

CHAPTER 2

THIN FILM TECHNOLOGY

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2.1 INTRODUCTION

The productivity enhancement of manufacturing processes always is a strategic research and industrial objective. [1] For centuries, liquid lubricants were used to limit the contact pressure and facilitate sliding. Contact is inevitable and lubricants are used to reduce the temperature produced by friction. But, in many cases the presence of liquid is not recommended or forbidden for contamination reasons. The application of cooling lubricants during machining poses a considerable problem. The disposal costs for these environmentally dangerous machining aid materials can in some cases be estimated as a multiple of the manufacturing costs. Furthermore, the toxic effects of the cooling lubricants do not make their further application at the workplace desirable. Effects are particularly important in vacuum or at high temperature, for food, medical apparatus, or the nuclear industry. [2, 3]

Coating is not only used to increase hardness but also used on cutting tools to provide improved lubrication at the tool/chip and tool/work piece interfaces and to reduce friction and consequently reduce the temperatures at the cutting edge. [4]

Hard coatings have been successfully used for protection of materials and particularly to enhance the life of cutting tools since the 1970s. Both the technological process of their production and their properties, i.e. hardness, wear and oxidation resistance, however, are continuously being improved. [5]

The earliest methods used for imparting increased surface hardness and wear resistance to cutting tools involved heat treatments, such as carburizing and nitriding, when the tools were essentially made of carbon steels and high speed steels. In mid-1960s, chemical vapor deposition (CVD) was used for the first time to deposit thin coatings of hard, refractory compounds on cutting tools, to provide increased hardness, chemical stability and wear resistance. The physical vapor deposition (PVD) techniques were introduced in the commercial markets in the late 1970s and early 1980s, and now enjoy an almost equal status with the CVD techniques in this market. [6]

Ceramic thin hard coatings are of interest in a number of technological fields due to their physical, chemical and mechanical properties. Ceramic thin films have the characters of good corrosion resistance, good oxidation resistance, high hardness, good wear resistance and high temperature endurance. Combined with ceramic thin films, the surface properties of metals and their alloys will be changed greatly. [7]

2.2 DEPOSITION OF THIN FILMS

Hard physical vapor deposition (PVD) and chemical vapor deposition (CVD) coatings have been extensively used to enhance the multi-functional properties of tools, dies and molds as the working conditions become increasingly severe. Especially the demand to develop wear resistant hard coatings with good thermal stability becomes crucial for the extension of tool life as machining speed increases and the machining of heat treated molds and die materials of high hardness over HRC 45-55 is needed. Hard Physical vapor deposition (PVD) and chemical vapor deposition (CVD) coatings have been extensively used to enhance the multifunctional properties of tools, dies, molds as the working conditions become increasingly severe. [8, 9]In chemical vapor deposition technique chemicals (sources) containing deposition constituents are transported in vapor phase to the substrate where they react to generate deposition constituents which then gets deposited over the substrate.[10]The term PVD is used to describe processes in which at least one of the coating species is atomized from a solid source within a coating chamber, to then condense on a substrate, forming a film.[11]PVD methods have been widely applied to deposit transition metal nitride films and is normally divided into three categories: evaporation, sputtering and hybrid PVD processes (ion plating, reactive evaporation and ion-beam assisted deposition, etc.).[12]

Physical vapor deposition includes number of vacuum coating processes during which material is physically removed from source by evaporation or sputtering and then transported through vacuum using the energy of the vapor particles and finally condensed as a film on substrate. All PVD processes can be separated into three stages:

1. Emission from Vapor source
2. Vapor transport in a vacuum
3. Condensation on substrate. [12]

Table 2.1 Chart showing comparison of PVD & CVD coating processes: [13]

PVD	CVD
Performed in a vacuum (10^{-2} to 10^{-4} Torr)	Performed in a controlled atmosphere
Low process temperature (200°-800°F)	High temperature process (1900°F)
Line of sight process	Reactive gas process coats wherever atmosphere contacts surface
Coating exhibits a physical bond to the substrate	Diffusion bond to substrate (much stronger than PVD's physical bond)
Average thickness: 2-5 μm , or .00008-.0002"	Average thickness: 6-10 μm , or .00024-.0004"
Suitable for a wide range of substrates	Smaller range of appropriate substrates
Ideal for closely tolerance components (+/- .0001" is appropriate)	Requires relatively loose tolerances (example: +/- .0005" per 1.0" diameter)
No heat-treating required	Post-coating heat-treating required on steel components
Good for sharp edges: no excessive coating build-up	Requires hone on cutting edges due to coating build-up
This process has the ability to coat mirror finishes without any post-coating polishing	Difficult to maintain mirror finish (post-coating polishing will improve finish beyond 4 μm .)

Over the last decade, PVD coatings have been successfully applied to round cemented carbide tools and metal-cutting inserts for applications involving interrupted cuts and/or those requiring sharp edges. The layers of wear resistant PVD coatings are only a few microns thick but can, to a large extent, change the performance of the basic cutting tool material and have a big influence on finish machining processes in today's production. [14-16]

The PVD is one of the most versatile processes. The advantages with PVD is, foremost, the relatively low deposition temperature (200–500°C), allowing most industrially important substrate materials to be coated, excellent adhesion, minimum effluent or pollutant products during deposition and no hydrogen embitterment problems. One of major limitation is that coating atoms reach the substrate surface more or less in a line-of-sight process, i.e., it is difficult to deposit coatings on surfaces with a complex geometry, e.g., narrow cavities in forming tools. [17]

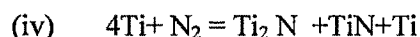
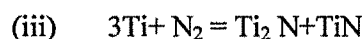
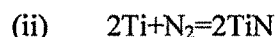
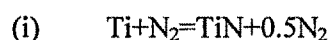
In an overwhelming majority of PVD techniques, there occur chemical reactions between plasma components or between components of plasma and the substrate (so called reactive PVD techniques). Similarly in the majority of CVD techniques, physical phenomena, e.g., reduced pressure and plasma, are utilized. The difference between CVD and PVD becomes even smaller. [18]

The two special characteristics of PVD process are:

- The same coating material deposited by different techniques usually does not feature same coating characteristics;

- Properties of coatings deposited by one technique with utilization of same materials do not have to be same because their chemical composition may be different; they may form stoichiometric, substoichiometric and super stoichiometric compounds.

For example, coating of TiN with general formula of TiN_x may contain nitrogen within the range of 28% to 50% (atomic) which corresponds to value of $0.42 \leq x \leq 1$. The chemical composition of layer depends on the conditions of deposition, on the proportion of reagents in the plane of substrate, in accordance with the formulas:



This proportion depends on the rate of condensation of titanium on the substrate and on partial pressure of nitrogen (uniform in different zones of the working chamber), as well as on the degree of ionization which, similar to degree of condensation, is not uniform in all zones of the working chamber. [19]

2.3 CATHODE ARC EVAPORATION (CAE) TECHNIQUE:

This technique was developed in the early 1970's at the Physico – Technical Institute in Kharkov and by way of license and sub-license purchase has been broadly propagated by US companies like Multi-Arc and Vec-Tec System, as well as Plasma and Vakuum Technik from Germany [20]

Amongst the physical vapor deposition (PVD) techniques, cathodic-arc evaporation is increasingly being used for tribological applications because of its high degree of ionization of the vaporized atoms, resulting in good adhesion and a dense morphology of

the coatings. During bombardment, high-energy metal ions generated from the cathode bombard the substrate surface which is kept at a high negative bias of 500–2000 V. In addition to cleaning and heating the substrate, energetic metal ions during ion bombardment knock off some metal atoms from within the substrate or may penetrate the substrate lattice to angstrom levels. This leads to defects and roughness on the substrate at an atomic level, and the atomic level of roughness is believed to be responsible for the improved adhesion of the coating. [21-23]

Apart from many advantages, such as the simplicity of the deposition process and plasma source structures, the method also has several disadvantages. The major disadvantage is higher roughness when compared with sputtered and E-beam-deposited coatings. Many researchers have attempted to attribute this problem to the droplet emission generated during arcing on the cathode surface. The protruding conical features on the coating surface are often called "macros", "macro particles" and "droplets". These defects contribute in part to the surface roughness of the coated substrates, resulting in dull-looking rough coatings. [24,25]

The reason for formation of macroparticles is the fast evaporation of the process, which produces excess atoms that are not completely ionized before they arrive at the substrates. The excess neutral atoms may coalesce to macroparticles during flight. Thus the macro particulates may cause effects that are undesirable in certain applications, such as decoration. [26]

The presence of Macroparticle (MP) in the vacuum arc plasma jet is the critical problem of the cathodic vacuum arc deposition technology as it is suspected that coatings have a deteriorated performance due to increase in surface roughness, micro holes in the coating and abrupt changes of microstructure and texture. [27, 28]

MP contamination in coatings depends on MP generation, MP transport to the substrate and the MP-substrate interaction. Plenty of features influence the share of the microdroplet phase in the deposited coating: the melting point of the cathode's material, the average temperature of the cathode's evaporated surface and the average cathode energy dissipation, bias voltage characteristics, such as the amplitude, mean value, frequency and duty cycle (in the case of unipolar pulsed voltage).[29,30]Several methods

have been demonstrated to eliminate MPs, including background gas pressure variation, negative substrate biasing and axial magnetic fields. [27]

However, the presence of the macroparticles in the TiN substrate interface may be useful to the adhesion of TiN coating to the substrate. The presence of macroparticles in the TiN coating is favorable for the release of internal stresses, because the Ti macro-particle has a much higher plasticity than the TiN phase. [26, 29-33]

2.4 GROWTH MODEL IN THIN FILMS

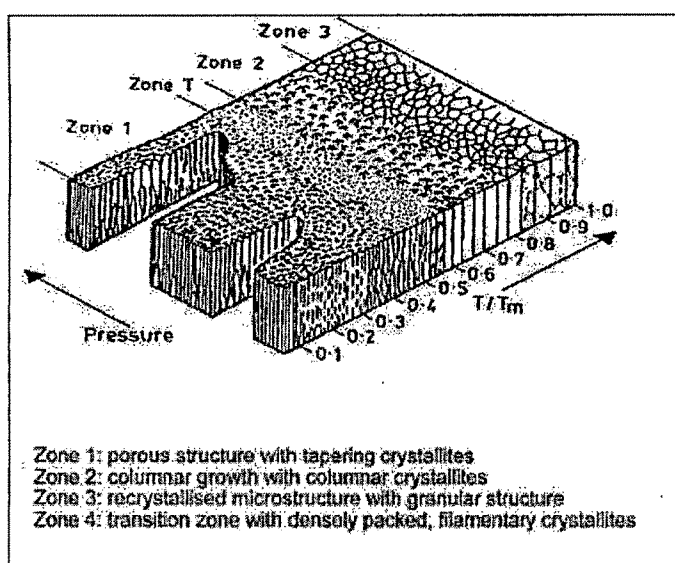


Fig 2.1 Growth Model in Thin Films.

Several film growth models for the influence of the deposition condition on the microstructure of the film have been developed. Commonly used are the empirical structure zone models where different growth modes (zones) are identified in a diagram for different temperature to melting temperature ratios (T/T_m). An extensive review of such models was published by John A. Thornton in 1977 and further developed by Movchan and Demchishin. They made the following classification: Zone 1 appears when $T/T_m < 0.3$ and is characterized by high surface roughness and voided grain boundaries. Zone 2 appears when $0.3 < T/T_m < 0.5$ and is characterized by a mat, smooth surface and columnar grains with distinct, dense boundaries. Zone 3 appears when $0.5 < T/T_m < 1$ and are characterized by a bright surface and equiaxed grains. The structure and properties of

this zone are close to bulk material. Further Thornton has proposed an extended model where the influence of the process gas pressure is added into a second axis in the diagram (fig 2.1). In this diagram a fourth zone (zone T, transition) can be identified between zone 1 and zone 2. The zone T structure is dense and fibrous without voided grain boundaries. The coatings deposited at the low deposition temperatures do not display the excellent wear resistance of the tool coatings because the microstructure changes from the dense columnar-type T to the open type I with its intergranular voids. [21, 34, 35]

2.5 VARIABLES IN CAE TECHNIQUE

(i) Gas pressure

Nitrogen pressure influences the properties of coatings. Nitrogen pressure lower than 1.0 Pa (0.01 mbar) produced a coating with poor adhesion, whereas, a good wear resistant coating was obtained at a pressure of 5.0 Pa (0.05 mbar), in cathodic arc deposition. [21] According to S.G. Harris et al to reduce the number of macroparticles in reactively deposited CAE coatings is to increase the partial pressure of the reactive gas during deposition [36]

(ii) Bias Voltage

The bias voltage is known to increase the kinetic energy of the ions extracted from the plasma and as a result, change the microstructure of the deposited film. When the substrate bias is more negative the surface is heated and re sputtering may occur. Furthermore, as the energy of the impinging ions increases the generation of defects increases. This, in turn, produces an increased number of preferential nucleation sites, resulting in the reduction of the grain size with more negative bias however increase in grain size with increasing negative bias may be by increasing ad atom mobility induced by increasing ion energy. It seems that both mechanisms i.e., the generation of defects and the enhanced atom mobility influence the coating microstructure. High substrate bias voltages and process temperatures provide an increase in adatom mobility and the re-sputtering rate; whilst inter diffusion mechanisms may be generated, causing less well defined and rougher layer interfaces. [23, 37, 38]

A dense, fine-grained structure can be obtained with the increase in bias voltage. Higher bias voltage leads to higher attraction energy and increases impact effect of arriving ions. Macroparticles can be reduced with respect to the increasing bias voltage or severe

contamination of larger macroparticles spread over the coating surface is improved with respect to the increase of bias voltage. [39]

(iii) Interlayer:

Considering most widely used TiN thin films, the purpose of Ti interlayer is many fold.

1. Ti interlayer hinder columnar growth
2. It increases the adhesion strength of TiN coating
3. Ti interlayer dissolve oxide layer remaining on the surface of substrate as well as to relieve shear stress in the interface
4. A very good epitaxial relation is established between TiN and Ti, and therefore the texture of the TiN coatings with a Ti interlayer showed enhanced preferred orientation when approaching the TiN/Ti interface. The texture enhancement may be due to similar atomic packing between (111) in TiN and (0001) in Ti, which leads to kinetically favorable conditions in forming TiN (111) on the pre-deposited Ti interlayer.
5. Ti interlayer can also favor the growth of both less defective nitride coatings and a titanium oxide passive barrier
6. Ti interlayer inhibits the bonding mismatch of the interface. [40,41]

(iv) Substrate temperature:

A rise in substrate temperature causes an increase of the force of adhesion of coating to substrate. Overheating the substrate may, however, cause a loss of acquired mechanical properties of substrate e.g. exceeding of tempering temperature causes a loss of hardness. For this reason, in the case of metallic loads, heating is carried out at a temperature approximately 50⁰K lower than that of tempering (150⁰-250⁰ C).[42]

2.6 COMPOSITION OF CERAMIC THIN FILMS:

Among the transition metal compounds, Titanium Nitride(TiN) sits in a preferential position with suitable average properties meeting most requirements for wear and corrosion-resistant coatings. It is reasonably hard, pleasant in aspect and cheap. TiN is known as the most universal coating and shares about the 90% of coating market [43-46] The first generation PVD coated tools featured TiN as the hard coating and were applied in interrupted cutting such as milling of steels. The superior performance of PVD TiN

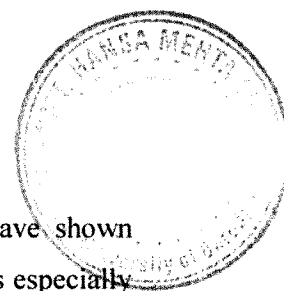
coated tools prompted their use in other machining applications, such as turning, as well as in industries as a wear-resistant or protective layer on the dies. PVD TiN coating deposited on sharp tool edges enhance machining productivity and also generate acceptable surface finish with moderate power consumption during machining operation. [47-48]

TiN_x has been the most widely studied due to the relatively wide compositional range ($0.6 < x < 1.2$) where the *B1* single-phase with rock salt (NaCl) structure is stabilized and also because it combines physical characteristics of typical metals, such as good electrical and thermal conductivity, with high hardness ($H \sim 20\text{--}22$ GPa), chemical inertness and high melting temperature ($T_m = 3222$ K) typical of covalent crystals. [49]

The reasons for extremely high hardness, chemical inertness, excellent wear resistance (widely utilized in many industrial areas where high abrasion resistance, low friction coefficient, high temperature stability, and high hardness are required) and high melting temperature is the bond structure in transition metal nitrides which consists of a mixture of covalent, metallic and ionic components and is responsible for high hardness. The reason for their high mechanical and chemical stability is thought to be the highly directional nature of the metal–nonmetal *pd* hybrid bonding. The unusual mixture of covalent and ionic nature in these hybrid bonds means that such compounds have ceramic-like hardness, while also exhibiting high thermal and electrical conductivity, characteristic of metals. [21, 50]

However, the main limitation of this coating is the oxidation at 550 or 600 °C which can be reached during the machining processes. TiN is most widely used but at Temp. >600°C TiO₂ layer is formed. Due to large difference in molar volume between TiO₂ and TiN, compressive stresses are developed in oxide layer this results in spallation and exposure of unoxidised nitride to further oxidation [23, 51-54]

Zirconium nitride (ZrN) coatings have similar structure and properties to TiN coatings, as both Ti and Zr belong to the same periodic element group. Further Zirconium nitrides exhibit very interesting properties such as high hardness, high melting point and high corrosion resistance. Its various applications include diffusion barrier, cryogenic thermometers, decorative coating and hard protective coatings, because of their high mechanical properties, better corrosion and wear resistance and exhibiting warmer golden



color than the corresponding properties of TiN films. ZrN-coated tools have shown significant performance advantages over TiN coated tools during drilling tests especially for Nonferrous metals. ZrN has a coefficient of friction lower than that of TiN and other transition-metal nitrides, while being comparatively hard. It is thus especially attractive material for protective coatings. [55-59] ZrN coated tools have shown significant performance advantages over TiN coated tools during drilling tests. It has been shown in previous reports that ZrN coated tools last from 200% to 1000% longer than uncoated tools and up to 500% longer than TiN coated materials. [61-63]

Since zirconium has a higher melting point, a lower vapor pressure, and higher contamination susceptibility by oxygen and carbon, it is more difficult to deposit ZrN film than TiN or CrN films. [60]

The mass of Ti atoms is almost half of the Zr, there is a greater loss of kinetic energy of Ti atoms by collision than those of the Zr, generating a coating of coarse columnar grains that would have many voids and other structural defects that can absorb oxygen. The smaller roughness of a coating offers a greater resistance to corrosion and this is why ZrN has a better behavior to corrosion tests than TiN. However ZrN film presents a greater micro strain than the TiN film when the discharges number is increased. This indicates that the ZrN film has a greater presence of dislocations densities and/or lattice defects. This residual stress plays key role in the performance of the protective coating mechanical behavior, adhesion and corrosion resistance. Since corrosion and wear properties depend on both of above parameters these contradictory properties of deposited film will in turn determine their functional capability. [22, 64, 65]

TiN had a very low oxidation resistance, a drawback that made it less suitable for applications where the service temperature could reach several hundreds of degrees Celsius, as it is the case in the tip of cutting tools working at very high cutting speed

For the further development of conventional hard material with improved properties of thin films lies in depositing compounds with a complex structure, *i.e.* ternary or quaternary mixed phases. Single layer PVD TiN coatings have been improved through partial or complete substitution of N with C (TiCN), B (TiBN, TiB₂), or partial substitution of Ti with Al (TiAlN), Zr (TiZrN), or V (TiVN). Both Al and Zr could increase the temperature for initiating oxidation of the coatings by more than 200⁰C, in

comparison to TiN. Nevertheless, researchers soon realized that the alloying procedure also had a beneficial effect on the coating's mechanical properties, with significant improvements in hardness, maintaining high values of fracture toughness and coating adhesion. Several explanations were given based on well-known hardening mechanisms such as those based on lattice distortion (solid solution, precipitation), decrease in grain size (grain boundaries), or electronic structure (valence electron concentration). The substituting atoms can also impart higher chemical stability and improved oxidation resistance. These characteristics can in turn improve metal-cutting productivity by allowing the tool user to increase machining speeds. [39, 66-69].

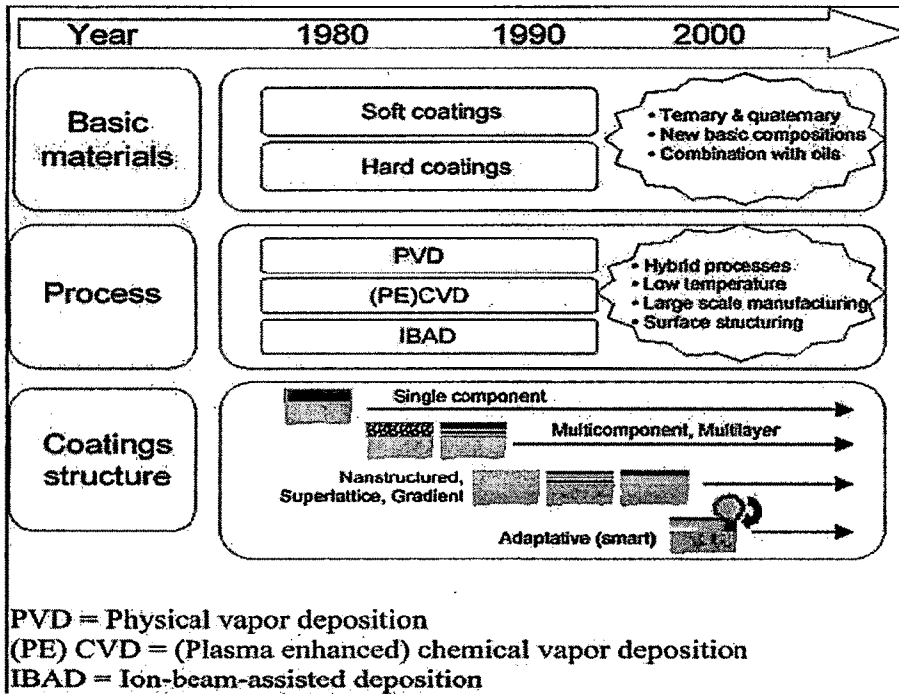
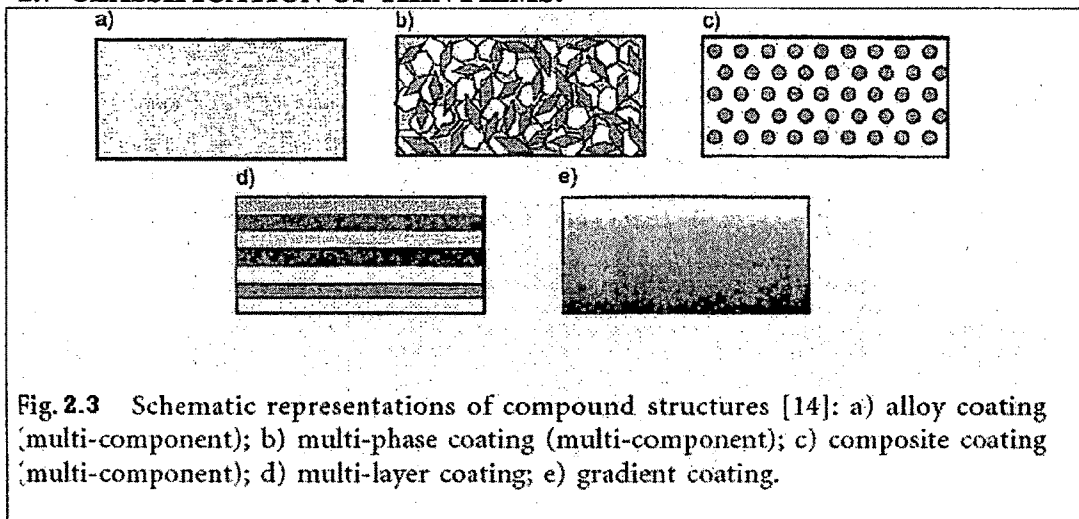


Fig 2.2 Development in thin film deposition technique. [69]

2.7 CLASSIFICATION OF THIN FILMS:



Coatings deposited by PVD techniques can be divided into two groups:

2.7.1 Simple, known as monolayer coatings, comprising one material—a metal (e.g., Al, Cr, Mo, Cu, Ag, Au) or a phase (e.g., TiN, TiC)

2.7.2 Complex, comprising more than one material (metal, phase or compound), with the materials distributed in a varied manner relative to each other.

Five types of complex coatings are distinguished:

(a)-alloyed (multi-component) coatings in which the sub lattice of one metallic element is partially filled by another metallic element, similar to substitution-type solutions. Marked effect on the coating performance, an improvement was seen in ‘alloying’ of the binary components by metal and/or metalloid components. Particularly carbonitrides of various compositions [e.g. Ti(C, N)] and additions of aluminum [(Ti, Al)N] resulted in promising progress.

(b)-Multi-phase coatings constituting a mixture of two or more divisible phases e.g. TiN/Ti₂N or TiC/TiN

(c)-Composite Coatings comprising a mixture of two or more phases and constituting a specific type of multiphase coating in which one phase is discreetly dispersed in another phase, occurring in a continuous manner, e.g., Ti/Al₂O₃

(d)-Multilayer Coatings, known as micro laminates, comprising consecutive simple layers of different materials, deposited on top of one another with different properties and also forming between themselves transition layers.

Monolayer constituting the multilayer coating should be arranged in such a way that the transition layer formed between any of them allows best mutual adhesion, i.e., that the transition layer forms a coherent interphase zone. Coherent connections are formed by coating materials with metallic bonds with metals or other coating materials which also feature metallic bonds, e.g. TiC/TiB₂. Weaker connections are formed between materials with metallic bonds and materials with ionic bonds (and strongly depend on the chemical composition and structure of the transition layer), e.g., TiC/ Al₂O₃. Weakest connections occur between materials with covalent bonds and other materials with the same type of bonds or ionic bonds, e.g., B₄C. Good connections are obtained between those materials which are mutually soluble, forming alloys, e.g., TiC and TiN or Al₂O₃ and AlN.

(e)-Gradient Coatings, constituting a modification of multi-layer coatings, in which the change of chemical composition and of properties of the individual layers does not occur in leaps (as in typical multi-layer coatings), but in a continuous manner. An example of a gradient coating is TiN/Ti(C, N)/TiC. [70-73]

2.8 TOOLS FOR THIN FILM CHARACTERISATION: [74]

a) Tools for measurement of coating properties such as

- + Chemical composition by EDX, ESMA, Auger, SIMS etc.
- + Residual stresses by X-ray diffraction or by mechanical methods
- + Topography by mechanical or optical methods as well as Atomic Force Microscopy
- + Morphology and growth by SEM analyses of fractures
- + Plastic hardness by micro hardness HV or
- + Nano-hardness and elasticity by universal hardness and nano-indentation
- + Thermal conductivity by the thermal wave method

b) Tool for measurement of tribological properties such as

- + Coating-substrate adhesion by scratch test or Rockwell indent
- + Resistance to abrasion by the spherical calo test or the pin on disk method
- + Resistance to tribo oxidation by abrasion testing on thermally pre-loaded coatings
- + Adhesion resistance by measurement of material transfer between sliding partners
- resistance to diffusion by ESMA analysis of clamped and heated tool material
- + work material specimens friction between sliding partners on a tribometer with realistic pressings

+ Resistance to fatigue by means of an impact test.

c) Tools for measurement of Corrosion resistance such as

+Open circuit potential using Potentiodynamic testing

+Electrochemical impedance spectroscopy

+Tafel Plot using Potentiodynamic testing

Amongst various characterization tools, in the present investigation SEM, XRD, Potentiodynamic test and Pin on disc method to characterize thin film have been selected, depending on the easy availability of the tools. The principle and working of SEM & XRD is discussed. However detailed study of corrosion and wear equipment is presented in chapter 3.

2.8.1. Scanning electron microscopy

SEM is one of most versatile instrument for investigating corrosion and wear resistance of thin films.

Scanning electron microscopy (SEM) is a technique where electrons from an electron gun are accelerated by a high voltage (5 – 50 kV) towards the sample surface where they cause emission of secondary electrons and scattering of electrons from the sample surface. Detection of low energy (50eV secondary electron) permits the imaging of the sample surface topography. These primary electrons can also be backscattered from the surface. The electron beam is focused to a small spot and scanned over the sample so that an image of the surface geometry can be recorded.

The resolution of a SEM reproduction depends on instrument and sample material. The limit is set by how well the beam can be focused and by scattering processes in the sample surface. Typical values of this limit are 10 – 20 Å, implying that smaller features than that cannot be detected. The image contrast can arise from several different phenomena of which one is the topographical contrast that means that it is more probable to detect electrons scattered from sample surfaces near the detector than from more distant surfaces. (Fig 2.4) Two types of electrons are used for images Secondary electron which gives more information about surface structure and back scattered electrons which gives information about composition, topography and crystallite shape. This kind of contrast gives images that are easy to interpret. Sample preparation is uncomplicated, the samples should be clean and preferably electric conducting and nonmagnetic. Insulating surfaces cause problem with saturated charges. This requires either lower acceleration

voltage for the beam (with consequently lower sensitivity) or an auxiliary coating of the surface by a thin conductive film, e.g. a gold film.

The application of SEM includes imaging grain size, roughness, porosity, material homogeneity, mechanical damage, micro crack location, film and coating thickness determination, dimension verification etc. [34, 74, 75]

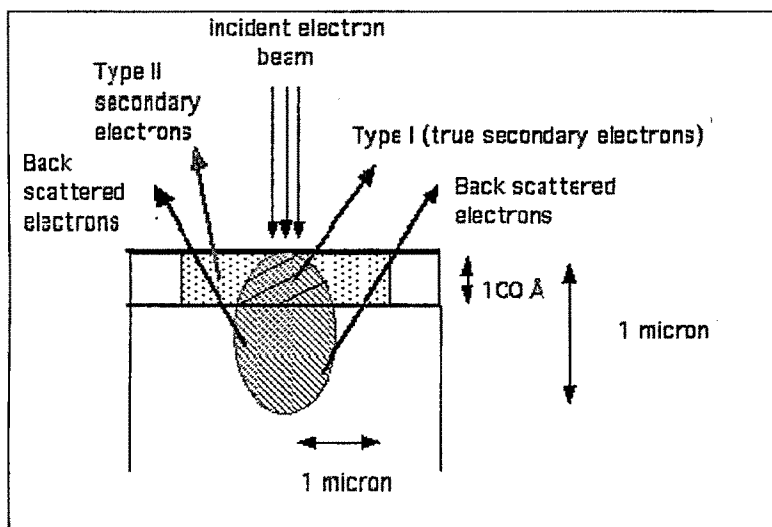


Fig 2.4 Depth of the secondary and Back scattered electron within the sample.

Energy Dispersive X ray Spectroscopy:

It can provide a rapid nondestructive quantitative analysis of elemental composition of top 1-2 micron of sample. A highly energetic ($>10\text{KeV}$) focused electron beam is directed onto an electrically conducting solid sample in vacuum, X-rays are emitted from target. Characteristic X-rays are emitted via excitation and subsequent electron transfer in atoms which have absorbed sufficient energy from bombarding electrons. The emitted X-rays are quantified as number of photons vs energy. The measurement is performed using solid state p-i-n Si(Li) detector cooled with liquid nitrogen.[74,75]

2.8.2 X-ray diffractometer

X-ray diffraction (XRD) is a versatile material analysis technique for crystalline materials. The application of XRD to nanocrystalline solids, powders, single crystal, thin films or multilayer helps in determining their crystal structure(from analysis of direction and intensities of diffracted beams). XRD can provide information on nano crystal size(strictly coherence length),micro stresses and micro strains(from analysis of line broadening), macro strains(from analysis of line shifts),repeat distances(or superlattice

wavelengths) and total thickness in multilayer films (from analysis of low angle Bragg peaks) and orientation distributions or texture (from analysis of pole figures or orientation distribution function) other advantages include is that it is rapid and nondestructive.

The idea behind X-ray diffraction is that a crystal, with its regularly repeating structure, will diffract electromagnetic radiation with a wavelength of the same size as the crystal's inter-atomic distance, just like an optical grating will diffract visible light.

One way to understand the x-ray diffraction is to regard the atom planes in the crystal as a stack of semi-transparent mirrors. The diffraction can now be treated like reflections in the atom planes where every plane reflects a part of the radiation so that there will be several reflections. These reflections will interfere constructively when they are in phase, i.e. the difference in path length equals an integer multiple of a wavelength. This occurs only when the angle of incidence satisfies Bragg's law:

$$2d \sin\theta = n\lambda$$

Where d is the distance between two adjacent atom planes,

θ is the Bragg angle,

n is an integer, and

λ is the x-ray wavelength.

For all other angles there will be a destructive interference and no reflection. As there are several sets of atom planes with different spacing in a crystalline substance there will be strong reflections in several directions for a polycrystalline sample. Every strong reflection has two properties, diffraction angle and intensity and this data can be compared with databases and an unknown substance and its crystal structure can be determined. In the case of very thin films the intensity of the reflections from the film can be so weak that they will drown in the background radiation, e.g. from the substrate. This problem can be avoided by using a grazing incidence method, (GAXRD) which means that the incidence X-rays have a very small angle with respect to the surface and this increases the intensity so that the technique becomes more surface sensitive.

By the use of a Goebel mirror parallel incidence x-rays are obtained that gives higher intensity and simplifies GAXRD. For an ordinary XRD this also makes it possible to analyze non-flat samples. [34, 76]

2.9 CORROSION RESISTANCE OF THIN FILMS

Hard wear resistant coatings are more and more being used to protect less noble materials like steels against corrosive attack. These coatings are mainly based on the nitrides, carbides and borides of the refractory metal elements. They exhibit an ideal combination of hardness, wear resistance, chemical resistance and nice colors. In applications such as chemical apparatus processing and the food industry, the mechanical loads occurring are superimposed by corrosive attack. The hard coating itself has a high chemical resistance in corrosive media. Despite this very good chemical property coated parts are often severely corroded, especially if the hard coatings which were deposited directly to less noble substrates and then exposed to a corrosive environment. This corrosive attack is due to imperfections within the coating, e.g. micro cracks, pores, pinholes and transient grain boundaries. They open possible paths for the corrosive media to reach the less noble substrate. [77-80]

Concerning corrosion, generally a distinction has to be made between a homogeneous attack of the complete surface area and a local corrosion attack. This means, for coating-substrate systems, that either the total area of the coating is attacked (as in the case of so called sacrificial coatings) or the substrate is locally corroded at damaged areas, depending on the nobility ratio of coating and substrate material. The corrosion process is determined by the ion release of metallic species and is, therefore mainly surface phenomena. [81]

2.9.1 Factors Affecting Corrosion Resistance of Thin Films

(a) Substrate Material:

Vapor deposited coating exhibit micro cracks, pores, pinholes and transient grain boundaries through which a corrosive attack on the (less noble in most cases) substrate material takes place. As mentioned by H A Jehn[89] the corrosion potentials E_{corr} and corrosion current densities I_{corr} for some TiN and ZrN coatings on steel and glass substrates. All samples with hard coatings on glass show positive E_{corr} values, those of ZrN being lower than those of TiN. The nitride coatings on steel substrates show almost the same (negative) values given by the steel substrate. The corrosion current is strongly increased too, when compared with coating-glass systems. This reflects the high

contribution of the substrate corrosion to the total corrosion process. The extent of damage depends on nobility ratio of coating substrate material. [81-83]

(b) Coating Thickness

Increasing the thickness of coating increases the corrosion resistance as, the likelihood of having the through-thickness pinholes is lowered. However in case of PVD thin films stresses increases with increases in thickness. This is due to atomic peening of substrate by depositing species. Hence depending on the magnitude of residual internal stresses corrosion resistance may increase or decrease. [75]

(c) Substrate Temperature

Increasing substrate temperature affects coating morphology. Also it reduces the stresses as film undergoes densification or expansion. Hence corrosion resistance increases with increase in temperature to certain extent.

(d) Substrate Roughness

A higher substrate surface roughness results in a less complete coverage of the substrate with the coating material because of shadowing effects during PVD film growth. Hence smooth surface with good surface finish is desirable for high corrosion resistance.

(e) % Cold Work of Substrate.

Deformation due to cold work disturbs the crystalline structure of alloys and raises the value of surface energy of the superficial layer. The disturbance is due to increase in number of defects in the lattice and enhancement of carbon and nitrogen atom mobility near lattice defects. Both single factor and their joint interaction favor the susceptibility of alloys to corrosion. Corrosion resistance depends on degree of cold work. With the critical cold work (for steels it is 5-10%), corrosion resistance deteriorate very significantly with less amounts of cold work-it deteriorate too but to a lesser degree. Higher % Cold work of substrate increases the internal stress and decreases corrosion resistance of thin films.

(f) Process variables

(a) % of ions

(b) Plasma power density

High % of ions and Plasma power density increase corrosion resistance this is due to change in chemical composition of the coatings. Also high packing factor film may

reduce the penetration of the corrosive medium onto the substrate material hence increasing corrosion resistance.

(g) Effect of environment

The same object coated with same type of coating, exhibit different corrosion resistance in different environments. For that reason generally problem of corrosion resistance is extremely difficult. It depends most significantly on: chemical composition, structure of the coating, three dimensional structure of coating surface, on defects, residual stresses, type and condition of substrate, type and intensity (temperature and concentration) of the corrosive medium and time of exposure.

(h) Coating Composition:

(i) Chemical Composition of coating

Each composition has different corrosion resistance depending on oxidizing power / ionizing capacity of coating composition.

(ii) Nature of coating:

Due to electrochemical nature of corrosion the corrosion resistance of coatings should be considered jointly with the substrate, with respect to which the coating may be either anodic or cathodic. Anodic coatings are made of metal which in given environment exhibits potential lower than that of the substrate i.e. made of less noble metal than the protected substrate. Cathodic coatings are made of a metal whose electrode potential in given environmental conditions is more electropositive than the potential of substrate metal, i. e made of nobler metal than substrate. Consequently they protect the substrate metal only when they are totally tight (without porosity, crack, flaking, spalling & scratches).

(iii) Structure of coating

The properties of alloys, such as corrosion resistance depend not only on the alloy composition but also on their microstructures. When the compositions are fixed, the micro-structure is very important to the corrosion behavior of materials

An amorphous like structure is thought to be beneficial in terms of improved corrosion resistance as grain growth is disrupted, potentially reduces the effects of growth defects and the absence of grain boundaries reduces the pathways for corrosion. Implanted layers are usually characterized by anticorrosion properties.

(iv) Residual Stresses within coating

Residual stresses are formed in coating as the result of difference in thermal expansion coefficients of substrate and coating materials (Stresses of the I kind), as well as significant defects in the structure of the coating material (stresses of II and III kind). Residual stresses may play positive or negative role depending on their character. Usually, compressive stresses are favorable, while tensile stresses are unfavorable. In order to reduce stresses of I kind, multi layered coatings are deposited, comprising composition of layers with successively changing thermal expansion coefficient relative to substrate material. Residual stresses may be reduced by the selection of appropriate materials and process parameters. The sign (kind) of stresses depends on the coefficient of thermal expansion of substrate, coating layers and on character of structural defects. If the layer contains more atoms in interstitial positions than there vacancies in lattice, tensile stresses are formed, while the reverse situation leads to formation of compressive stresses. Generally superficial layers with residual stresses are more susceptible to electrochemical corrosion in the presence of corrosive environment than layers which are free of stresses. It is assumed that a difference in the state of stress causes the creation of differences of potential in metal. Stress corrosion causes the metal to crack.

(v) Alloying additions

Addition of alloying elements increases corrosion resistance. The effect is based on “chemical” interaction increasing the corrosion potential of coating material and there is “physical” effect also i.e. denser and more fine grained coatings are formed.

(i) Porosity:

Pores negatively affect the tightness of the coatings, substantially reducing their corrosion resistance. These local defects form direct paths between the corrosive environment and the substrate. If the coating is anodic to the substrate (i.e. it behaves sacrificially), the presence of open porosity is not a critical parameter because cathodic protection of the substrate is achieved. If the coating is cathodic to the substrate, the defects lead to a rapid localized galvanic attack and ‘pitting’ corrosion of the substrate occurs. This galvanic effect localized to each open porosity, is increased by an unfavorable surface ratio (cathodic surface \gg anodic surface). As the corrosion reactions are initiated at the

coating–substrate interface, determination of the porosity is essential in order to estimate the overall corrosion resistance of the coated pieces

(j)PVD interlayer and Multilayer

Addition of interlayer and multilayer will result in lower porosity than a single layer coating, since the open structure, reaching from the surface to the substrate, will be interrupted by repeated nucleation at the interfaces between sub layers and new structures of hard coatings are formed on the top of the interlayer.[75,84-90]

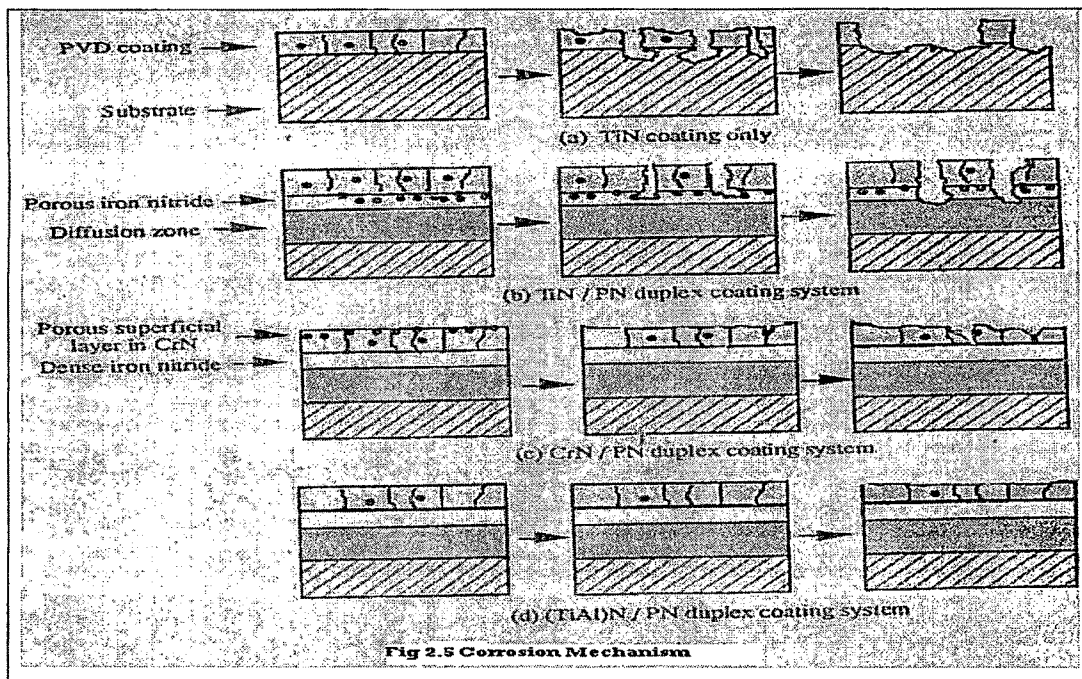


Fig 2.5 Corrosion mechanisms in (a) Single layer, (b) multilayer with porous interlayer, (c) multilayer with dense interlayer and (d) multi layer with dense interlayer and multiconstituent top layer.

In case of single layer Fig 2.5 (a) coatings pits penetrate into the substrate. However in case of duplex coatings, depending on the characteristic of interlayer the pits may penetrate the porous interlayer 2.5(b) or may stop at the interface,(2.5C) indicating total resistance to the corrosion. However fig 2.5(d) indicates better corrosion resistance because of top multiconstituent coating. [91]

2.10 WEAR RESISTANCE OF THIN FILMS:

In addition to increase lifetime of tool, application of coating results in other positive effects like:

- The improved wear resistance of coated metal cutting tools is usually utilized to increase the cutting speed and thereby the productivity, in addition to prolonged tool life.
- Reduced friction often means reduced energy consumption. In some cases, a lowered friction may permit the exclusion of lubrication or of cooling stages.
- Increased or controlled friction may be a beneficial effect in other applications such as brakes, bolted joints and safety connectors.
- Reduced tendency to sticking and material pick up from the counter surface is crucial to the performance of forming tools and many sliding applications. Anti sticking agents may be omitted in forming tool applications.
- Components of reduced weight can be designed by application of coatings. Reduced weight means e.g. an increased ratio of power to weight of car engines, which in turn may give lower fuel consumption. [88]

2.10.1 Factors Affecting Wear Resistance of Thin Films

The success of hard coatings for various applications like cutting tool, coating on bearing substrates results from a combination of the coating's physical and mechanical properties. From a functional standpoint, chemical stability, hot hardness, and good adhesion to the substrate are essential; optimum coating thickness, fine microstructure, and compressive residual stresses can further enhance their performance [89]

(a) Substrate Coating Combination

Depending upon the application, substrate-coating combination or system is selected. Because of vastly differing properties of substrate and coating materials, only a few combinations have been successful in achieving the requirement level of system integrity. The deposition parameters (substrate temperature, plasma characteristics, etching time, substrate bias, etc.) together with the *substrate characteristics* (e.g. composition, microstructure, topography) determine the *coating characteristics* (thickness, chemical composition, microstructure and topography, etc.). Here, the influence from the substrate is primarily related to the nucleation and growth of the coating, and to the coating

topography. Consequently, the substrate material and surface preparation is crucial to the coating topography and adhesion which in turn influence the performance of the coating composite. [88] The important material parameters to be considered in achieving better performance are elastic module (stress discontinuity), thermal expansion coefficients, crystal structures and chemical compatibility of coating and substrate material. [89,90]

(b) Adhesion

The single most important property of a coating/ substrate composite is the adhesion of the coating to the substrate. If this is inadequate, premature failure of the coated part can occur due to coating detachment. [91] Good adhesion of the coating to the substrate is necessary for satisfactory performance of the coated tool. Initial coating nucleation on the substrate should feature inter diffusion of coating and substrate atoms at the interface. [88,89]

(c) Young's modulus

The Young's modulus of the coating (E_c) is a useful parameter, for measurements and calculations of the stress state and the cracking and delamination behavior of coating composites. [88]

(d) Residual stresses

Tribological PVD and CVD coatings usually display residual stresses (σ_{res}). Structural misfits in epitaxial nucleation, growth and ion bombardment during growth are two stress origins of intrinsic nature. The stresses induced during cooling from the deposition temperature due to mismatch in thermal expansion between coating and substrate materials and possible phase transformations occurring during cooling are two sources of the external origin. The final stress state is a combination of these components. The actual stresses during application (σ) is given by

$$\sigma = \sigma_{res} + \sigma_{app}$$

Where σ_{res} denotes residual stresses within the substrate

σ_{app} denotes the stress field induced by the application, including external forces and thermal mismatch stresses due to frictional heating.

Too high compressive stresses may result in spontaneous coating detachment, e.g. during cooling from the process temperature. In less severe cases, the coating may detach when the coated component becomes loaded externally. The risk for detachment is closely

related to the geometry and topography of the coating/substrate interface, the smoother the interface the less is the risk.[88]If the coating has a porous microstructure or has internal stresses which are tensile, coating will wear faster. [92,95]

(e) Hardness

Ceramic thin films prepared by plasma-assisted vapor deposition are known to have a non-equilibrium density of structural built-in defects. Therefore, the film hardness is increased compared to their corresponding bulk counterparts. [93, 94]

Hard coatings contribute to increased abrasive wear resistance as long as they maintain a higher hardness than the substrate at machining temperatures. [89] The hardness of a coating depends not only fundamentally on its bonding structure but also the way in which it is deformed during measurement. Coating materials with high degrees of cohesive energy, covalent bonding and short bond length exhibit high intrinsic hardness. High cohesive energy of a coating material however need not translate into higher hardness, as measured by indentation methods. This is because the hardness of a coating system depends upon other factors such as composition, microstructure, texture, substrate material, indentation load and testing method.

(f) Toughness

Coating cracking or fracture often precedes damage of PVD and CVD coatings. Thus, the ability of the coating composite to accommodate deformation in tension or compression without crack nucleation and propagation is crucial. Critical situations are found in applications of non-conforming sliding or rolling. Since cracking is initiated by tensile stresses, any compressive residual stress has first to be relaxed. Consequently, if the coating initially has a high compressive residual stress, the coated component can take more tensile strain before the coating will fracture. The critical component strain is thus a more important parameter than the critical intrinsic tensile strain of the coating. [88]

(g) Fracture Toughness

The coating fracture toughness is a parameter of great importance because crack initiation and propagation virtually always precede coating failure. Fracture toughness, can be estimated from the length of cracks developed during indentation in the hardness measurement exercise. [95]

(h) Roughness

The surface roughness of a material significantly influences the tribological performance of a mechanical system. If, for example, the harder member of an assembly is rough, the counter face may wear by abrasion due to micro cutting or micro ploughing mechanisms. It has been clearly established that under lubricated conditions the relative dimensions of the asperities and the lubricant film thickness are critical in avoiding metal-to-metal contacts i.e. to efficient lubrication and lower resultant friction and wear. Rough tool surfaces are not preferred in metal forming industries for obvious reasons - the surface finish of the product generally replicates the tool surfaces. [96]

(i) Chemical stability

The criterion for chemical inertness is either a high negative standard free energy of formation of the coating material or low solubility in the work piece material at temperatures encountered during machining. [88]

(j) Coating thickness.

In a film-substrate tribo-system, the thickness of the film plays an important role in determining the performance and characteristics of a system. In a general sense, the thicker the film, the longer service life it has, provided that it does not spall through high internal residual stress, but this is not always true. Practical experiences reveal that the optimum thickness of a film is a function of the working conditions. For instance, for turning, the thicker the film, the longer service life it has, while for milling and interrupted turning, there exists an optimum film thickness. The film thickness is indeed a key factor that influences the behavior of a coating system: it must be taken into account and cannot neglected. [97, 98]

To achieve maximum metal-cutting productivity, the thickness of the modified surface layer has to be optimized. If the modified tool surface region is too thin, the effect persists for too short a time during cutting. If the coating is too thick, the layer acts as a bulk material and the advantage of an engineered composite may be lost. It is established that functional tool coatings can range from 2 to 20 μm in thickness. [88]

(k) Microstructure and morphology

Coating process and process parameters influence the microstructure of hard coatings. The microstructure (e.g., grain size, grain structure, and grain- and phase boundaries) in

turn affects the mechanical properties of the coatings. It is known that finer grain sizes in PVD TiN are associated with higher micro hardness. PVD coatings with high lattice defect density are associated with high residual stress which can also contribute to their high micro hardness [88]

(I) Multilayer and Multicomponent coatings

The use of multilayers has often been cited as the way forward to improve the mechanical, tribological and chemical properties of coatings. A practical approach is to consider how the requirements of a surface differ at different locations within it — i.e. at the interface with the substrate, within the coating itself and at its surface as shown in Fig. 2.6 [99]

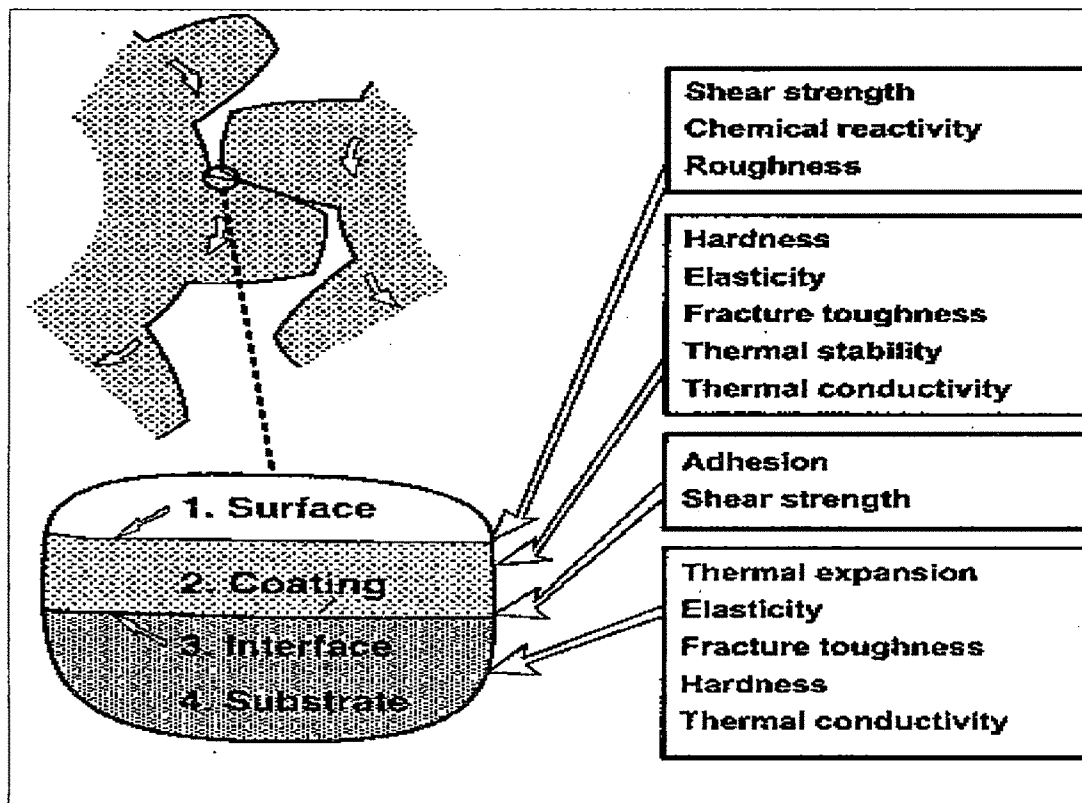


Fig. 2.6 Tribologically important properties in different zones of the coated surface

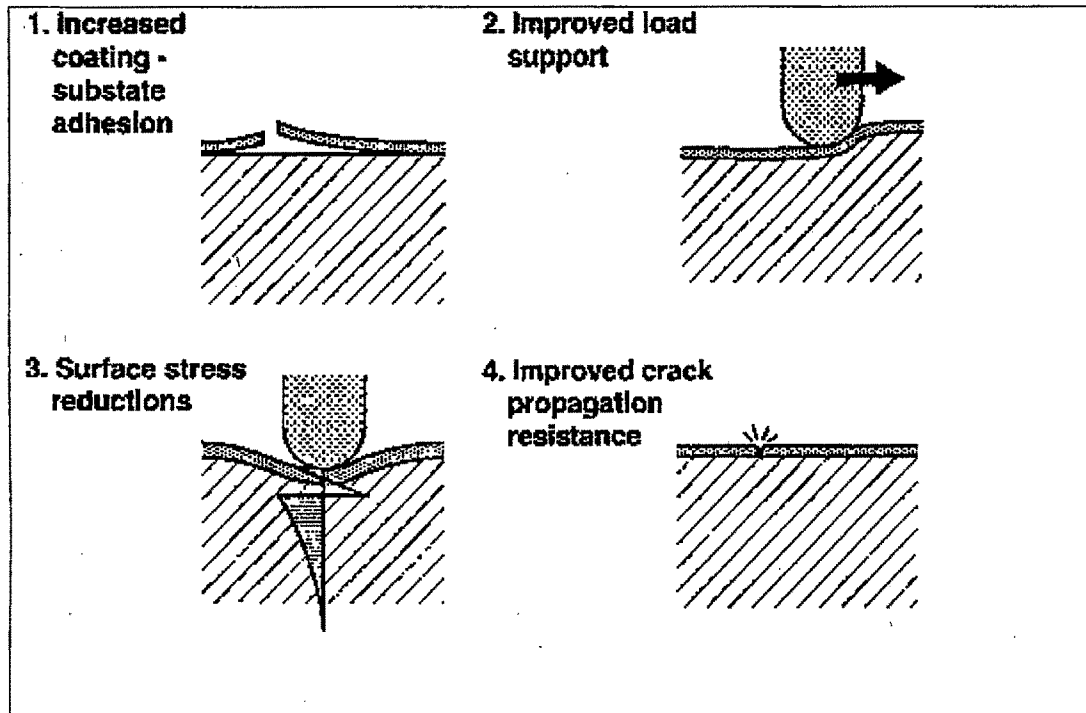


Fig 2.7 Improved wear resistance of multilayered coating.

As shown in fig. 2.7 a multilayer coating can improve the tribological properties of the surface by increasing the coating/substrate adhesion, improving the load support, reducing the surface stresses and improving the resistance to crack propagation. [99]

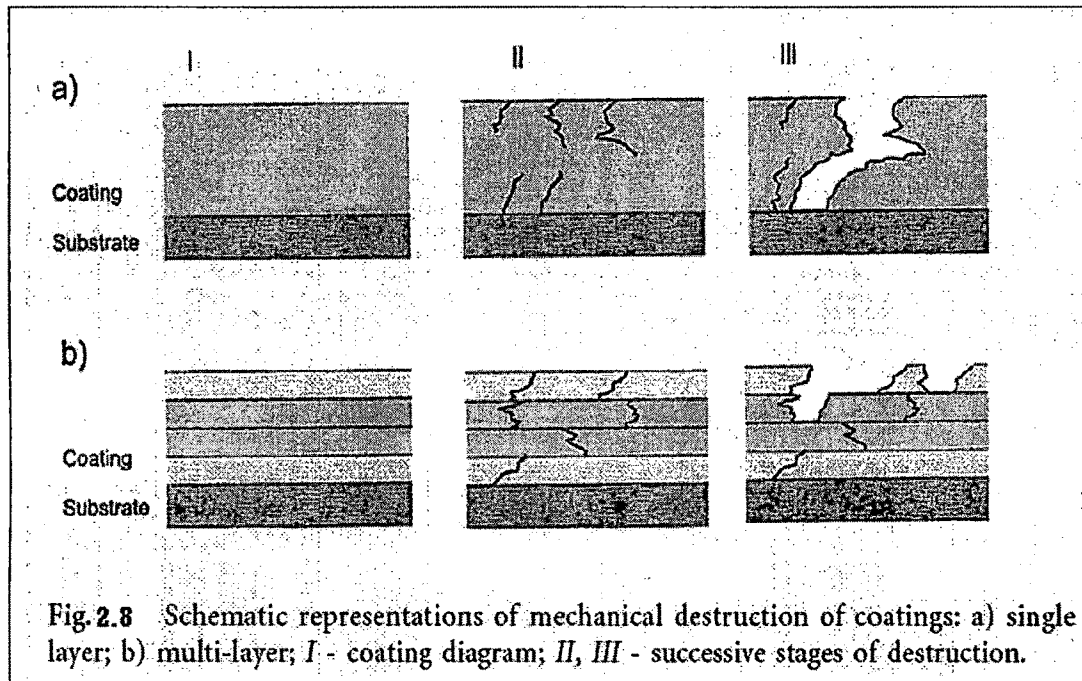


Fig. 2.8 Schematic representations of mechanical destruction of coatings: a) single layer; b) multi-layer; I - coating diagram; II, III - successive stages of destruction.

In a monolayer coating the initiation of micro cracks occurs both at the surface and at the interface with the substrate. Propagation and coalescence of micro cracks destroy the coating across its entire cross-section (Fig 2.8a). On the other hand, the mechanism of destruction of a multilayer coating is different. Initiation of micro cracks occurs mainly at the surface of the coating, while interfaces between layers change the direction of micro crack propagation, thus enhancing the mechanical resistance of the coating. This type of coating wears in a laminar manner (Fig.2.8b). [100,101]

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