CHAPTER 1

SURFACE ENGINEERING

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1.1 INTRODUCTION:

The majority of material failure originates at surface by mechanism involving wear, corrosion and fatigue. In case of metals, one technique for controlling surface initiated failure is through use of alloying elements throughout the bulk of these specimens to suitably modify the hardness, chemical passivity or strength characteristics. However this method is considered inefficient due to the use of costly strategic alloying elements like Chromium(Cr) and Cobolt (Co).[1]

The reorganization that vast majority of engineering components fails catastrophically in service through surface related phenomena, led to the development of broad interdisciplinary subject of "Surface Engineering". Surface Engineering could be best defined as design of surface and substrate together as a system to give cost effective performance enhancement of which neither is capable of its own. [2]

The definition of surface engineering as given by Bellis:[3] "The application of traditional and innovative surface technologies to engineering components and materials with properties unattainable in either the base metal or surface materials". Frequently the various surface technologies are applied to existing design of engineering components but ideally surface engineering involves design of component with knowledge of surface treatment to be employed. OR As per Definition by *ASM Handbook [4]*: treatment of the surface and near-surface regions of a material to allow the surface to perform functions that are distinct from those functions demanded from the bulk of the material. [3,4]

Surface engineering, is a discipline of science and technology, which meets the expectations of modern technical science: energy, material efficiency, as well as environment friendliness. [5, 6]

1.2 ADVANTAGES OF SURFACE ENGINEERING:

Surface engineering has significant role to play in our day-to-day lives as it has led to:

- The possibility of producing tools, machine components and whole appliances from the materials with lower properties, usually cheaper, and giving their surface improved characteristics. This is conducive to the mass and energy consumption necessary to manufacture them, retaining same strength characteristic and usually better tribological, decorative and numerous other properties.

- Improvement of reliability of work of tools, machine components and appliances and reduction of failures.
- Diminishing of energy losses to overcome resistance caused by friction, due to mass reduction of moving machine components and appliances, and due to enhancement of tribological properties of rubbing surfaces.
- Reduction of frequency of replacing used tools and machine parts, as well as frequency of maintenance overhauls.
- Reduction by 15 to 35% of losses due to corrosion, which is of great significance when it is realized that the impact of corrosion on economy may even reach 5% of gross national product.
- Minimization of environmental pollution, primarily due to reduction of energy consumption by burdensome branches of the industry and low rate of energy consumption by methods used in surface engineering, besides low amounts of waste, effluent, smoke, dust and industrial gases.[5,6]

1.3 CLASSIFICATION OF SURFACE ENGINEERING

(I) Changing the Surface Metallurgy:

None of these process changes the surface chemistry, but they improve properties like wear and fatigue by changing surface metallurgy

a) Localized surface hardening (flame, induction, laser, and electron-beam hardening): Improves wear resistance through the development of a hard martensitic surface. [7]

b) Laser melting:

Improves wear resistance through grain refinement and the formation of fine dispersions of precipitates on the surface. [7]

c) Shot peening:

Shot peening is a surface enhancement process which produces beneficial compressive residual stresses on metallic surfaces. This improves fatigue strength and relieves tensile stresses that contribute to stress-corrosion cracking. [8, 9]

(II) Changing the Surface Chemistry

Surface modification processes have advantage over coating primarily because they

(1) usually impart internal compressive stresses in near surface region and

(2) Will not delaminate off the substrate. [10]

The process includes:

(a)Chemical or electrochemical conversion treatment that produce complex phosphates, chromates/oxides on metal surface.

(b)Thermo chemical diffusion heat treatment that involves the introduction of interstitial elements like C, N or B into ferrous alloy surface at elevated temperature.

(c)Pack cementation diffusion treatments that involve the introduction of aluminium(Al), Cr or silicon(Si) into alloy surface.

(d)Surface modification by ion implantation, which involves introduction of ionized species (virtually any element) into the substrate using ion beam of high velocity electrons.

(e)Surface modification by combination of laser beam melting and alloying. [11]

(III) Adding a Surface Layer or Coating

This involves an intentional buildup or addition of new layer on metal substrate i.e. application of coating or lining.

A wide range of processes are used to deposit metal/ceramic and organic (paints or plastic and rubber coating).Coating methods commonly used are:[12]

I. Organic coatings and lining
II. Ceramic coatings
III. Hot dip metallic coatings
IV. Electroplating (metal or composite coating)
V. Weld overlays (metal or ceramic coating)
VI. Cladding (thick metal coating)
VII. Thermo reactive deposition/diffusion process (carbides, nitrides or carbonitrides)

Amongst all the above methods of coating deposition, ceramic coatings have advantages since Ceramic materials are noted for their high hot hardness and good chemical and thermal stability, making their surface properties ideal for number of engineering products, which encounter demanding operating conditions. The deposition of ceramic phases onto conventional metallic materials results in good combination of bulk toughness and load support with desirable surface characteristics and also making forming of complex shapes easier. [2]

1.4 METHODS OF DEPOSITING CERAMIC COATINGS:

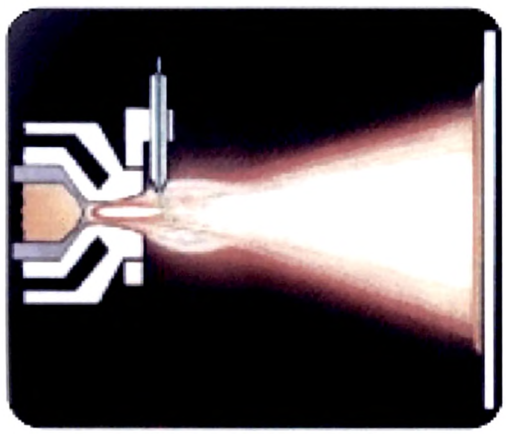
1. Thermal Spraying:
2. Sol Gel technique
3. Chemical Vapor Deposition Technique (CVD)
4. Physical Vapor Deposition Technique (PVD)

1.4.1 Thermal Spraying

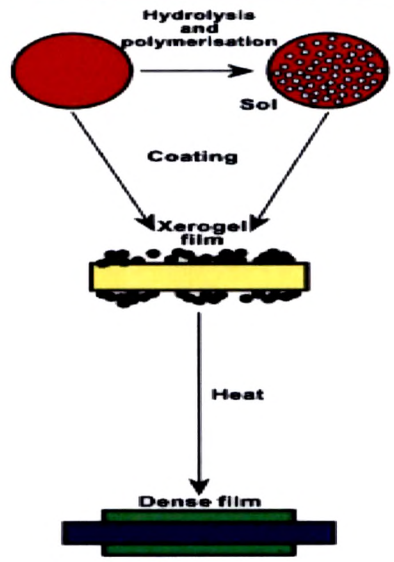
Thermal spray is one of the most versatile deposition processes for coating materials and its use for industrial applications has been greatly increase. Thermal spraying is, in fact, a generic group of processes in which the coating material is fed to a heating zone, where it becomes molten, and is then propelled to the surface to be coated . Metallic, ceramic, cermets and some polymeric materials can be used in the form of powder, wire, or rod for this purpose. (Fig 1.4.1)[13-15]

1.4.2 Sol Gel technique

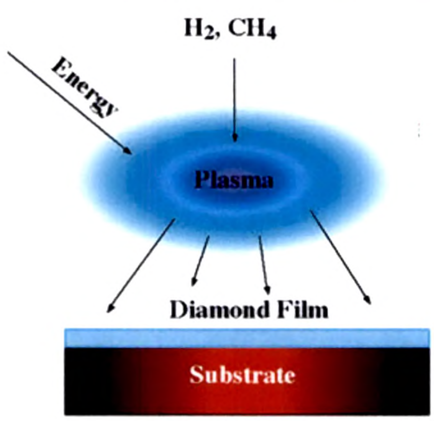
The sol-gel technique is based on hydrolysis of liquid precursors at low temperature and formation of colloidal sols. (Fig 1.4.2)[16]



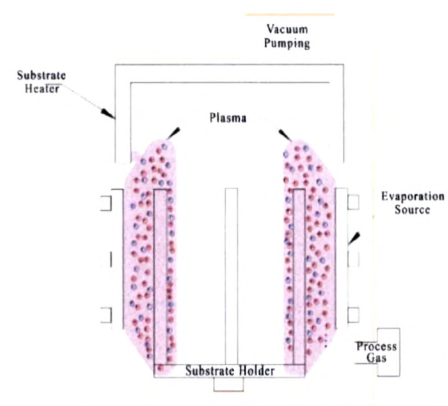
1.4.1 Thermal Spraying



1.4.2 Sol Gel Technique



1.4.3 CVD



1.4.4 PVD(Cathode arc Evaporation)

Fig 1.1 Schematic diagram of various processes for Ceramic thin film deposition

1.4.3 Chemical Vapor Deposition Technique(CVD)

CVD involves flowing a precursor gas or gases into a chamber containing one or more heated objects to be coated. Chemical reactions occurs on or near the hot surfaces resulting in deposition of thin films on the substrate, this is accompanied by the production of chemical byproducts that are exhausted out of chamber along with unreacted precursor gases. (Fig 1.4.3)[17]

1.4.4 Physical Vapor Deposition Technique (PVD)

PVD processes are atomistic deposition processes in which material is vaporized from solid/liquid source in form of atoms/molecules, transported in form of vapor through a vacuum or low pressure gaseous or plasma environment to the substrate where it condenses. PVD can be used to deposit films of metals or alloys as well as compounds using reactive deposition processes. (Fig 1.4.4) [18]The main advantage of PVD processes compared to CVD processes is the low deposition temperature (typically around 350^0C to 500^0C).Because of low temperature and high growth rates involved PVD coatings have high compressive stresses while those formed under CVD have low tensile stresses. If the layer contains more atoms in interstitial positions than there are vacancies in lattice and tensile stresses are formed like in case of CVD. While if layer contains more vacancies in interstitial position and atoms in lattice compressive stresses are formed. In Addition to this other advantages include excellent adhesion, good thickness uniformity, wide range of coating and substrate materials is possible and no hydrogen embrittlement problem [19- 21]

PVD Titanium Nitride (TiN) is superior to CVD TiN coating in increasing the metal-cutting performance of Cemented carbide tools owing to the former's greater resistance to abrasive wear and its associated higher surface fracture strength. This is due to fact that PVD TiN coating microstructure and beneficial compressive residual stress both of which contribute to higher micro hardness. [22]However main disadvantage of PVD process is they are generally line of sight between surface to be coated and source. [17, 23]

PVD thin films are widely used for surface protection, optical and electronic applications. Following figure shows the useage of thin films for various applications.

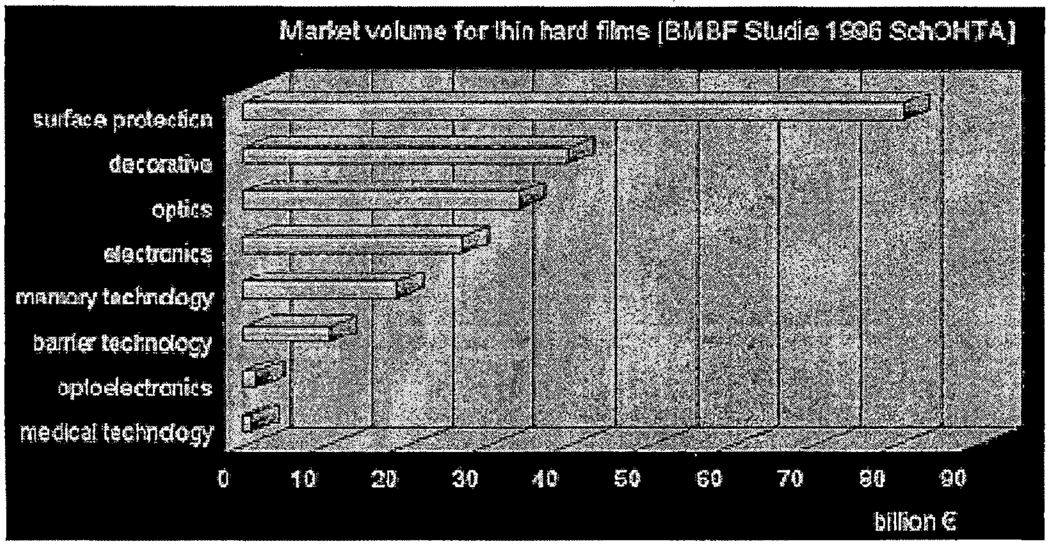


Fig 1.2 Application of PVD coatings.

As indicated in Fig 1.2 the largest application of PVD coatings is in surface protection for example in metal cutting field-particularly for twist drills, gear cutting tools, forming tools such as in cold backward impact of copper components, polymer processing machinery(injector screws),moulds for plastic, in food industry coating on stainless steel sleeve used for manufacturing of chocolate, in metrology field thread gauges and slip gauges, in medical applications for surgical tools, used in automotive parts of racing cars. Attractive golden color of TiN has led to its increasing use as decorative coating in jewellary applications. [2]

Cathode arc evaporation (CAE), one of the PVD processes has high deposition rates to produce dense and excellent adhesive coatings that offer a potential economical advantage. The industrial utilization of CAE is largely confined to mechanical applications, in particular to the deposition of hard coatings on the cutting tools. [24-26]

1.5 TiN, ZrN and ZrTiN Thin Films

The fourth-column transition metal mono nitrides have interesting properties resulting from their exhibition of both metallic and covalent bonding characteristics. The covalent crystalline properties are: high melting points; extreme hardness and brittleness and excellent thermal and chemical inertness. The metallic characteristics are electrical conductivity and metallic reflectance. Gold like appearance results from high reflectance of the materials at the red-end of the visible spectrum with Low reflectance near the ultraviolet region. First TiN Coating by PVD technique on Cutting Tools took place in 1960. Because of their extreme wear resistance, they are used as hard-coating thin films to expand lifetimes of mechanical compounds such as cutting tools and dies. Titanium nitride (TiN) has a NaCl structure that is stable over a broad composition interval allowing both under and overstoichiometric phases. At low nitrogen content in an inert carrier (e.g. argon) also a Ti_2N phase is possible. Titanium nitrides (TiN) and Zirconium nitrides (ZrN) have been the most successful in industrial application as decorative coatings and to Prevent Chip Welding in Cutting tools. [27, 3]

TiN and ZrN are thermodynamically stable but are susceptible to oxidation, which can be inferred from the heats of formation of TiN (-80 kcal/ mol) and ZrN(-87.3 kcal /mol).TiN is most widely used but at Temp.>600^0C TiO_2 (Titanium dioxide)layer is formed. Due to large difference in molar volume between TiO_2 and TiN, compressive stresses are developed in oxide layer this results in spallation and exposure of unoxidised nitride to further oxidation. Zirconium base thin films have high Melting point, high Hardness and high Corrosion and Abrasion resistance. It has better Hot hardness than other nitrides and better wear resistant Coating on cutting tools (30% harder than TiN). [28-34]

TiN and ZrN possess the same FCC crystal structure with a lattice misfit of 7.1% that can be easily overcome by misfit dislocations, a shear stiffness difference of about 30Gpa.

Compared with conventional metal nitrides, ternary nitrides such as (Ti, Al)N, (Ti,Cr)N and (Ti, Zr) N possess great advantages in micro hardness and oxidation resistance due to their respective alloying effects. Besides tribological applications the composition dependent color shifts find these ternary nitrides interesting usage in decorative application. [35]

The coatings used for functional applications are usually characterized by Corrosion and Wear resistance Wear is the erosion of material from a solid surface by the action of another solid. [36]Wear like corrosion is one of the most important failure modes of vast majority of mechanical components, is a surface property that can be minimized by altering the surface chemistry and microstructures.

In certain applications coating suffer combined corrosion attack and wear. Some examples include tools for plastic processing such as moulds for extrusion or injection molding which are in contact with corrosive media (eg. Softener and colors and free hydrochloric acid contain in certain polymers) and cutting tools where cutting fluid may contain sulphur. In some applications combined properties in terms of tribology, corrosion and fatigue are required. For example, pumps in chemical industries subjected to aggressive environments bearings and gears exposed to marine environment such as in naval aircraft which suffer from pitting corrosion due to localized attack by chloride ions.[37] In applications such as chemical apparatus processing and the food industry, however the mechanical loads occurring are superimposed by corrosive attack. Requirements for coatings withstanding this complex load include chemical inertness in the media concerned, but also microstructure demands a smooth surface, dense morphology without micro porosities and diffusion pathways, a homogeneous stoichiometry and a good adhesion between the coating and the substrate material [38]

Hence in practice wear, corrosion and fatigue are major concerns and coating life time is in many circumstances closely related to surface degradation problems. [37]

In the present investigation TiN, ZrN and ZrTiN of varying thicknesses (Film thickness was chosen as the controlling parameter) were deposited on 316 stainless steel by cathode arc evaporation technique. Since stainless steel is an important metal used in daily life, AISI 316 stainless steel (316 SS) was chosen as the metal substrate for evaluating the applicability of these coatings in the present study.[39] The deposited coatings were subjected to characterization technique like SEM(Scanning electron microscope) and EDX(Energy dispersive X rays) before and after Corrosion (Potentiodynamic test and Electrochemical impedance spectroscopy(EIS) in industrial corrosive environment) and wear test(pin on disc tribometer).Initially coatings were characterized by XRD (X-ray Diffratometer) to determine the composition and grain size of phases present.

The present research work is done from the view of a producer and characterizations of coatings for special demands by varying the basic parameters of thickness and the target material. An attempt has also being made to bring out characterization monograms for different CAE deposited thin films of nitrides of titanium and zirconium.

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