrogen to melt and propel the molten particles. This gives low performance coatings and have relatively low flame velocity, but has been used because of its economy.

HVOF SPRAYING

HVOF processing is basically combustion flame spraying with a specially designed torch in which the compressed flames undergo free expansion upon exiting the torch nozzle, with very high gas acceleration. By properly injecting the feedstock powder from the rear of torch and concentrically with the flame the particles are also subjected to near supersonic velocity. Therefore, upon impact onto the substrate,

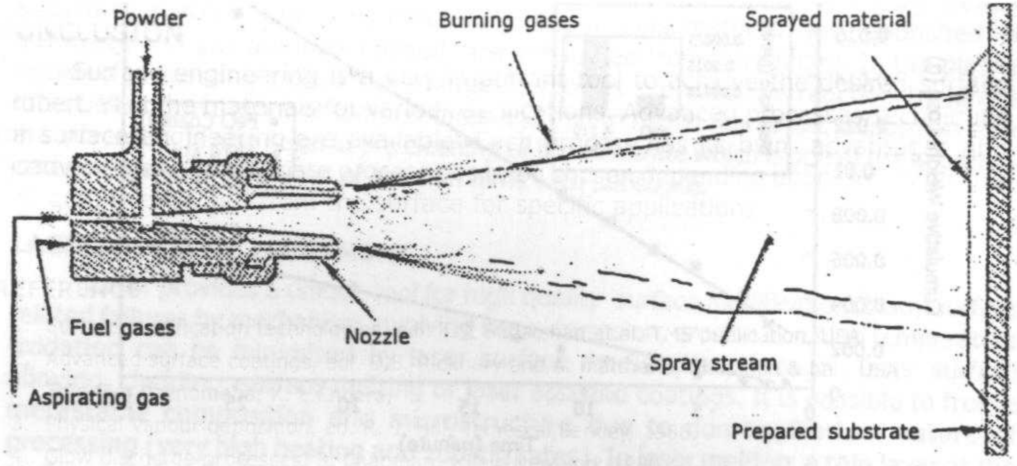


Fig. 8 : Schematic of combustion thermal spray process

the particle spread out and bond well to the substrate and to all other splats in its vicinity yielding a dense well adhered coatings. Hard ceramics with metal binders have been successfully coated for different industrial applications. It can be used to deposit coatings on very large components (Fig. 9). Figure 10 shows an example of enhancement in wear and abrasion resistance in aluminium alloys due to deposition of WC-Co by different thermal spray process. However, the flame temperature is not high enough to melt the ceramic particles, hence plasma spraying was invented.

PLASMA SPRAYING

In plasma spraying, a plasma gas (generally argon is complemented with a few percent of enthalpy enhancing gas such as hydrogen) is introduced at the back of the gun interior; where it swirls in a vortex and leaves at the front exit of the anode nozzle. The electrical arc from the cathode forms an existing plasma flame, which rotates due to the vortex momentum of the plasma gas. The temperature at the exit point is very high (about 1500K at DC torch operating at 40kw. The powders are accelerated and melted in the flame on their high speed (100-300m/s) path to the substrate, where they impact and undergo rapid solidification. Ceramics and refractory metals can be coasted by this method.

COLD SPRAYING

Cold Spraying a newer technique is under study since 1994. It consists of injecting microscopic powders, metals or solids at supersonic jet of rapidly expanding gas and shooting them at a target surface. The advantage of this process is that no oxidation of the particle or the surface takes place and high density deposits can be obtained at atmospheric Pressure.

PLASMA IMMERSION ELECTRODEPOSITION

This process is new but is similar to anodisation process with the addition that the work piece is immersed into plasma during anodising. Hence the process is called plasma electrolytic oxidation or the electrodeposition. Electrolyte provides oxidation as well as co-deposition. It has been successfully used in automotive, textile, marine, oil, pharmaceutical, robotic industries.

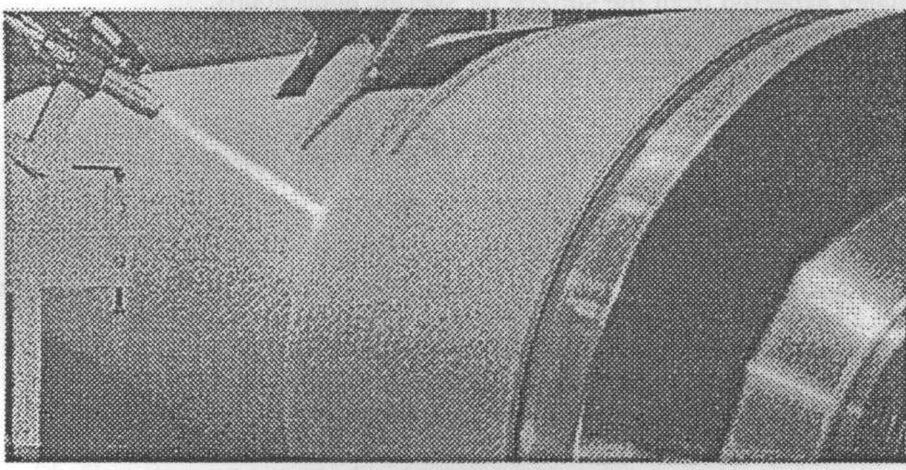


Fig. 9 : Ceramic coating by HVOF process on large components

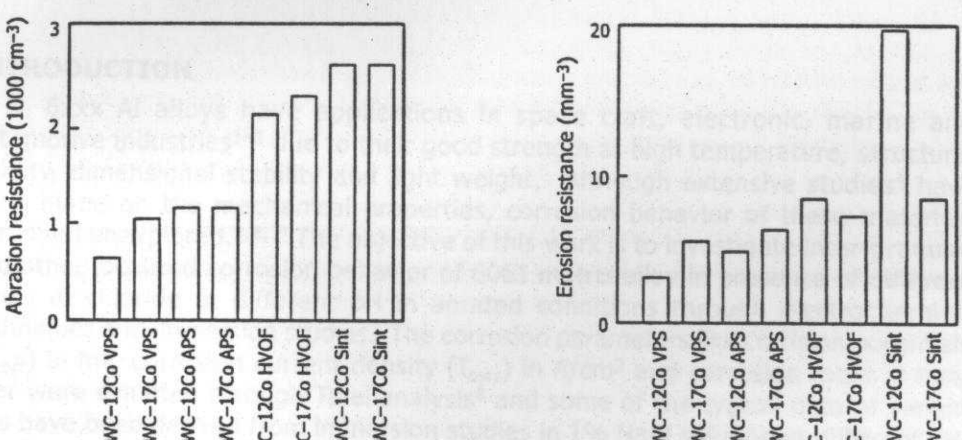


Fig. 10 : Enhancement of erosion and abrasion resistance by WC-Co coating by different spraying processes and sintered composite

CONCLUSION

Surface engineering is a very important tool to achieve the desired surface properties in the materials for various applications. Advanced processes/techniques for surface engineering are available. Each process has its own advantages and disadvantages . Appropriate process has to be chosen depending upon the properties and quality expected from the surface for specific applications.

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