THE EFFECT OF THIN FILM COATINGS AND NITRIDING ON THE MECHANICAL PROPERTIES AND WEAR RESISTANCE OF TOOL STEEL

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DCU

DECLARATION

I hereby certify that this material, which I now submit for assessment on the programme of study leading to the award of MEng. is entirely my own work and has not been taken from the work of others save and to the extent that such work has been cited and acknowledged within the text of my work.

Signed: ———————— ID No.: 99144964
Adel Zeghni

Date: 30th- September- 2003

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Finally to my wife Nuwara, son Ahmed and daughter Nosaiba, who in varying degrees had to contend with a less than full-time husband and father for the period of my study.

DEDICATION

TO

my wife Nuwara,

son Ahmed

and

daughter

Nosaiba

THE EFFECT OF THIN FILM COATINGS AND NITRIDING ON THE MECHANICAL PROPERTIES AND WEAR RESISTANCE OF TOOL STEEL

ABSTRACT

A.E. ZEGHNI, B.Sc. Eng.

The wear characteristics and mechanical properties of three different coatings deposited on different types of tool steel have been investigated. Four types of tool steels D2, D3, Vanadis 4 and Vanadis 10 were used as substrate materials. These materials were cut to the desired dimension 55mm x 25mm x 5mm and prepared for treatment and coating. The specimens were nitrided using gas nitriding, a case depth of 150 µm was achieved in all cases. Three types of coating TiC, TiN and Al_2O_3 were commercially deposited on the treated and untreated samples using the magnetron sputtering technique. A thin film coating of ~ 4µm thickness was measured on each sample. The coatings were characterized in their thickness, hardness, adhesion and chemical composition. A wear test rig designed, constructed and commissioned at DCU was adapted for the wear tests. Wear characteristics of coated, nitrided, and prenitrided coated samples were investigated and compared to the uncoated samples characteristics. The microhardness of the surfaces coated and nitrided show an increase in hardness, with the highest hardness in the case of TiC coated Vanadis 10 samples. Wear test results show that titanium carbide coatings and nitriding treatment prove to have good wear resistance, on the other hand titanium nitride showed slight improve in wear resistance while alumina did not. Nitriding of the samples prior to the deposition of the coatings improved the wear resistance of the substrate materials particularly in the case of TiN and Al_2O_3 coatings. Adhesion evaluation of the coatings confirmed the observation of the wear and hardness. The substrate materials have a profound effect on the wear resistance and mechanical properties of the coated surfaces.

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LIST OF ABBREVIATIONS

AES	Auger Electron Spectroscopy
ARE	Activated Reactive evaporation
CRT	Cathode Ray Tube
CVD	Chemical Vapour Deposition
dc	Direct Current
EDX	X-ray Energy Dispersive Analysis
fcc	Face Centred Cubic
HSS	High Speed Steel
IBAD	Ion Beam Deposition
OECD	Organisation for Economic Co-Operation and Development
PECVD	Plasma Enhanced Chemical Vapour Deposition
PVD	Physical Vapour Deposition
RBS	Rutherford Backscattering
RCF	Rolling Contact Fatigue
rf	Radio Frequency
SEM	Scanning Electron Microscopy
SIMS	Secondary Ion Mass Spectroscopy
TEM	Transmission Electron Microscopy
ULSI	Ultra Large-Scale Integration
XRD	X-ray Diffraction

CHAPTER 1

INTRODUCTION

1.1 SURFACE ENGINEERING AND WEAR

Surface treatment and coatings are being used more and more frequently in the industrialised societies in order to reduce or control friction and wear of engineering materials. The principal impetus behind this endeavour is related to economic and environmental aspects [1]. The need to save cost of replacing worn machine elements, to optimise energy consumption and reduce the use of hazardous lubricants are some of the examples.

Wear is of enormous economic importance. As an example, it was estimated that its cost to the British economy in 1988 was £ 2 billion [2].
It is believed that proper attention to tribology lead to savings of between 1.3 and 1.6% of the UK GNP per year over the last 10 years [3].

For a tool to be able to resist wear it must have high hardness and mechanical strength, be chemically stable and possess a high toughness [4,5].

As is generally recognised, it is difficult to combine all these properties together in a single conventional tool material. However, nowadays, surface-engineered materials are developed so as to tailor desired material properties for a specific application.

A large variety of functional properties can be optimised separately for the bulk material and the surface by applying the appropriate coating or treatment. For example, in cutting tools, the bulk material is chosen to provide the toughness while the coating is responsible for the wear resistance and for reducing friction.

In the last three decades surface engineering has become an enabling field of science and technology. Surface engineering includes surface coatings, mechanical work-hardening processes, implantation processes, heat treatment and surface shape design [6]. The combination of the properties of both the bulk substrate and its surface treatment is required in the fields of application of coatings and surface treatment.

1.2 OBJECTIVES OF THE STUDY

This study aims to contribute to the ongoing effort of understanding the low friction and wear resistance coatings and surface treatment and to understand the analytical tools used in the characterization of thin films, the main objectives of this study were:

i) To characterize the surface coatings and the nitrided layers obtained on the surface of the substrate materials.

ii) To compare the behaviour of treated and untreated surfaces under dry sliding wear test conditions.

iii) To examine the performance of the coating-substrate combination and the influence of the different substrates on the wear resistance and the mechanical properties of the system.

iv) To study the effect of pre-treatment on the adhesion, hardness and wear resistance of the coatings.

v) To compare the behaviour of the different coatings on the same substrate material.

vi) To study the effect of the number of wear cycles on the wear resistance of the coatings at the same normal load.

1.3 METHOD OF APPROACH

The method of approach is outlined in Fig. 1.1. The method of approach consists of (i) sample preparation,(ii) coating and nitriding,(iii) film characterization, (iv) wear test and wear measurement, (v) examination of the samples tested and analysis of the results.

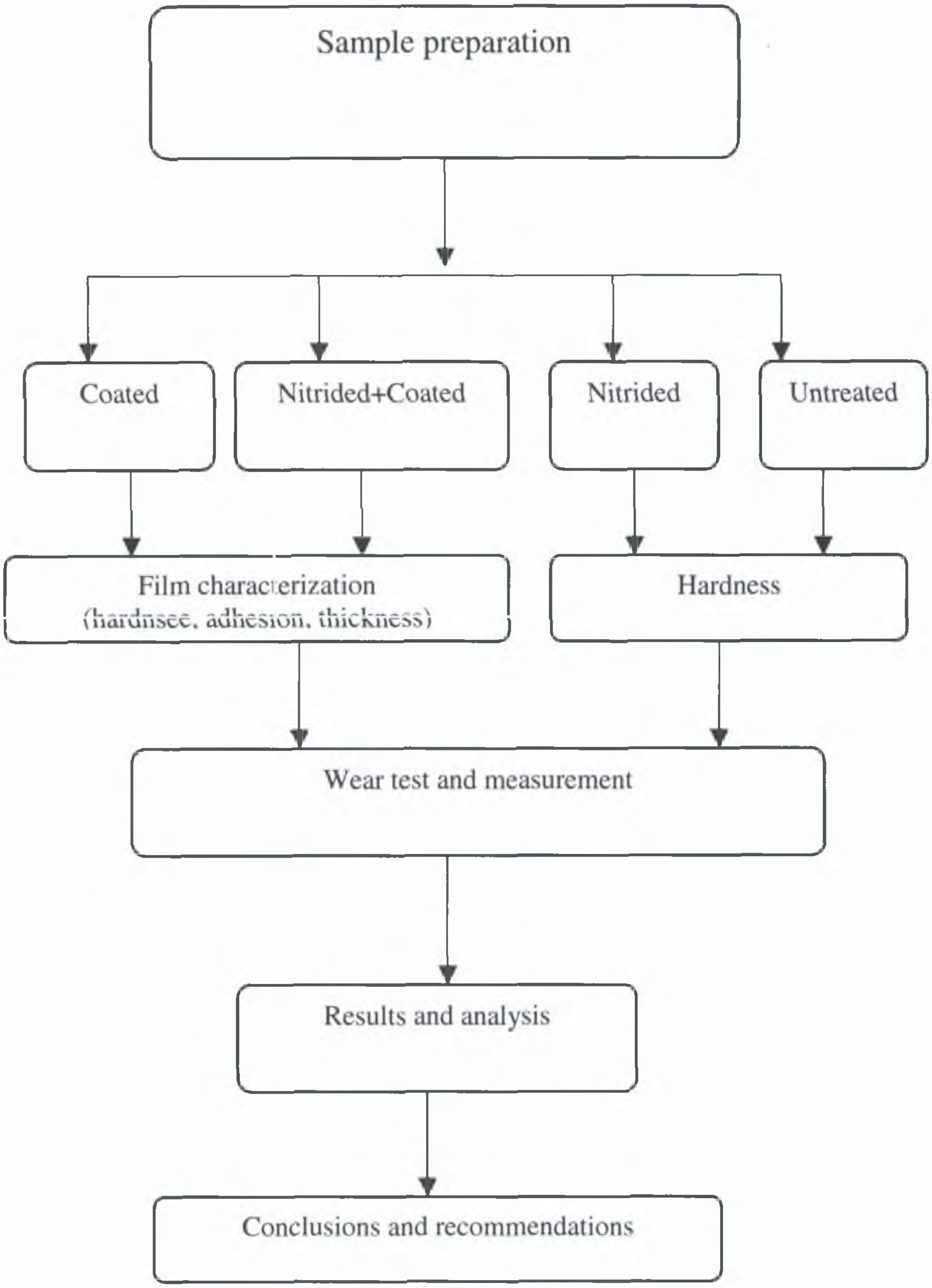


Fig. 1.1 Method of approach of the study

CHAPTER 2

SURFACE ENGINEERING TECHNOLOGY

1.4 THESIS OUTLINE

The thesis is divided into seven chapters. Following the introduction chapter two reviews the area of surface engineering, provides information regarding surface coatings and treatments and coating deposition techniques. Chapter three covers the area of wear and wear testing. Chapter four presents the experimental equipment, while chapter five concentrates on the experimental procedure. Chapter six presents the main results of the thesis and the analysis and the discussion of the results. Chapter seven highlights the main conclusions drawn from the work and it makes recommendations for further work.

2.1 INTRODUCTION

Surface engineering encompasses the research and technical activity aimed at the design, manufacturing, investigation and utilization of surface layers, both for technological and for end use, with properties better than those of the core [7] Surface engineering can be the key to improve performance for many products by improving their properties, such as corrosion resistance, wear resistance, fatigue limit etc

Surface engineering practices play a major role in ameliorating problems and enhancing prospects for advancement in three major areas of technology, corrosion, wear and manufacturing [8] The expanding use of surface engineering generated a need for understanding or at least an awareness of the physical and chemical properties of materials (coatings/substrate), their mechanical properties and especially structure/property relationships in materials

In this chapter some of the principles and concepts of this field of science and technology are highlighted

2.2 SURFACE COATINGS

2 2 1 Concept of Coatings

A coating is a layer of material, formed naturally or synthetically or deposited artificially on the surface of an object, made of another material, with the aim of obtaining the required technical or decorative properties [7]

Coatings can be formed in different structures as the following

The Single Layer Coating is a coating deposited in one process, comprising of one layer of material. This could be a single constituent coating consisting of one material element or compound, such as; titanium, titanium nitride, or a multi-component coating such as Ti(C, N) or Ti(Al, N).

The Multi-Layer Coating is one, which consists of two or more materials. These may be layers of the same material, separated by a sub layer, or they may be of different materials. The aim of applying multi-layer coatings is the intensification of the protective or decorative or other function. For example, the double layer nickel-chrome electroplated coatings on automotive and motorcycle component. The external chromium layer gives the coating a shiny appearance and the internal nickel layer binds to the substrate.

2.2.2 Types of Coatings

Coating can be classified in different ways, depending on the criteria used. Division of coatings can be made by material, by application and by method of manufacturing of the coating [7].

Classification of Coatings by Material

Metallic Coatings

These coatings are made of different metals, such as zinc, nickel, chromium, aluminium, tin etc., or metal alloys such as steels, brasses, W-Co, W-Ni, Ni-Fe, Zn-Al, etc.

Non metallic Coatings

A wide range of non-metallic coatings are available of natural and synthetic origin, amongst them are:

Rubbers
Plastics

Enamels
Ceramics

Classification of Coating by Application

This classification depends on the task of the coating and can be divided into the following groups

Protective coatings
Decorative coatings
Protective-Decorative coatings
Technical coatings

Classification of Coatings by Manufacturing Methods

Depending on the way the coating is manufactured, five groups of coatings can be distinguished [7]

Electroplated coatings
Immersion coatings
Spray coatings
Cladded coatings
Crystallizing coatings
Some of these groups will be discussed in more detail later on in this chapter

2.3 SURFACE COATING METHODS

In the recent years surface coating science and technology has grown worldwide into a major research area. The importance of coatings and the synthesis of new materials for industry have resulted in a tremendous increase of innovative coating processing technologies. There exists a huge variety of coating deposition processes and technologies, which originate from purely physical or purely chemical processes. The more important coating processes are based on liquid phase chemical techniques, gas phase chemical processes, glow discharge processes and evaporation methods [9].

Rickerby and Matthews [10] divided the process into the following four categories:

Gaseous state process
Solution state process
Molten or semi-molten state processes, and
Solid state processes
A general classification of surface coating techniques is shown in Fig.2.1.

2.3.1 Gaseous State Process

Gaseous state process covers surface engineering techniques in which the coating material passes through a gaseous or vapour phase prior to depositing onto the substrate surface [11].

The vapour deposition technique includes vacuum evaporation and sputtering. Sputtering is based on the bombardment of the target with excited ions. Vapour deposition includes chemical vapour deposition (CVD) and physical vapour deposition (PVD).

The name physical vapour deposition describes the process of obtaining a coating of the required material using a physical method of evaporating and condensation on the substrate surface

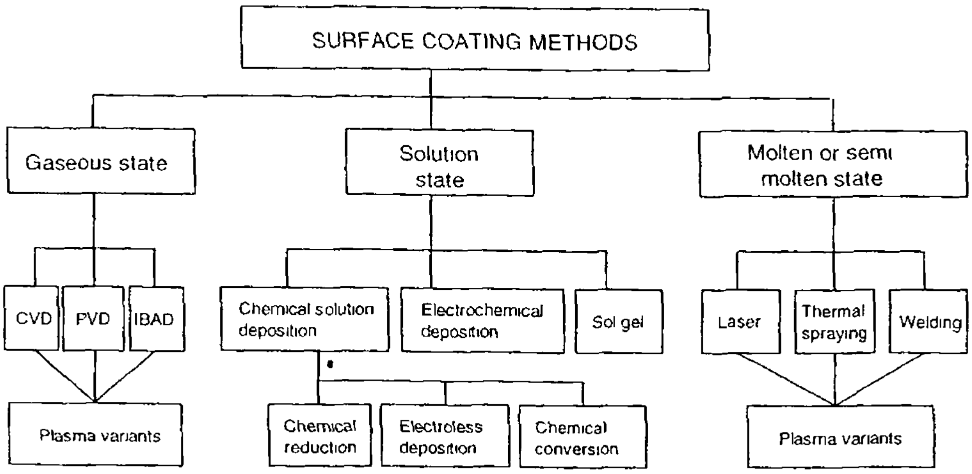


Fig 2 1 A general classification of surface coating methods [35]

2.3.1.1 Chemical Vapour Deposition

Chemical vapour deposition (CVD) methods have been widely used in the industry worldwide since the late 1960s to produce anti-abrasive and anti-corrosion layers because of their versatility for depositing a very large variety of elements and compounds covering a wide range of materials from amorphous deposits to epitaxial layers having a high degree of perfection and purity [12-14].

The CVD coating process consists of heating parts to be coated in a sealed reactor with gaseous reactants at atmospheric or lower pressure. The gaseous chemical reactants are transported to the reaction chamber, activated thermally in the vicinity of the substrate and made to react chemically to form a solid deposit on the substrate surface.

CVD is the main method for coating sintered carbide inserts used as cutting tools. For the deposition of TiC, the coating temperature between about 950 ^{o}C and 1100 ^{o}C and system pressure ranging from about 1 torr to atmospheric pressure are used [15].

CVD coatings in the hard metal industry have been employed in two fields:

The first is CVD coated steel metal forming tools. This concerned the coating of forming, stamping and press tools where the applications are concerned with high pressure sliding and shaping process . The life of these tools was in a number of cases dramatically improved by the application of TiN or TiC CVD coatings.

The second field of application concerns the process of machining. Use of CVD coatings can increase the cutting speed and thus productivity of the chip producing technique. Furthermore the cutting force is reduced and the cutting temperature is markedly lower than in the case of the uncoated inserts [16]. More details about coatings for CVD processes and their applications are listed in reference [17]. A schematic of a conventional CVD process is shown in Figure 2.2.

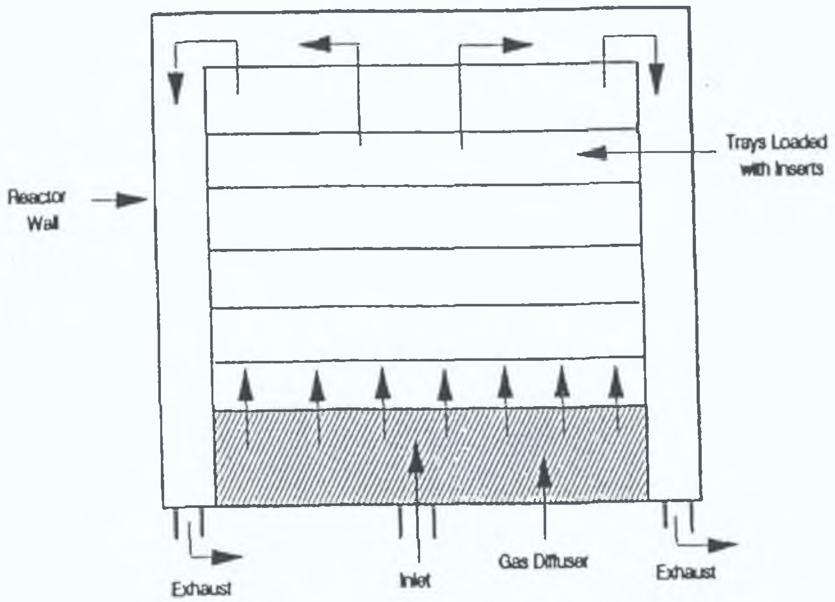


Fig. 2.2 Schamatic showing CVD reactor [83]

2.3.1.2 Physical Vapour Deposition

Many investigations have been carried out to find a way of reducing the high temperature of CVD-processes. However, the greatest advances in the coating of hard materials at low temperatures have been achieved using the PVD technique [18]. This process enables coatings to be deposited at a temperature as low as 200 °C, thus allowing tools manufactured from temperature sensitive tool steels to be included. The temperature/pressure zones, which are used by the current depositing processes are shown in Figure 2.3.

The PVD technique involves the atomisation or vaporisation of material from a solid source and the deposition of that material onto the substrate to form coatings, see Fig.2.4.

That said, there are several versions and modifications of PVD techniques, all utilizing different phenomena, which take place at pressures reduced to 10^{-5} Pa. These phenomena are the following:

- Obtaining of vapour of materials through erosion of the vapour source due to evaporation (electron beam and arc evaporation) or sputtering.

- Electrical ionisation of gases supplied and metal vapour obtained.

- Crystallisation from the obtained plasma of metal or compound.

- Condensation of components of the plasma (particles, atoms, ions) on the substrate.

The above stages of the process of physical vapour deposition occur with different intensity in different versions [19].

The PVD techniques have certain advantages and disadvantages when compared to their CVD counterparts. PVD techniques allow the deposition of coatings at low temperature, which is advantageous for maintaining the mechanical properties of the substrate. Since CVD processes operate at high temperatures, because of the coating interfaces become less well defined because of the inter-diffusion, which takes place during the process. This inter-diffusion improves adhesion if brittle intermediate phases are not formed [3].

The high deposition rate of most PVD techniques permits the more rapid build up of material and allows easier production of multi layer coatings [20, 21]. PVD coatings are deposited at low pressure (10^{-3} to 10^{-2} torr) which means the atoms and molecules have long mean free path and undergo fewer collisions, making PVD a line-of-sight deposition technique. This necessitates moving the tool fixtures during the deposition process to ensure uniformly thick coatings on the tool. The PVD films are extremely fine grained and individual crystallites contain large concentrations of point defects. In contrast, CVD films are generally formed under thermal equilibrium, resulting in high angle grain boundaries and grain sizes in the range of 0.5μm [22,23]. Consequently, PVD coatings show a high compressive stress, whilst those formed by CVD are under relatively low tensile stress [24].

The compressive residual stresses in a coating improve the surface fracture strength or toughness of the coated tool, which improves the fatigue wear resistance. On the other hand, it can cause low adhesion between coating and substrate [25,26]. In addition, the lower deposition temperature used in PVD processes leaves the stress state of the substrate unaffected, whilst the CVD process anneals out any beneficial compressive stresses, which had been presented in the uncoated tool [27].

Magnetron Sputtering

Sputtering is one method of creating the flux of source material in PVD process. Sputtering can be defined as the ejection and dislodge of atoms from a solid surface following momentum exchange due to surface bombardment by energetic particles as shown in Figure 2.5. The high-energy particles are usually positive ions of a heavy inert gas (argon is a commonly used inert gas). The sputtered material is

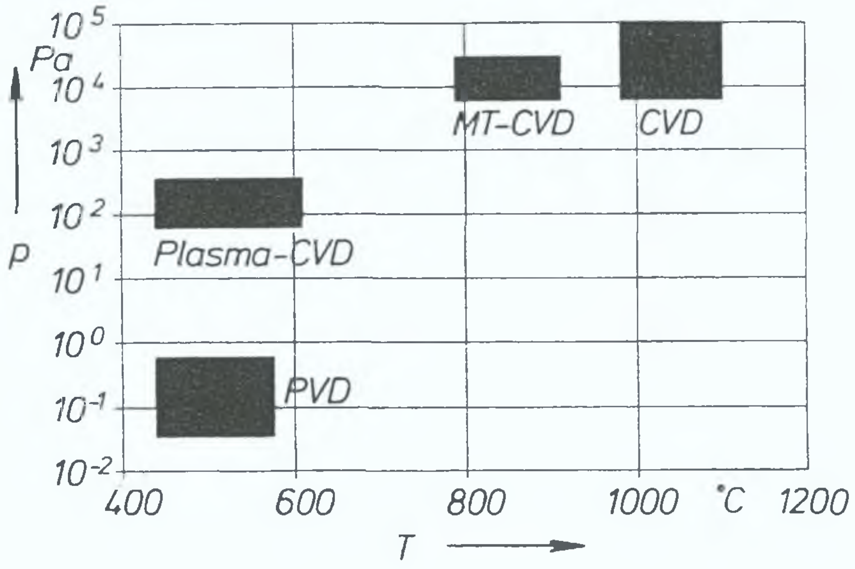


Fig.2.3 Pressure-Temperature zones for methods of hard material coating [16]

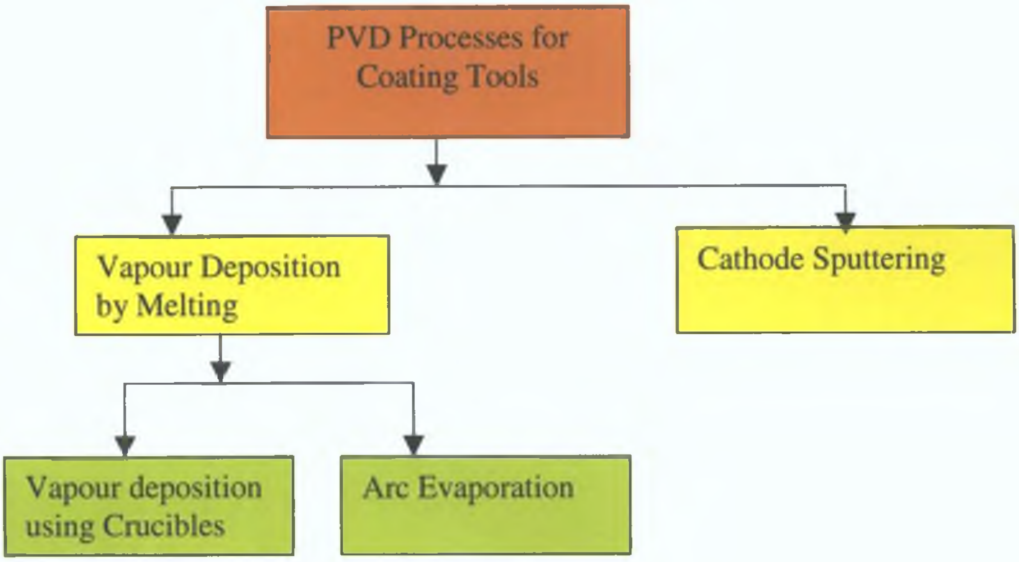


Fig. 2.4 PVD processes for tool coating

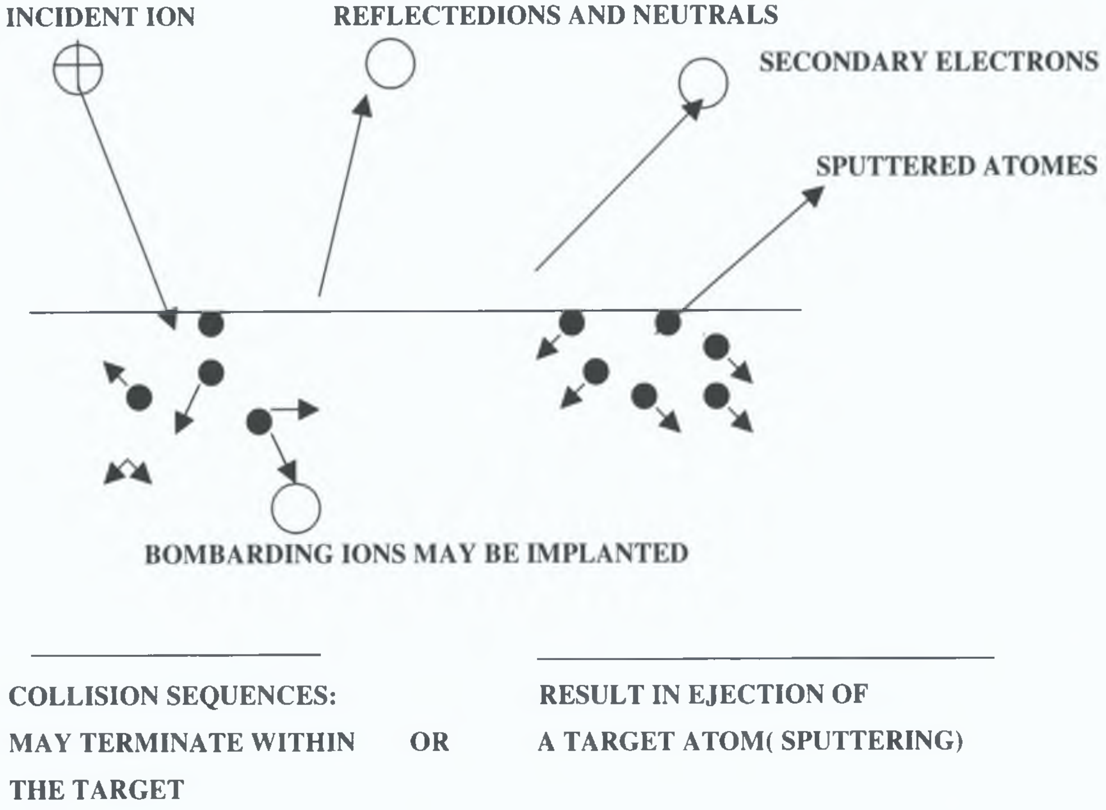


Fig. 2.5 The sputtering process[131]

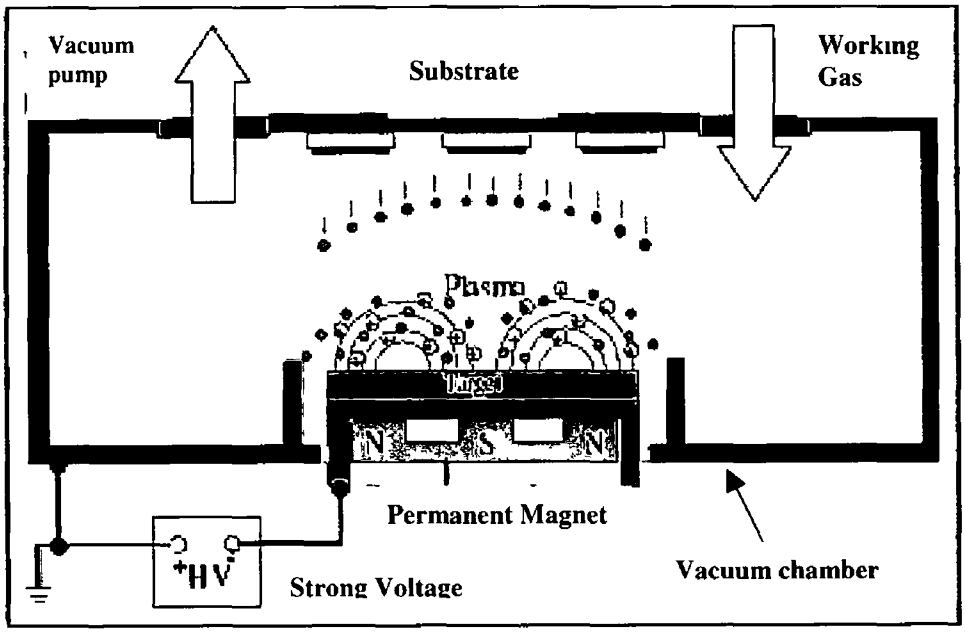


Fig 2.6 Schematic diagram of magnetron sputtering process [83]

ejected primarily in atomic form from the source of the coating material called the target The substrate is placed in a position in front of the target to intercept the flux of sputtered atoms Ions in the sputtering process can be produced using glow-discharge ionisation or an ion beam source [28] In the glow-discharge sputtering process, the target is placed into vacuum chamber which is evacuated to $10^{5} - 10^{3}$ Pa and then pack filled with a working gas to a pressure 5×10^{1}-10 Pa to sustain a plasma discharge As the gas (say Ar^{+}) strikes the target creating secondary electrons which then form more ions A negative bias (0 5-5 kV) is applied to the target so that it is bombarded by positive ions from the plasma Ions accelerated by this voltage impact on the target cause ejection sputtering of the target material The following are the categories of glow-discharge sputtering i) diod sputtering, ii) triod sputtering and iii) magnetron sputtering

Magnetron sputtering is a magnetically assisted glow-discharge sputtering, where magnetic fields are used to enhance the sputtering rate by increase the ionisation efficiency of the electrons The closed magnetic field traps the fast secondary electrons that escape from the cathode surface and forces them to undergo ionising collisions with inert gas atoms away from the cathode surface and a dense secondary plasma forms in the region where the substrate is placed as shown in Figure 2 6 This plasma causes the bombardment of the growing film

2.3.2 Solution State Processes

The main coating techniques in this category are electroplating and electroless plating The solutions used are usually aqueous, and deposits can be produced on metallic or non metallic substrates Solution state processes can be divided into chemical and electrochemical, but according to Lowenheim [29] this division may not be straightforward since some reactions, which appear to be chemical may in fact be electrochemical One of the advantages of the solution processes over the vapour deposition methods, is that they have no upper limitation thickness, which is limited in the vapour deposition method due to the stress build up leading to debonding, which limits the use of films with less than 10 μm thick when hard ceramic materials are deposited [30]

The main methods of solution state process are

Chemical solution deposition
Electrochemical deposition
Sol-gel processing

2 3.3 Molten and Semi-Molten State Processes

These processes include laser surface treatments, the hard facing techniques of thermal spraying and welding Each of these techniques covers a very wide range of methods A review of these techniques can be found in references [6, 31-33]

2 4 COATING SELECTION

The protection of materials by hard coating is one of the most important and versatile means of improving component performance There are a tremendous number of hard coatings and techniques of depositing these coatings, therefore it is important to have criteria for the selection of the most suitable coating material for specific needs This is a difficult task to achieve because the requirements for the composite (substrate/coating) are often very complex and many compromises must be accepted Problems with the coating selection for specific applications arise mainly because many desired properties such as good adherence at the substrate-coating interface or high hardness and high toughness cannot be achieved For example, increasing hardness and strength usually lead to the decrease in toughness, adherence, low notch sensitivity and poor resistance to crack propagation [34,35]

There are some points of interest, which should be considered in the design of the coating system

(i) The objective of the coatings

(ii) The bulk material must manage to withstand the processing steps required to deposit the coating

(iii) The coating should not impair the properties of the bulk material One must take a system approach to coating design, it is not useful to improve wear resistance if the corrosion of the bulk material is negatively affected

(iv) The coating material must be able to be applied to the bulk material, and the deposition process must be capable of coating the component in terms of size and shape

(v) The coating method must be cost effective, but factors such as reduced down-time, longer service life, more favourable workings conditions, higher production quality and renewal of the coating at a later stage should be considered in addition to the coating cost

Smart [36] and James [37] were probably the first to propose coating selection criteria Smart presented a checklist based on two sets of subheadings

Process Selection

(i) General factors such as process availability and quality required

(ii) Job factors such as, size, weight and machine ability

(iii) Surface preparation factors such as undercutting and tolerances

(iv) Finishing factors such as required finish and post-surfacing activities

Materials Selection

(i) General factors such as knowledge of similar applications and cost

(ii) Operating environment, including wear types and lubrication

(iii) Substrate factors such as previous surface treatment and size

James made the selection more straightforward by designing interdependencies of the criteria. He divided the selection method into three headings:

Requirements: Before any selection begins, it is important to understand the function of the coating. James suggests that by comparing surface and bulk requirements the designer will be able to decide whether a bulk material is sufficient or a coated surface is needed.

Limitations: These refer to the constraints that may be imposed on the designer by environmental, use, social, supply and process factors.

Interactions: These are divided into these parts:

(i) Coating/substrate interaction; which may have high influence on adhesion.

(ii) Coating/process interaction; different properties may be achieved when different depositing techniques are used for the same coating material.

(iii) Process/substrate; the effect of the process on the substrate must be considered.

2.5 CERAMIC COATINGS

Ceramic materials are often very hard and stiff, even at elevated temperature and they are usually chemically stable, due to their fundamental bond type. For these reasons ceramics have attracted much interest as material choice in engineering applications subjected to surface wear in harsh and corrosive environments at high temperature [38, 39]. Often these desired properties are only needed at the surface and hence a thin ceramic coating on an engineering component of another material such as steel can be the best solution. The bulk ceramics can exhibit very low wear rate compared with bulk metals, but they are very brittle and costly in production, and they are not good because of the risk of cracks and fatigue. This problem can be avoided by the application of this ceramic coating onto cheap and shock resistance materials [7, 40]. Ceramic coatings are also being developed on ceramic substrates mainly to limit chemical interactions between the tool and the work material. To take advantage of high temperature resistance deformation of cemented carbide and silicon nitride and to minimize chemical interactions when machining steel at high speeds, multilayer coatings of TiC/TiN or Al_2O_3/TiC were developed [41 – 44].

2.5.1 Titanium Nitride Coatings

Titanium nitride is one of the most widely applied and most thoroughly studied hard coating material. The bond structure in transition metal nitrides consists of a mixture of covalent, metallic and ionic components, and is responsible for high hardness, excellent wear resistance, chemical interactions, good electrical conductivity and superconductivity properties. The use of TiN films as diffusion barriers in contact structures in silicon integrated circuits [45], solar cells [46], microelectronics [47] and in advanced metallization scheme for ultra large-scale integration (ULSI) applications [48] has been investigated. Although TiN is mainly used as a protective hard coating because of its attractive tribological properties, TiN has also been used in decorative applications because of its golden colour.

TiN coatings are applied by a variety of techniques such as activated reactive evaporation (ARE), ion plating, cathodic ion plating and sputtering ion plating, rf/dc reactive/non reactive sputtering and magnetron sputtering and CVD [49 – 54]. The most successful application area of TiN is that of coatings on various carbide and high-speed tool steels. PVD TiN is especially attractive for HSS tools because of the low temperature of deposition compared to the CVD technique.

Sprouland Rothstein [55] reported the improvement of 50 times life of magnetron sputtering TiN coated M – 7 HSS drills over the uncoated drills both in dry and lubricated conditions. Ramalngam and Winer [56] observed that TiN coated cemented carbide tools experience significantly lower wear than those uncoated tools.

Hochman *et al* [54] tested TiN coating in rolling-contact-fatigue (RCF) tests They deposited 0 2 and 0 8 μm thick coatings by dc magnetron sputtering on 440 C stainless steel and AM55749 bearing steels They found that TiN coatings improved RCF life by a factor of more than 10

Sundquist *et al* [57] found that the wear rate of PVD TiN coating on D3 tool steel was between 4 and 24 % of the wear rate of the uncoated samples depending on the surface roughness They proposed that increase in wear resistance of the tool coated with TiN can be expected only when the roughness of the surface is less than the coating thickness Up to 10 times improvement due to decreased wear for thin PVD deposited TiN coatings on steel substrate have been reported by several authors [58-62]

Han *et al* [63] reported the enhancement of micro hardness of STD 11 steel coated by TiN using IBAD technique, up to 1400 kg/mm^2 corresponding to 70 % increase in hardness ratio, and therefore highly improved wear resistance against Al_2O_3 and WC – Co balls in un-lubricated conditions They also reported that the performance of TiN coated STD 11 steel moulds and dies, the dimensional tolerance of which is less than 5 μm, which proved to have potential for application in semi conductor manufacturing

Rickerby and Burnett [64] examined PVD TiN coatings of varying thickness Their observations were that thicker coating deterioration was due to spalling at wear groove intersections followed by micro chipping of the coating at the edge of the spalled region

M Scholl [65] examined the abrasive wear of TiN coatings on HSS substrate under low stress abrasion, his observations were that as the coating was harder than the silica abrasive, conventional abrasion mechanism was not evident and no adhesion failure was observed The SEM investigations showed micro fissuring of the surface. His results indicated that as long as coating integrity is maintained under the flow of abrasive material, the wear rate of the TiN is small.

Efeoglu and Arnell [66] studied the sliding fatigue behaviour of TiN coated by close field unbalance magnetron sputtering technique (CFUBMS) by modified scratch test. The tests showed that the number of cycles to failure increases with decreasing applied load. One of their observations was that the high applied sub-critical loads generated heavily plastic deformation, which lead to the extrusion of the substrate from both sides of the scratch track without any coating failure or detachment. This condition is a sign of excellent coating-substrate adhesion.

An increase in tool life by a factor between 3 and 10 for TiN coated tool steel turning tools was reported by Kowstubham and Philip [67].

TiN-coated turning tools were found to be more resistant to flank wear than uncoated tools [68].

Y. Iwai *et al* [69] evaluated the wear resistance of PVD TiN coated on HSS substrate using the solid particle impact test for wear evaluation. They found that the coatings proved to have much higher erosion resistance than the substrate material, and consequently, the wear rate increased significantly to the higher level of the substrate material when the coatings were penetrated.

Bienk *et al* [70] and Bromark *et al* [71] reported the reduction of adhesion wear and, friction and abrasive wear of PVD TiN coating.

An area of interest in the field of application of TiN is the addition of certain elements to the titanium nitride. The addition of these elements cause more stabilisation to the fcc phase in TiN coatings.

Vaz *et al* [72] and Pal Dey and Deevi [73] reported that the presence of silicon in TiN improve the oxidation resistance of the coating. The improvement of the wear resistance (flank wear) of the TiN coated cutting tool by adding Zr has been reported by several authors [74 – 81]

An important aspect of TiN is its stoichiometry, which is the proportionality between Ti and N The stoichiometry determines the colour of the coating and effect of the hardness TiN_x coatings with $x < 1$ are silver coloured, stoichiometric coatings with $x = 1$ are golden colour and coatings with $x > 1$ are copper coloured [82] The composition of the coating or the ratio (N/Ti) has significant influence on the micro hardness as shown in Fig 2 7 For under stoichiometric (N/Ti<1), has been shown to increase the hardness up to values between 3500 kg/mm^2 and 1500 kg/mm^2 depending on the substrate material and process parameters For over stoichiometric coatings (N/Ti >1) all results show decreasing hardness value as the ratio of N/Ti increases and value as low as 340 kg/mm^2 are reported as shown in Figure 2 7 [83]

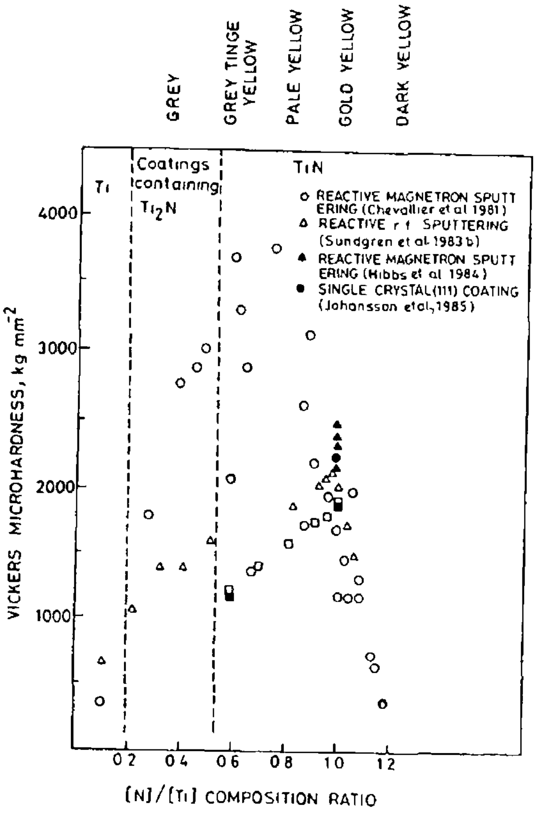


Fig 2 7 Effect of stoichometry of sputtered TiN coating on hardness and colour [83]

Zhang and Zhu [84] reported an increasing hardness and elastic modulus for x increasing from 0 5 to 1 11 for TiN coatings The relation between micro hardness deposition parameters and mechanical properties of TiN coating was studied in detail in reference [85]

2.5.2 Titanium Carbide Coatings

Titanium carbide, the first commercially successful CVD coating used on a cutting tools was introduced in late 1969 and was found to improve the wear resistance when used to machine steel and cast iron Titanium carbide is the most widely used ceramic carbide coating [15] The application of TiC includes cutting tools to increase their life, onto balls of gyro application ball bearings, and as first-wall materials in the tokamak-type nuclear fusion reactor [83] TiC coating is today applied to forming tools, such as punches and dies, and where abrasive wear is predominant TiC coatings provide high hardness about 3-5 GPa HV and abrasion resistance, with low coefficient of friction and resistance to cold welding They have high melting point and good tribiological properties They have in general shown low friction in the range of 0 1 to 0 4, for both PVD and CVD when they slide against steel [35] The properties of TiC coatings strongly depend on coating deposition technique and coating conditions

TiC coatings have been applied by plasma spray, ARE, ion plating, sputtering CVD, and PECVD techniques TiC coatings have been deposited by sputtering process on various substrates such as steel, stainless steel, copper, molybdenum and Ti based alloys [86-88]

The stoichiometry of TiC sputtered coatings has significant influence on the microstructure, mechanical and physical properties Sundgren et al [89] examined the effect of the composition on the microhardness of TiC coating deposited by rf-sputtering onto various substrates They found that the hardness increases with increasing C/Ti ratio

The density and the electrical resistivity also change with change in the composition The density decreases as the carbon content increases [83]

Many investigations have been made to measure the residual stresses in TiC coating produced by the sputtering process The results of these investigations showed that all the TiC coatings are in state of compression Residual stresses have been shown to be a function of deposition parameters The very high compressive stresses in TiC coatings (1 to 10GPa) could give rise to lattice distortion which would affect the dislocation propagation and thus increases the hardness of coatings However, such high stresses may reduce the coating substrate adhesion [90-92]

Fraklin [93] reported that the erosion and corrosion resistance of tools for moulding have been improved using PVD TiC coating Mathews and Leyland [35] have achieved considerable improvements in wear resistance in knives used in the packing industry when these were coated by PVD TiC

Gun et al [94] studied the tribiological behaviour of PVD TiC, TiN and Ti (CN), they found that TiC coatings have high wear resistance and low friction

Feng et al [95] studied the tribiological and mechanical properties of magnetron sputtering TiC with different kinds of interlayers (Ti, Cr, Mo) They found that inserting a Cr or Ti interlayer between TiC coating and the substrate reduces the wear and friction and improves the hardness and elastic modules of the coating, but inserting a Mo interlayer had the opposite effect Even though TiN more widely used as a coating for tools by PVD techniques than TiC, the outperformance of TiC in certain tribiological conditions has been reported [96-98]

2 5 3 Aluminium Oxide Coatings

The Al_2O_3 coating was the third commercially successful coating that emerged for use for cutting tools in the 1970's The outstanding wear resistance of Al_2O_3 coated tools when used for high speed machining of cast irons and steels was attributed to the superior thermodynamic stability, high hot hardness and lower chemical dissolution wear rate relative to TiC and TiN [99,100]

Al_2O_3 has the high hardness of the oxides One of their primary assets is greater resistance to oxidation at elevated temperatures than any other refractory material The tribiological applications for Al_2O_3 include cutting tools, bearing, seals and other sliding/rolling applications

Alumina can exist in a number of metastable polymorphs in addition to the thermodynamically stable α- Al_2O_3 as shown in Figure 2 8 Amorphous Al_2O_3 coatings are soft and are used as protection against chemical corrosion or as electrical insulators Alfa Al_2O_3 coatings are hard and are used for wear applications

Al_2O_3 coatings have been commercialised using CVD and plasma sprayed processes However, PVD Al_2O_3 coating in the tribiological applications are not yet commercially available

In the last years efforts have been increased to deposit crystalline aluminium oxide layers by PVD processes such as magnetron sputtering These coatings specially developed for dry machining, additionally open up the opportunity to combine a reduction of friction at elevated temperature with high wear resistance The using of magnetron sputtering allows the deposition of γ- Al_2O_3 phase at substrate temperatures approximately of 350°C and of α- Al_2O_3 phase at a substrate temperature of 680°C [101,102] The K- Al_2O_3 phase could be deposited at 370°C using an additional RF coil for ionisation [103] See Figs 2 8 and 2 9

Zywitzki et al [104] deposited Al_2O_3 layers with hardness between 20 and 22GPa using electron beam evaporation technique, thus the application of the process for the deposition of wear resistance Al_2O_3 layers for cutting tools may become widely used in recent years.

Matthews et al [105] studied the wear and friction of PVD Al_2O_3 coated pin sliding on a steel disc at a speed of 0.2 m/s and a load of 5 N. They measured a low coefficient of friction of 0.3 and a wear rate of the same order of magnitude as that for TiN or TiC coatings in the same condition.

In addition to the application of Al_2O_3 in tribiological applications it is used in optics, corrosion, dielecrical, microelectronics and catalysis.

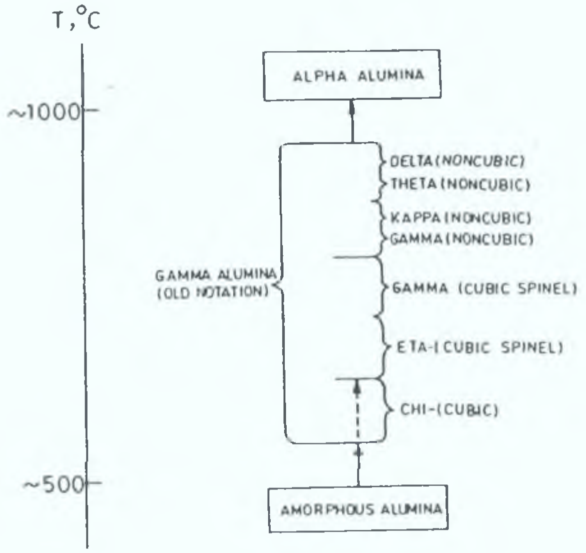


Fig. 2.8 Schematic of aluminium oxide phases [83]

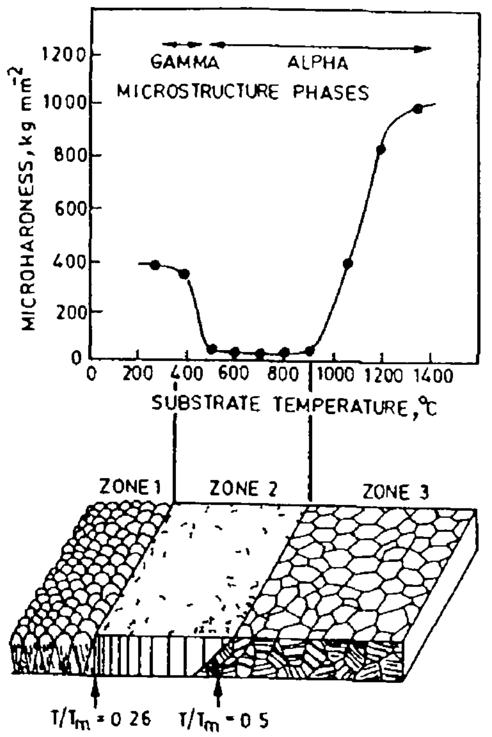


Fig 2 9 Influence of substrate temperature/coating material melting point on the microstructure, phase and hardness of alumina deposited by electron beam evaporation [83]

2 6 SURFACE TREATMENT PROCESSES

Surface treatment processes can be divided into two categories

i) Those in which only the surface structure is changed by thermal or mechanical means This process includes, induction hardening, laser hardening, electron beam hardening, chill casting and work hardening

ii) Those in which both composition and structure are changed either by diffusion or ion implantation This process includes carburizing, boriding, chromizing, nitriding, aluminizing, siliconizing, ion implantation and ion beam mixing

Many of the surface treatment techniques can be applied very economically to large and complex components Most surface treatments are employed to increase surface hardness, wear resistance, minimize adhesion and to improve the corrosion resistance of the tool steel base The surface treatments are normally applicable to ferrous alloy, but some of them can be applied even to non ferrous alloys The practical case depth versus wear resistance is shown in Table 2 1 [83]

Surface treatment covers very wide range of process and techniques, some of them will be discussed in this chapter and more details about surface treatment techniques can be found in references [106,107] Figure 2 10 shows a comparison of process temperature and depth of hardened material produced by different methods of surface modification of steel

2.6.1 Shot peening

Shot peening is a method of cold-working process in which compressive stresses are induced in the surface of metallic materials due to the impact of a high stream of

Light case	<50 μm	Good wear resistance at low stresses
Medium case	50-200 μm	Good wear resistance at higher stresses
Heavy case	200-500 μm	Sliding and abrasive wear resistance Resists crushing and fatigue
Extra heavy case	>500 μm	Wear and shock resistance at severe conditions

Table 2 1 Wear resistance as function of case depth of surface treatments [83]

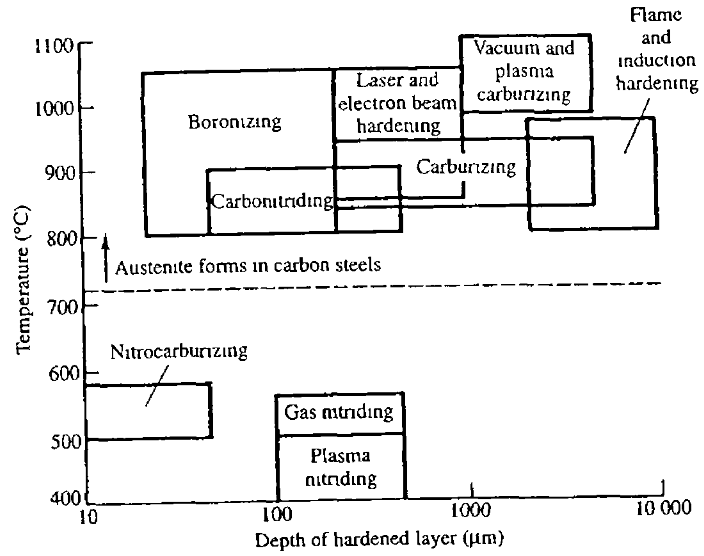


Fig 2 10 Comparison of process temperature and the depth of the hardened material produced by different methods of the surface modification of steel [35]

shots, which cause plastic flow of surface metal at the instant of impact Up to 0 5mm beneath the metal surface may be affected during the process, but the normal effect usually extends from to about 0 12 to 0 25mm

This process improves the fatigue resistance and thus improves wear resistance in situations involving the repeated application of load, however, it appears to have little effect on other wear processes [106]

2.6.2 Induction hardening

This process relies on heating a thin surface layer of carbon or alloy steel (0 3 to 0 5 per cent carbon) into the austenitic temperature range, then this layer is rapidly quenched, either by immersion or spraying the heated part after heating has been completed

The heating source in this process is a high frequency alternating current, which induces eddy currents in the surface of the steel components The typical case depths are in between 0 5-2mm The time required for induction hardening is up to 30s [106]

2 6 3 Ion implantation

This process involves the introduction of other elements to the substrate surface by using high-energy ion beams of the elements to be introduced in vacuum chamber, at pressure on the order of 10^{4} Pa The ions of the foreign material lodge below the surface and lock into place [108,109] Ion implantation processes have many advantages over the other surface treatments including

i) No distortion of the substrate due to the low temperature of the process
ii) No surface damage
iii) It is a vacuum process, thus no oxidation takes place

iv) No mechanical weakness or interface corrosion, because it is not a coating process

On the other hand the main disadvantages [110] of the process are

i) The extremely shallow treatment depth (~100nm), which limits its tribiological application to the light loaded cases
ii) It is a line of sight method, thus the need for the target or the beam to be manipulated in order to achieve uniform surface thickness
iii) It requires a high capital investment and an associated high running cost

2.6.4 Carburizing

Carburizing is thermo-chemical process relying on the diffusion of carbon atoms to the substrate surface at temperature of 950°C The source of carbon can be solid, molten salt, gas or plasma These parts are then directly quenched in oil or water A thick case depth can be produced with hardness up to 850 HV [83] Carburizing is restricted to steels with low carbon content (0 1 to 0 2 %C) Carburizing is not recommended for high speed steel cutting tools because of the extreme brittleness of the case produced The high hardness of the case hardening produced by carburising is accompanied by improved wear resistance, however, the high temperature of the process causes some distortion

2 6 5 Nitriding

Nitriding is a surface-hardening ferritic thermochemical treatment for low alloy and tool steels that introduces nitrogen into the steel surface at a temperature range of 500-550°C [106]

The nitrogen is introduced into the steel surface by reaction with solid (powder) or gas phase or more recently, by nitrogen- containing plasma

$$2NH_3 \longrightarrow 2(N) + 3H_2 \qquad (2.1)$$

$$\text{N (atomic form)} + \text{steel surface} \longrightarrow \text{various nitrides} \qquad (2.2)$$

The chemical reaction of nitrogen with steel produces various iron-nitrides, which are hard and wear resistant. Therefore the treated components do not require quenching to achieve full hardness [111].

At the nitriding temperature steel is in ferritic condition and thus there is no chance for grain growth. The process results in minimum distortion and excellent dimensional control compared with other surface hardening techniques.

According to the Fe-N binary diagram [112], as shown in Figure 2.11,nitrogen has partial solubility in iron and can form a solid solution with ferrite at nitrogen contents up to about 6%. When the nitrogen content exceeds 0.1wt % a compound called γ' – nitride (Fe_4N) is formed. At nitrogen contents exceeding about 8% the equilibrium reaction product is ε compound, Fe_3N. The γ' layer (called white layer) is undesirable because of its excessive brittleness. Its presence can be minimised by using special nitriding techniques, e.g. liquid nitriding. Although the case depth and the hardness of the nitriding layer depends strongly on the nitriding time, these properties are sharply dependent on the type of steel. Alloy steels containing alloying elements such as Al, Cr, Mo, V and W form shallow and very hard surface layers. These elements have strong affinity to form stable nitrides [106, 107, 113].

Nitriding, mainly because of its cost effective, easy and non-toxic nature (with the exception of salt nitriding) has been of particular importance for various industrial applications, including bearings, gears and tooling [114]. There are three types of nitriding are employed to hardening steels, gas nitriding, liquid nitriding and plasma nitriding. In gas nitriding technique the nitrogen is introduced to the surface of ferrous materials by holding them in contact with a nitrogen-containing gas, which is usually ammonia at a temperature at about 550°C. In liquid nitriding technique (nitriding in a molten salt bath), the process takes place approximately at the same

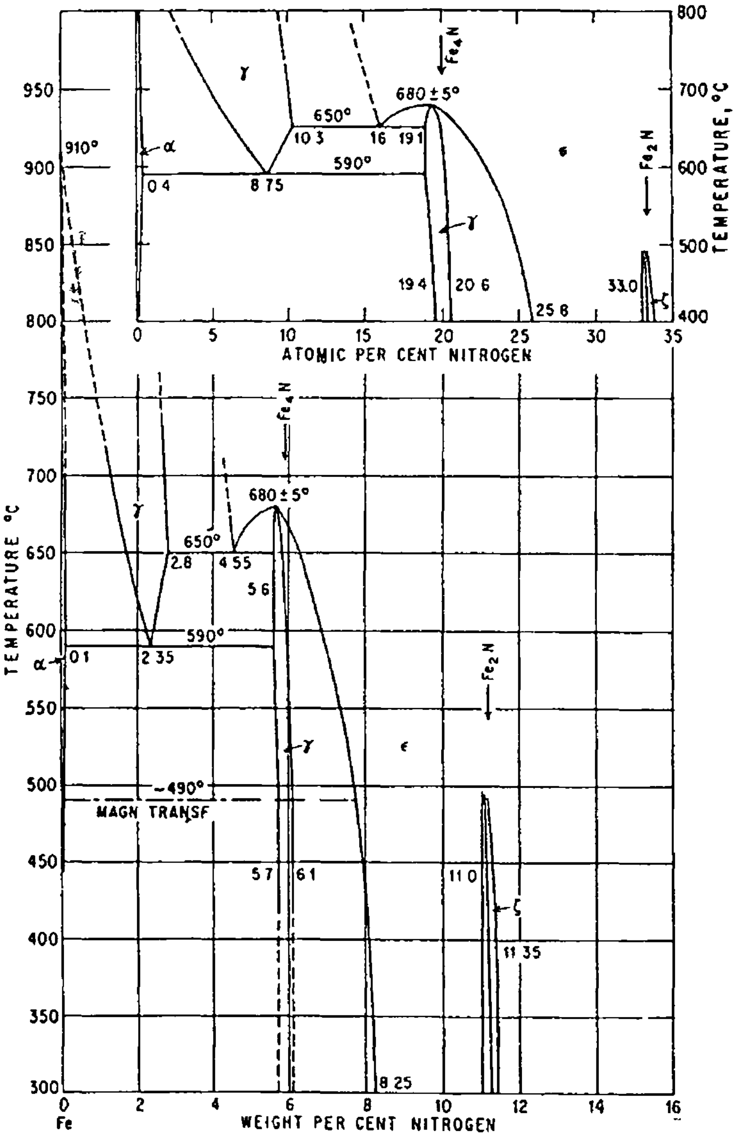


Fig 2 11 Fe-N Binary phase diagram [175] temperature as gas nitriding. The salt bath consists of mixtures of sodium and potassium cyanide (from which nitrogen is released during the process) and sodium carbonate, potassium carbonate and potassium chloride.

Liquid nitriding is preferred to gas nitriding for high-speed steel cutting tools because it can produce a more ductile case with a lower nitrogen content [113].

Recent advances in ion-beam and plasma-based technologies have led to process optimisation and a more effective diffusion processes called plasma nitriding is also known as ion nitriding or glow-discharge nitriding [106,115]. The material to be treated is placed in a processing chamber which is then filled with the working gas (nitrogen). Plasma consisting of nitrogen ions and electrons is formed in the processing chamber when a high voltage electrical energy is applied to the substrate. The subsequent ion bombardment of the heated substrate surface allows the nitrogen ions to penetrate and diffuse into it.

The use of plasma nitriding permits better quality cases in lower times or temperatures. The temperature used in the process can be as low as 350 °C. Nitriding,in general, is a well known as surface hardening technique to improve the hardness, the wear resistance and the fatigue of low alloy and tool steels because of the significant improvement in properties such as hardness, fatigue resistance and in some steels, corrosion resistance.

2.7 DUPLEX TREATMENT

Duplex or multilayer coatings, comprise consecutive layers of different materials or treatments, deposited on top of one another, to intensify the protective or decorative or other functions of the material. The development of such multilayer coatings has been shown to provide an improvement of the performance over comparable single layers [116]. PVD hard coatings such as TiN, TiC and TiCN are well known for providing engineering surfaces with high hardness and good tribiological properties, however application of single PVD hard coatings to the substrate materials cannot guarantee the optimal tribiological performance without pretreatment of the substrate materials due to plastic deformation of the substrate which results in eventual coating failure. The surface treatment provides a hardening and increases load support effect on the substrate [117-120]. By comparing the cutting ability of indexable inserts coated with TiC and TiN, it has been found that TiC gives good protection against wear, whilst TiN reducing crater wear. These advantages of the two coatings can be used as a duplex coating of TiC/TiN [16].

Many approaches aim to enhance the load bearing capacity of the coated surfaces and improve the adhesion of the coatings such as deposition of an interlayer material or compound prior to the coating or the treatment of the surface by nitriding or carburizing. In terms of the cost and complexity, surface treatment such as nitriding and carburizing are better candidates. Sun and Bell [121] and Van Stappen et al [122] studied the beneficial effect of nitriding steel before PVD coating and found reduced wear on TiN under these conditions. Fox-Rabinovich et al [123] concluded that ion nitrided sub-layer improved by >1.5 times the wear resistance of the tool with PVD coatings.

It is well known that wear resistance of a coated tool strongly depends on the coating adhesion to the substrate. It has been found that pre-nitriding of tool steel can improve coating adhesion [124]. Plasma nitriding, for example, was found to increase the adhesion of 3μm thick TiN coating on HSS substrates [125]. Nickel et al [126] made a comparison between the wear characteristics of TiN coated HSS drills and that of pre-nitrided TiN coated HSS drills. They found that the pre-nitrided drills had longer life than the only coated drills. Also the wear features of the pre-nitrided drills indicated that the coatings were subjected to progressive wear. On the other hand the TiN coated only drills experienced interfacial spalling.

Zeng et al [127] examined the development of (Ti, Al) multilayered coatings for high speed machining tools using unbalanced magnetron-sputtering technique. The results showed that the tool life with this coating was improved by factor of 4 or better under the testing conditions used compared to the uncoated tools.

2.8 STRESSES IN THIN FILMS

The residual stress field is a very important parameter in coating technology since it influences the stability and coating properties. All metallic and compound films are in a state of stress. Residual stresses of the order of several giga pascal can be measured in thin films [128,129]. Very often such stresses limit the film thickness that can be realized before spalling.

Very high residual compressive stresses also can cause low adhesion between coating and substrate. If the substrate is not perfectly smooth a high residual stress in combination with a weak interface can cause the coating to spall in advance of the coated component ever being used [22, 23, 130]. The stress in the films depends on both the materials and the deposition process. The total stress is composed of thermal stress and the intrinsic stress (internal stress). The thermal stresses arise from the different thermal expansion coefficients of substrate and deposited material. The intrinsic stresses, have two main causes, the mismatch between the lattices of film and substrate and the coupling of film grains. While thermal stresses can be limited by simple cooling devices during the deposition, intrinsic stresses cannot always be controlled due to the complex nature of these stresses. The thermal stresses in thin films is given by:

$$\alpha_{th} = E_f(\alpha_f - \alpha_s)(T_s - T_a) \tag{2.1}$$

where E_f is the Young's modulus, α_f and α_S the coefficients of thermal expansion for film and substrate, T_s is the temperature during deposition and T_a is the temperature during measurements [131]. A considerable effort has been devoted in order to establish the relationship between the residual stress, process parameters and performance of PVD coatings. Ton Shoff and Seegers [132] reported that the cutting performance of PVD-coated tools is strongly influenced by the stress distribution in the subsurface of the substrate. Janack et al [133] investigated the effect of collimation on internal stress in sputtered-deposited coatings. They found increase in the level of accumulated compressive stress of collimated films compared to the uncollimated films.

The film stress of PVD coating was found to depend on gas pressure, target-to-substrate distance and the substrate temperature condition during deposition [127]. With agreement with theoretical models, low pressures and low distances lead to compressive stresses while high pressures and high distances lead to tensile stresses. Substrates coated with compressive stressed layers show a higher resistance to microcracking and wear when compared to those coated with films in tensile stress state [129, 134-137].

CHAPTER 3

WEAR OF MATERIALS AND WEAR TEST METHODS

3.1 INTRODUCTION

According to the OECD wear is defined as the progressive loss of substance from the operating surfaces of a body occurring as a result of relative motion at the surface [138].

Wear, corrosion and breakage are the main cause of failure of engineering components. Statistical analysis shows the main reason for the failure of machines in not breakage, but the wear of the moving machine components. Wear is of tremendous economic importance, not only because of the cost of the replacement of the parts, but also the expenses involved in machine downtime, lost production and the efficiency of the worn equipment which lead to inferior performance and increase the energy consumption. Therefore controlling wear can result in considerable savings. One of the main uses of coatings and surface treatments is to reduce friction and control wear.

Wear as a function of time or sliding distance evolves in three stages as shown in Fig.3.1. The first is the running-in stage which represents a small portion of the overall wear process and a number of mechanical wear mechanisms, especially those depend on the adhesion or abrasion are likely to be operating simultaneously. The second stage which is the steady state condition is maintained for the operational life of component. In this stage wear is low but progressive. The third stage is one of catastrophic wear, in which the wear rate rises again and the third body mechanisms come in to play [139,140].

In general the rate of removal of material from one or both of the solid surfaces is slow but steady and depends on many factors such as, hardness, load, speed, surface roughness and temperature as illustrated in Fig. 3.2. The need to improve the wear resistance of engineering components is ever increased and many approaches have been tried in order to address this issue. Surface treatments, coating and lubrication are examples Wear particles are an important source of information and by studying their size, composition and physical and mechanical properties, it is possible to establish highly specific ideas on the process of their formation

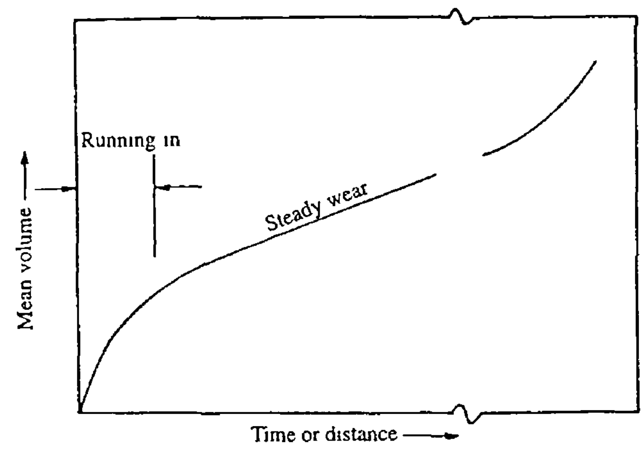


Fig 3 1 Wear as function of the operating time/sliding distance [139]

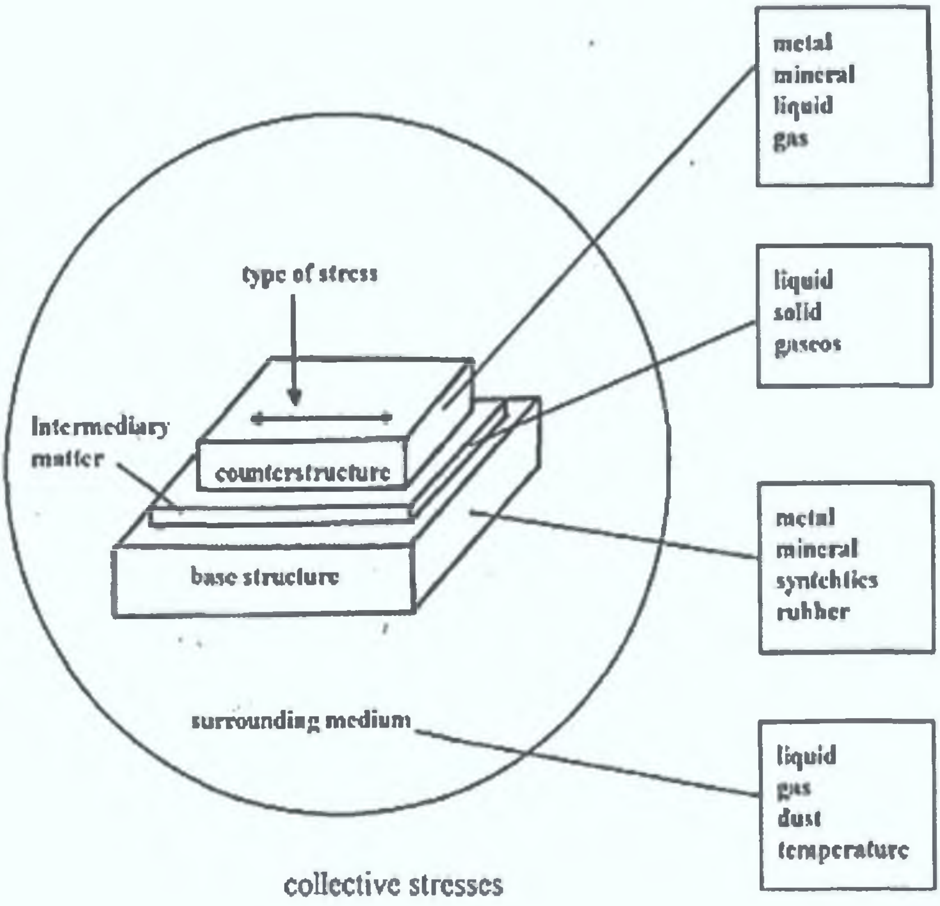


Fig.3.2 Principle factors influencing wear [35]

3.2 WEAR MECHANISMS

3.2.1 Adhesive Wear

Adhesive wear is often called galling or scuffing, where interfacial adhesive junctions lock together as two surfaces slide across each other under pressure [83]. As normal pressure is applied, local pressure at the asperities become extremely high. Often the yield stress is exceeded, and the asperities deform plastically until the real area of contact has increased sufficiently to support the applied load, as shown in Fig. 3.6a. In the absence of lubricants, asperities cold-weld together or else junctions shear and form new junctions. This wear mechanism not only destroys the sliding surfaces, but the generation of wear particles which cause cavitation and can lead to the failure of the component. Wear rate of the adhesive wear process described theoretically by Archard is equation

$$W = k\,(N/H) \tag{3.1}$$

where W is the wear rate, k is the wear coefficient, N is the normal load and H is the hardness of the softer material. This equation suggests that the adhesive wear rate is proportional to the load and sliding distance and inversely proportional to the hardness of the softer material. An adequate supply of lubricant resolves the adhesive wear problem occurring between two sliding surfaces.

3.2.2 Abrasive Wear

Abrasive wear occurs when material is removed from one surface by another harder material, leaving hard particles of debris between the two surfaces. It can also be called scratching, gouging or scoring depending on the severity of wear. Abrasive wear occurs under two conditions:

1. Two body abrasion; In this condition, one surface is harder than the other rubbing surface . Examples in mechanical operations are grinding, cutting, and machining.

2. Three body abrasion; In this case a third body, generally a small particle of grit or abrasive, lodges between the two softer rubbing surfaces, abrades one or both of these surfaces.

In the micro scale, the abrasive wear process is where asperities of the harder surface press into the softer surface, with plastic flow of the softer surface occurring around the harder asperities. This often leads to what is known as microploughing, microcutting, and microcracking, when a tangential motion is imposed. Abrasive wear may be reduced by the introduction of lubricants at various film thickness to separate the surfaces and to wash out any contaminant particles.

3.2.3 Erosive Wear

The impingement of solid particles, or small drops of liquid or gas often cause what is known as erosion of materials and components. Solid particle impact erosion has been receiving increasing attention especially in the aerospace industry [141]. Examples include the ingestion of sand and erosion of jet engines and of helicopter blades. As shown in Figure 3.3 the erosion mechanism is simple. Solid particle erosion is a result of the impact of a solid particle A, with the solid surface B, resulting in part of the surface B being removed. The impinging particle may vary in composition as well as in form. The response of engineering materials to the impingement of solid particles or liquid drops varies greatly depending on the class of material, materials properties (dependant on thermal history, exposure to previous stresses or surface tensions), and the environmental parameters associated with the erosion process, such as impact velocity, impact angle, and particle size / type. Movement of the particle stream relative to the surface and angle of impingement both have a significant effect on the rate of material removal, according to [142]. Cavitation erosion occurs when a solid and a fluid are in relative motion, due to the fluid becoming unstable and bubbling up and imploding against the surface of the solid, as shown in Figure 3.4. Cavitation damage generally occurs in such fluid-handling machines as marine propellors, hydrofoils, dam slipways, gates, and all other hydraulic turbines [142] Cavitation erosion roughens a surface much like an etchant would [82]

3.2 4 Surface Fatigue

When mechanical machinery moves in periodic motion, stresses to the metal surfaces occur, often leading to the fatigue of a material All repeating stresses in a rolling or sliding contact can give rise to fatigue failure These effects are mainly based on the action of stresses in or below the surfaces, without the need of direct physical contact of the surfaces under consideration When two surfaces slide across each other, the *maximum shear* stress lies some distance below the surface, causing microcracks, which lead to failure of the component These cracks initiate from the point where the shear stress is maximum, and propagate to the surface as shown in figure 3 5(c) Materials are rarely perfect, hence the exact position of ultimate failure is influenced by inclusions, porosity, microcracks and other factors Fatigue failure requires a given number of stress cycles and often predominates after a component has been in service for a long period of time

3.2 5 Corrosive Wear

In corrosive wear, the dynamic interaction between the environment and mating material surfaces play a significant role, whereas the wear due to abrasion, adhesion and fatigue can be explained in terms of stress interactions and deformation properties of the mating surfaces In corrosive wear firstly the connecting surfaces react with the environment and reaction products are formed on the surface asperities Attrition of the reaction products then occurs as a result of crack formation, and/or abrasion, in the contact interactions of the materials This process results in increased reactivity of the asperities due to increased temperature and changes in the asperity mechanical properties

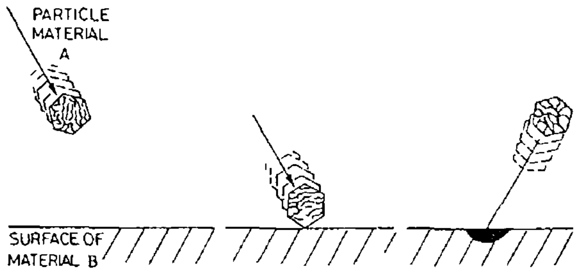


Fig 3 3 Typical events in erosive wear [83]

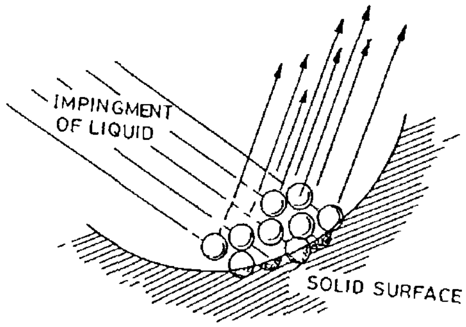


Fig 3 4 Schematic of cavitation erosion due to impingement of liquid bubbles [83]

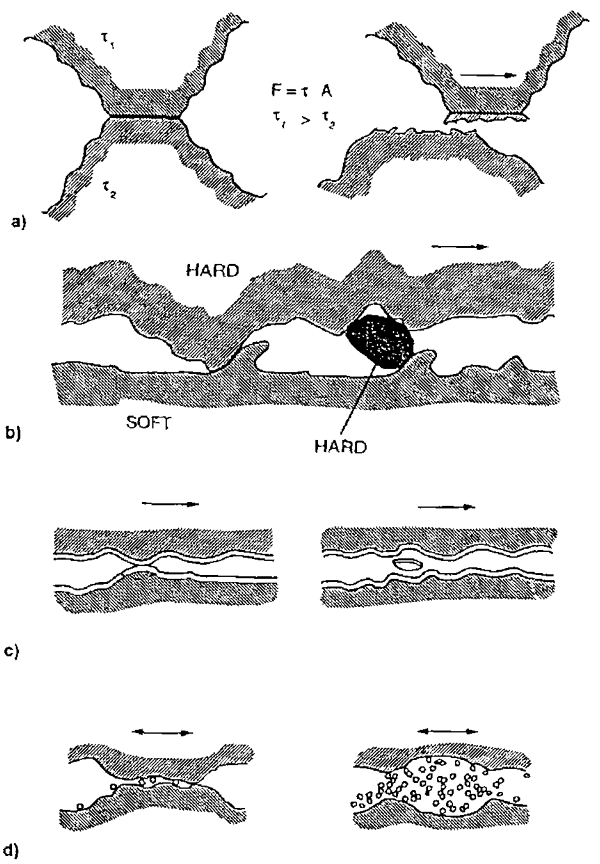


Fig 3 5 The basic mechanism of wear (a) adhesive (b) abrasive (c) fatigue (d) chemical wear [35]

3.3 DEVELOPMENT OF THE WEAR THEORY

Increasing the wear resistance of engineering components is one of the main factors in extending their life However it is impossible to extend the life of the rubbing components with out establishing engineering theories and methods for calculating the wear taking in to account the physical and mechanical properties of the materials and the operating conditions

The problem of wear has been concerning scientists for long time Leonardo da Vinici at the end of the fifteenth and the early sixteenth century investigated and studied friction and wear Contact theory wasinitiated by Hertz in 1882, later developed by Johnson and Kaller Others such as Euler, Reynolds, Ertel and Grubin have contributed to the development of the wear theory and knowledge [2,138,140] The first attempt to relate wear to the mechanical properties of materials was by Tonn [143], who proposed an empirical formula for abrasive wear Holm [144] calculated the volume of substance worn over unit sliding using the atomic mechanism of wear, i e

$$W = z\ (N/HB) \tag{3 1}$$

where W is the wear rate, z is the probability of removing an atom from the surface when it encounters an atom of the opposing surface, N is the normal load and HB is brinell hardness of the softer material

Burnwell and Strang [145] and Archard and Hirst [146] developed an adhesion theory of wear Archard [147] on the assumption that the wear particles are hemispheres of radius equal to the radius of the contact point showed that

$$W = k/3\ (N/HB) \tag{3 2}$$

where k is the probability of the removing of the wear particle from the contact point

The relation between the wear rate and hardness of the softer material as stated in Archard's law is supported by much experimental work, notably that of Kruschov [148], although materials properties other than hardness are also important in determining wear rates. Hornbogen [149] extended the Archard equation. He proposed a model to explain increasing the wear rate with increasing toughness of the metallic materials. This model is based on a comparison of the strain that occurs during asperity interactions with the critical strain at which crack growth is initiated. If the applied strain is smaller than the critical strain, the wear rate is independent of toughness and Archard's law is applied. However if the strain applied is larger than the critical strain leads to increased probability of crack growth and therefore to higher wear.

The next stage in the development of the wear theory was the introduction of the fatigue theory of solids. Kragelsky [150] published the first paper in this regard. Further papers were published soon afterwards giving a wider view of the theory [1451,152]. This theory incorporates the individual frictional bond deformed by the bulk of the rubbing bodies and the stress distribution as a function of the load, friction, and the geometrical profile of the microasperities. The main concept of this theory is that destruction of the sliding surfaces requires repeated sliding effects, the number of which can be expressed quantitatively as a function of the stress distribution.

The fatigue theory of wear has been widely accepted among scientists worldwide. Endo *et al* [153] provide important evidence of the fatigue nature of wear. Based on the fatigue theory of wear Bayer et al [154] developed a method for calculating the wear of various machine components. The authors consider the life of machine contact is inversely proportional to $N^{1/3}$, i.e. they use the connection between the actual stress and the number of cycles required to damage the material.

Yoshimoto and Tsukizoe [155] published an important study in which wear is associated with the thickness of the oxide film formed on the metal surface. According to these authors the oxide film is ruptured at the real contact point, the thickness of the film depending on the time interval between two successive contacts, the interval depending on the density of the contact point

Khruschov [148] studied the influence of material properties on the abrasive wear and has shown that direct proportionality exists between the relative wear resistance and the hardness He has also shown that heat treatment of the structural steel improves the abrasive wear resistance Zum Gahr [156] considers the detailed process of the microcuttings, microploughing and microcracking in the abrasive wear of the ductile metals In his model he includes other microstructural properties of the materials worn beside the hardness It has been shown that the homogeneity of the strain distribution, the crystal anisotropy and the mechanical instability have an influence on the abrasive wear mechanisms

3 4 WEAR TEST METHODS

Standard wear test methods have been developed under the supervision of ASTM technical committees, such as G-2 committee on wear and erosion [157] These test methods are designed to determine a material's resistance to specific wear type in order to help solve important industrial problems However, there occasions where no ASTM tests satisfactorily meets the current need for wear data Furthermore it is seldom possible for one worker to take full advantage of tests carried out by others as reference data, because there will be usually be some differences in the operating parameters such as speed, load and specimen geometry or surface roughness [35]

Every wear test can be complicated by equipment problems and test conditions Many of the abrasion wear test depend on their accuracy on the abrasive paper used Thus slight difference in the particle size or shape cause test results to vary This results in the lack of standardization in the field of wear testing

Appropriate wear testing is a prerequisite for material to be considered for possible wear applications The need to improve the performance of the engineering components has driven the development of new engineering materials, new surface treatment and new coatings Before the use of these new materials and substrate treatment or coatings, they should be tested to evaluate their properties Engineers need wear test results to confidently select the best material or coating for certain service situation

Wear test can be carried out either in the laboratory or in a service trial When materials are to be tested in laboratory in order to classify them with respect to wear resistance the outmost care should be taken that the test environment should as close as possible to the practical environment

Wear tests are conducted for many reasons

1- to characterize the wear resistance of the material
2- to determine the friction coefficient between the rubbing materials
3- to estimate the life time of the tool materials
4- to test the performance of the lubricants
5- to investigate the wear mechanisms under certain and controlled conditions

In selecting a suitable wear test the following points should be considered[158]

i) The test method should be similar to the actual service environment
ii) Ensure that the test selected is measuring the desired properties of the material
iii) What type of the contact between the surfaces (sliding, rolling, etc)?
iv) Are temperature and humidity important factors?
v) Is the material to be tested in bulk form or thin or thick coating?

vi) What forces and stress limits are suitable for the test?

vii) The duration of the test

In the selection of wear test rig there are two approaches, to design a test rig for specific situation or to use a standard rig The use of specially designed wear test rig will usually permit a closer simulation of the required service conditions On the other hand it will be restricted in the range of situations which can be simulated [138]

The use of the wear test results depends on the degree of simulation of the service situations If the wear tests were carried out in high degree of simulation, then the results can be used with considerable confidence in selecting the wear resistant material or coating

On the other hand according to Subramanian[159] the best way to test a coating for its wear behaviour is to put it in the service Table 3 1 gives details about some of the wear test machines and their applications A schematic of typical wear test methods is shown in Fig 3 6

Pin-on-Disc

In the pin-on-disc test the pin pressed against a rotating disk The pin can be a ball, a hemispherically tipped rider, a flat-ended cylinder or even a rectangular parallelepiped [83] This test apparatus is used to measure sliding wear and friction properties Pin-on disc is the most widely used wear test method followed by pin-on-flat according to Glaeser and Ruff [160]

Pin-on-Flat

In the pin-on-flat test apparatus a flat moves relatively to a stationary pin in reciprocating motion In some cases the flat is stationary and the pin is reciprocates By using small oscillation amplitude at high frequency fretting wear test can be conducted_

Block-on-Ring

This test, ASTM G77-83 [161], makes use of rotating metal against a fixed block. This test allows variation in materials, speed, loads, lubricants, and coatings. Wear is measured using volume loss on the block and weight loss of the ring.

Taber test

The Taber test (manufactured by Teledyn Taber) is widely used to evaluate the abrasion resistance of various materials and coatings at low stresses. Wear action results when a pair of abrasive wheels is rotated in opposing directions by a turntable on which the specimen is mounted. Two and three body abrasive wear can be conducted by this method. The weight used is 250,500, or 1000g. The wear in this method is normally measured using weight loss.

Dry sand rubber wheel test

In the dry sand rubber wheel test ASTM G65, the specimen is loaded against the rotating rubber wheel. The load is applied along the horizontal diametrical line of the wheel. The abrasive is typically 50 to 70 mesh (200to 300μm) dry AFS (American Foundry Society) test sand [82]. Swanson [161] used this method to compare laboratory and field tests under sandy soil working conditions, and concluded that there was close correlation between the two. Specimen weight loss is used to measure the wear in this method.

Disc-on-Disc

The disc-on-disc is one of the apparatus used for testing materials and lubricants in the rolling contact fatigue applications. This apparatus uses two discs or ball on disc rotating against each other on their outer surfaces The disc samples may be crowned or flat Usually the samples rotate at different sliding speed to produce some relative sliding (slip) at the interface [162]

Solid particle erosion test

Erosion testing is generally conducted at room temperature using an air blast test apparatus The tester is operated by feeding the eroding particles from a vibrating hopper into a stream of gas A known amount of eroding particles is directed onto one or more test specimens The wear measurement in this method conducted using weight loss [163]

Wear Testing Machine	**Conditions**	**Applications**
Pin-on-disc sliding wear tester	0.1-300N load 0.0016-3 m/s speed	Ion implanted, CVD, PVD, elecroless coating, laser processed, plasma sprayed
Dry and Rubber wheel	30-250 N load 195rpm speed	Laser processed, Cr plated plasma processed
Taber abrasion	10N load; 60rpm speed	Electroless plating, PVD
Polishing wear	6-10 Kpa pressure 0.23 m/s speed	Ion-implanted, PVD, CVD thin coatings
Erosion	150-200 m/s speed	Plasma sprayed, PVD, CVD
Roll-on-roll	49-2000 N load 250-3000rpm speed	PVD, CVD, Laser treated, Diffusion treated, Plasma nitrided
Pin –on-rolling	0.5-100 N load 0.002-0.8 m/s speed	PVD, electroless coating
Cross cylinders	90-300 N load 11-100 rpm speed	Ion-implanted, electrosparkdeposited

Table 3.1 various wear testing methods for surface treated and coated materials [159]

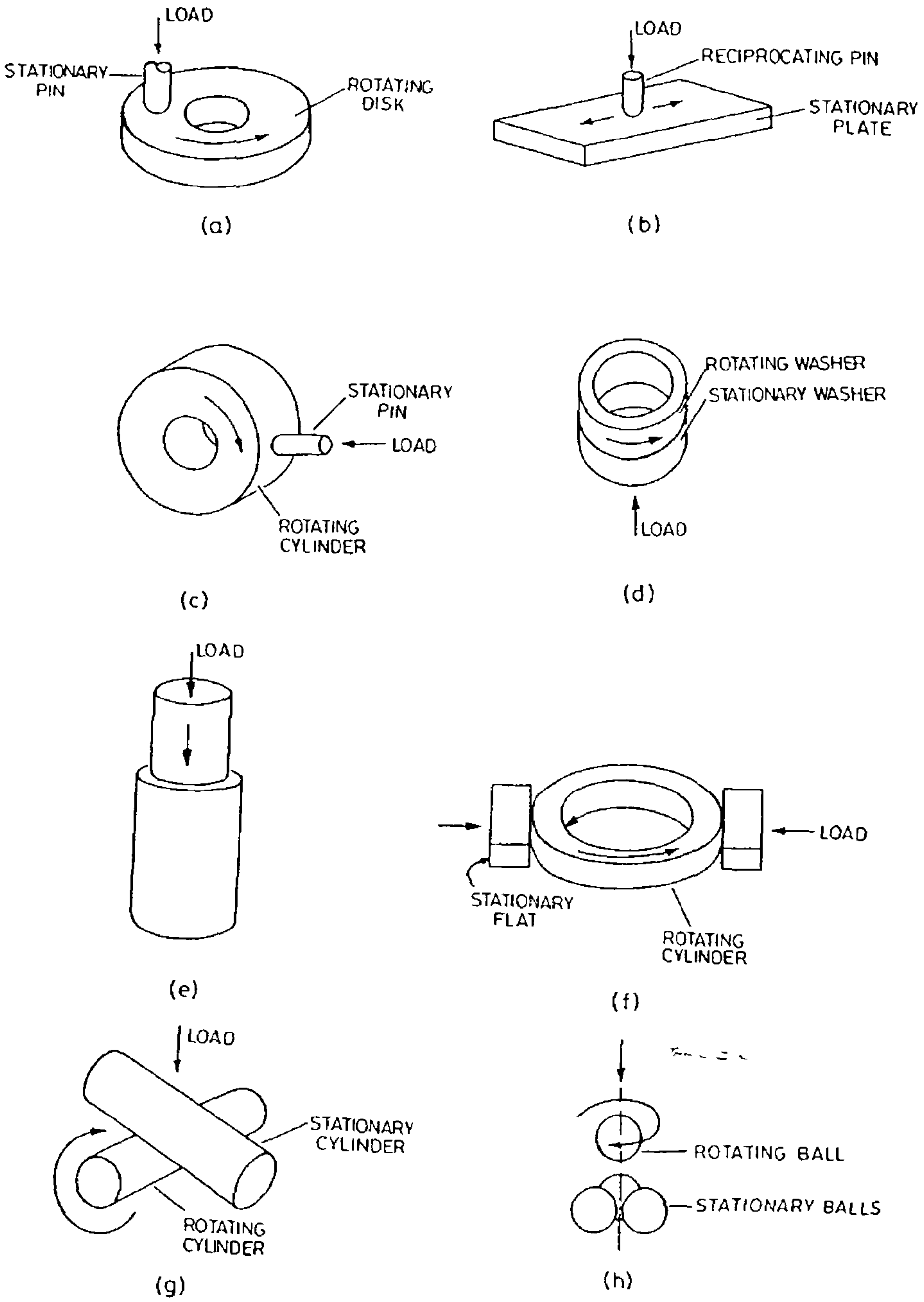


Fig 3 6 Schematic of typical wear test methods (a) pin-on-disc (b) pin-on-flat (c) pin-on-cylinder (d) thrust washer (e) pin into bushing (f) rectangular flats on rotating cylinder (g) crossed cylinder and (h) four ball [83]

CHAPTER 4

EXPERIMENTAL EQUIPMENTS

4 1 INTRODUCTION

The aim of the experimental work in this study is to evaluate the mechanical properties and the wear resistance of different coatings deposited on different substrate materials

The wear tests were carried out using a novel wear rig test The wear rig as shown in Fig 4 1 was designed, constructed and commissioned in the School of Mechanical and Manufacturing Engineering, DCU [164] A schematic diagram of the wear test rig is shown in Fig 4 2 Wear tracks on the surface of coated samples obtained from the wear rig is shown in Fig 4 3

To characterize the deposited films and the hardened layers the following apparatus has been used microhardness tester, profilometer, optical microscope, SEM/EDX unit, and Rockwell hardness tester

4 2 WEAR RIG COMPONENT

Drive system

A three phase motor (0 75kW, Hanning Elektro Werke) is used to drive the linear and also an impact mechanisms Toothed belts are used to drive the intermediate shaft and cam The sliding mechanism provides sliding motion to the wear tool as shown in Fig 4 1 One end of the connecting arm is hinged to the linear guide unit (platform) The other is attached to the motor shaft with an offset from the centre of the shaft as shown in Fig 4 4(a), where r is the crank arm length and L is the connecting arm length The offset distance yields the crank effect to the sliding mechanism The linear driving unit is used to locate the wear tool (stylus) in relation to the test piece It is attached to and supported by four pillars, which allow vertical adjustment of the linear unit These pillars are fixed to the base plate of the test rig
As the motor shaft rotates, crank and connecting arm translates rotary motion to reciprocating motion and the platform starts sliding The rotational speed of the

output shaft is 106 rpm. The sliding distance can be varied, subjected to maximum sliding distance of 6 cm as shown in Fig. 4.4(b).

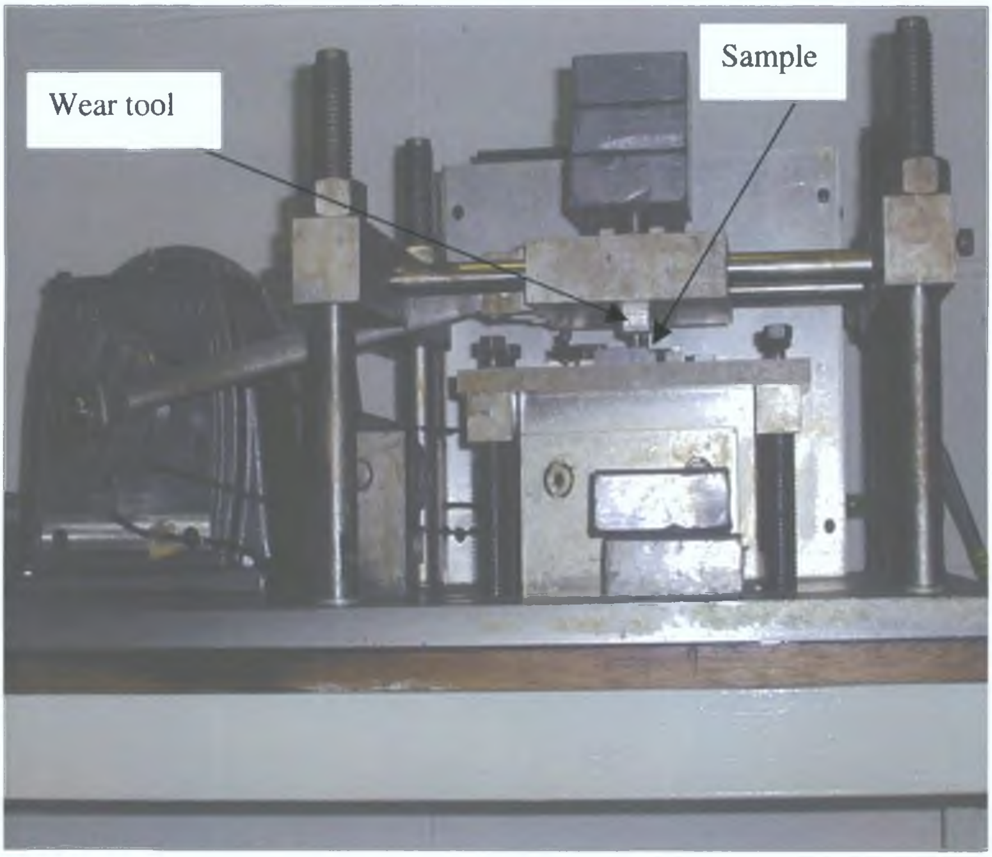
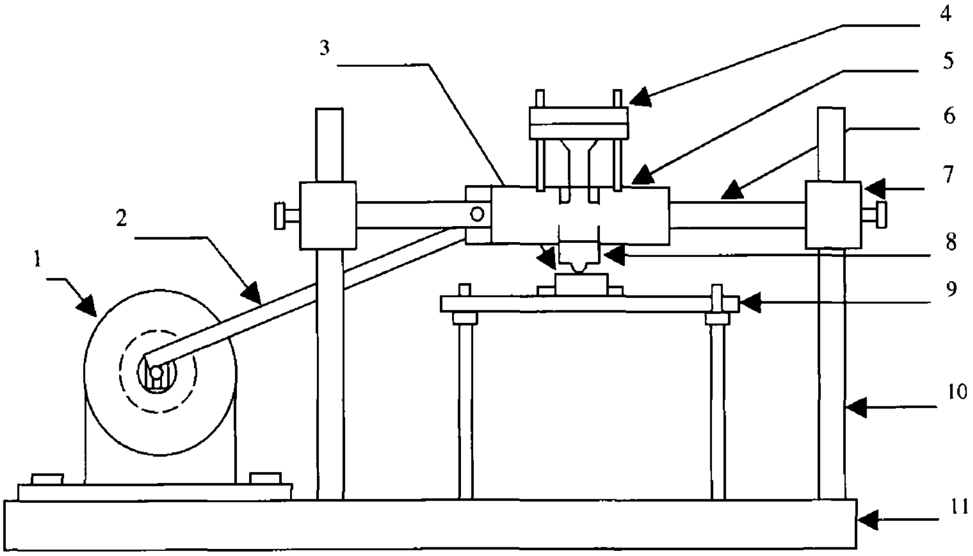


Fig. 4.1 Wear test rig



1 Motor

2 Connecting arm

3 Substrate

4 Load

5 Platform

6 Guiding rod

7 Rectangular bar

8 Wear tool

9 Substrate table

10 Ball screw shaft

11 Base plate

Fig 4 2 Schematic diagram of the wear test rig

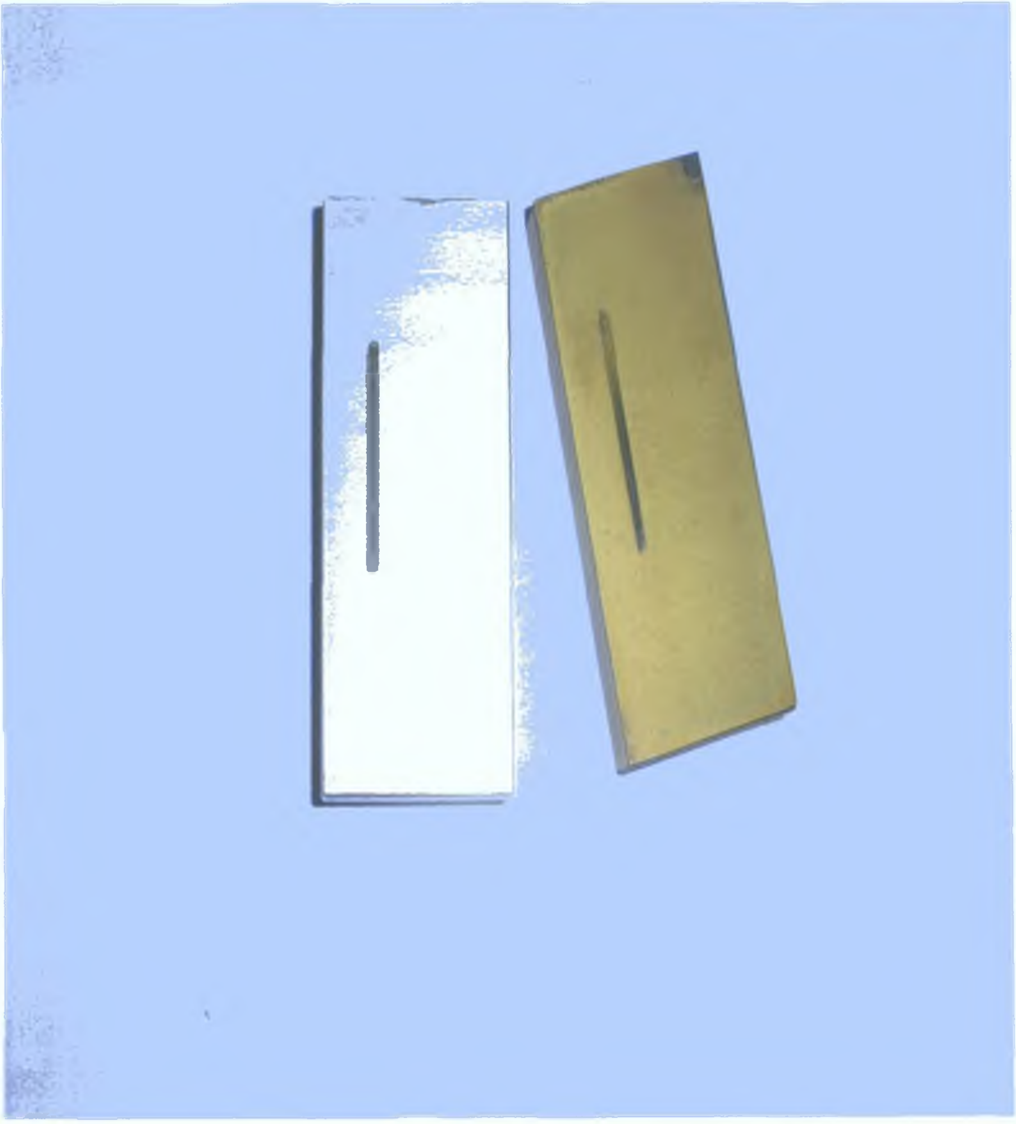


Fig. 4.3 Wear tracks in coated samples

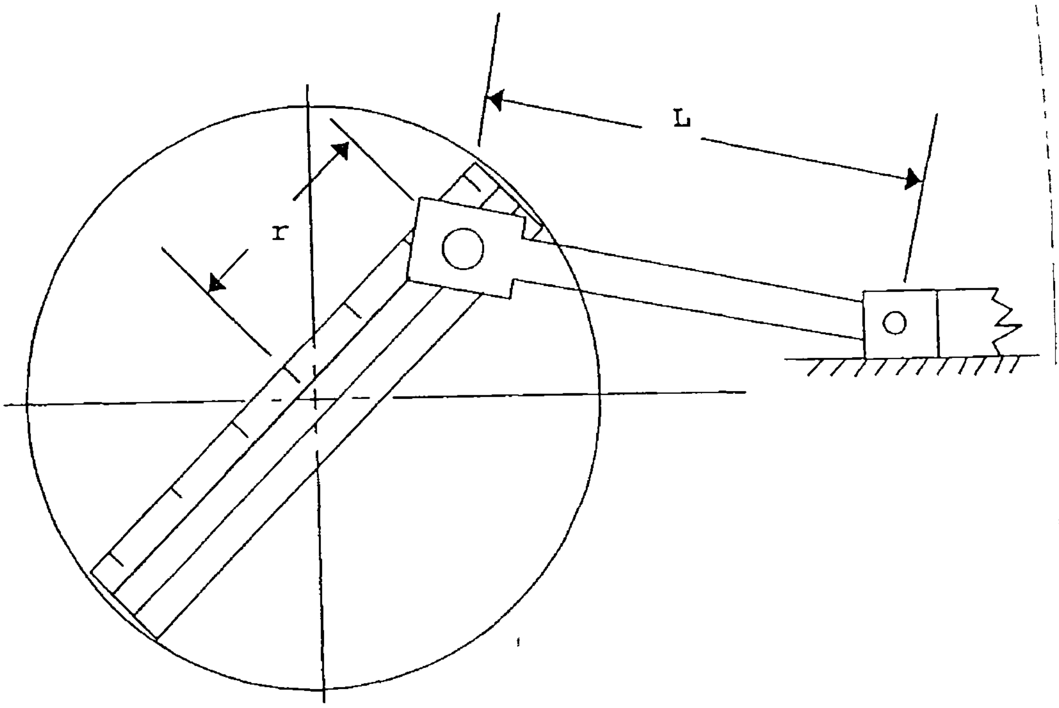


Fig 4 4(a) Transformation of the rotational motion into reciprocating motion by crank and connecting arm [97]

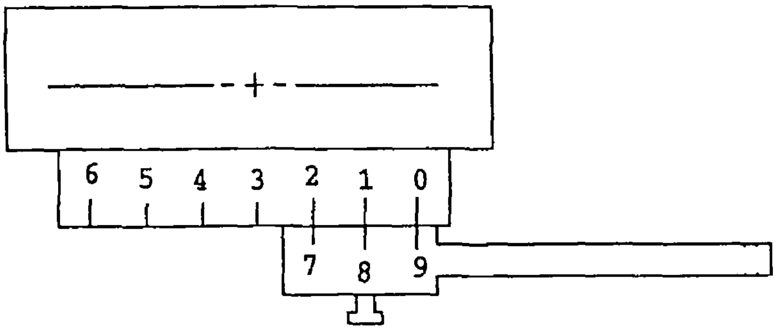


Fig 4 4 (b) Adjustment of sliding length [97]

Substrate table

The substrate table as shown in Fig.4.2, is made of D2 tool steel mounted on the base plate. The substrate plate is used to hold the sample to be tested in a position against a fixed locating face.

Tool wear and tool wear holder

The tool wear (stylus) used in this study consists of 2mm radius, round nose tool as shown in Fig.4.5. It is produced from tungsten carbide of ISO grade, P50. It is located in a tool holder fixed with a lock screw to ensure it cannot move during the test process. There is no restriction on the shape of the stylus tip, and any substrate material coated or uncoated can be used. The wear tool holder is produced from an AISI-D3 tool steel, and heat treated to 58 HRc.

Revolution counter

A revolution counter (RS 260-937, RS components Limited) is used to record the number of cycles the test piece is subjected to during each test process.

Wear load

The wear load rests on the wear tool holder and is guided by two rods as shown in Fig. 4.2. The loads are made of cubic blocks of lead. The load can vary but subjected to a maximum load of 10 Kg.

Sample size

The sample size can vary but must be longer than the stroke of the tool wear when reciprocating on the surface under test. Typical sample dimensions are 80mm ± 30mm in length, 35mm ± 20mm in width, and 10mm ± 3mm in thickness. Two clamps are used to hold the samples to the substrate table in a position against the wear stylus. Circular samples can be also accommodated and small pieces such as cutting inserts can be fixed to a suitable base plate before testing.

4.3 WEAR MEASUREMENT

A profilometer, also known as stylus instrument [83,131], is used in wear measurements [159,160]. The essential features of the stylus instrument are shown in Fig 4.6. The profilometer amplifies and record the vertical motion of a sharp and very light stylus displaced at constant velocity on the surface to be examined. It consists of the following components: a pickup driven by transverse unit that draws the stylus over the sample to be measured, an electronic amplifier to boost the signals from the stylus, data logger, and chart recorder for recording the amplified signal. The transducer is a linear variable differential transformer and produces an electrical signal that is proportional to the stylus displacement. In its simplest form the analogue signal is fed, after suitable amplification, to a chart recorder so providing a magnified view of the original profile. In order to provide data that is representative of the surface as a whole the horizontal travel of the stylus needs to be many times the maximum amplitude of the its vertical motion; thus to contain this information in a manageable length of chart it is usual to use a much greater magnification in the vertical direction than in the horizontal [165]. The stylus is tipped by a diamond of a few microns radius. The stylus of the profilometer used in the present study is a cone of tip radius of 5μm and has a resolution of up to 0.05μm for a range of 10μm [165]. A profilometer (Surf test 402, Series 178, Mitutoyo Corporation) with the added feature of chart recorder (Mini Recorder for Surftest 402, Series 178, Mitutoyo Corporation) as shown in Fig.4.7 was used in the wear measurements. The chart recorder is a thermosensitive type recorder which provides profile curve and roughness curve of the surface texture at profile mode and roughness mode respectively. The surface test provides the surface roughness in any of the following: R_a, R_q, R_z and R_{max}. The record chart is a section of paper divided into divisions, each of which is equal to 0.1″x 0.2″. The chart recorder has the following features. The horizontal magnification can be varied from 5 to 100. The vertical magnification can be varied from 80 to 10,000 depending on type of roughness data (R_a, R_q, etc.) and the range used.

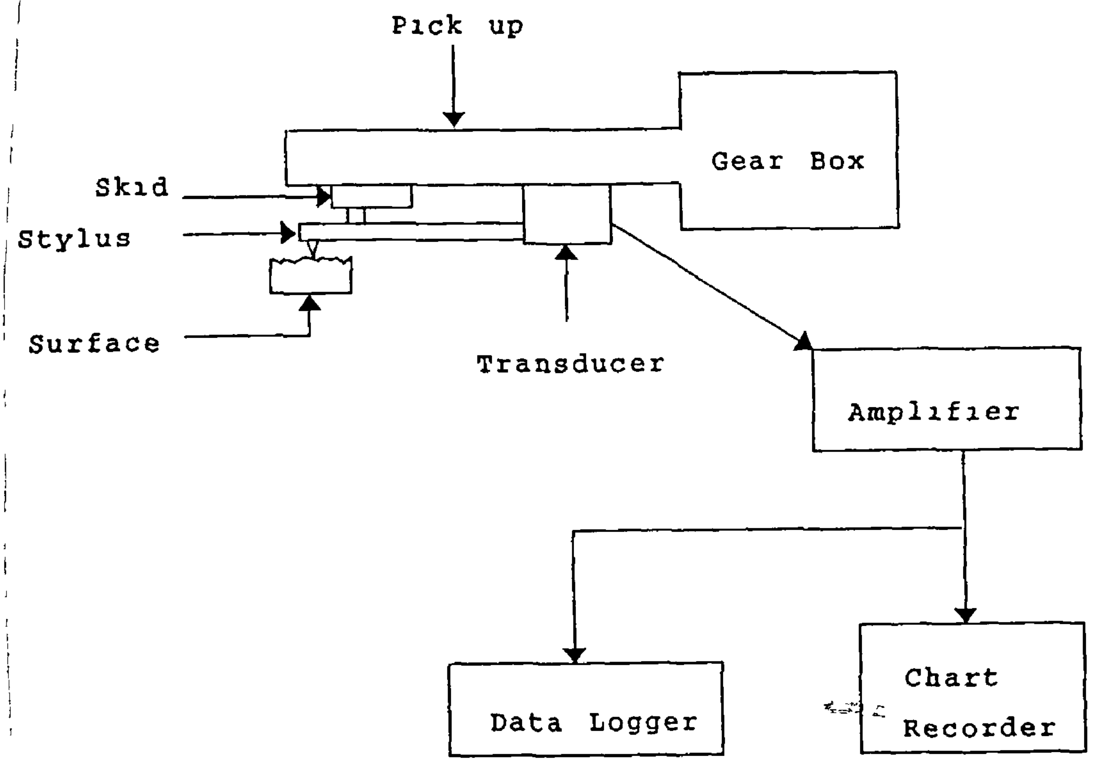


Fig 4 5 Component parts of typical stylus instrument [139]

4.4 FILM THICKNESS

Film thickness is the coating characteristic most often measured. It is very significant to coating characteristics such as wear, corrosion, porosity, and other mechanical properties. Thickness of the coatings can be measured by in situ monitoring of the deposition rate or by tests after the coated part is taken from the deposition chamber. Several techniques are employed to measure the film thickness, some proved to be successful than others, but all reflected the difficulty in assessing accurately the thin film thickness.

The techniques are used in the assessment of the film thickness can be divided in to six categories [83] as following:

Optical techniques such as interferometery, ellipsometry,etc.

Mechanical techniques such as stylus technique.

Electrical techniques such as capacitance, ionisation,etc.

Magnetic/electromagnetic, such as attractive force, etc.

Radiation such as x-ray absorption, x-ray emission, etc.

Micellaneous such as microbalance, etc.

The technique used in the present work for measuring the thickness is stylus instrument technique. If a step is made in a coating by masking a portion of the substrate during deposition or by removing part of the coating from the substrate, then a stylus instrument can be used to measure coating thickness. A range from 100μm to 5nm can be measured using this technique [83]. As shown in Fig. 4.9 the idea in this method is that the stylus is drawn across the step and the horizontal and vertical motion of the stylus are magnified and recorded.

The equipment used for thickness measurement is the one described in section 4.3.

4.5 HARDNESS TESTER

Hardness is an important material property of concern in films utilized for mechanical, tribological, optical and electronic applications. It affects wear resistance and plays an important role in friction and lubrication of surface films in contact. Hardness is a complex and not a fundamental property of a material as it depends on more than one variable such as; yield strength, elastic modulus, and ultimate strength. Hardness of a surface, defined as the average pressure under the indenter, and calculated as the applied force required to induce plastic penetration divided by the area between the indenter and the specimen. Hardness of materials is measured by forcing an indenter into its surface. The indenter material, which is usually a ball, pyramid, or cone, is made of harder material than the material being tested. For example hardened steel, diamond, or tungsten carbide are commonly used materials for indenter. For most the standard hardness tests a known load is used by pressing the indenter into the surface of the material. After the indentation has been made, the indenter is withdrawn from the surface. An empirical hardness number is then calculated or read off a dial or digital display.

The common hardness tester are: Brinell, Vickers, Knoop, and Rockwell. The hardness number of each of these tests depends on the shape of the indenter and the applied load. The hardness test is simple to conduct and can be non-destructive, for these reasons it is widely used in industry for quality control.

In thin film technology the depth of the penetration must be as small as possible to get a more accurate picture of the film hardness independent of the substrate. Film thickness to indentation depth ratios ranging from 5 to 10 appear to be safe in most situations. If the ratio D/t (D is the indentation depth and t is the film thickness) exceeds a critical value, the hardness influenced by the substrate material.

Microhardness instruments are widely used for measuring the hardness of thin film coatings because they allow the indentation to be shallow and of small volume. These instruments include Vickers and Knoop hardness testers

Vickers microhardness technique was used in the characterization of the thin film coatings in the current work. The Vickers microhardness also known as the diamond pyramid hardness employs diamond indenter in the form of square pyramid with face angle of 136°. The Vickers hardness number is obtained as the ratio of the applied load to the actual surface area of the indenter, and is given by [131]

$$H_v = 2\cos 22^\circ \frac{L}{l^2} = \frac{1.854L}{l^2} \text{ Kg/ mm}^2 \qquad (4.1)$$

where

L = applied load
l = indentation diagonal

Nanoindentation instrumentation has been developed to measure the hardness of extremely thin films, it can measure indentation depth as small as 20 nm[131,166]. This tester continuously monitors the load and the indentation depth during the indentation process and produces a curves of load versus the indentation depth.

In this study the hardness was measured using Leitz Miniload Vickers microhardness tester [167].

4.6 ADHESION EVALUATION

Adhesion of coating to the substrate is the most important property of a coating. Good adhesion of the coating to the substrate is obviously necessary for any practical application; a film that is rapidly removed will be useless. According to the American Society for Testing Materials (ASTM), adhesion is defined as the condition in which the two surfaces held together by valance forces or by mechanical anchoring or by both together [131]. Even though adhesion is of critical importance it is one of the least understood properties. Adhesion is dependent on the interfacial region between the film and substrate and the bonding across this region. This bonding may be due to van der waals forces, ionic, covalent or metallic bonds.

The interfacial region may be divided in to four main categories

1. Mechanical interface, a mechanical interlocking of the film with a rough surface
2. Monolayer to monolayer interface , this is seen as an abrupt change from the substrate to the coating material Such an interface occurs when there is no diffusion of the depositing atoms into the substrate material
3. Compound interface, when a chemical compound is formed at the interface
4. Diffusion interface, this is a gradual change in composition and lattice parameter across the interfacial region

Cleaning of the substrate prior to film deposition, considering the film-substrate properties and the presence of intermediate layers between the film and the substrate are very important factors to control and improve the adhesion strength

There is an urgent need to develop easy, quick and reliable technique for adhesion evaluation to ensure user confidence The ideal adhesion test should fulfil the following requirements (1) quantitative (2) reproducible (3) simple to use (4) not very time consuming (5) non-destructive (6) feasible for geometrically complex samples (7) the test samples are real production samples (8) creates an electronic record of the test results [168]

Many techniques have been developed to evaluate the coating adhesion According to Mittal [169] these techniques can be divided in to three categories *nucleation methods* such as, nucleation rate measurement, *mechanical methods* such as, pull-off and indentation methods, and *miscellaneous methods* such as, abrasion method

In the indentation method the coating is indented under sufficient load so that a lateral crack initiates and propagates Indentation tests have been performed using pyramid [170] and hemispherical indenters [171]

Static indentation tests are in widespread use in industry as a quick and convenient means of obtaining a qualitative indication of adhesion This is usually carried out using Rockwell C indentation and microscopic observation of the cracking around the indentation area. Jindal et al [172] described how static indentation could be used to obtain quantitative measure of adhesion.

A Rockwell indenter (O.M. A.G. 21056 INDUNO) was used to measure adhesion properties of the films on tool steels. This Rockwell indenter machine consists of:

1- Dial gage: This shows the load applied and corresponding hardness scale.
2- Indenter: In the case of Rockwell C a diamond brale is used.
3- Anvil: This is the workbench of the machine. Samples are mounted on it and lifted up to the indenter.
4- Crank handle: This acts as a mechanical switch to activate load into the indenter.

4.7 SURFACE ROUGHNESS TESTING

Surface roughness measurements were carried out using a Mitutoyo Surftest 402, Series 178 (see Fig. 4.7). Some of the measurements were conducted using Non-Contact WYKO NT 3300 Optical 3D Profiling system (Veeco Metrology Group) which combines non-contact interferometry with advanced automation for highly accurate, fast, 3D topography measurements from 0.1 nm up to several millimetres [173].

4.8 OPTICAL MICROSCOPE

The most obvious way to examine an engineering surface is to view it optically. The surface is illuminated by a beam of visible light, which is focused on the area of interest. The reflected light rays are then collected by the objective lens and an image of the surface produced by a suitable optical system. This can be formed on viewing screen, a photographic plate, or directly to the eye. The image obtained is a two dimensional representation of the features of the surface, and it can be the exact representation of the surface if it is flat or plane. The optical microscope as shown in Fig. 4.9 was used for general observation of the worn tracks and the area surrounding the Rockwell C indentation used for adhesion evaluation.

4.9 SEM/EDX

The scanning electron microscope is perhaps the most widely used instrument for the direct observation of the surface especially in thin films and coatings It offers better resolution and depth of field than optical microscopes In the scanning electron microscope a fine beam of high energy electrons thermionically emitted from a tungsten or LaB_6 cathode filament are drawn to an anode and focused to a point on the surface of the specimen by condenser lenses This causes the emission of secondary electrons which are collected and amplified to give an electrical signal, this in turn is used to modulate the intensity of an electron beam in a cathode ray tube (CRT) The intensity of the spot on the CRT screen mimics the intensity of electron emission from the specimen To build up a complete image the electron beam in the microscope is scanned over an area of the surface while the CRT beam is scanned over a geometrically similar taster The image on the CRT is a map of the electron intensities emitted from the specimen just as the image in an optical microscope is a map of the light reflected from the surface As well as emitting electrons the bombardment by the primary electron beam leads to an electron from the outer shell lowers its energy by filling the hole and an X-ray is emitted This X-ray detected by a Si(Li) detector and correlated to the atomic number of the element within the sampling volume This is what is known as X-ray energy dispersive analysis (EDX) Hence, some qualitative and quantitive elemental information can be obtained The analysis of characteristic X-rays emitted from the sample gives more quantitative elemental information It is thus possible to combine visual observation with chemical analysis of a selected area SEM, accompanied by EDX, is considered a relatively rapid, inexpensive, and basically non-destructive approach to surface analysis It is often used to survey surface analytical problems before proceeding to techniques that are more surface-sensitive and more specialized Elements of low atomic number are difficult to detect by EDX The SiLi detector is often protected by a Beryllium window The absorption of the soft X-rays by the Be precludes the detection of elements below an atomic number of 11 (Na) In windowless systems, elements with as low an atomic number as 4 (Be) have been detected, but the problems involved get progressively worse as the atomic number is reduced There are several techniques which are used for chemical analysis [131] such as, X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), Secondary ion mass spectroscopy (SIMS), Rutherford backscattering (RBS), X-ray diffraction analysis (XRD)

In this work a LEO Stereoscan 440 scanning electron microscope equipped with EDX analysis was used for the elemental analysis of the thin films (see Figure 4 11) It is equipped with ultra thin window (UTW), and digital processing helps because it is inherently more sensitive to small pulses from soft X-rays

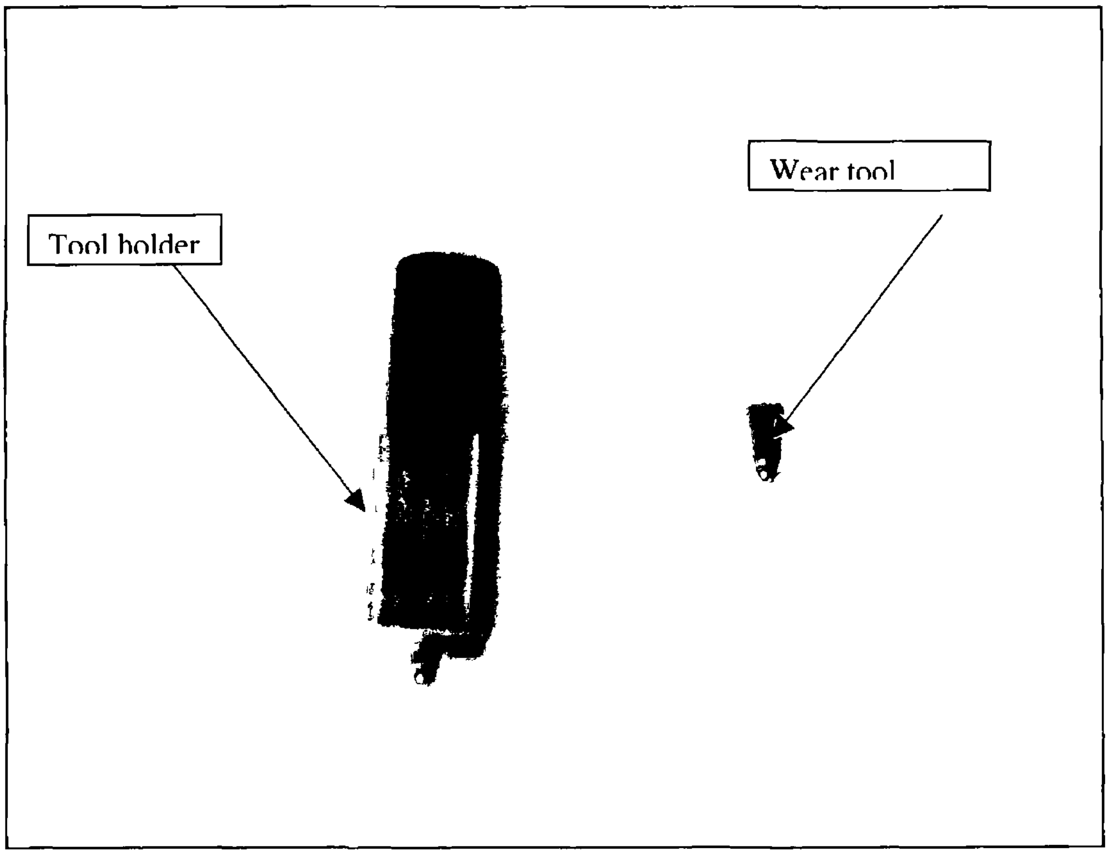


Fig 4 5 wear tool and wear tool holder

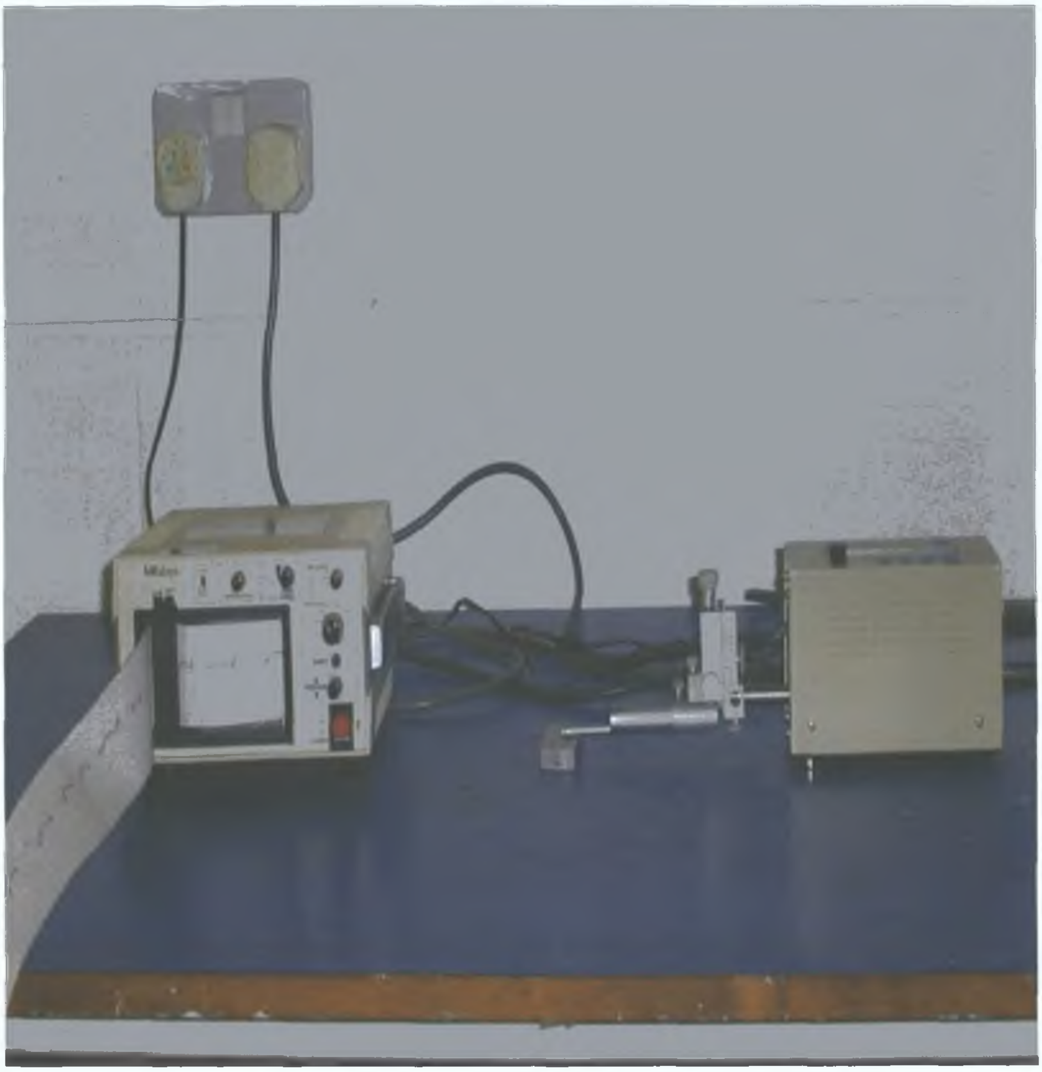


Fig. 4.7 Surface profile equipment

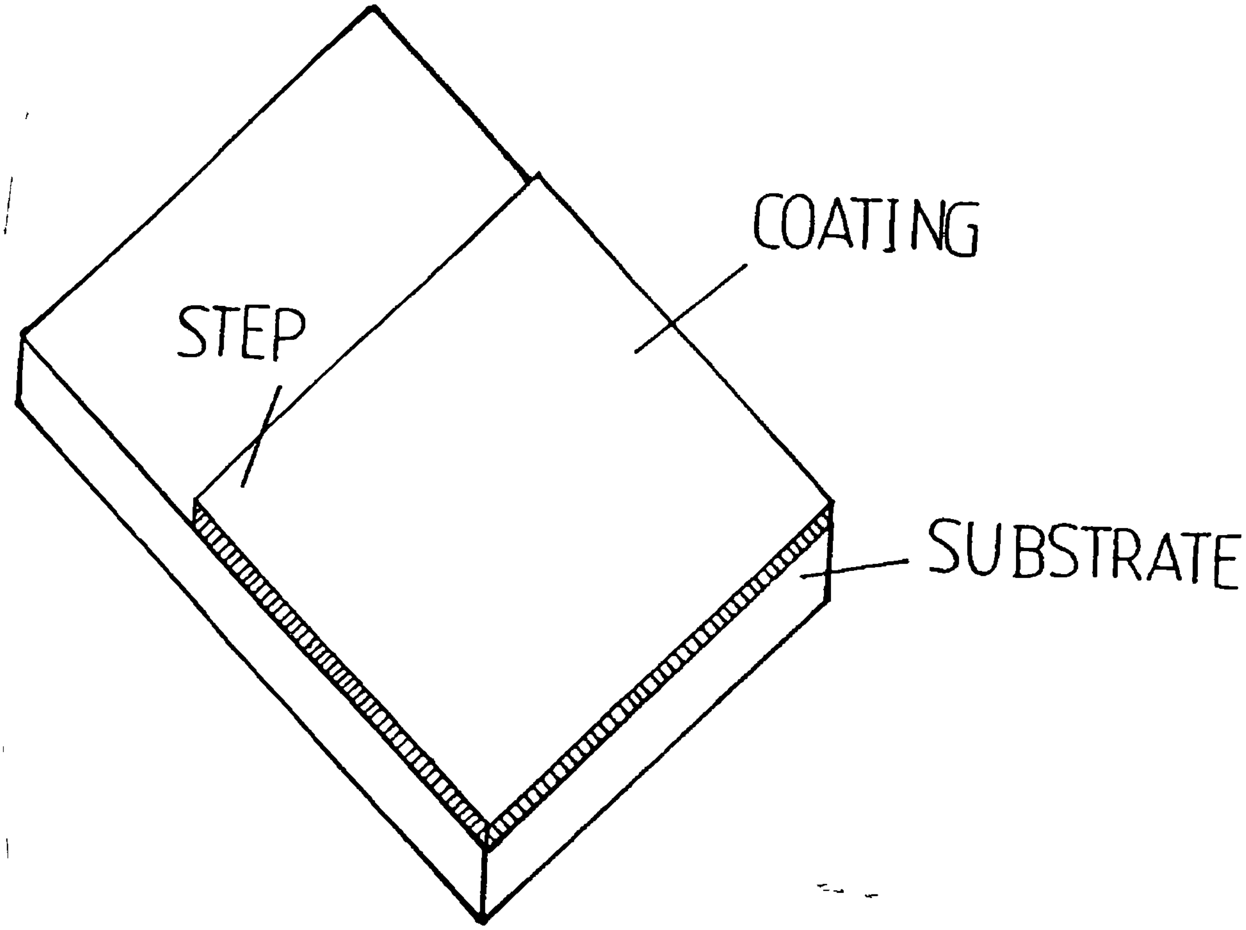


Fig 4 8 Step coverage

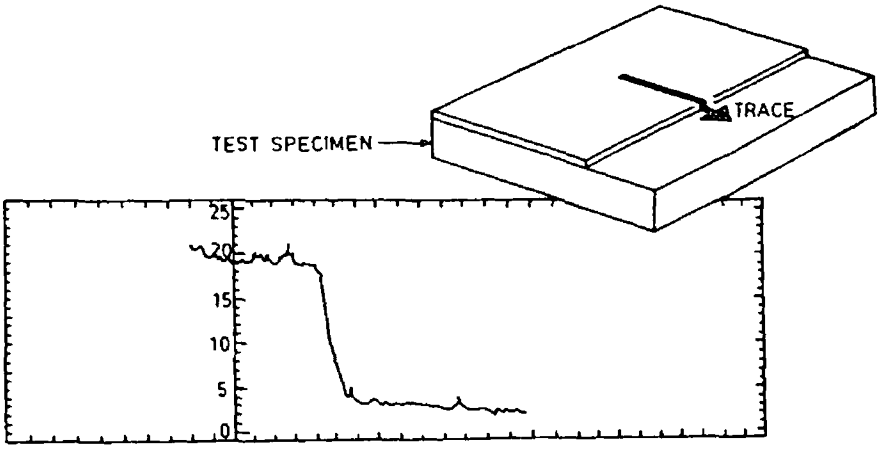


Fig 4 9 Stylus profile trace of silver coating on glass substrate[83]

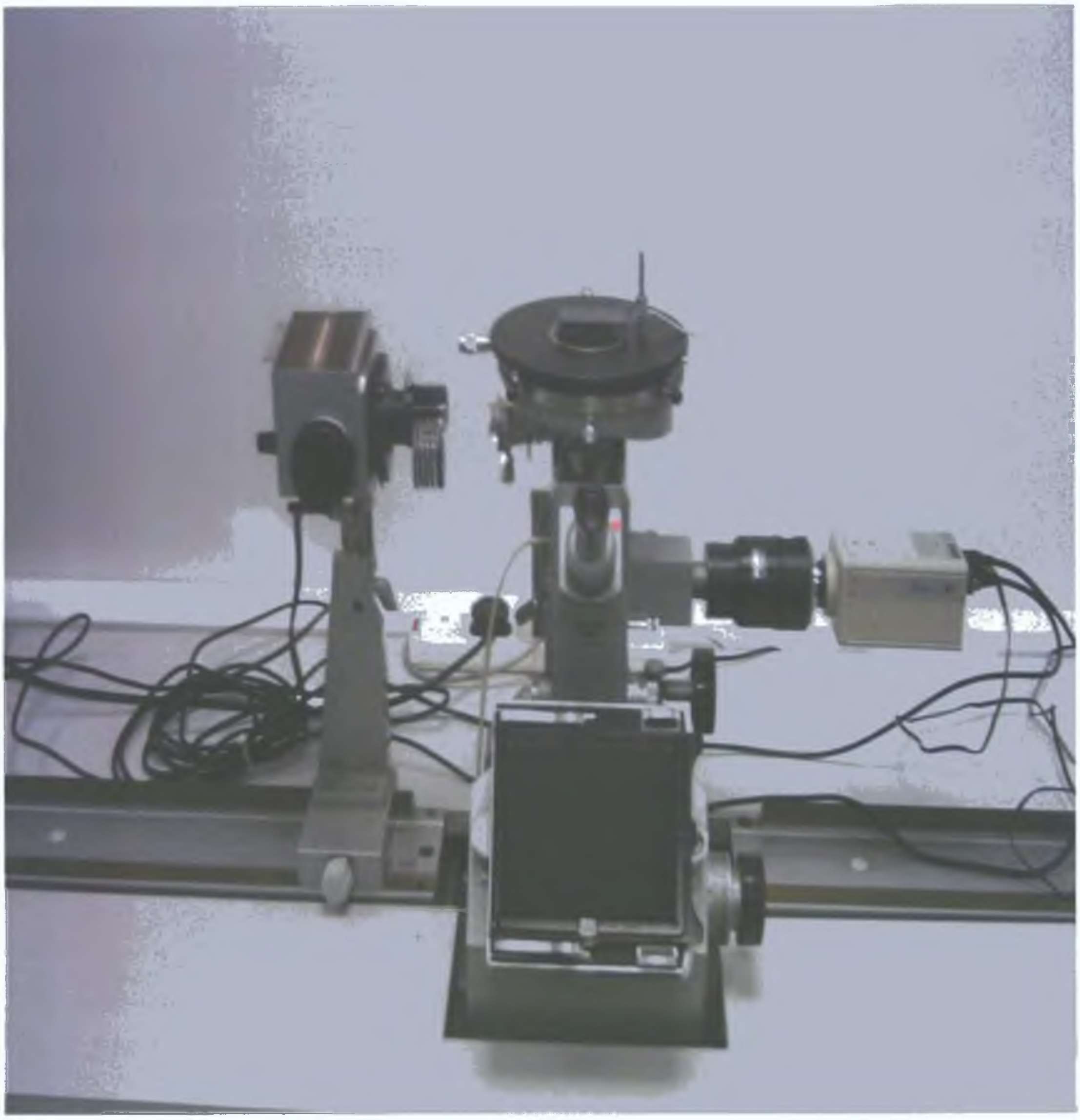


Fig. 4.10 Optical microscope

Fig. 4.11 SEM/EDX unit

CHAPTER 5

EXPERIMENTAL PROCEDURE

5 1 TEST MATERIAL

5 1.1 Substrate materials

Four different, widely used in industral tool steels were used as substrate materials in this study Two high carbon high chromium cold-worked tool steel and two powder metallurgy Vanadis 4 and Vanadis 10 Table 5 1 shows the chemical composition and the hardness value (HRc) of the four materials All substrates were cut to small pieces of 55mm length, 25mm width, and 5-8mm thick The substrates, then were polished with different grade of emery paper in the following sequence 250, 600, 800, 1200, after that the substrates were polished on polishing cloth using SiC powder of size 0 3 µm

	Contents wt% (Balance Fe)							Hardness
Material	C	Si	Mn	Cr	Co	W	V	HRc
AISI D2	1 55	0 3	0 3	12	0 8		0 8	63
AISI D3	2 05	0 3	0 8	12		1 3		60
Vanadis4	1 5	1 0	0 4	8 0	1 5		4 0	62
Vanadis10	2 9	1 0	0 5	8 0	1 5		10	63

Table 5 1 Substrate materials

5 1 2 Coatings

Coatings deposited and characterized in the experimental work include

1 Titanium Nitride TiN

2 Titanium Carbide TiC

3 Aluminium Oxide Al_2O_3

5.2 NITRIDING

The four type of steel samples were nitrided using gas nitriding in the Heat Treatment Centre, UCD, Dublin, Ireland The samples were submerged in degrease solution for 30 min then removed and rinsed and then submerged in conditioning solution for 30 min then rinsed and dried Then the samples were placed in a fluidised bed furnace at temperature of 525 °C for 150 min in an atmosphere of N_2 and NH_3 After that the ammonia was switched off for 30 min and continued with N_2 only to obtain ε layer at the surface The above process was repeated as necessary When the process was completed the samples were removed to a fluidised bed quench until they are cool enough for a test A case depth of 0 15 mm was achieved

5.3 COATINGS DEPOSITION

Three types of coating TiC, TiN and Al_2O_3 were commercially (Teer Coating, UK) deposited on the four substrate materials using the magnetron sputtering technique A photograph of the coated samples is shown in Figure 5 1 The substrate materials were degreased by scrubbing in Lotoxane solvent, followed by dry blasting with fine glass bead media to remove any surface rust/oxide etc , followed by 15 min ultrasonic clean in Lotoxane and then drying using hair dryer The coating temperature was approximately 200-250°C in each case The deposition rate was ~ 1 4 microns/hr for TiN, 1 micron/hr for TiC and 2 5 microns/hr for Al_2O_3 A thin film of ~ 4μm thickness is achieved for the three coatings on the four substrate materials, Fig 5 1

5 4 CHARACTERIZATON OF FILMS AND NITRIDING LAYER

5 4 1 Indentation and Adhesion tests

A 120° sphero-conical diamond indenter was used for the adhesion tests The sample is set on the work bench and a minor load is applied Application of minor load eliminates backlash in the load train and causes the indenter to break through slight roughness and crush foreign particles, thus contributing greater accuracy during the test A set position is established on the dial gage of the indentation apparatus Then the major load is applied When the indenter penetrates the coating, cracks propagate from the indentation point Two indentations were made for each sample The technique is a comparative measurement, which gives the picture of comparative adhesion properties considering the crack network from the indentation spot A scale is considered from HF1 to HF6 showing the adhesion properties in a sequential way as shown in Fig 5 2 HF1 shows the best adhesion while HF6 shows the poorest adhesion on the scale In all the cases a load of 150Kg was used The observations were done using optical microscope and a photograph of the indentation spot was taken at magnification of 100x

5.4.2 Microhardness

Hardness is one of the most important parameters influencing the tribological properties of coated surfaces The microhardness measurements were conducted using a conventional Vickers microhardness tester 30 indentations were made on each of the uncoated, coated, nitrided, and pre-nitrided coated samples within a specified area of 55mm x 25mm Once the diagonal length is measured using the microscope, the hardness values can be obtained either using the tables provided or using the following formula [167]

$$HV = 1854\ \frac{4 * f}{d^2} \qquad (5\ 1)$$

where

f = applied load in grams

d = mean value diagonal in μm

The mean of the 30 hardness values was taken for each set of tests.

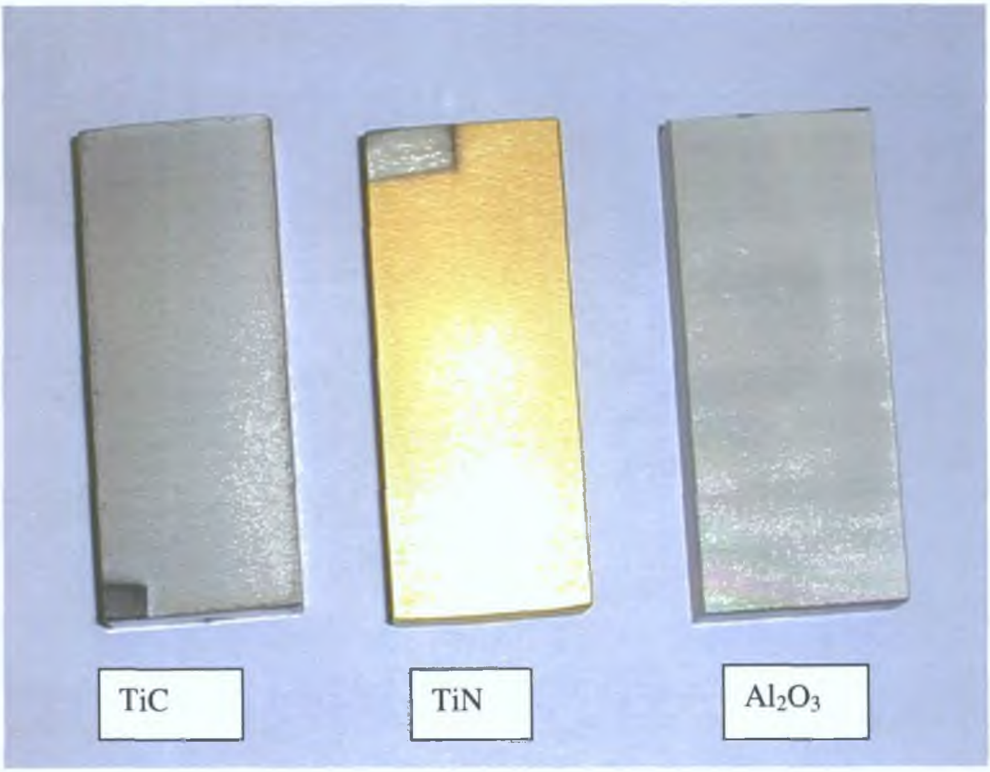


Fig.5.1 Coated substrates

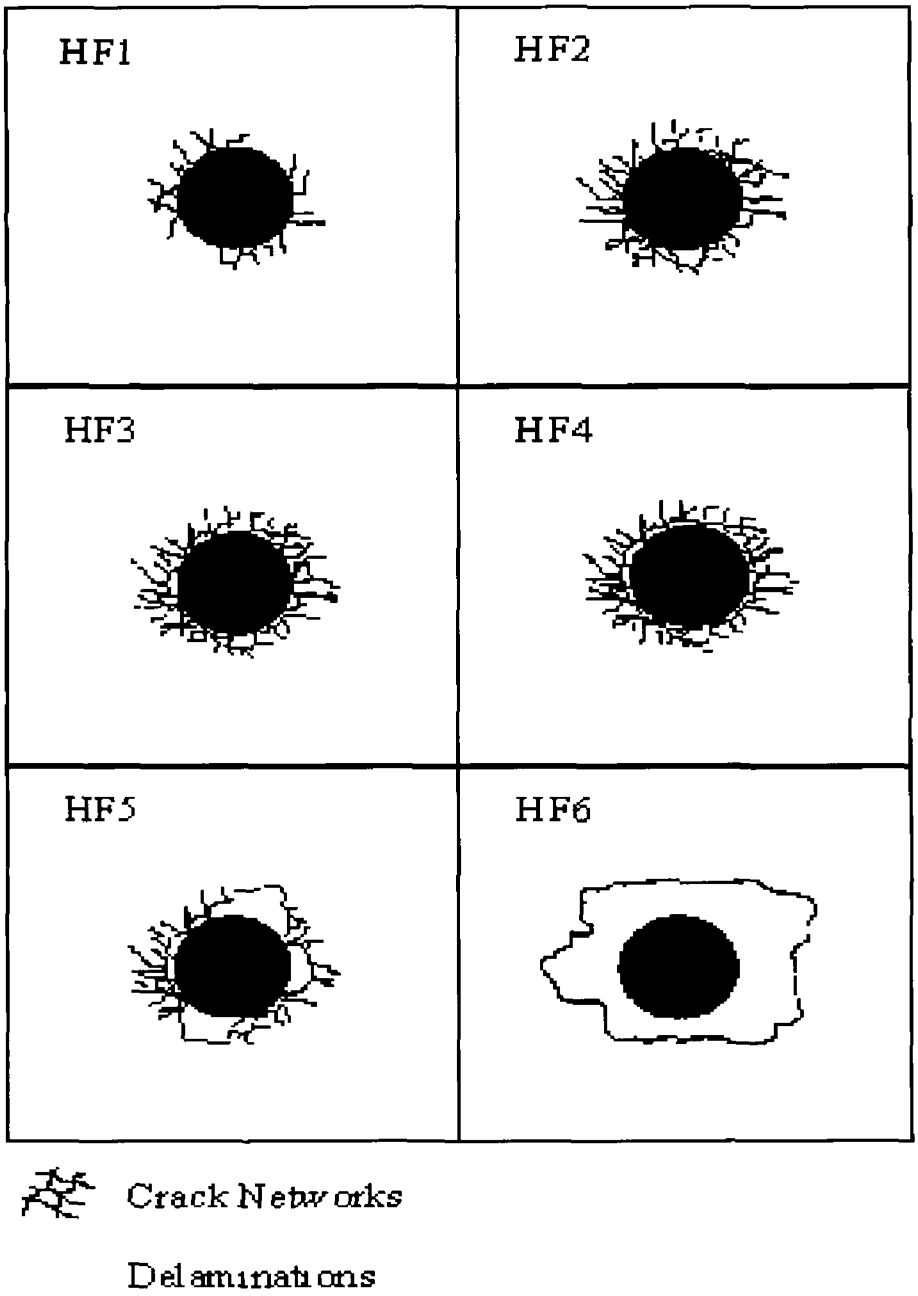


Fig 5.2 Scale of the adhesion evaluation [178]

5.4.3 Chemical composition

The deposited films and the nitriding layer obtained on the surface of the substrates were elementally analysed using X-ray dispersive energy analysis (EDX). The objective of the chemical characterization was to measure the element composition of the coatings and to trace the presence of the nitrogen in the nitriding layer.

5.5 MORPHOLOGY OF THE WEAR TRACK

A comprehensive optical microscopic scanning of all the worn specimens was performed to detect any features or signs of certain wear mechanism.

The interface between the coatings and the substrates was investigated. The samples were cut to a suitable size with low speed and lubricated conditions to prevent any distortion of the samples examined. The samples were mounted, polished and then examined using optical microscope. Micrographs were taken of the interesting features.

5.6 WEAR TESTING

The quality of most metals and their products depends on the condition of their surfaces and on surface deterioration by use. Wear may be considered essentially a surface phenomenon and one of the most of destructive influences to which metals are exposed. For that the wear test has special importance in this investigation since the coating and treatment are mainly applied to improve the surface properties of the materials.

The wear rig was described in detail in Section 4.2 of the previous chapter. With reference to that section the samples were prepared and held in a position by two clamps fixed to the test table. The wear tool (tungsten carbide stylus) is located over the sample in a linear drive unit driven by the motor. The normal load is placed over the stylus. As the motor shaft rotates, crank and connecting arm translate rotary motion into reciprocating motion and the plate form starts sliding. As the tool holder is placed through the square hole in the platform, the stylus comes in contact with the sample surface to produce wear once the stylus slides A revolution counter records the number of revolution of the motor output shaft The connecting arm is adjusted for the desired sliding distance (20mm) After setting the wear tool on the sample surface, the desired wear load (5Kg) is applied As the motor is switched on the tool starts sliding, and the revolution counter records the number of cycles to which the sample is subjected in order to produce wear After low number of cycles the sample is declamped and is taken for wear measurement To continue the sample is placed in the same position under the same load with the same or different number of cycles Then the process is repeated until the desired wear depth is attained

5.7 WEAR MEASUREMENTS

The wear loss of the coatings was too small to be resolved by weighing Depending on the densities, some times the weight loss method may be misleading, especially when comparing several coatings with different densities [158] Instead the depth of the wear track was measured as an indication of the wear resistance of the different coatings Common wear measurements are weight loss, volume loss or displacement scar width or depth, or the prediction of wear life depending on time required to wear the material or load required to cause damage to the surface A stylus instrument is easy to use for measuring depth of wear with a resolution of up to fraction of a nanometer, then a stylus instrument can be used to measure a depth ranges from about 100μm to 5nm [83, 158] To record the profile curve from which the depth is measured the specimen must be properly levelled, the higher the magnification the higher the importance of the levelling [165] When the stylus traverses across the worn surface, the profile of the surface as well as the specimen surface is recorded on the chart Fig 5 3 shows an example of a wear track profile obtained using the stylus instrument

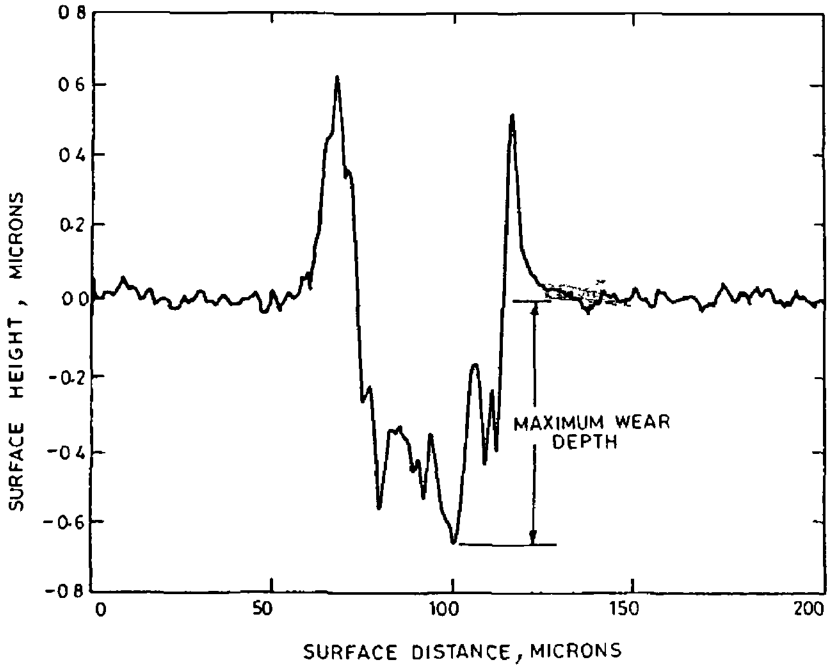


Fig 5 3 Profile curve across wear track [83]

CHAPTER 6

RESULTS AND DISSCUSION

6.1 INTRODUCTION

The substrate materials, which have been used in this study, were subjected to three types of surface treatment:

i) Coating
ii) Nitriding
iii) Nitriding and coating

These treated samples have been tested to investigated the effect of the treatment on their mechanical properties and wear resistance. Surface roughness, microhardness, adhesion, chemical composition and wear were the main properties characterised in this work. Several techniques such as, stylus instrument, Vickers microhardness, SEM/EDX were employed in the experimental procedure. Untreated samples were also tested and compared to the treated samples. The results obtained during these studies are introduced in this chapter.

No. of samples	Four	Four	Four	Four	Four	Four	Four	Four
Type of treatment	Uncoated	TiN Coated	TiC caoted	Al2O3 coated	Nitrided only	N*+TiN	N+TiC	N+Al_2O_3

*N= Nitrided

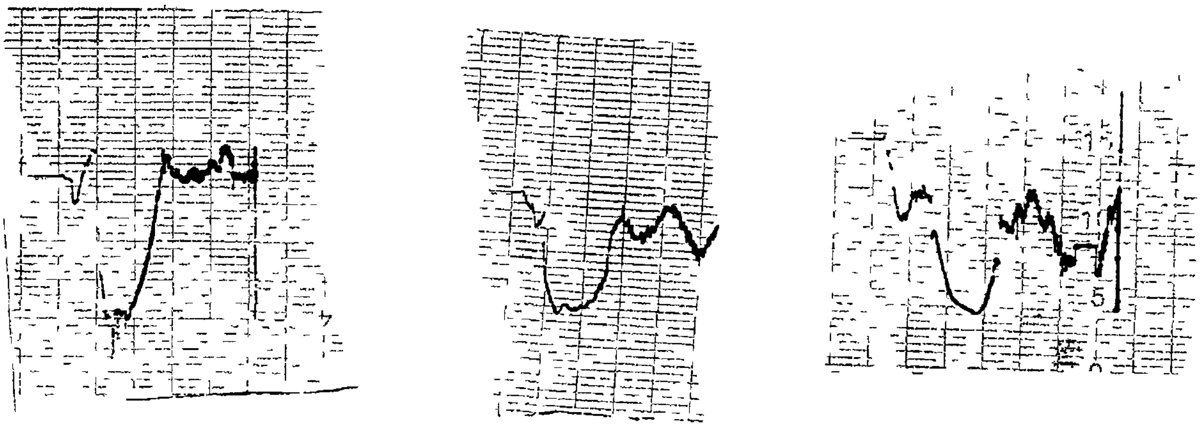
Table 6.1 Number of samples characterised in each case

6.2 SURFACE ANALYSIS OF THE SAMPLES

6.2.1 Profile across the wear track

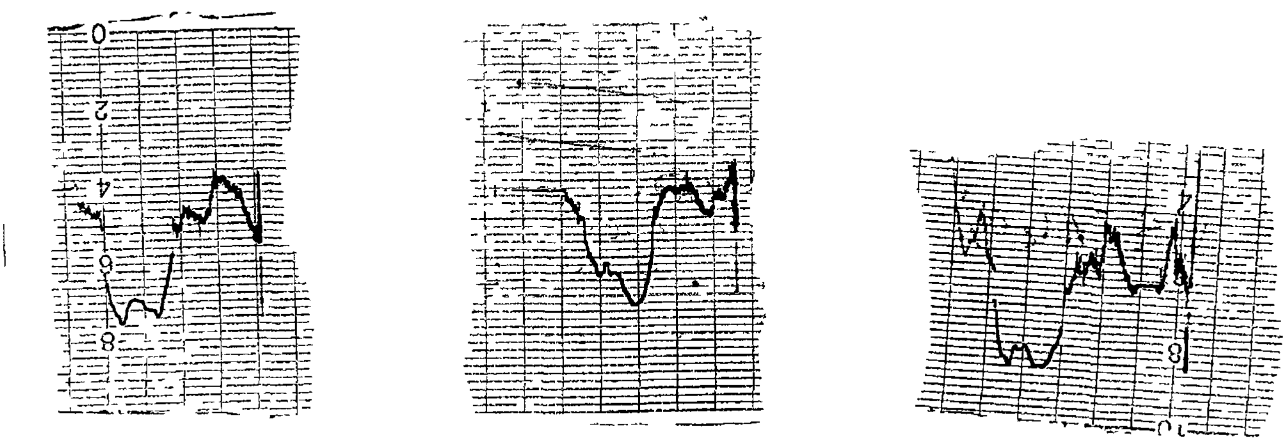
Wear profiles across the wear track of the coated and uncoated samples are shown in Figs. 6.1 to 6.5 all the profile curves shown in these figures are of tracks generated under the same load (5 Kg) and sliding distance of (20mm) unless stated otherwise. For the stylus profilometer the horizontal magnification was 5 for all the cases. Optical non-contact profilometer was also used to record the surface profile across the samples as well as the surface data and 3D image of the wear tracks as shown in Figs.6.3a and 6.6 to 6.8. The samples shown in Figure 6.1 subjected to 5000,90000 and 25000 cycles respectively and those samples shown in Figure 6 2 subjected to 50000, 80000 cycles respectively Nitrided and TiC coated samples show lower wear track depth and better surface finish, which are associated with the improvement in the wear resistance of these samples over those uncoated and coated with TiN and Al_2O_3 The shape of the wear track profile is almost semi-circular

Figures 6 3 (a) to 6 8 show 3D image of the wear track in D2 tool steel, profile curves of coated and uncoated samples and surface data inside and outside the wear tracks obtained using a non-contact optical profilometer in this figures (6 6 to 6 8) the red areas are of high roughness while the blue areas are of the lower roughness Surface data inside and outside the wear track show the increase in surface roughness in the worn surface over unworn surface These data also show the distribution of the roughness values in the same area especially in worn surfaces as shown in Figs 6 6 to 6 8



(a) (b) (c)

Fig 6 1 Profile across the wear track of (a) uncoated D2 tool steel (b) Nitrided D2 (c) uncoated Vanadis 4



(a) (b) (c)

Fig 6 2 Profile across the wear track of (a) Vanadis 10 TiN (b) D3 TiC (c) Vanadis4 Al_2O_3

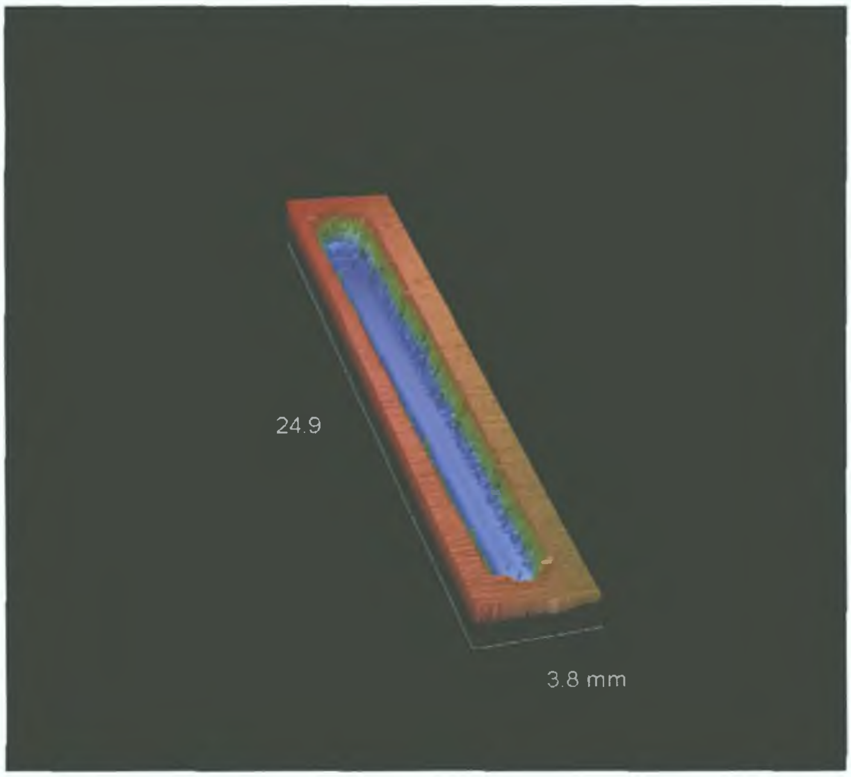
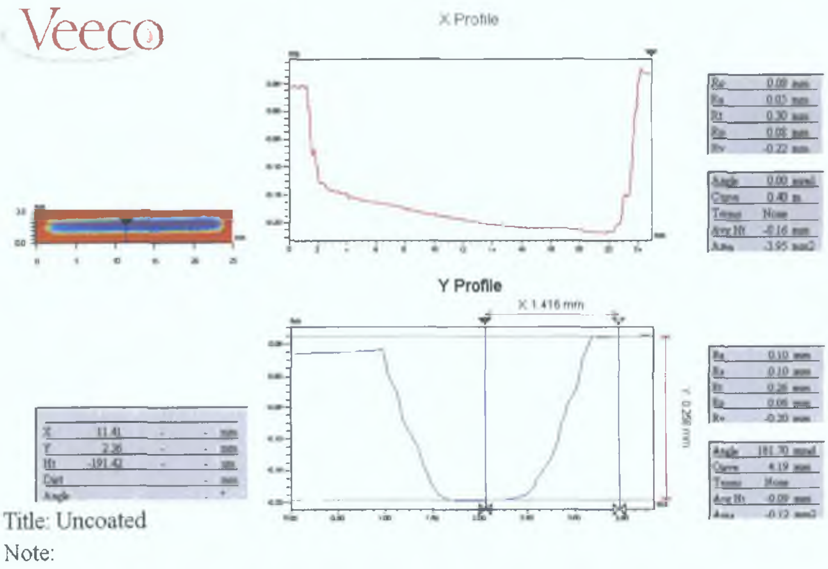


Fig 6.3 (a) 3 D image of uncoated D2 tool steel (10 Kg, 10000 cycles)



Rq	0.09 mm
Ra	0.05 mm
Rt	0.30 mm
Rp	0.08 mm
Rv	-0.22 mm

Angle	0.00 mrad
Curve	0.40 m
Terms	None
Avg Ht	-0.16 mm
Area	-3.95 mm2

Rq	0.10 mm
Ra	0.10 mm
Rt	0.26 mm
Rp	0.06 mm
Rv	-0.20 mm

Angle	181.70 mrad
Curve	4.19 mm
Terms	None
Avg Ht	-0.09 mm
Area	-0.12 mm2

X	11.41	-	-	mm
Y	2.36	-	-	mm
Ht	-191.42	-	-	um
Dist			-	mm
Angle			-	°

Title: Uncoated
Note:

Fig 6.3 (b) Profile across the wear track of uncoated D2 tool steel (10 Kg, 10000 cycles)

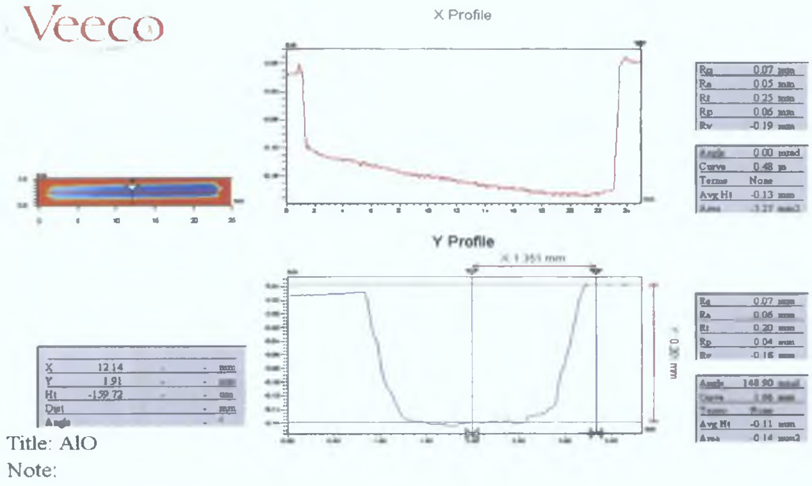


Fig. 6.4 Profile across the wear track of Al_2O_3 coated D2 (10Kg, 2000 cycles)

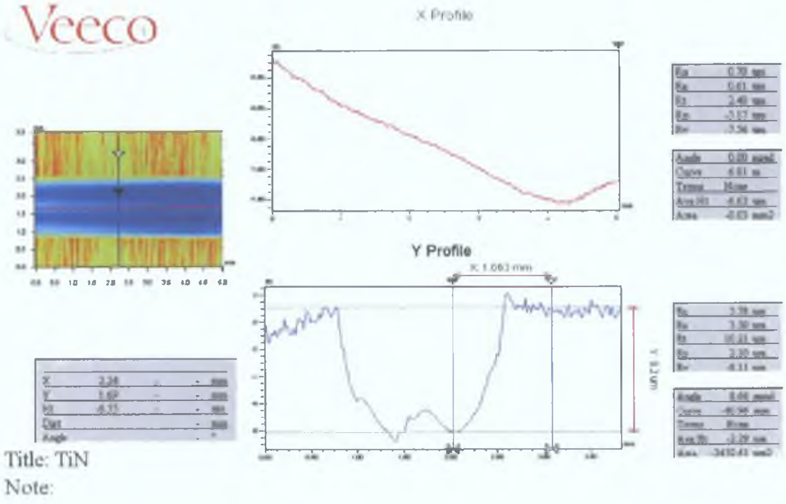
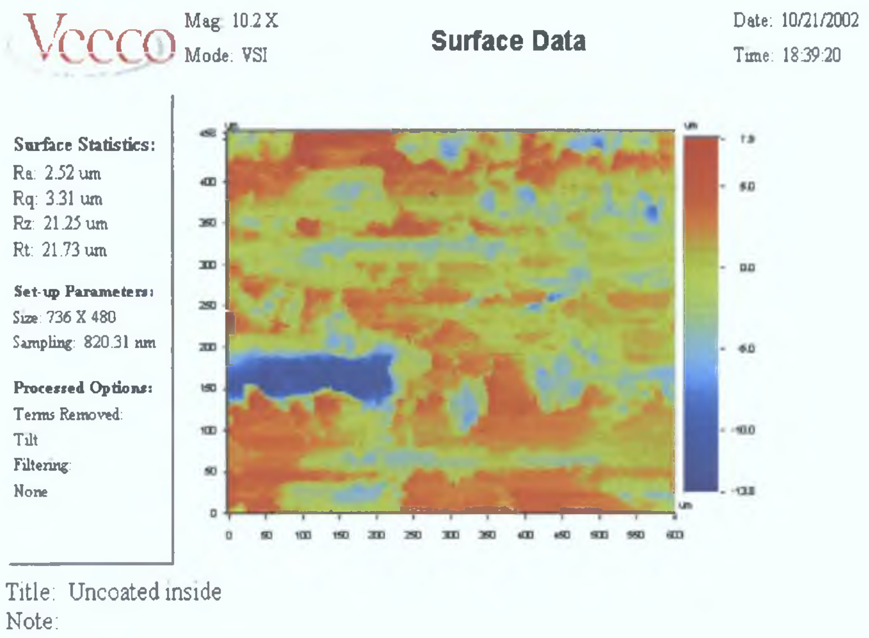


Fig. 6.5 Profile across wear track of TiN coated D3 (10 Kg, 10000 cycles)



Veeco

Mag: 10.2 X
Mode: VSI

Surface Data

Date: 10/21/2002
Time: 18:39:20

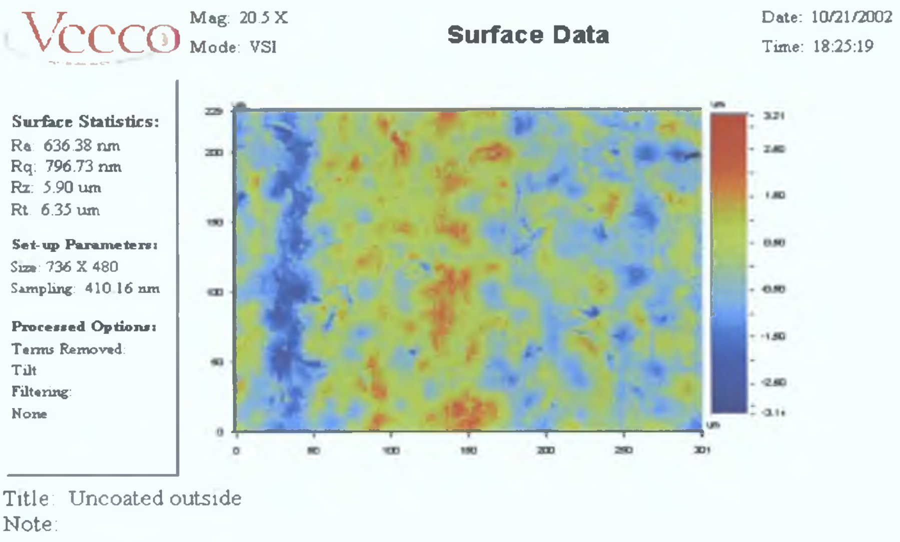
Surface Statistics:
Ra: 2.52 um
Rq: 3.31 um
Rz: 21.25 um
Rt: 21.73 um

Set-up Parameters:
Size: 736 X 480
Sampling: 820.31 nm

Processed Options:
Terms Removed:
Tilt
Filtering:
None

Title: Uncoated inside
Note:

(a)



Veeco

Mag: 20.5 X
Mode: VSI

Surface Data

Date: 10/21/2002
Time: 18:25:19

Surface Statistics:
Ra: 636.38 nm
Rq: 796.73 nm
Rz: 5.90 um
Rt: 6.35 um

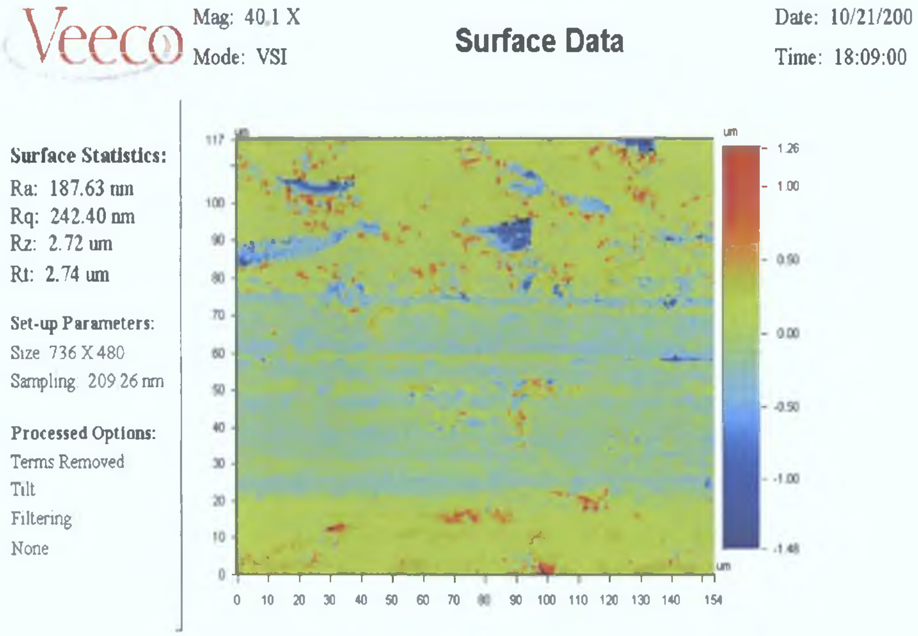
Set-up Parameters:
Size: 736 X 480
Sampling: 410.16 nm

Processed Options:
Terms Removed:
Tilt
Filtering:
None

Title: Uncoated outside
Note:

(b)

Fig. 6.6 Surface data of uncoated D2 tool steel (a) inside the track (b) out side the track.



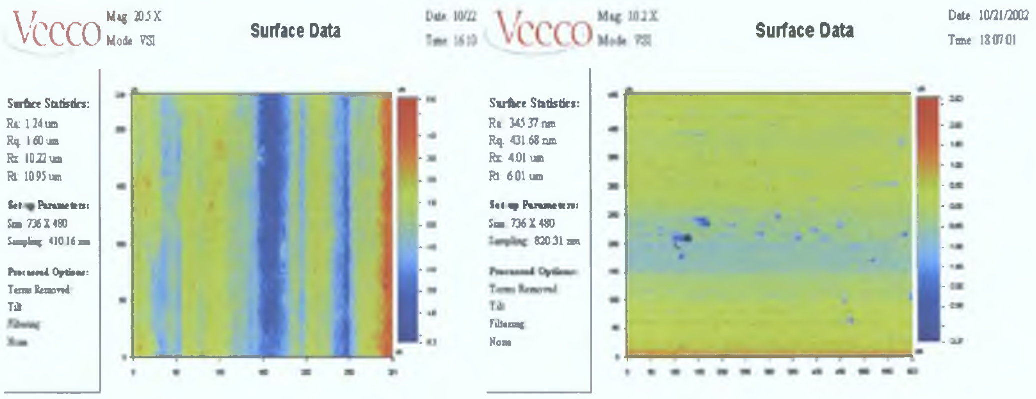
Mag: 40.1 X
Mode: VSI
Date: 10/21/200
Time: 18:09:00

Surface Statistics:
Ra: 187.63 nm
Rq: 242.40 nm
Rz: 2.72 um
Rt: 2.74 um

Set-up Parameters:
Size: 736 X 480
Sampling: 209.26 nm

Processed Options:
Terms Removed
Tilt
Filtering
None

Fig 6.7 Surface data of Al_2O_3 coated D2



Mag: 20.5 X
Mode: VSI
Date: 10/22
Time: 16:10

Surface Statistics:
Ra: 1.24 um
Rq: 1.60 um
Rz: 10.22 um
Rt: 10.95 um

Set-up Parameters:
Size: 736 X 480
Sampling: 410.16 nm

Processed Options:
Terms Removed
Tilt
Filtering
None

Mag: 10.2 X
Mode: VSI
Date: 10/21/2002
Time: 18:07:01

Surface Statistics:
Ra: 345.37 nm
Rq: 431.68 nm
Rz: 4.01 um
Rt: 6.01 um

Set-up Parameters:
Size: 736 X 480
Sampling: 820.31 nm

Processed Options:
Terms Removed
Tilt
Filtering
None

(a) (b)

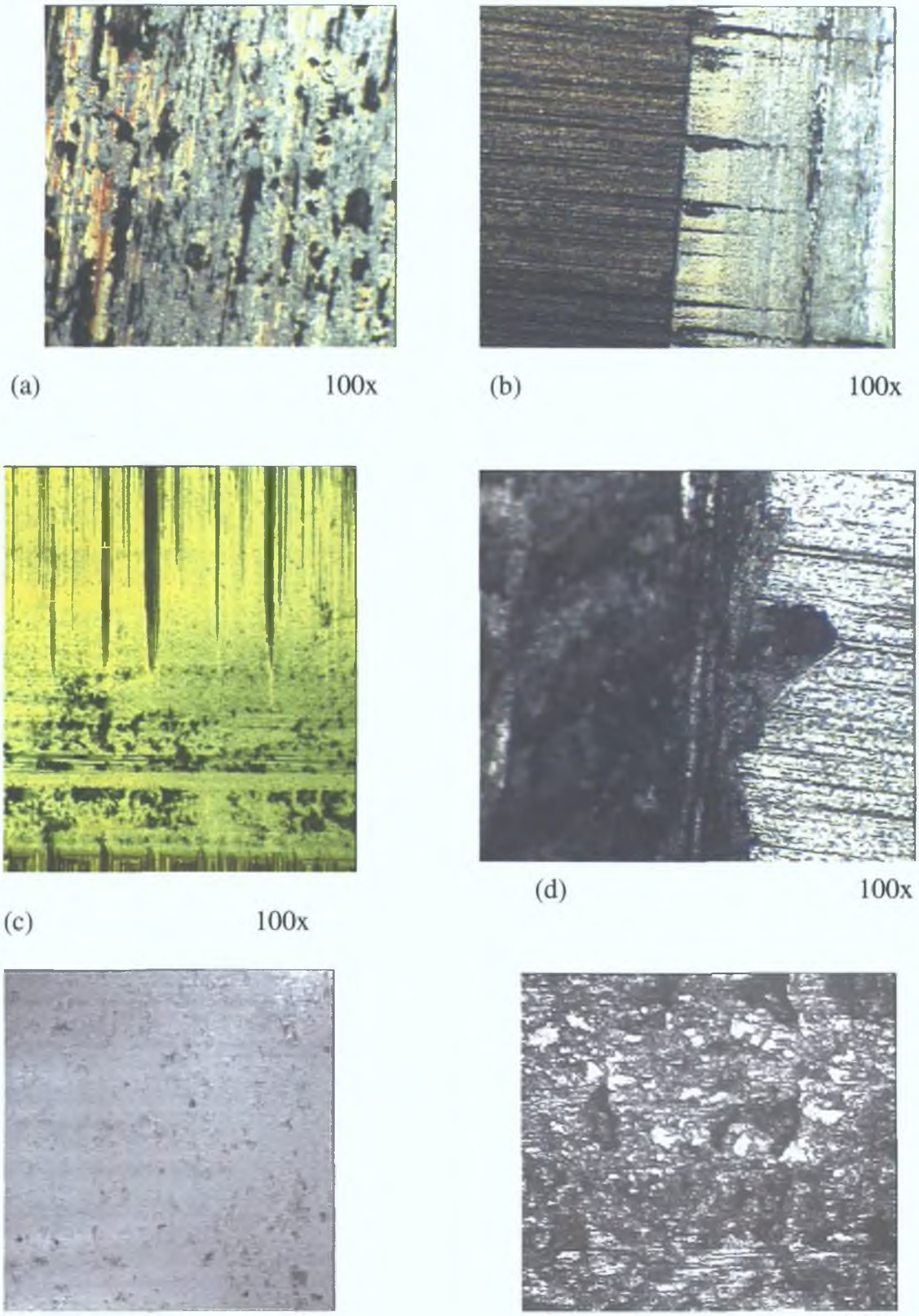
Fig. 6.8 Surface data of TiN coated D3 (a) inside track (b) outside track

6.2.2 Microscopic observations

The preliminary visual inspection of the coated surfaces revealed different thin film coatings, Al_2O_3 coating with silver colour, TiN coating with golden colour and TiC coating with dark grey. Wear tracks of the coated and uncoated samples were analysed by optical microscopy. Samples were examined under magnification of 100x. Fig. 6.9 shows a plan view section of the wear tracks obtained during the wear test of the treated and untreated samples. These worn samples were caused by the wear tool under a 5 Kg load. Fig 6.9 (a) shows the wear track of TiN coated D3 tool steel after 12000 cycles. Fig 6.9 (b) shows part of the coating and part of wear track of TiC vanadis 10 after 90000 cycles. Fig.6.9 (c) shows the wear track of uncoated vanadis 10 after 65000 cycles. Fig.6.9 (d) shows part of the wear track and part of the coating of Al_2O_3 coated Vanadis 4 after 4000 cycles. Fig. 6.9 (e) shows the wear track of the Nitrided D2 after 90000 cycles. Fig.6.9 (f) shows the wear track of uncoated D2 after 5000 cycles. These figures show the effects of wear on the treated and untreated samples under the conditions stated of load, sliding distance, number of cycles, and absence of lubrication. Microscopic observations show the abrasion and scuffing of the coated and uncoated surfaces with grooves running along the sliding direction as shown in Figure 6.9(a, b and c). Figure 6.9 (d) shows the flaking of the Al_2O_3 coating along, and at the edge of the track, with a large area of removed coating. Grooves are much finer on the surface of nitrided D2 tool steel and TiC coated vanadis 10 as a result the worn surfaces appear much smoother as shown in Figure 6.9(e) and Figure 6.9(b). On the other hand a rough worn surface appears in the case of uncoated D2 tool steel as shown in Figure 6.9 (f). The quality and the enhanced wear resistance can be shown by these micrographs. The wear tracks of TiN and TiC coatings are shown in Fig. 4.3. A cross section of TiN coated D2 steel is shown in Figure 6.10

6.3 CHEMICAL ANALYSIS RESULTS

Physical and mechanical properties of TiN and TiC coatings are highly depending on C/Ti and N/Ti ratio. In this study EDX analysis has been carried out to determine the atomic% of each of the constituents of the coatings used in this study. The composition of any coatings depends on several factors during the deposition process. The knoeldge of the composition of the coatings can help in understanding the behaviour of the coating under different situation. Figs. 10 to 12 show the x-ray patterns and the at % of TiN , TiC and Al_2O_3 respectively For TiN coatings it was found that 44 18 at % N and 53 87 at % Ti which an understoichiometric coating TiN coating with this composition is expected to have hardness equal to or greater than 1000 kg/mm^2 and with golden colour The maximum hardness of TiN coating achieved in this work is 800 kg/mm^2 This hardness value achieved, which, lower than expected, can be due to the influence of the substrate material on the overall hardness of the coating/substrate composite For TiC it was found that 49 31 at % Ti and 49 78 at% C which, is almost stoichiometric coating With C/Ti ratio of 1 the hardness approaches 2800 kg/mm^2 [83] The maximum hardness measured in the current work is 1470 kg/mm^2 For Al_2O_3 the ratio was found 58 53 at% O and 33 97 at % Al The EDX analysis of the nitrided layer on D3 tool steel show a 0 35 wt% N as shown in Fig 6 13 This value is considerably low to form the desirable ε phase, though it is enough to form iron nitrides according to the Fe-N binary diagram [112]



(a) 100x (b) 100x

(c) 100x (d) 100x

(e) 100x (f) 100x

Fig 6.9 Micrographs of wear track of (a) D3TiN (b) Vanadis 10 TiC (c) uncoated Vanadis 10 (d) Al_2O_3 Vanadis 4 (e) Nitrided D2 (f) Uncoated D2 (100x magnification in all cases).

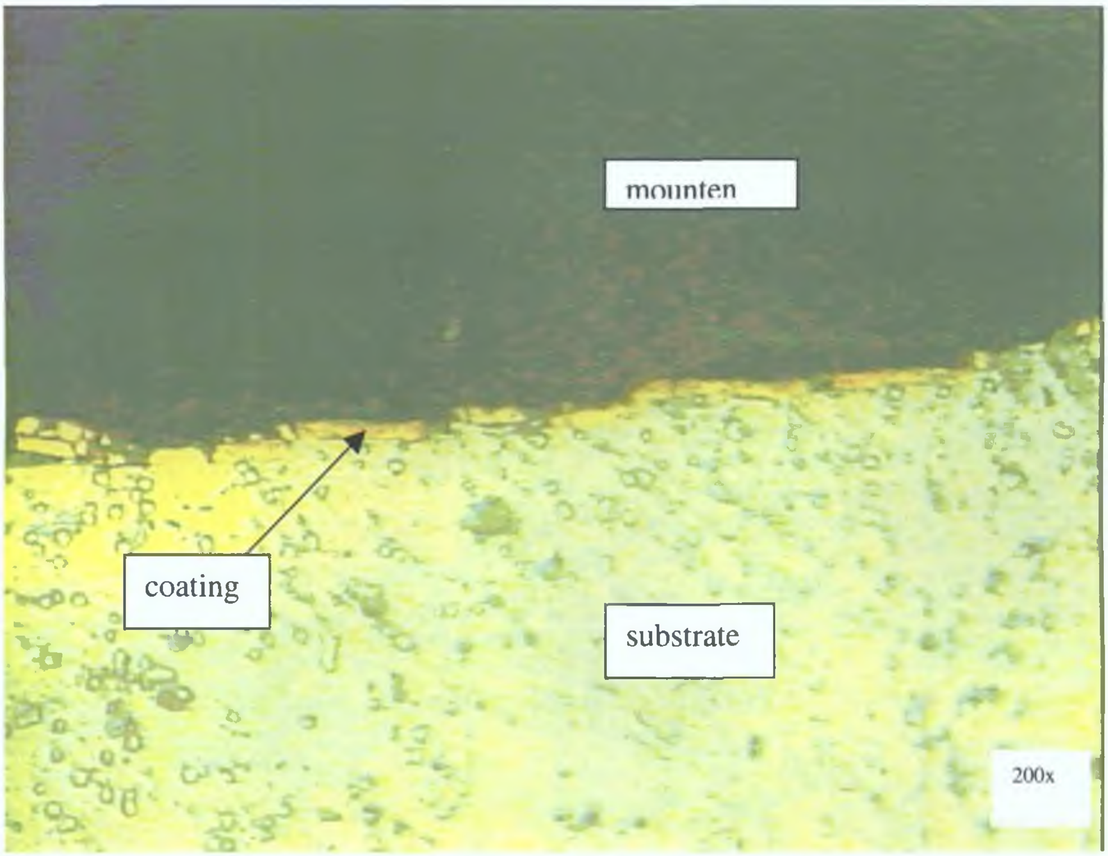
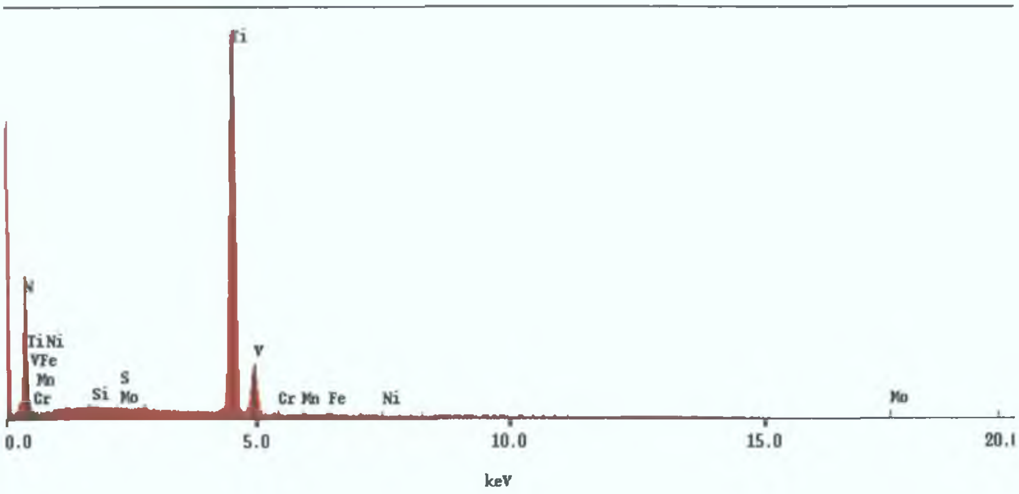


Fig. 6.10 Cross sectional image of TiN coated D2 tool steel shows the coating substrate interface. (magnification 200x)



```
PGT Bulk sample analysis      Wed Oct  9 11:22:04 2002

Phi-Rho-Z Method, variable-width filter


Sample /xd1/window1/#1,TiNd2.spt
Accelerating Voltage:          13.26 keV
Takeoff Angle:                 35.00 degrees
Library for system standards: /imix/spectra/system_standards.dir

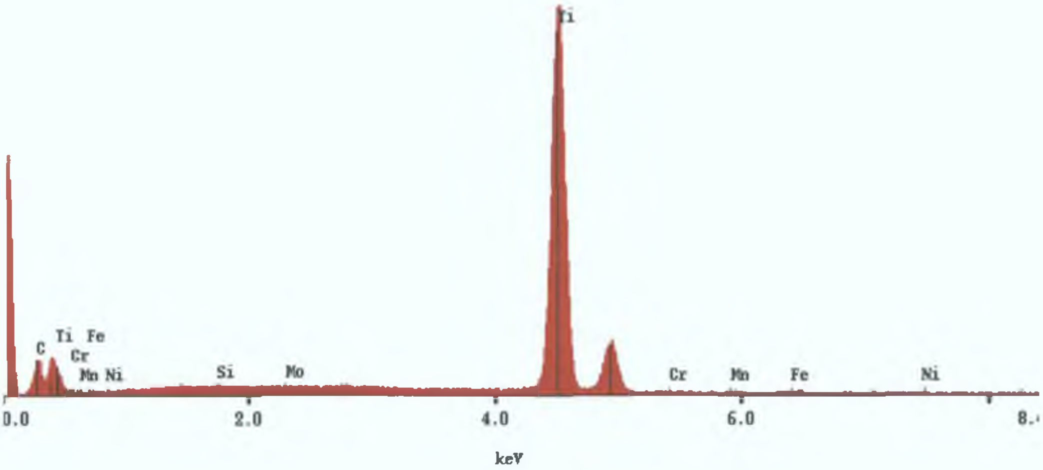
Elm   Rel. K      Z     A     F     ZAF    Norm wt% Prec. Atomic %

 N    0.0000    0.000 0.000 0.000 0.0000    18.74   0.00   44.18
 Ti   0.7510    1.044 0.997 1.000 1.0408    78.16   2.13   53.87
 V    0.0209    1.069 0.994 0.999 1.0628     2.22   0.67    1.43
 Fe   0.0079    1.061 1.047 1.000 1.1106     0.88   0.60    0.52
 Si   0.0000    0.918 1.290 0.997 1.1805     0.00   0.00    0.00
 Mn   0.0000    1.077 1.064 1.000 1.1451     0.00   0.00    0.00
 Cr   0.0000    1.054 1.084 0.999 1.1416     0.00   0.00    0.00
 Mo   0.0000    1.134 0.963 0.983 1.0732     0.00   0.00    0.00
 Ni   0.0000    1.054 1.026 1.000 1.0814     0.00   0.00    0.00
 S    0.0000    0.928 1.103 0.986 1.0100     0.00   0.00    0.00

Total                                      100.00         100.00

Goodness of fit     2.44
```

Fig. 6.11 EDX analysis of TiN coating on D2 steel



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PGT Bulk sample analysis      Wed Oct  9 12:07:57 2002

Phi-Rho-Z Method, variable-width filter


Sample /xd1/window1/#1,TiNCd2.spt
Accelerating Voltage:          13.26 keV
Takeoff Angle:                 35.00 degrees
Library for system standards: /imix/spectra/system_standards.dir

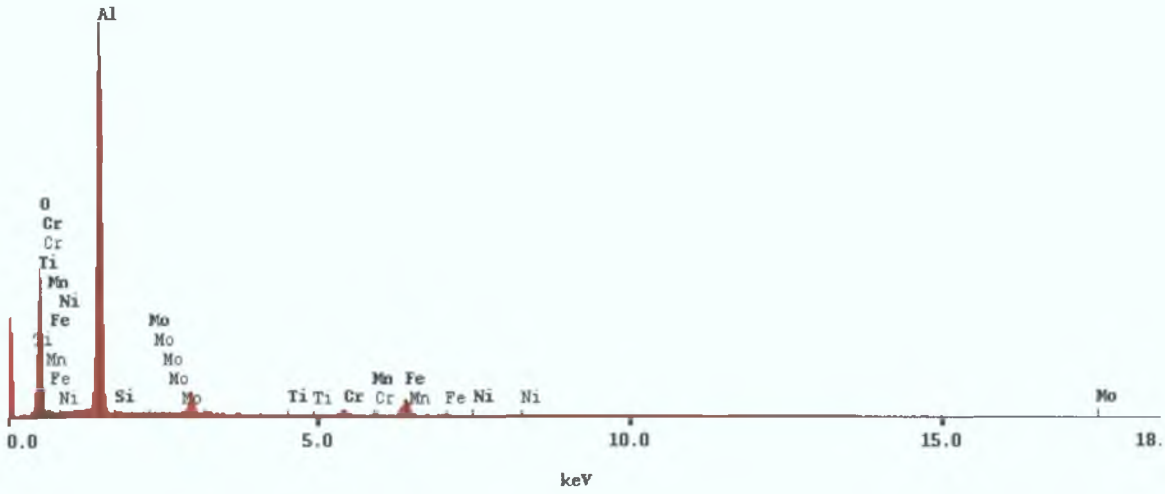
Elm   Rel. K      Z     A     F     ZAF    Norm wt% Prec. Atomic %

 Ti   0.7501    1.051 0.996 0.999 1.0464    78.49   1.77  49.31
 Fe   0.0091    1.068 1.045 0.999 1.1159     1.02   0.49   0.55
 Si   0.0004    0.923 1.276 0.997 1.1741     0.05   0.07   0.06
 Mn   0.0000    1.084 1.061 1.000 1.1500     0.00   0.00   0.00
 Cr   0.0000    1.060 1.084 0.999 1.1487     0.00   0.00   0.00
 Mo   0.0000    1.141 0.958 0.982 1.0734     0.00   0.00   0.00
 Ni   0.0052    1.062 1.025 1.000 1.0883     0.57   1.41   0.29
 C    0.0000    0.000 0.000 0.000 0.0000    19.87   0.00  49.78

Total                                       100.00         99.99

Goodness of fit     2.27
```

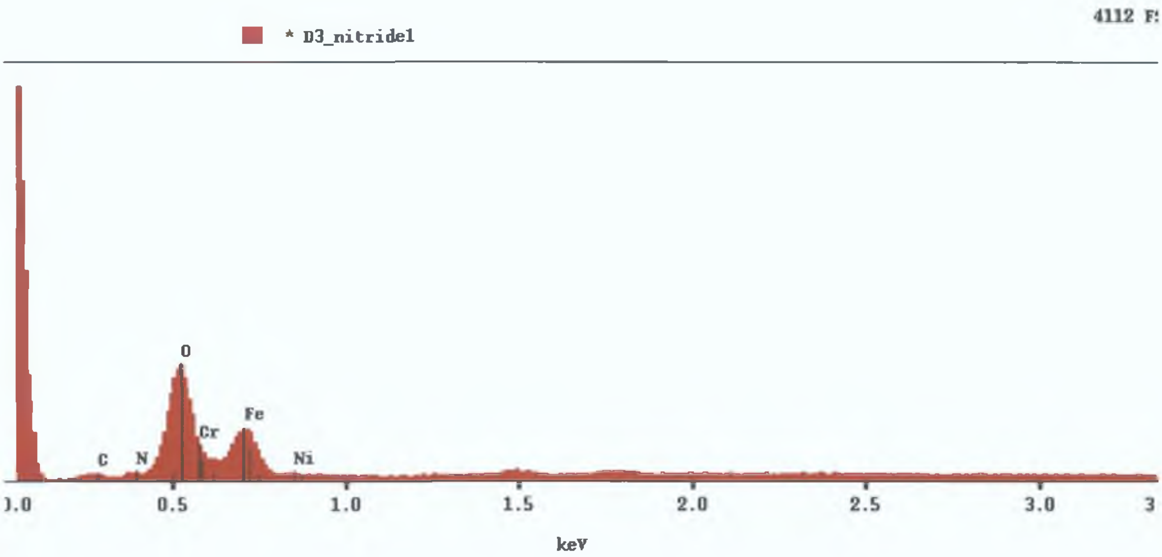
Fig 6.12 EDX analysis of TiC on D2 tool steel



Elm	Rel. K	Z	A	F	ZAF	Norm wt%	Prec.	Atomic %
O	0.0000	0.000	0.000	0.000	0.0000	41.79	0.00	58.83
Al	0.3091	1.020	1.290	1.000	1.3162	40.69	0.81	33.97
Cr	0.0222	1.158	1.001	0.957	1.1082	2.46	0.48	1.07
Mn	0.0027	1.185	0.998	1.000	1.1830	0.32	0.50	0.13
Fe	0.1245	1.170	0.999	1.000	1.1691	14.56	1.24	5.87
Si	0.0011	0.994	1.563	1.000	1.5531	0.17	0.96	0.14
Mo	0.0000	1.230	1.055	1.000	1.2965	0.00	0.00	0.00
Ni	0.0001	1.167	1.006	1.000	1.1743	0.01	0.00	0.00
Ti	0.0000	1.143	1.009	0.978	1.1288	0.00	0.00	0.00
Total						100.00		100.01

Goodness of fit 5.18

Fig. 6.13 EDX analysis of Al_2O_3 coating on D3 tool steel



```
        C :  K line:     161  L line:      0  M line:      0
        O :  K line:    6575  L line:      0  M line:      0
        Cr:  K line:    2879  L line:    285  M line:      0
        Fe:  K line:   11539  L line:   3062  M line:      0
        Ni:  K line:     426  L line:     69  M line:      0
        N :  K line:     167  L line:      0  M line:      0

     Normalized chi squared:    6.66


PGT Bulk sample analysis      Tue Jul 15 12:12:06 2003

Phi-Rho-Z Method, variable-width filter


Sample /xd1/window1/#1,D3_nitride1.spt
Accelerating Voltage:            14.45 keV
Takeoff Angle:                   35.00 degrees
Library for system standards: /imix/spectra/system_standards.dir

Elm   ZAF     Norm wt% At prop Line

 C   3.4622     0.77    0.96  K line
 O   0.0000    25.45   24.00  K line
 Cr  0.9015     8.16    2.37  K line
 Fe  1.0650    61.21   16.53  K line
 Ni  1.1028     4.06    1.04  K line
 N   2.1465     0.35    0.38  K line

Total          100.00   45.28
```

Fig. 6.14 EDX analysis of Nitrided D3 tool steel

6.4 WEAR TEST RESULTS

6.4.1 Wear of coated and uncoated tool steels

Wear tests have been performed on four tool steel materials D2, D3, Vanadis 4 and Vanadis 10. These materials were coated, nitrided, and pre-nitrided coated. The coatings were deposited using the magnetron sputtering technique. Three ceramic thin films TiC, TiN, and Al_2O_3 were applied to the treated and untreated substrates. Wear tests were carried out using a round nose of radius 2mm tungsten carbide wear tool. The tests were carried out in dry conditions at room temperature, with normal load of 5 Kg and sliding distance of 20mm. Wear depth as function of number of cycles of each of the tested the coated and uncoated is shown in Figs 6.15 to 6.18. In the generation of wear, material was removed continuously with increasing number of cycles. In Figure 6.15 it is shown that the TiN coated D2 tool steel suffered slightly lower wear than the uncoated substrate. However TiC coated D2 tool steel showed much lower wear than the uncoated D2 tool steel. On the other hand the D2 tool steel samples coated with Al_2O_3 experienced higher wear than the uncoated surfaces. The same observation can be seen for D3 tool steel as shown in Figure 6.16. From Figures 6.17 and 6.18 it is shown that both vanadis 4 and vanadis 10 coated with TiN and Al_2O_3 experienced higher wear than the uncoated vanadis 4 and vanadis 10 but, TiC coated vanadis 4 showed much lower wear than uncoated vanadis 4. In the case of TiC vanadis 10 the wear was nearly the same.

6.4.2 Comparative wear resistance of different coatings

Figures 6.15 to 6.18 show the wear track depth of TiC, TiN and Al_2O_3 coatings on each of the substrate materials as a function of number of cycles. From these results it is evident that TiC coatings offered the greatest wear resistance when compared to TiN and Al_2O_3. In comparison Al_2O_3 coated samples demonstrated much lower wear resistance. The poor performance of Al_2O_3 can be explained by the fact that amorphous Al_2O_3 coatings are soft and unstable, and most PVD alumina coatings are of this form due to the low temperatures used in PVD technique. The maximum hardness of α- alumina PVD coatings has been reported is 1000 Kg/mm^2. α- Al_2O_3, which is hard and used for tribological application cannot be obtained with PVD techniques with temperatures lower than 680°C [83,101,102,174,175] The temperature used for the deposition of the alumina in this work is ~ 250°C which means the phase formed is the soft amorphous phase which suitable for protection against corrosion but it is not suitable for protection against wear It was observed also from these results that TiN coatings demonstrated in general slightly lower wear than the uncoated and the alumina coatings on D2 and D3 tool steels but there was no sign of improvement on Vanadis 4 and Vanadis 10 The high performance of the TiC coated samples can be attributed to the coating/substrate hardness and the good adhesion of the coating to the substrate The only explanation, which can be suggested for the poor performance of the TiN coatings that the properties of the substrate especially the surface roughness affected significantly the adhesion between the substrate and the coating It was observed that when the coatings break, the wear rate increases, and then it resumed at the same level as that the uncoated surfaces As shown in Fig 6 15 the wear rate of the TiC coated D2 tool steel increased when the wear depth exceeded the thickness of the coating This may be explained by the fact that as the coatings break, the hard fragments acted as third body and increased the loss of material, and when the coating is totally removed wear became similar to that of the substrate material This leads to the suggestion that hard coatings may cause sever wear when they are broken

6 4 3 Wear resistance of the nitided surfaces

The effect of the nitriding on the wear resistance of D2, D3, vanadis 4 and vanadis 10 tool steels is shown in Figures 6 19 to 6 22 The wear track depth of the nitrided and untreated steel is shown as a function of number of cycles These figures show that the nitriding improved the wear resistance for the four substrate materials, with the nitrided vanadis 10 providing the best wear resistance The tremendous increase of the wear is due to the hard nitriding layer formed on the surfaces of the substrate materials

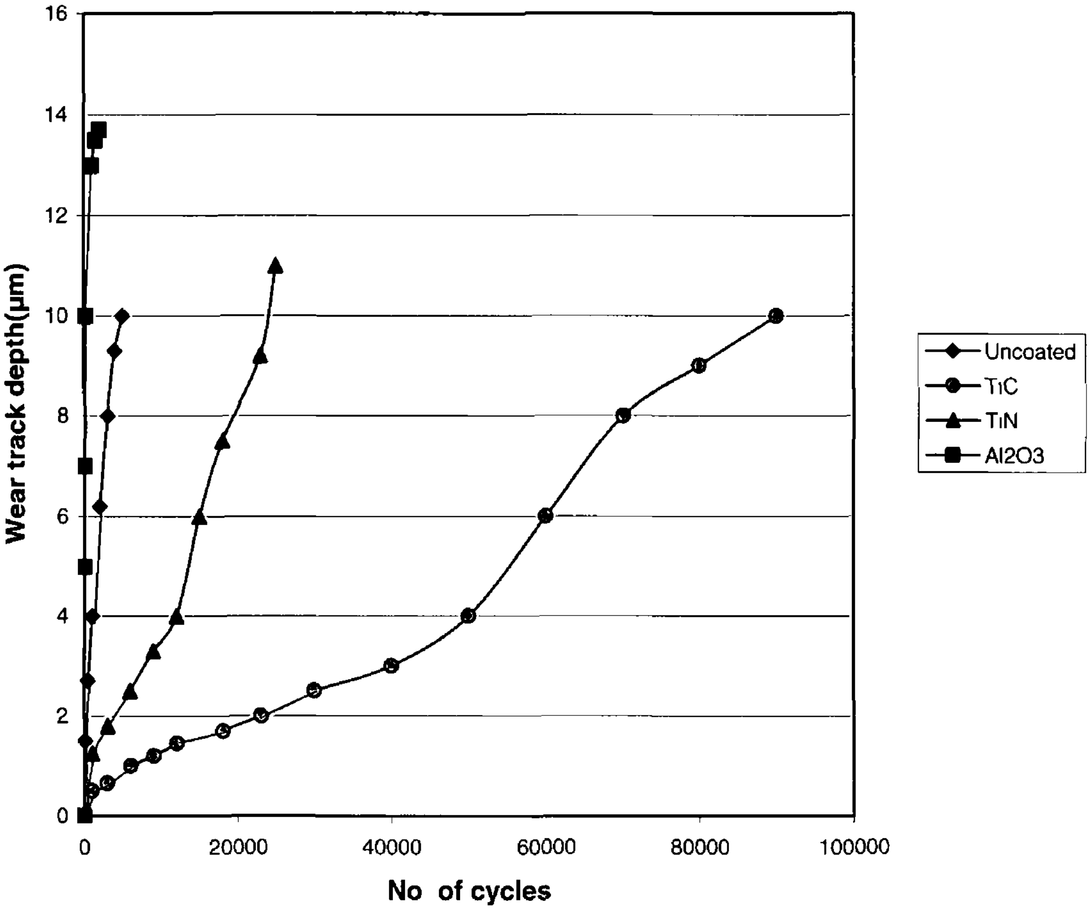


Fig 6.15 Wear track depth vs No of cycles of coated and uncoated D2 steel.

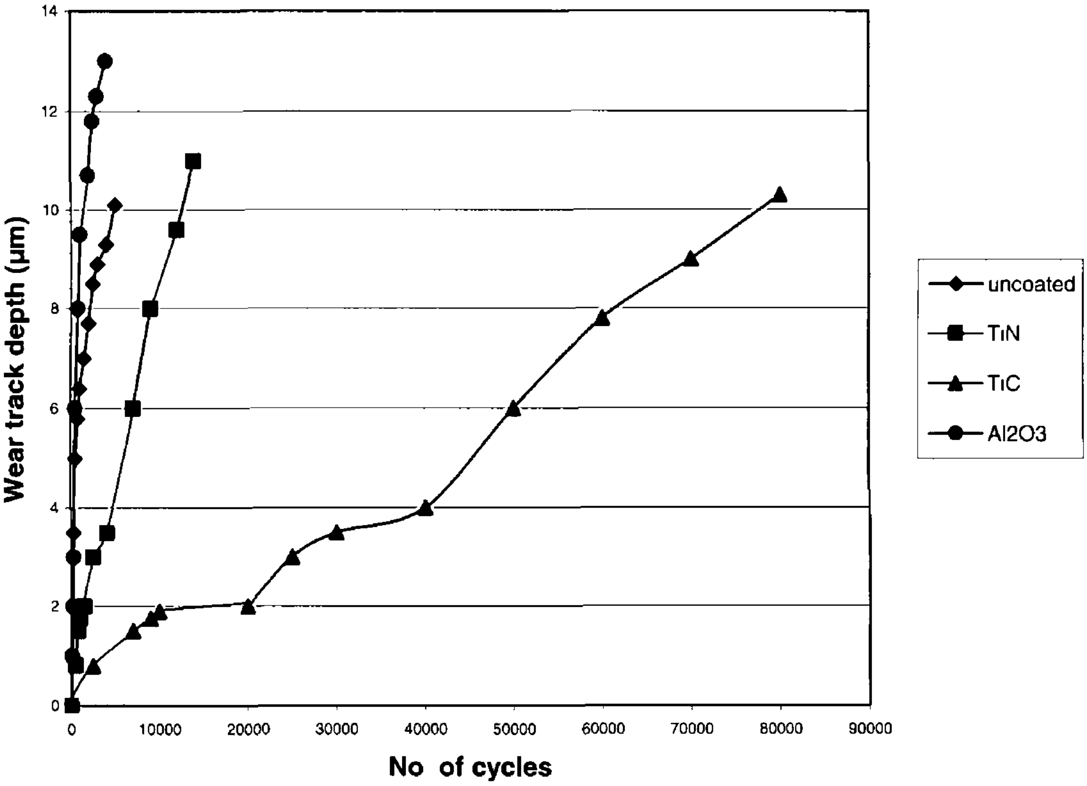


Fig 6 16 Wear track depth vs No of cycles of coated and uncoated D3 steel

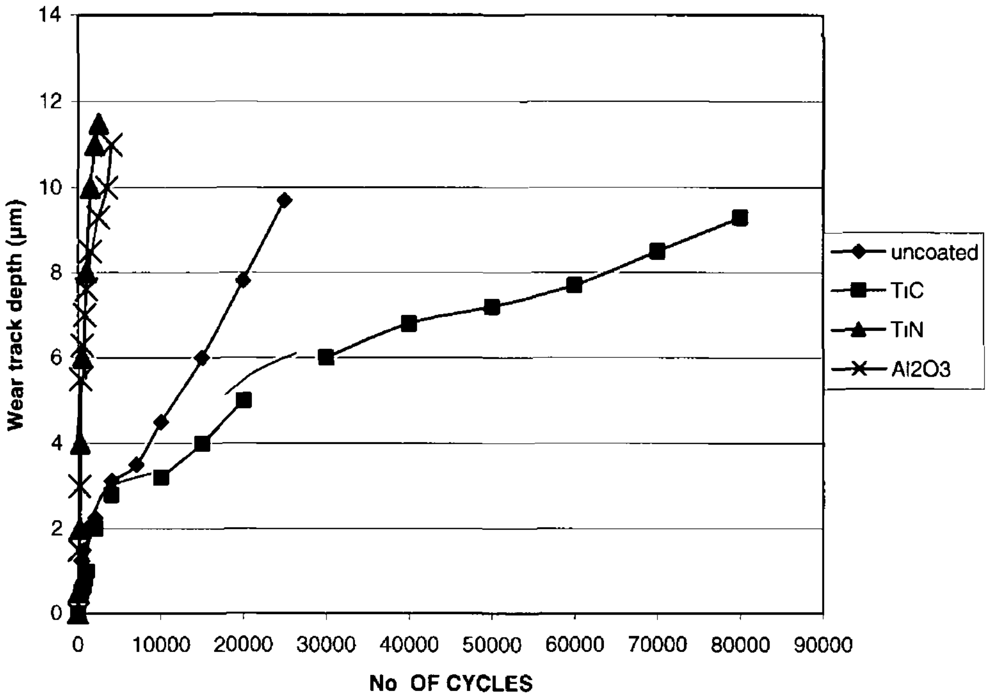


Fig 6 17 Wear track depth vs No of cycles of coated and uncoated Vanadis 4.

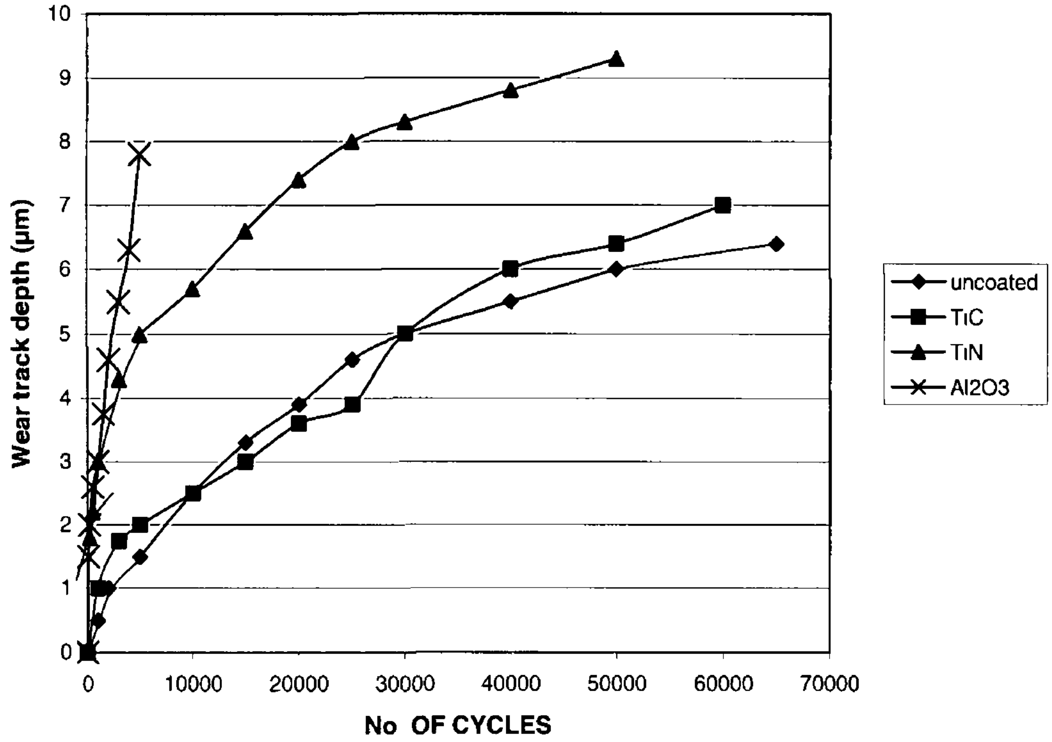


Fig. 6.18 Wear track depth vs No. of cycles of coated and uncoated Vanadis 10

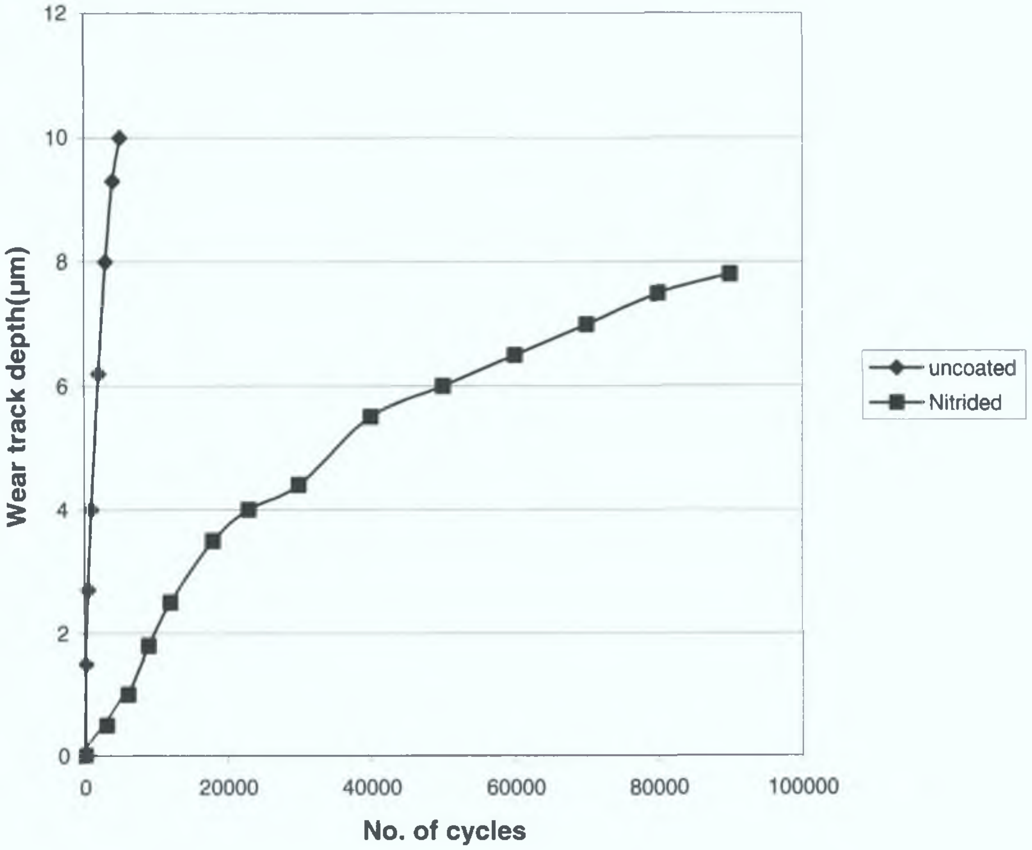


Fig. 6.19 Wear track depth vs No. of cycles of nitrided and untreated D2 steel.

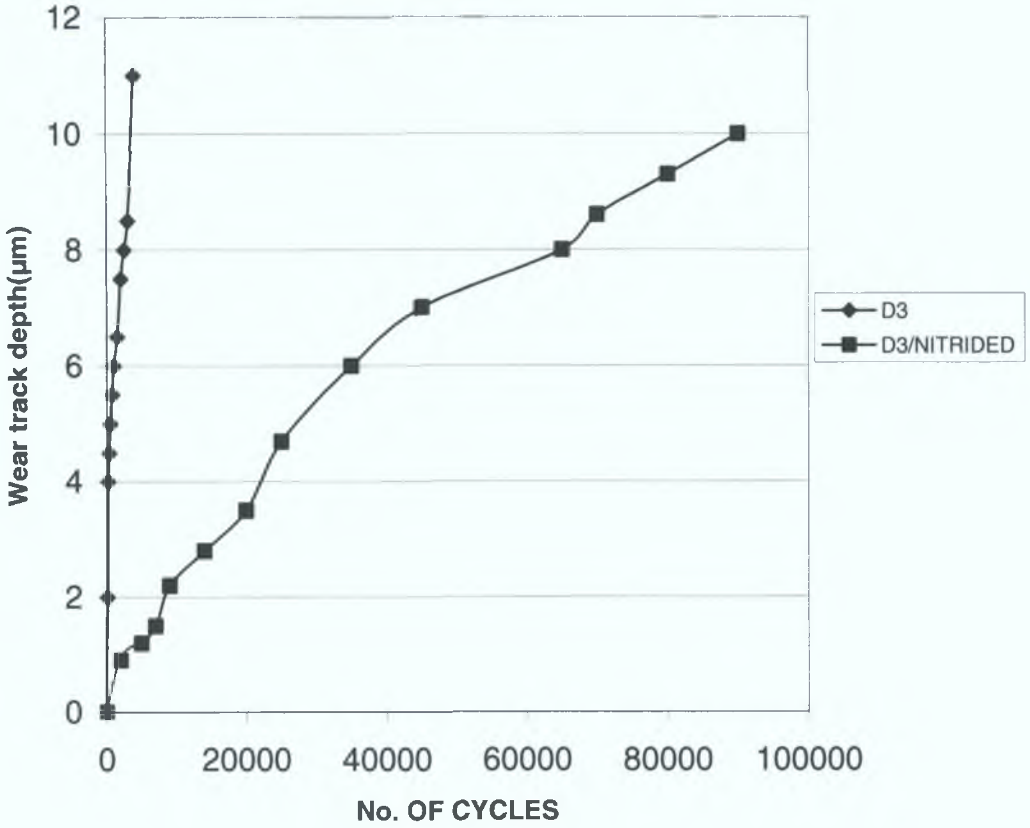


Fig. 6.20 Wear track depth vs No. of cycles of nitrided and untreated D3 tool steel

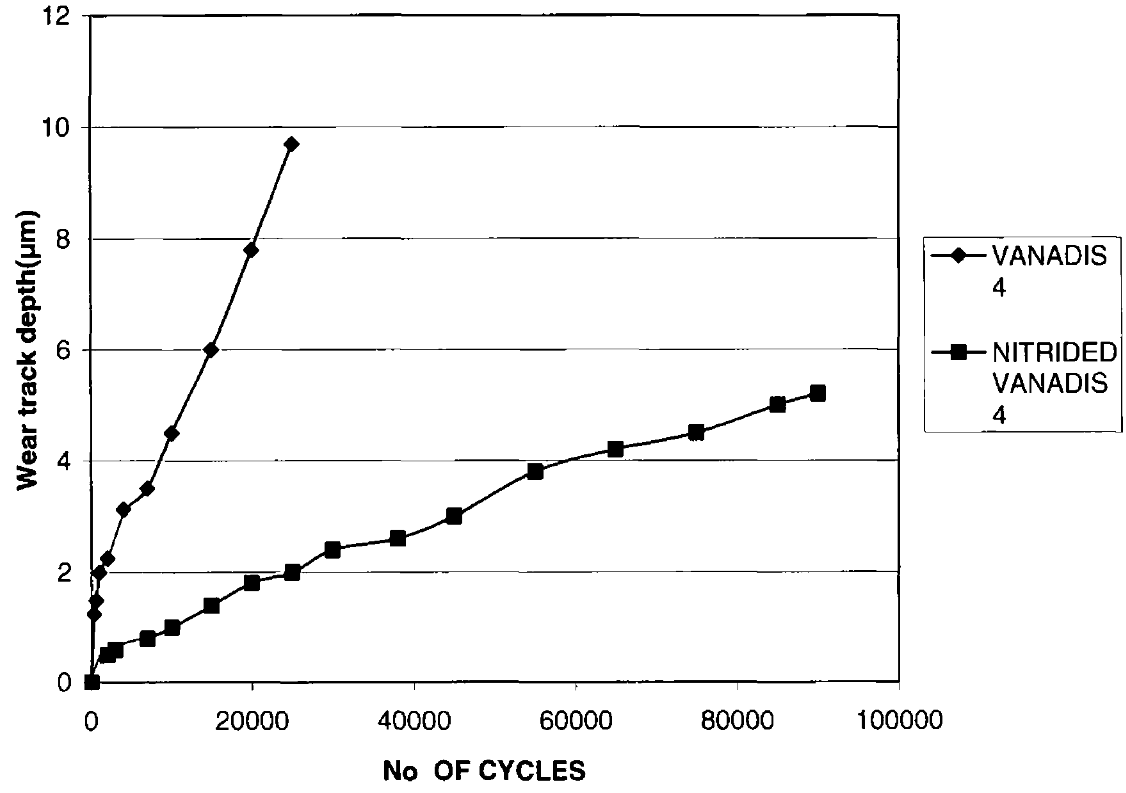


Fig. 6 21 Wear track depth vs No of cycles of nitrided and untreated Vanadis 4 steel

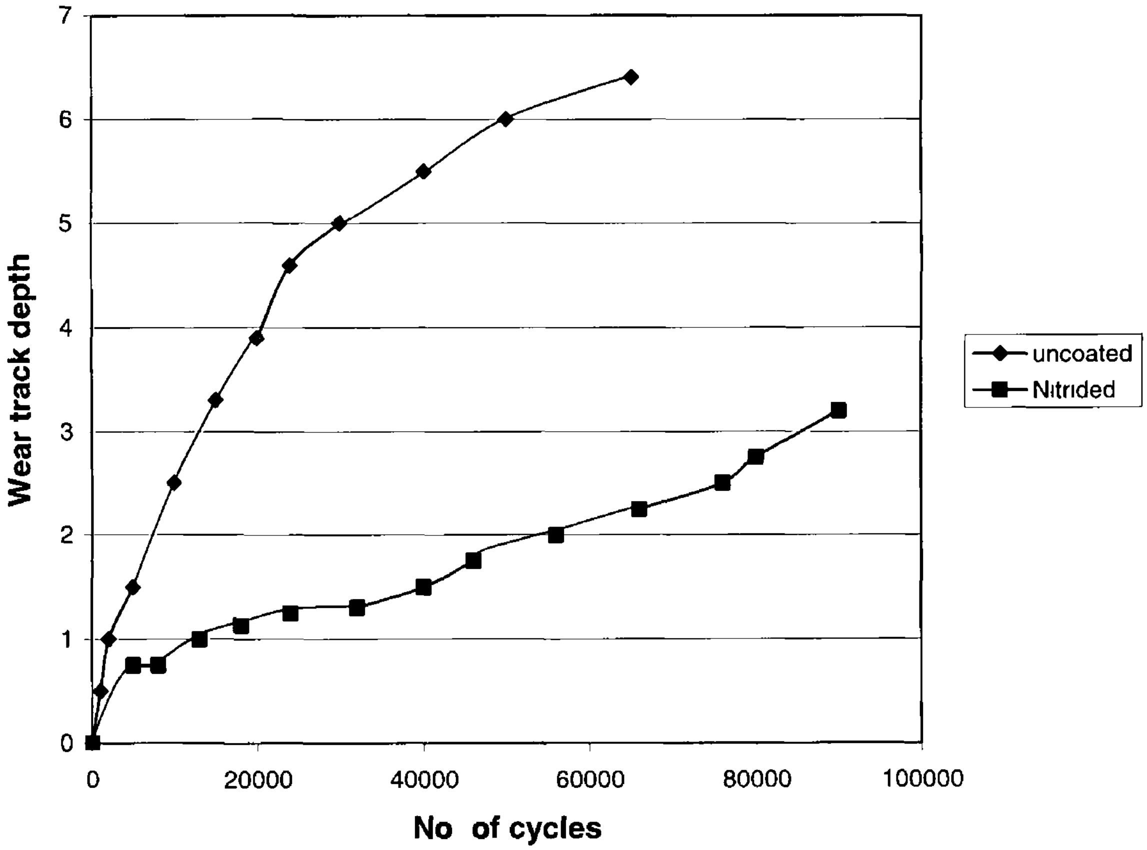


Fig. 6.22 Wear track depth vs No. of cycles of nitrided uncoated vanadis 10

6.4.4 Effect of pre-nitriding on wear

The effect of pre-nitriding on the wear resistance of the coatings was observed. The results obtained as shown in Figs 6.23 to 6.34 strongly suggest that nitriding treatments of tool steels prior to the deposition of thin films can improve the wear resistance of the coatings by enhancing the hardness and the adhesion of the coating and the load bearing of the substrate material. Pre-nitriding of the substrates before coating with TiN and Al_2O_3 significantly improved wear resistance due to the presence of the hard nitriding layer on the lower surface. In the case of Al_2O_3 coatings the tremendous improvement of the wear resistance can be due to the affinity of Al to form stable and hard nitrides and the effect of N_2 on the stabilizing of amorphous alumina [171]. On the other hand nitriding did not improve the wear resistance of TiC coatings as shown in Fig. 6.23. This lower wear resistance is due to the poor quality of the pre-nitriding TiC coated samples as shown in Table 6.2 and Fig.6.93.

6.4.5 Influence of substrate materials

Wear track depth as a function of number of cycles of TiC, TiN and Al_2O_3 coated substrates are shown in Figs.6.35 to 6.37. The material has a great influence on wear resistance of the coated surface because the load applied to produce wear is supported through the coating by the substrate material. The influence of the substrate material can be observed from these Figs. Combination of D2 tool steel with TiC coatings showed better wear resistance than TiC coated Vanadis 4 and D3 steels. On the other hand TiN coatings improved the wear resistance of D2 and D3 but did not improve that of Vanadis 4 or Vanadis 10 steels with the same coatings thickness and under the same condition of wear . This finding supports what some researchers such as Bromark et al. [176] concluded about the effect of the substrate material properties on the overall tribological properties of the coating-substrate composite. Fig. 6.38 shows the wear track depth of the treated and untreated samples subjected to the same number of cycles (4000 cycles) It seems to show that nitriding is the best treatment for any of these coatings

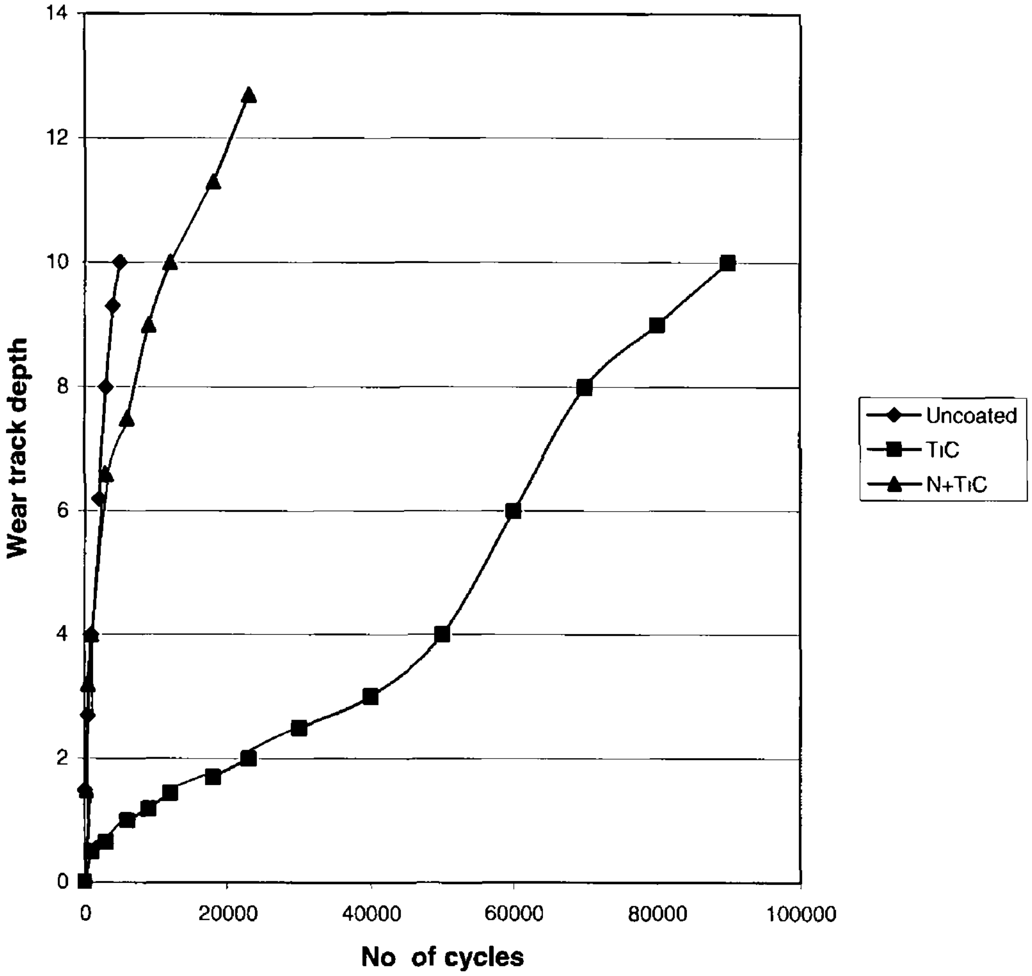


Fig 6 23 Wear track depth vs No. of cycles of pre-nitrided TiC coated D2 tool steel (compared to the uncoated and TiC coated)

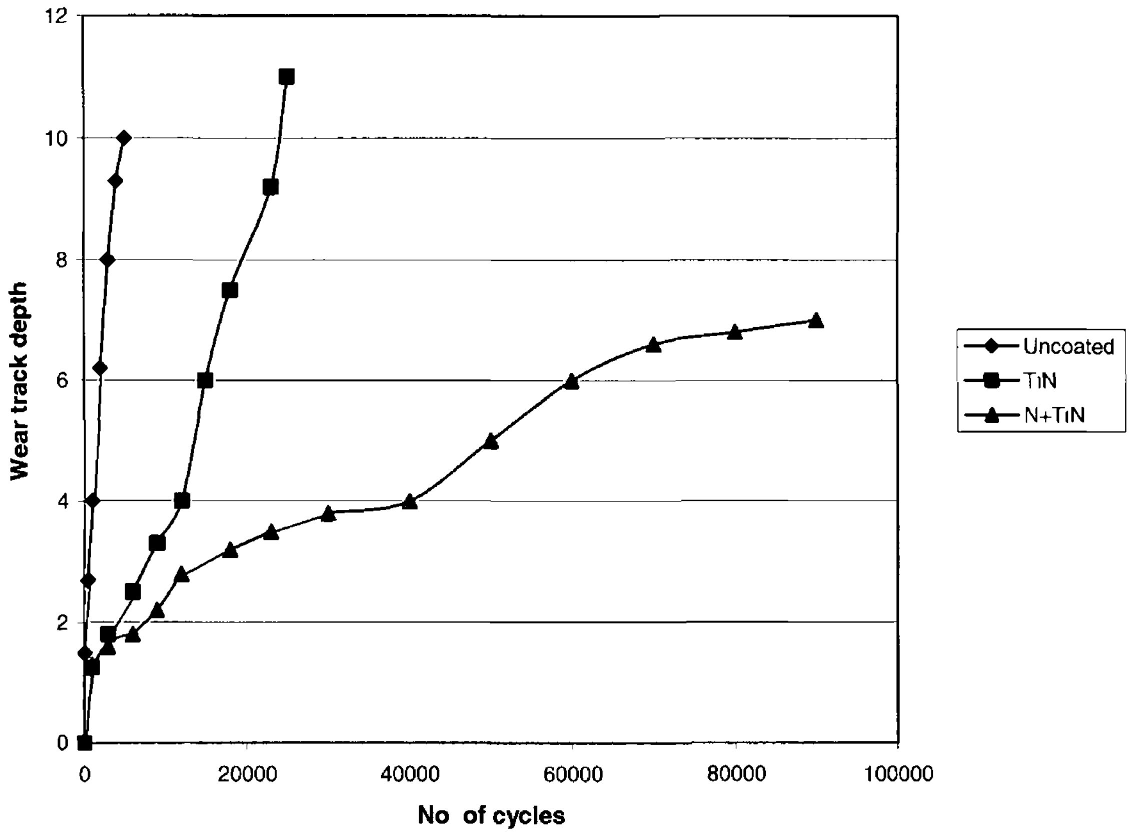


Fig. 6 24 Wear track depth vs No of cycles of pre-nitrided TiN coated D2 tool steel (compared to the uncoated and TiN coated)

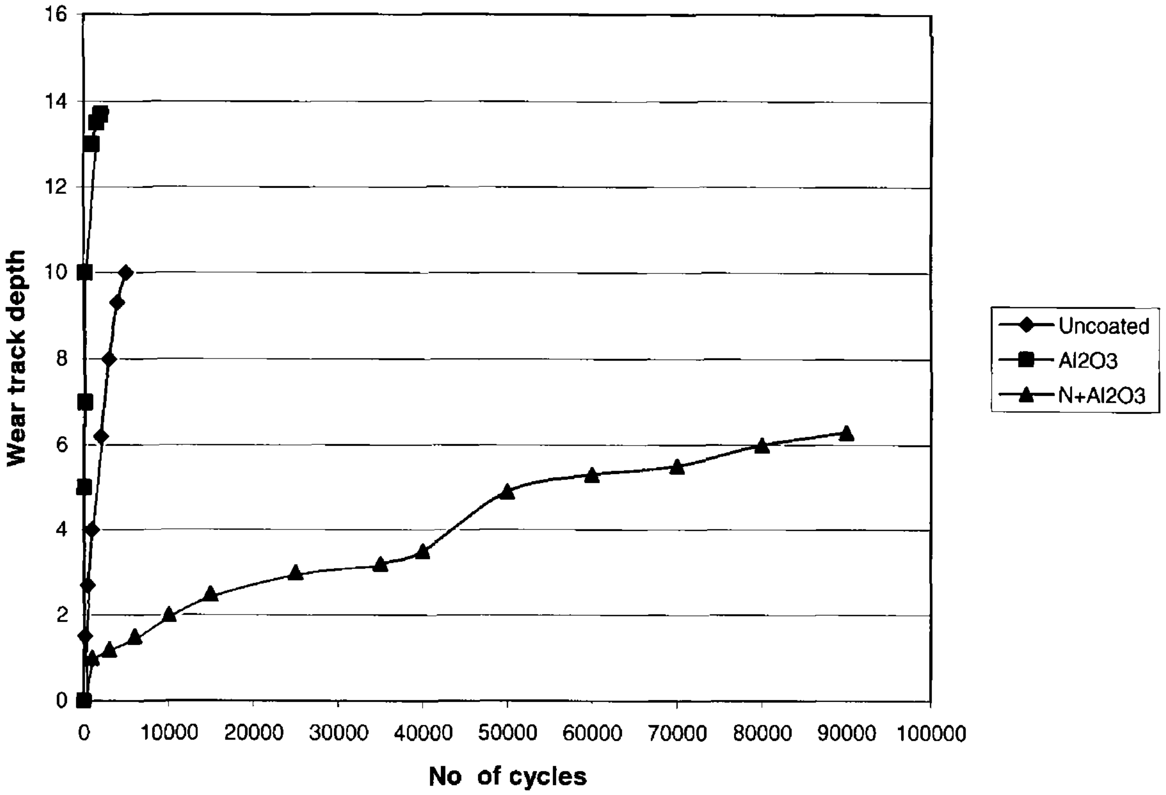


Fig. 6 25 Wear track depth vs No of cycles of pre-nitrided coated Al_2O_3 D2 steel(compared with the uncoated and coated Al_2O_3)

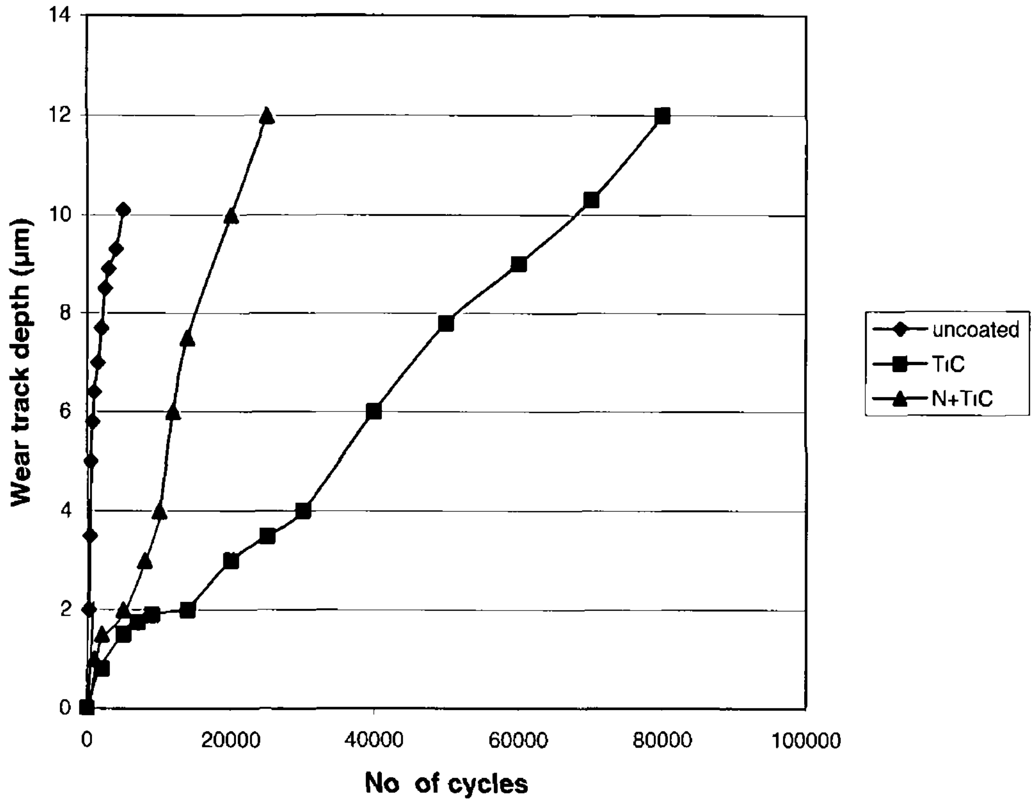


Fig. 6.26 Wear track depth vs No of cycles of pre-nitrided TiC coated D3 steel (compared with the uncoated and coated TiC)

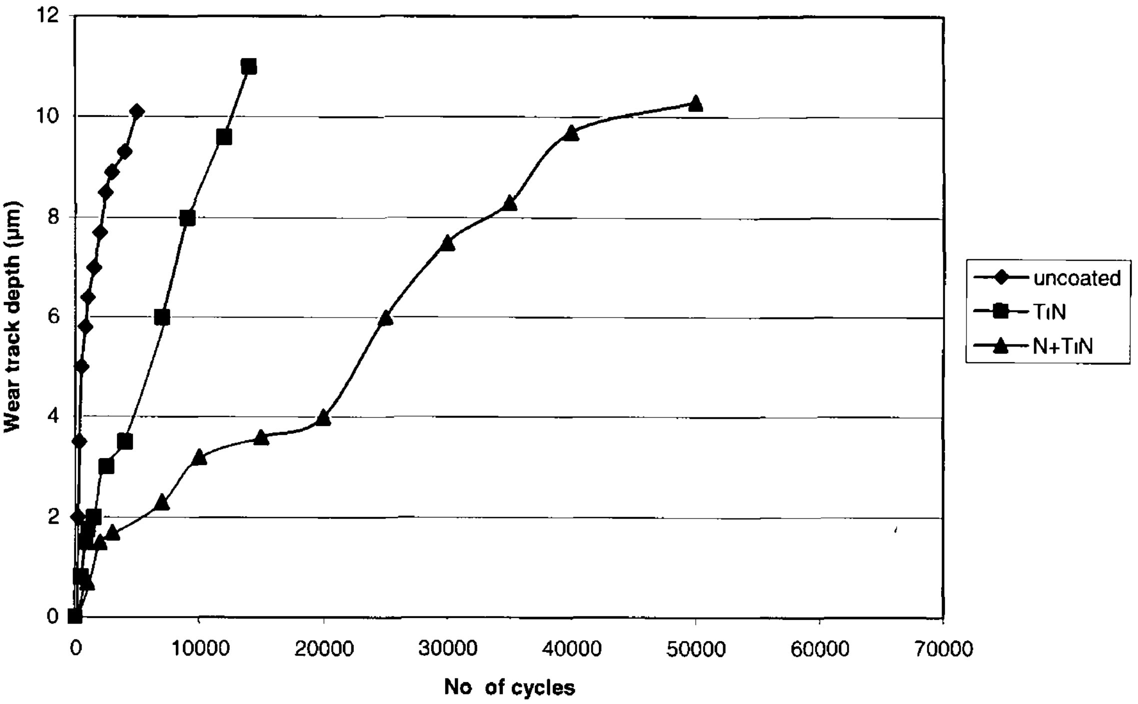


Fig 6.27 Wear track depth vs No of cycles of pre-nitrided TiN coated D3 steel (compared with the uncoated and coated TiN)

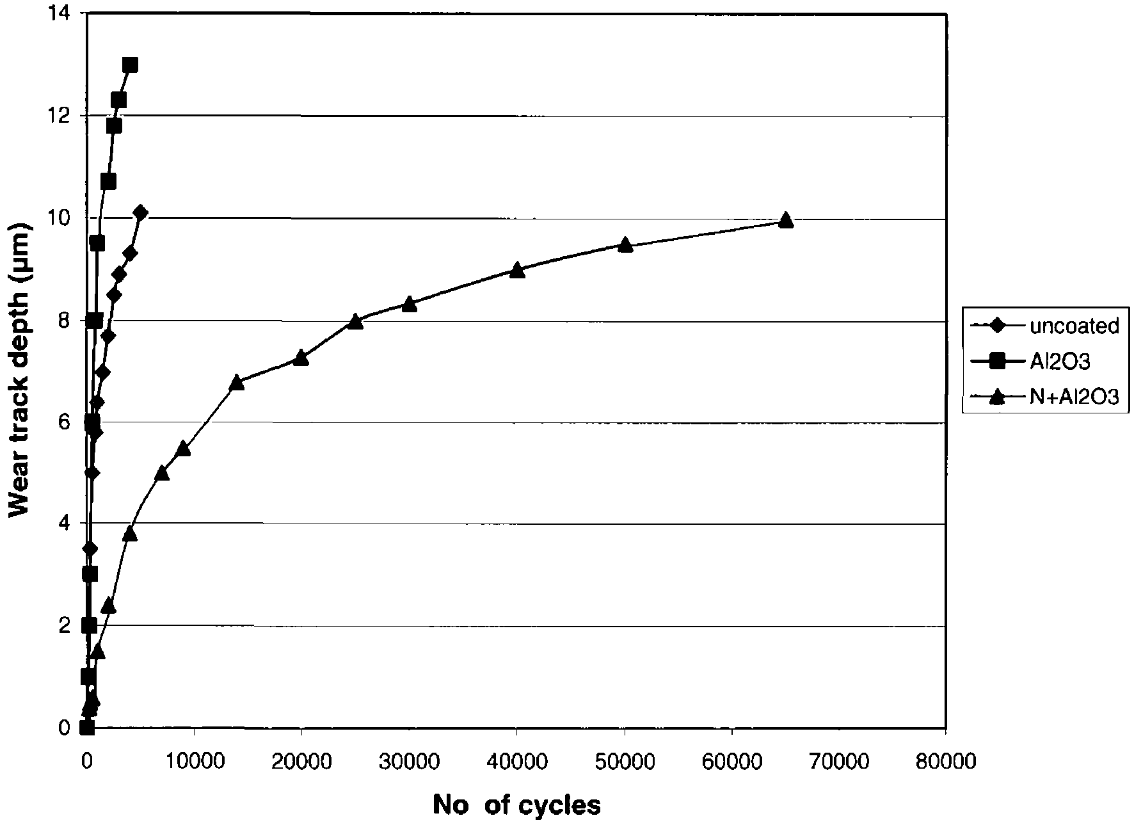


Fig. 6.28 Wear track depth vs No. of cycles of pre-nitrided Al2O3 coated D3 Steel(compared with the uncoated and coated Al_2O_3)

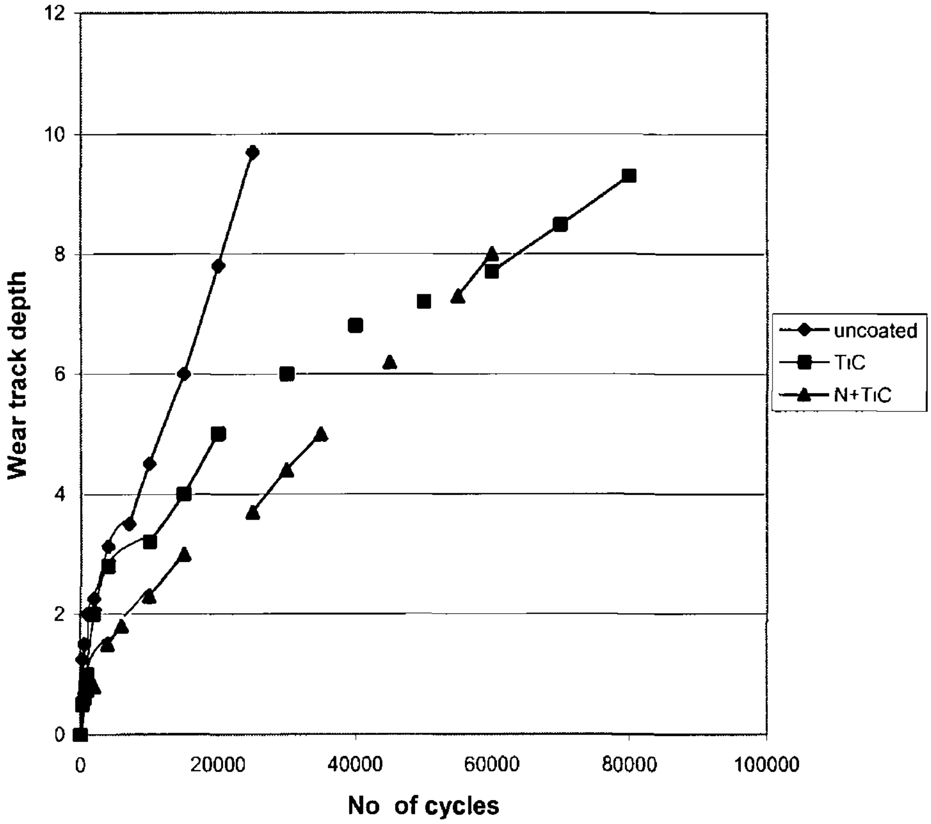


Fig 6 29 Wear track depth vs No of cycles of pre-nitrided TiC coated Vanadis 4 (compared with the uncoated and coated TiC)

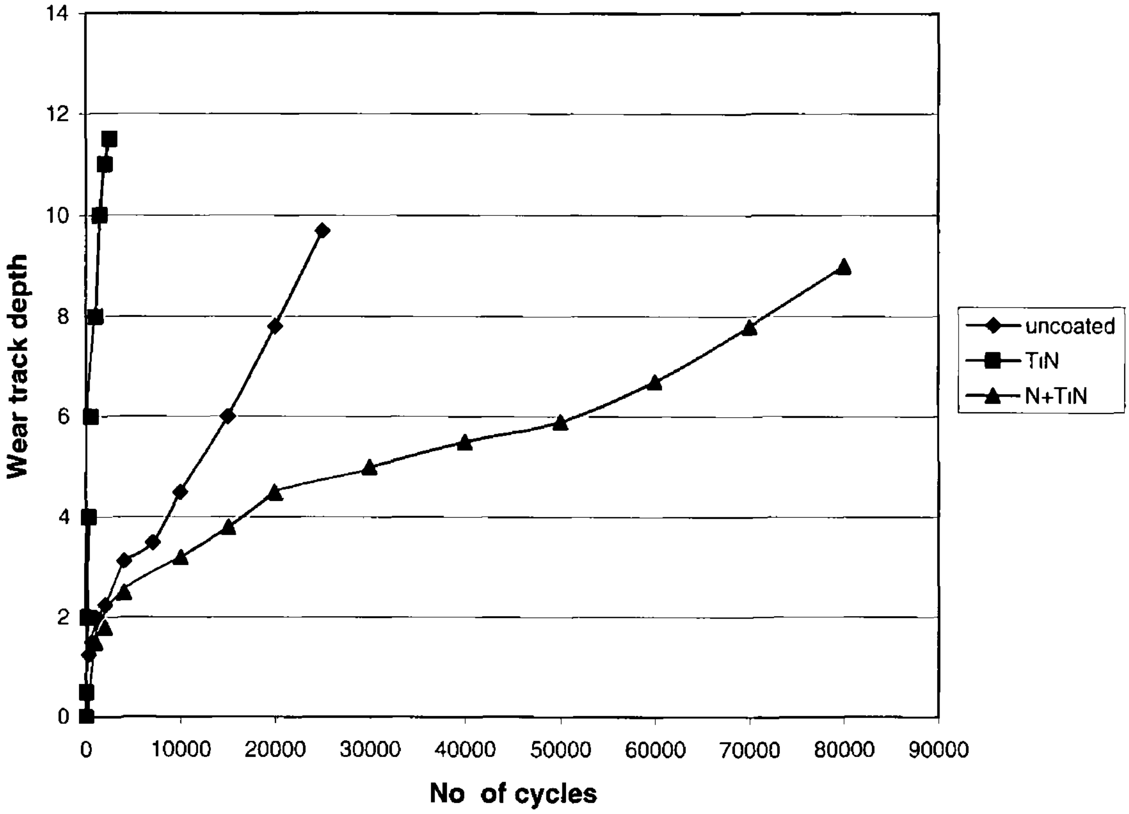


Fig 6 30 Wear track depth vs No of cycles of pre-nitrided TiN coated Vanadis 4 (compared with the uncoated and coated TiN)

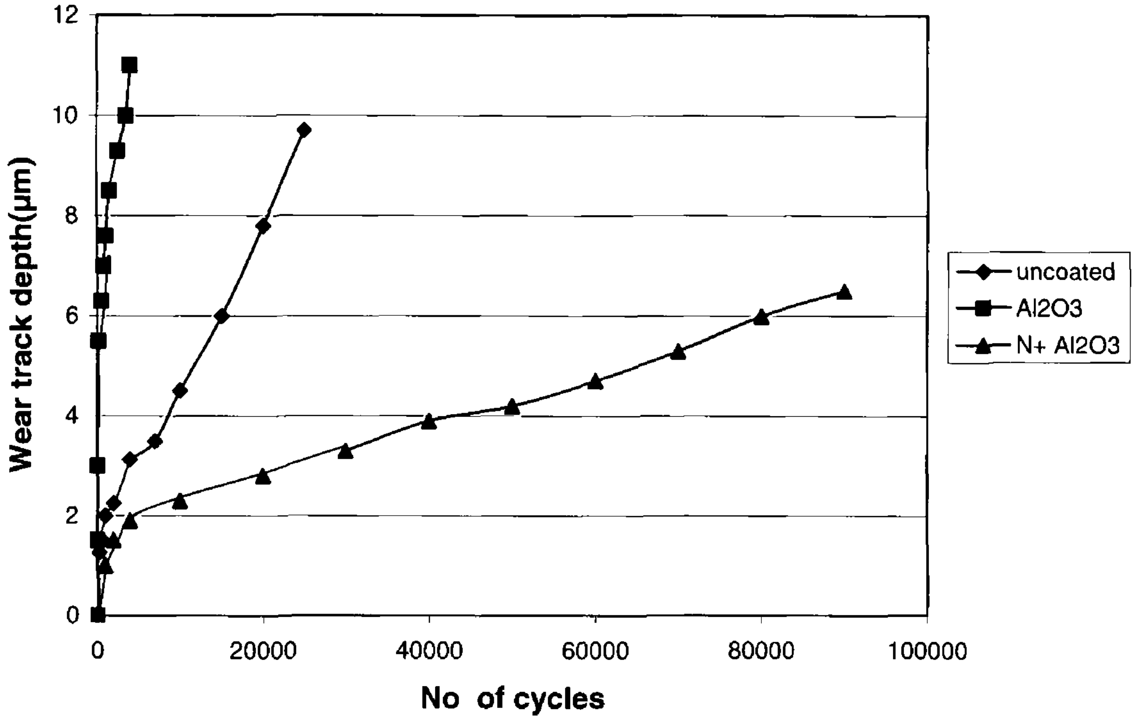


Fig 6 31 Wear track depth vs No of cycles of pre-nitrided Al2O3 coated Vanadis 4 (compared with the uncoated and coated Al_2O_3)

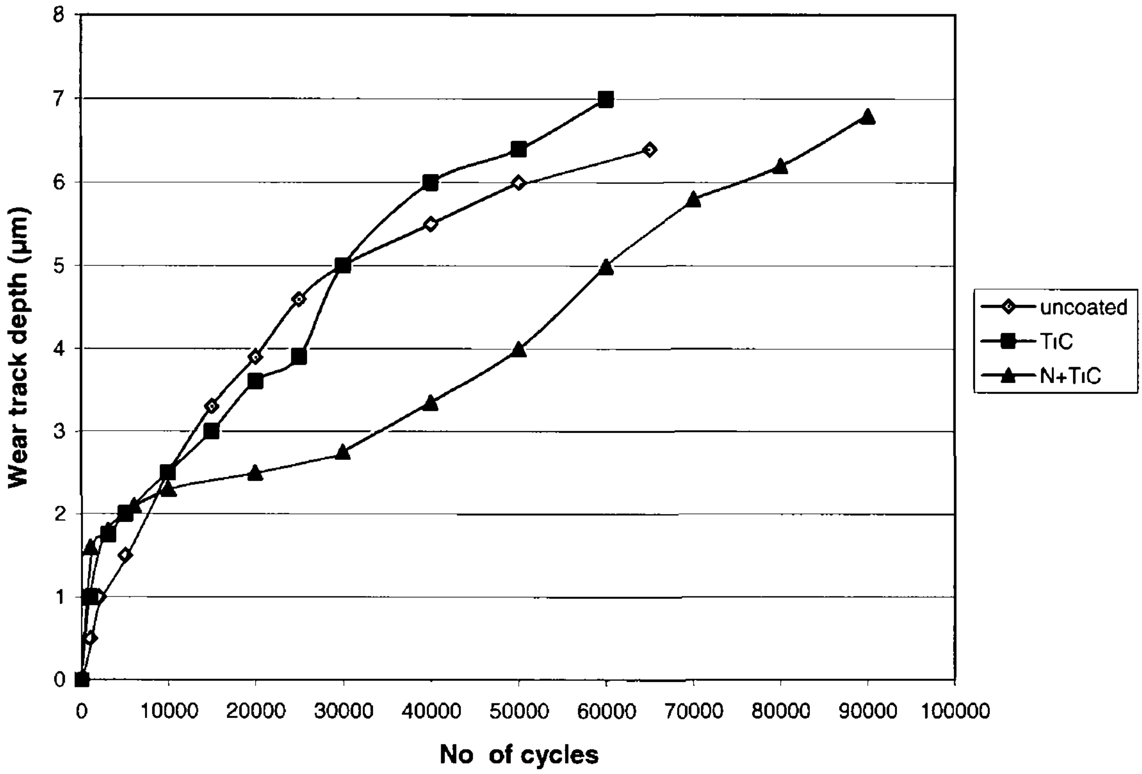


Fig 6 32 Wear track depth vs No of cycles of pre-nitrided TiC coated Vanadis 10(compared with the uncoated and coated TiC)

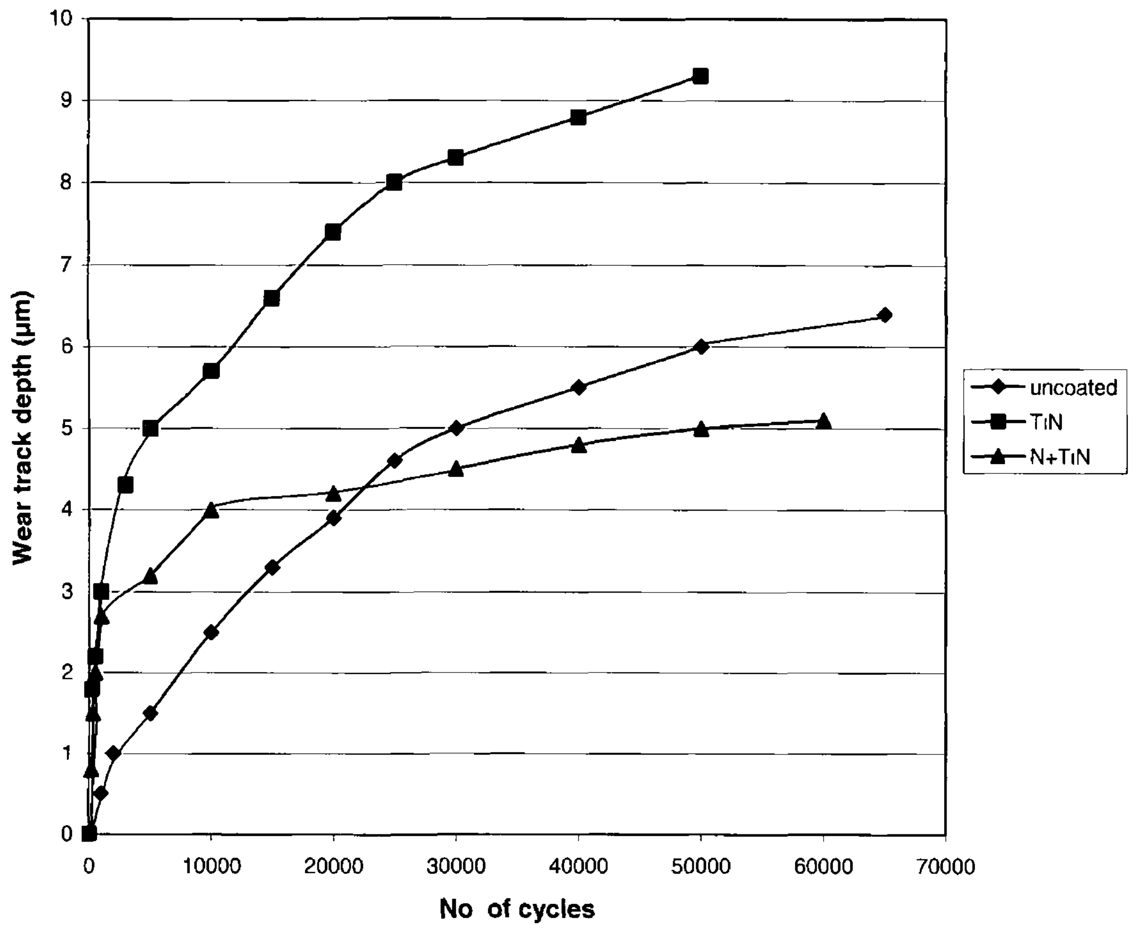


Fig 6.33 Wear track depth vs No. of cycles of pre-nitrided TiN coated Vanadis 10 (compared with the uncoated and coated TiN)

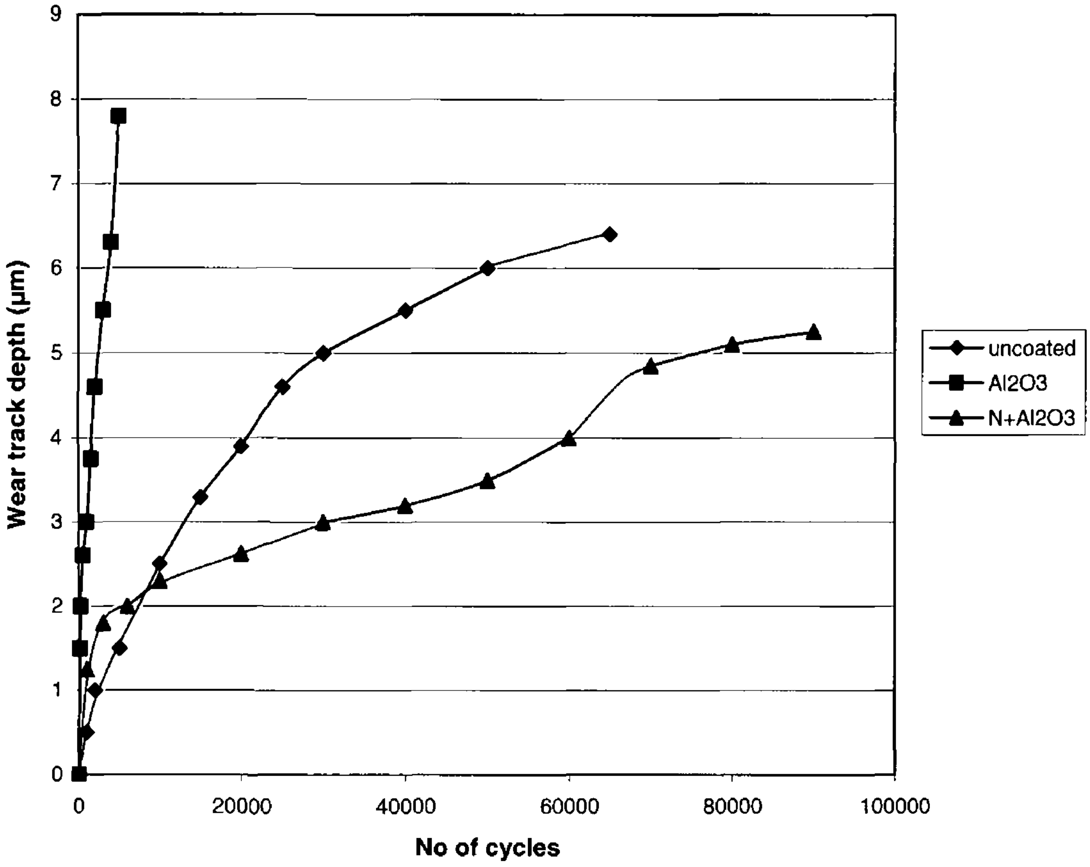


Fig 6.34 Wear track depth vs No of cycles of pre-nitrided Al_2O_3 coated Vanadis 10 (compared with the uncoated and coated Al_2O_3)

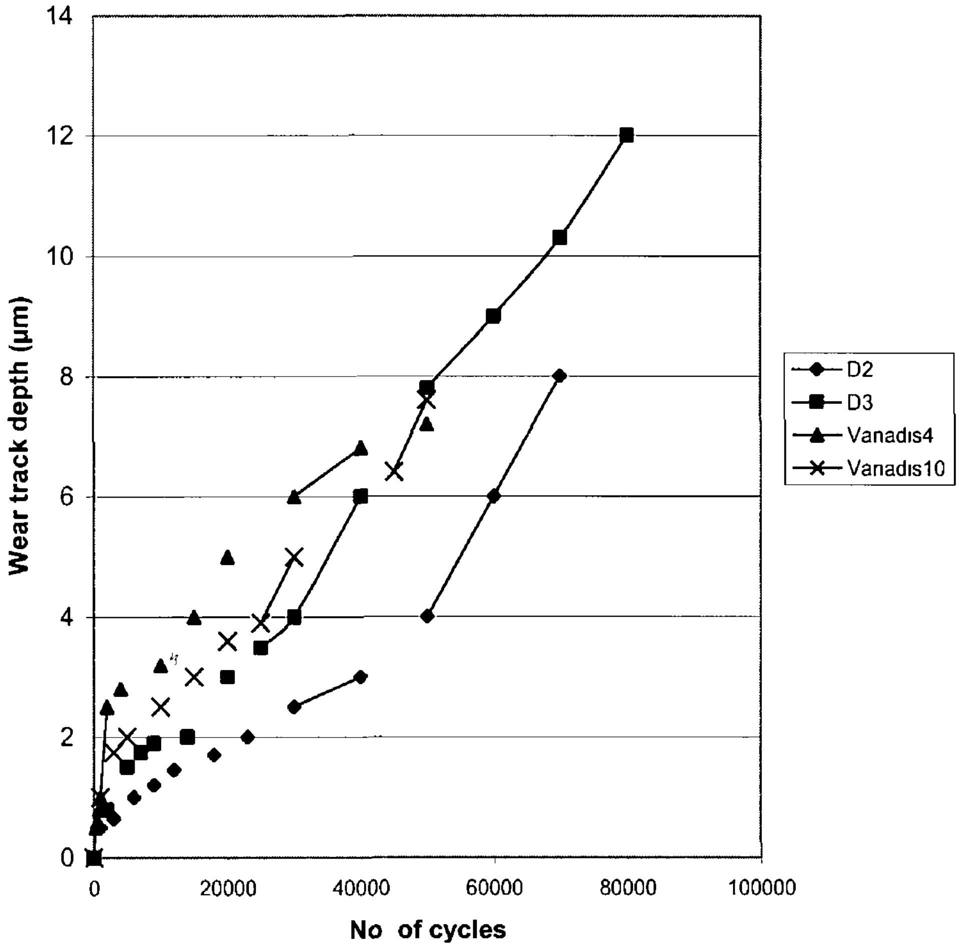


Fig 6 35 Wear track depth vs No cycles of TiC coating on different substrates

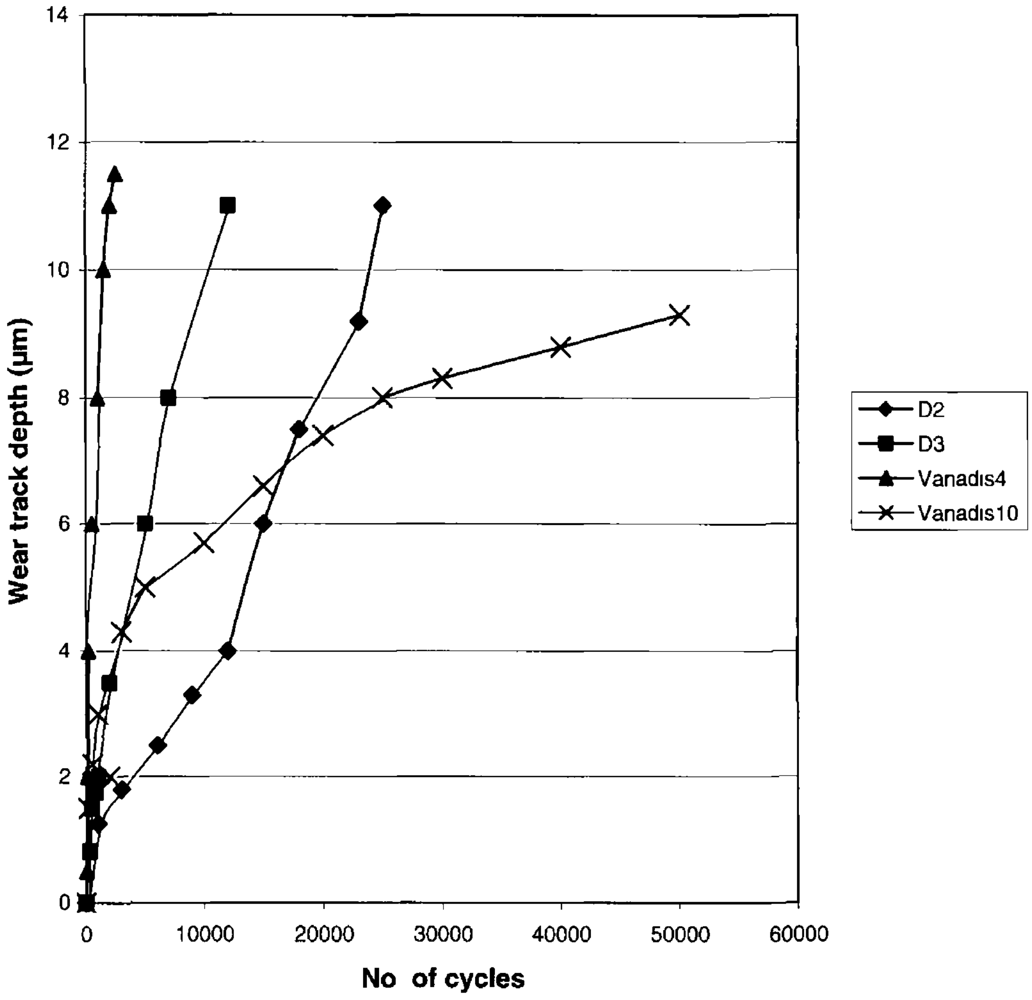


Fig. 6.36 Wear track depth vs No cycles of TiN coating on different substrates

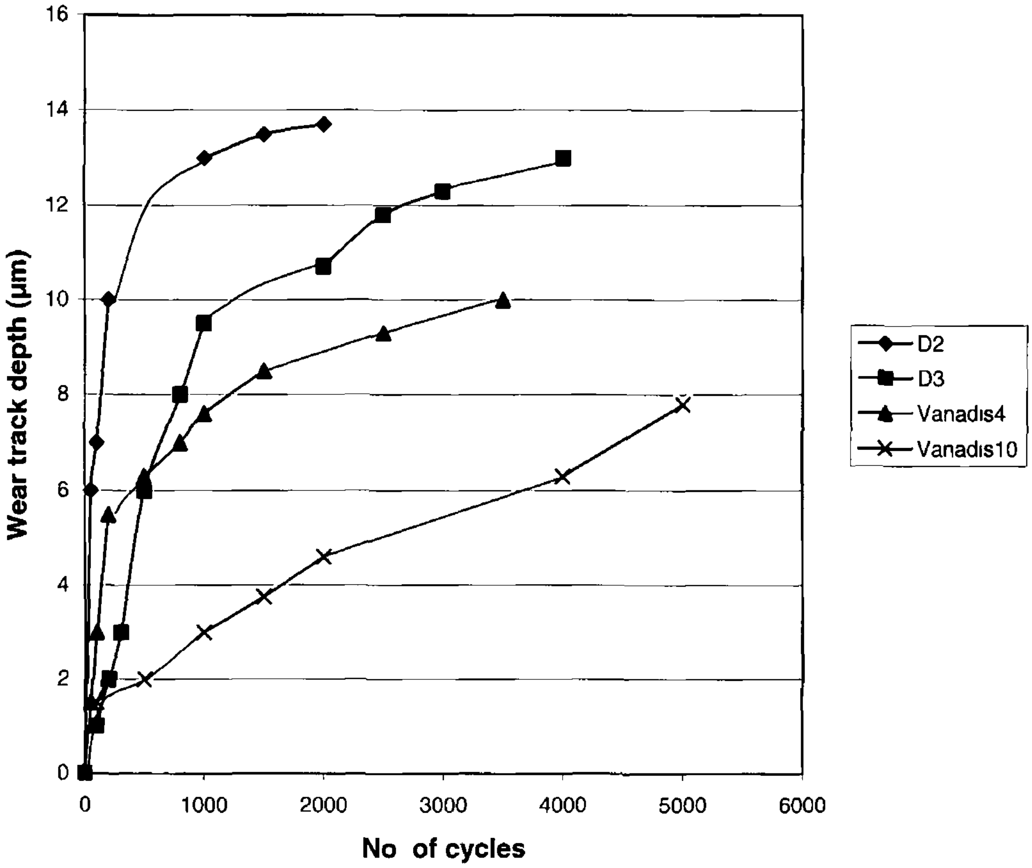


Fig 6 37 Wear track depth vs No. of cycles of Al_2O_3 coating on different substrates

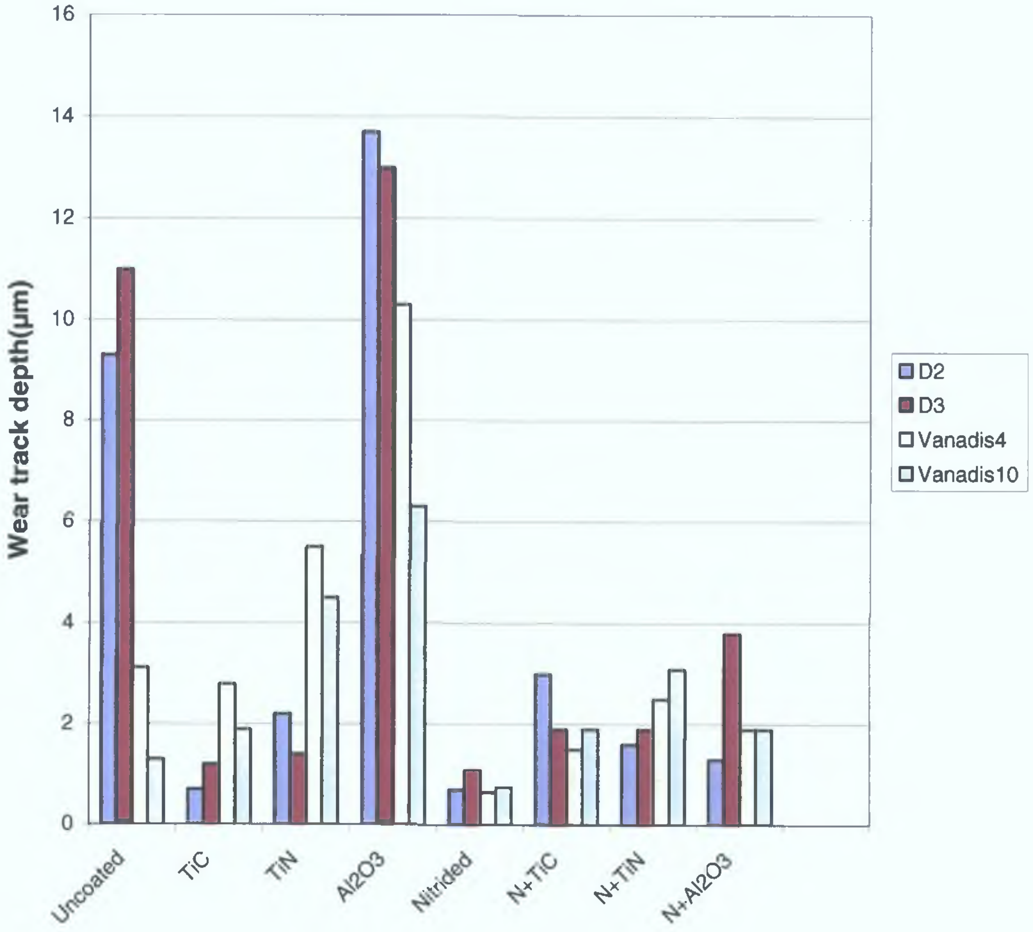


Fig. 6.38 Wear track depth of treated and untreated samples subjected to the same number of cycles (4000 cycles)

6 6 ADHESION EVALUATION

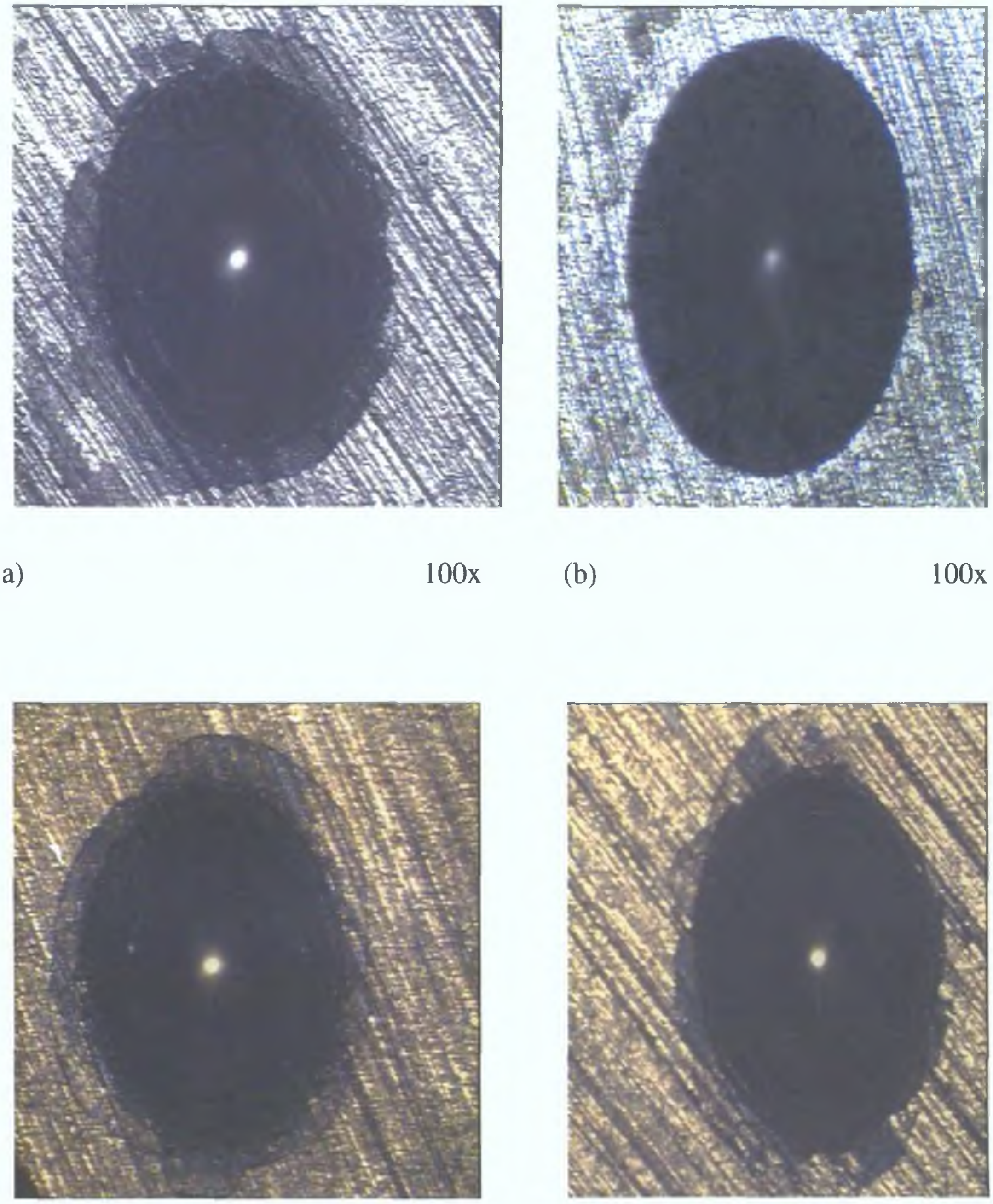
24 samples were evaluated for adhesion Adhesion tests were done by the Rockwell C indentation technique by comparing the indentation pattern, which scaled from HF1 to HF6 Fig 6 39 shows the indentation photographs with the magnification of 100x in all cases It is seen in Fig 6 39 and Table 6 2 that the Al_2O_3 coated samples show the poorest adhesion on the Rockwell evaluation scale HF6 The TiN coated samples showed slightly better adhesion The TiC coated samples showed good adhesion quality It is also shown that nitriding before coating improved the adhesion of the coatings to the substrate except in the case of TiC coatings Adhesion results are in consistent with wear and hardness results The summary of the Rockwell evaluation tests is given in Table 6 2

6.7 Microhardness

The Vickers microhardness values of the combined coating/substrate composite and treated substrates are shown in Fig 6 40 The lower hardness values of uncoated substrates and Al_2O_3 coated substrates corresponds with the lower wear resistance for these samples It was observed that the hardness value of the single TiN and Al_2O_3 are lower than TiC coated samples This is consistent with the higher wear rate of TiN and Al_2O_3 As a result TiC coatings improved the wear resistance of all the samples, but Al_2O_3 did not, while TiN slightly improved the wear resistance of D2 and D3 tool steels In Fig 6 48 the effect of the prenitriding on the hardness values is shown Except in the case of TiC coatings, nitriding of the samples before coating improved the hardness of the system The improvement in the hardness of the TiN and Al_2O_3 is due to the presence of the nitriding layer This can be considered as a sign of the wear resistance improvement

sample	Roughness R_a µm	Rockwell Evaluation	
		Single	Duplex
D2/TiN	0 4	HF4	HF2
D2/TiC	0 5	HF2	HF4
D2/Al_2O_3	0 8	HF6	HF2
D3/TiN	0 4	HF5	HF3
D3/TiC	0 5	HF2	HF4
D3/Al_2O_3	0 3	HF6	HF4
Vanadis4/TiN	0 5	HF5	HF3
Vanadis4/TiC	0 5	HF2	HF3
Vanadis4/Al_2O_3	0 4	HF6	HF2
Vanadis10/TiN	0 5	HF4	HF3
Vanadis10/TiC	0 3	HF2	HF4
Vanadis10/Al_2O_3	0 4	HF6	HF3

Table 6.2 Rockwell adhesion evaluation



(a) 100x (b) 100x

(c) 100x (d) 100x

Fig.6.39 Rockwell Evaluation photographs (a) Vanadis 4/TiN (b) D2/TiC (c) D3/Al_2O_3 (d) Vanadis 10 TiC pre-nitrided. (magnification 100x)

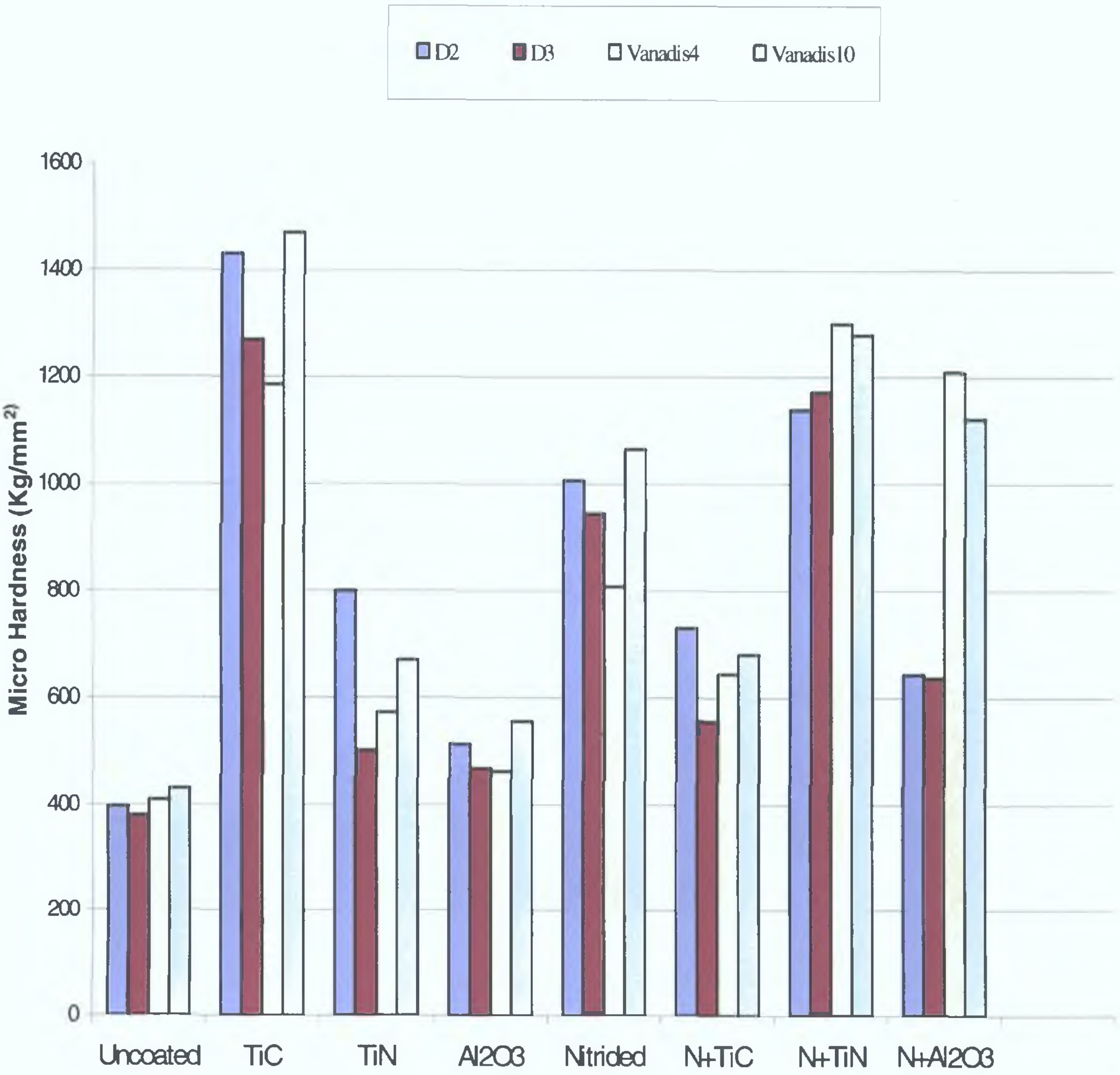


Fig. 6. 40 Microhardness of the samples

CHAPTER 7

CONCLUSIONS AND RECOMMENDATIONS

7.1 INTRODUCTION

In this thesis four widely used industrial tool steels AISI D2, AISI D3 cold worked tool steels and Vanadis 4 and Vanadis 10 powder metallurgical tool steels have been selected as substrate materials. These materials were prepared for coating and nitriding in an attempt to improve their mechanical and tribological properties. These substrate materials were nitrided using gas nitriding technique, and a case depth of .15mm was achieved. Three types of coatings (TiN, TiC,and Al_2O_3) were commercially deposited on these substrate materials (Teer Coating, UK). In order to evaluate the coatings and the nitriding layer the following characterizations were carried out:

Microhardness tests
Adhesion evaluation
Thickness measurements
Chemical composition analysis
Wear tests

The above characterizations were conducted on uncoated, coated, nitrided, and nitrided and coated samples. The results of the experimental work have been concluded and comparison has been made between the different samples.

7.2 CONCLUSIONS

These are the main conclusions to be drawn from this work

1- The quality of the coating has a great influence on the mechanical and tribological properties of the system, especially the coating adherence to the substrate material.
2- Better hardness and wear resistance have been shown for substrates coated with TiC, on the other hand the worst has been shown with Al_2O_3 coating.

3- The nitriding of the substrates improved their hardness and wear resistance in all the cases
4- The hardness of substrates has been improved with all the coatings However TiC coating on Vanadis 10 demonstrated the highest hardness value
5- Pre-treatment of the substrate by nitriding prior to the deposition proved to improve the quality and properties of TiN and Al_2O_3 coatings However the pre-treatment negatively affected TiC coatings
6- The performance of the same coating may be affected by different substrate properties

7 3 RECOMMENDATIONS FOR FURTHER WORK

Further experiments in lubricated conditions could be undertaken to assess the difference in wear rate of coated and uncoated samples Modelling the experimental work using wear measurement equations would be interesting Using plasma nitriding as the surface treatment might give better results than using gas nitriding For the chemical analysis it is recommended to use other techniques rather than EDX, with high sensitivity to elements with atomic number < 11 The identification of the phase formed during the deposition of Al_2O_3 is a very important, thus the use of Scanning Tunnelling Microscope(TSM) in conjunction with XPS or XRD is recommended For greater confidence instead of 1 sample, 3-5 samples should be tested Furthermore it would be useful to obtain coatings from different suppliers

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