Fabrication, characterisation and property modelling of TiB₂ based nanostructured coatings

Nurot Panich

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**Fabrication, Characterisation and Property
Modelling of TiB₂ Based Nanostructured Coatings**

Nurot Panich

School of Materials Science and Engineering

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ABSTRACT

Fabrication and development of TiB_2 -based nanostructured coatings and the development of finite element (FE) models to simulate the nanoindentation and micro-scratch test processes in various coating systems were investigated in the present work. By varying the sputter-target power density, substrate temperature, deposition time, substrate-to-target distance, substrate rotation, substrate biasing and substrate sputter cleaning, the relationship between the sputtered structure properties and sputtering conditions were established. In order to increase the coating/substrate adhesion, interlayer and multilayer techniques between TiB_2 and tough material, e.g. Ti and Cr were proposed and employed. Furthermore, techniques to strengthen the sputtered interlayer such as Ti by annealing the resultant coatings at various temperatures and introducing nitrogen gas during interlayer deposition were carried out.

The experimental results showed that the target-to-substrate distance played a major role in the coating structure and properties. Sputter cleaning of substrate helped to improve TiB_2 coating hardness and adhesion. The deposition process could be controlled to produce a TiB_2 coating with both high hardness and good adhesion strength. This was achieved by introducing substrate sputter-cleaning and then biasing for the early stage of deposition, followed by deposition without biasing. Annealing at optimum temperature helped to promote the (001) orientation of the TiB_2 coating and improved its hardness, coating adhesion and elastic recovery ability. Substrate rotation was focused to have a significant effect on the structure, orientation, hardness and adhesion strength of sputtered TiB_2 coatings. Significant enhancement of the adhesion for the TiB_2 coating-HSS substrate was found by optimum doping nitrogen into the Ti interlayer, the use of multilayer and the use of Cr interlayer. During dry sliding wear against an alumina ball, failure of the coating was correlated with the hardness and adhesion of the coating-substrate system. With increasing coating hardness and coating-substrate adhesion the wear resistance was increased.

The developed nanoindentation FE models were able to simulate the indentation loading-unloading curves of the coating/substrate system as well as multilayer systems. The model could also be used to extract the intrinsic values of mechanical properties, e.g. hardness and yield strength. In addition, the models were used to analyse the plastic deformation behaviour of coating-substrate systems during indentation process and investigate the effect of penetration depth on nanoindentation. The developed micro-scratch FE model was able to demonstrate the elastic and plastic behavior of the coating and substrate around the contact area during scratch test. The adhesion force between the stylus and the coating surface, which was difficult to measure by experiment, could be estimated.

Keywords: TiB₂-based nanostructured coating, Nanoindentation, Micro-scratch, XRD, SEM, FESEM, Planar-magnetron, ball-on-disc test, HSS, Finite element analysis, Hardness, Modulus, Plastic deformation, Tribology.

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List of Symbols

a	Radius of the contact circle of indenter
A	Projected area
A_1	Cross sectional area of scratch track
$^{\circ}\text{C}$	Degree centigrade
C	Compliance
C_f	Load frame compliance
C_s	Compliance of specimen
d	Scratch channel
DC	Direct current
ϵ	Geometric constant of indenter tip
E	Elastic modulus (Young's modulus)
E_i	Modulus of indenter
E_r	Reduced modulus
E_s	Modulus of specimen
F	Friction force
FT	Total friction
FE	Finite element
G	Shear modulus
h	Displacement
H	Hardness
h_c	Specimen displacement or contact depth
h_f	Final displacement
h_{cr}	Critical indentation depth
h_s	Displacement of the surface at the perimeter of the contact
HSS	High speed steel
L	Normal applied load
L_c	Critical length
mTorr	Milli Torr
P	Load

ν	Poisson's ratio
R_a	Average roughness
RF	Radio frequency
RT	Room temperature
s	Second
S	Stiffness
σ	Compressive stress
T	Temperature
τ	Shear stress
ξ	The difference in depth between the ideally sharp tip and the round tip
W	Watt
W_{AD}	Work of adhesion
Y	Yield strength
Y_c	Yield strength of the coating
Y_s	Yield strength of the substrate

Chapter 1

Introduction

1.1 Background and Motivation

In recent years, nanostructured materials have been attracting growing scientific and industrial interests due to their novel properties. In terms of mechanical properties, nanostructured materials show extraordinarily high hardness, tribological performance and yield strength. These unusual properties may provide great potentials for the application of this new class of materials in many fields, including mechanical, automobile, aerospace and microelectronic engineering [1-3]. Nanostructured materials can be defined as materials with microstructures on length scales from several nanometers to 100 nm in at least one dimension. Using this working definition, nanostructured materials can be in the form of cluster, thin film, coating and bulk materials. In terms of chemical composition, nanostructured materials can include nanostructured pure metal, alloys and nanocomposites.

Increasing applications have been found for thin, hard, wear resistant (ceramic) coatings in metal cutting and metal forming tools. The invention of low temperature (below 500 °C) physical vapour deposition (PVD) processes such as magnetron sputtering has made possible the deposition of various hard and wear resistant coatings onto commonly used tool steels. When applied properly, protective coatings on cutting tools and other tribological components can extend component lifetimes. It is usually desirable to have coating with high hardness and low internal stress. Protective coatings with high hardness provide better wear resistance of coated tool steel against abrasion at high contact pressures [4].

Among the many materials of interest, titanium diboride (TiB_2) has notably been chosen. TiB_2 possesses many interesting physical, mechanical and chemical properties, such as high hardness, high melting point, good chemical stability and good thermal and electrical conductivity. There have been increasing interests in fabrication of this material in thin film and coating forms for many potential applications, for example to reduce wear and corrosion in engineering components and particularly in material processing tools and dies [5-6].

Although TiB_2 coatings have been widely studied by many researchers, their real applications have been very limited. The existing problem of TiB_2 coating is that its adhesion is poor for the coating-substrate system.

Since many technologies have moved to ever smaller scale, characterization of the intrinsic mechanical properties of materials and thin films has become more difficult and complicated. Among the techniques to measure the mechanical properties of nanostructured thin films, nanoindentation techniques have been widely used to measure thin film mechanical properties, for instance hardness, elastic modulus, scratch resistance, creep, etc. Other reasons for the popularity of the nanoindentation method are that the mechanical properties can be measured without removing the film from its substrate as is done in other types of testing and that it provides the ability to probe a surface at numerous points, in both lateral and depth dimensions. In order to obtain the intrinsic properties of thin film materials, it is essential that the effect of the underlying substrate is eliminated during the test and/or through proper modelling and simulation.

In the present investigation, attempts have been made to fabricate TiB_2 -based nanostructured engineering coatings on high speed tool steel substrate. The characterisation of their structures and properties has been carried out. In this dissertation, modelling simulation has also been carried out to simulate the mechanical testing of the TiB_2 -based nanostructured coatings under nanoindentation and micro-scratch conditions.

1.2 Objective of This Dissertation

The need to develop nanocomposite thin film materials is stimulated by the ever increasing operation severity in machinery, where superhard surfaces, good coating/substrate adhesion and good tribological properties are required. Since nanostructured coatings can possess excellent mechanical and tribological properties, the main objective of this investigation is to design, fabricate and test a new nanocomposite system capable of achieving a variety of high performance. The specific objectives of this work are:

1. To develop a sputtering technique for the fabrication of the TiB_2 -based nanocomposite coatings.
2. To control the process conditions for the optimization of the coating/substrate combination.
3. To characterise the structures and properties of the resultant coatings and correlate the structural features with coating performance.
4. To develop and implement the nanotest technique to evaluate the mechanical properties of the coating/substrate system.
5. To investigate the wear behaviour of the resultant and treated coatings.
6. To model and simulate the mechanical performance of the nanostructured coating under indentation and scratch conditions.

1.3 Contribution

A series of experiments have been carried out in order to achieve the above listed objectives. The main contribution of this dissertation is summarised as follows:

1. Fabrication of magnetron sputtered single-layer TiB_2 coating with a Ti interlayer, single-layer TiB_2 coating with Ti (N) interlayer, single-layer TiB_2 coating with Cr interlayer and TiB_2 -Ti multi-layer coating systems.
2. Structural characterisation of the resultant nanostructured coating systems.
3. Nanoindentation and micro-scratch tests of the coating/substrate systems.

4. Development of a finite element (FE) model for the simulation of the nanoindentation process of hard coating-on-soft substrate system.
5. Development of a multi-layer finite element (FE) model for the simulation of the nanoindentation process of multi-layer systems.
6. Development of three dimensional micro-scratch model by finite element (FE) techniques

1.4 Dissertation Organisation

In this dissertation, a review on TiB_2 coating, nanoindentation and scratch test is given in Chapter 2. Chapter 3 and Chapter 4 outline the experimental procedures and modelling simulation, respectively. In Chapter 5, experimental results and finite element analysis results are presented and the results obtained in Chapter 5 are discussed in Chapter 6. This is followed by a summary of work done in Chapter 7 and suggestions for future work are given in Chapter 8.

Chapter 2

Literature Review

This dissertation is mainly concerned with the fabrication of TiB_2 -based coating and mechanical properties characterisation of the resultant coating systems. Hence, in this chapter, the four main topics are discussed i.e. relevant properties of bulk TiB_2 , preparation of titanium diboride coatings, structural characterization of titanium diboride coatings, and mechanical properties of titanium diboride coatings

2.1 Relevant Properties of Bulk TiB_2

Titanium diboride (TiB_2) is well known as a ceramic compound with a hexagonal crystal structure and with relatively high strength and durability as characterised by its relatively high melting point, hardness, strength to density ratio, abrasion resistance, oxidation resistance and wear resistance [5, 6]. Recently, one of the major uses of TiB_2 is as a wear resistant material in such areas as impact resistant armor, cutting tools, bearings, sand-blasting nozzles, crucibles, and wear resistant coatings [3, 5]. For such applications, the friction and wear characteristics represent limiting benchmarks on the performance and durability of the material.

2.1.1 Crystallography and Structure of TiB_2

TiB_2 is a boron-rich transition metal based ceramic existing at the narrow range of stoichiometry as shown in the Ti-B phase diagram (Figure 2.1) [6]. The chemical bonding in TiB_2 is a mixture of covalent, metallic and ionic components [2]. The Ti-Ti bonding is mainly metallic, which is the principle reason for the metallic characteristics, whereas minor contributions of covalent nature also exist. In addition, metallic nature of bonding is revealed by the electrical conductivity of TiB_2 , which is high and almost similar to metals [7]. The B-B bonding is purely covalent, with strong interaction between boron atoms owing to the formation of the graphite-like boron ring. The bonding between Ti and B is mostly covalent, coupled with a substantial ionic contribution [8].

Figure 2.1: Titanium-boron binary phase diagram [6]. Note TiB₂ has a narrow homogeneity range in the equilibrium state.

TiB₂ crystallizes with hexagonal symmetry, space group P6/mmm. It is a simple hexagonal lattice in which Ti layers alternate with graphite-like B layers. This structure, which is dominated by metallic and covalent bonds, consists of titanium atoms located at the corners of the cell, and boron atoms positioned at $\left(\frac{1}{3}, \frac{2}{3}, \frac{1}{2}\right)$ and $\left(\frac{2}{3}, \frac{1}{3}, \frac{1}{2}\right)$ as shown in Figure 2.2 [9].

Figure 2.2: The hexagonal unit cell of single crystal TiB₂ [5, 9].

The lattice parameters (a , c) have a slight quadratic dependence on temperature, which accounts for the linear temperature dependence of the coefficient of thermal expansion. The ratio c/a ranges from 1.066 ± 0.001 at $25\text{ }^{\circ}\text{C}$ to 1.070 ± 0.001 at $1500\text{ }^{\circ}\text{C}$. Individually, the lattice parameters may be expressed as:

$$a/\text{\AA} = 3.0236 + 1.73 \times 10^{-5} (T/\text{K}) + 3.76 \times 10^{-9} (T/\text{K})^2$$

$$c/\text{\AA} = 3.2204 + 2.73 \times 10^{-5} (T/\text{K}) + 3.95 \times 10^{-9} (T/\text{K})^2$$

where T is in the range from 293 K to 2000 K [8].

2.1.2 Physical Properties

From the Ti-B binary phase diagram in Figure 2.1, it can be seen that the melting point of TiB_2 is very high ($T_m = 3,225\text{ }^{\circ}\text{C}$). This extremely high melting point value, attributable to very strong covalent bonding, is beneficial as far as the chemical stability and lattice diffusion are concerned. It is well-known that a compound with a high melting point normally has high chemical stability [8]. Furthermore, a high melting point value also suggests the low lattice diffusivity, which was verified by Schmidt et al [10] recently. Schmidt et al. suggested that the diffusivity for Ti in TiB_2 is more than 3 orders of magnitude lower than that for B [10]. The extremely low lattice diffusivity suggests a high thermal stability. Concurrent with a high melting point, the heat of formation for TiB_2 is also high ($-H_f^0 = 328\text{ kJ/mol}$) [11], indicating high hardness and corrosion resistance [12], as well as high thermodynamic stability as a diffusion-barrier layer [13].

2.1.3 Mechanical Properties

The elastic moduli of TiB_2 rely crucially on its density, and reduce with porosity. For fully dense TiB_2 ($\rho = 4.52\text{ g/cm}^3$) at room temperature, the measured values for the Young's (E) and shear (G) moduli are 551 GPa and 255 GPa, respectively, with the poisson's ratio (ν) of 0.11. These moduli are in agreement with the theoretical values derived from single-crystal elastic constant by using the Hashin-Shtrikman bounds [14]. Furthermore, a theoretical Poisson's ratio of 0.104 can be deduced from these Hashin-Shtrikman bounds,

which is in agreement with the measured Poisson’s ratio value. In terms of hardness, bulk TiB₂ shows a relatively high value of 33 GPa in Vickers hardness [15], which can be expected from its high shear modulus [15].

2.1.4 Other Properties

Bulk TiB₂ exhibits very good chemical stability and excellent corrosion resistance. It is very inert and not easily dissolved in any solvents [16]. This outstanding and valuable property can be deduced from its extremely high melting point, since the melting point of a material is generally associated with its chemical stability [12]. Another outstanding property of TiB₂ is high conductivity, which can be used in semiconductor applications. The electrical resistivity of polycrystalline TiB₂ at room temperature is in the order of 10 μΩ.cm [17, 18], which is lower than that for pure Ti [13]. Indeed, it is this high conductivity, associated with high stability and low diffusivities, that make TiB₂ a candidate as a diffusion barrier [13]. The significant properties of TiB₂ at room temperature, such as physical and mechanical properties, are listed in Table 2.1 [5, 6].

Table 2.1: The significant properties of titanium diboride (TiB₂).

Property	TiB ₂
Crystal Structure	Hexagonal
Lattice Parameter	$a = 3.03 \text{ \AA}, c = 3.23 \text{ \AA}$
Melting Point	$3,225 \pm 20 \text{ }^{\circ}\text{C}$
Density	4.52 g/cm^3
Hardness	33 GPa
Modulus of Elasticity (E)	551 GPa
Shear Modulus (G)	255 GPa
Poisson’s Ratio (ν)	0.104
Thermal Conductivity	64.4 W/mK
Coefficient of Thermal Expansion	$\alpha_c = 8.65 \times 10^{-6} \text{ K}^{-1}$
Electrical Resistivity	10 μΩ.cm
Fracture Toughness	5 MPa.m ^{1/2}

2.2 Preparation of TiB₂ Coatings

Since TiB₂ has attracted growing interest from industry as a result of its many interesting properties as mentioned in section 2.1, a wide variety of coating techniques have been developed and investigated to produce TiB₂ and TiB₂-based coatings ranging from 1 to 5 μm thick. For instance, chemical vapour deposition (CVD), physical vapour deposition (PVD), plasma spraying, electron beam vapourisation, magnetron sputtering and laser assisted techniques, are available to deposit TiB₂ on different substrates. However, each of these coating processes is limited by several factors, such as the properties of the coating and the coating/substrate adhesion as well as cost of operation. Table 2.2 summarises some available TiB₂ deposition techniques and processing conditions, as well as resultant structures and properties reported in the literature.

Table 2.2: Some available TiB₂ deposition works from literature.

No.	Coatings	Deposition Technique	Deposition Conditions	Resultant Structures	Hardness	Elastic Modulus	Critical Load (L _C)	Ref.
1	TiB ₂	DC magnetron sputtering	Bias voltage : -100 V Substrate temp : 300 °C Ar pressure : 0.8 Pa	Very fine crystalline TiB ₂ phase	6900 HV (~70 GPa)	N.A.	N.A.	19
2	TiB ₂	DC magnetron sputtering	Magnetron power 6 kW Ar 3 × 10 ⁻³ mbar Substrate temp : 580 °C	Strong (001) hcp TiB ₂ phase	52 GPa	590 GPa	70 N 60 µm thick Rockwell C R = 200 µm	20
3	TiB ₂	Plasma-assisted CVD (PACVD)	Substrate temp : 530 °C Voltage : 480-550 V Pulse duration : 600 µs Pressure : 100-300 Pa	Nanocrystalline Strong (100) peak	33 GPa	352 GPa	35 N Rockwell C R = 200 µm	21
4	TiB ₂	DC magnetron sputtering	Bias voltage : -200 V Magnetron power : 6 kW	Strong (001) hcp TiB ₂ phase	48-53 GPa	420-605 GPa	20-42 N Rockwell C R = 200 µm	22
5	TiB ₂	Laser surface engineering (LSE)	Laser power: 1.5 kW Transverse speed : 200 cm/min	Strong (001)	N.A.	477.3 GPa	N.A.	23
6	TiB ₂	Ion-beam-enhanced deposition (IBED)	Ion energy : 25-85 keV Working pressure : 5×10 ⁻⁷ Torr Working gas : Xenon	Nanocrystalline hcp phase (100), (101), (110)	25-39 GPa	190-230 GPa	N.A.	24

No.	Coatings	Deposition Technique	Deposition Conditions	Resultant Structures	Hardness	Elastic Modulus	Critical load (Lc)	Ref.
7	TiB ₂	DC magnetron sputtering	With and without N ₂ flow rate (0-80 sccm)	hcp phase Amorphous	10-40 GPa	280-390 GPa	N.A.	25
8	Multilayer Ti/TiB ₂	Magnetron sputtering of TiB ₂ and electron beam gun evap. of Ti	Magnetron power : 6 kW Substrate bias 0 V Ar pressure 2.25 mtorr	Strong Ti (002) phase with strong (001) hcp TiB ₂ phase	2.6-50 GPa	160-550 GPa	8-40 N Rockwell C R = 200 µm	26
9	Multilayer TiN/TiB ₂	Plasma-enhanced CVD (PECVD)	Voltage : 550 V Pressure : 150-170 Pa Substrate temp : 530 °C	Small TiB ₂ grain size and broad diffraction peak	17.5-45 GPa	N.A.	25 N Rockwell C R = 200 µm	27
10	Ti-B-N	DC magnetron sputtering co-sputtering	Sputtering power densities : 2 W cm ⁻² Ar pressure : 3 Pa Substrate temp : 400 °C	Nanocrystalline fcc and hcp Ti-B-N phases	50 GPa	N.A.	N.A.	28
11	Ti-B-N	DC magnetron sputtering	Substrate temp 200 °C Substrate bias -200 V Chamber pressure : 4×10 ⁻⁴ Pa	Well - Crystallized TiB ₂ (001)	44 GPa	N.A.	6-15 N Rockwell C R = 200 µm	29

In the present study, magnetron sputtering has been chosen due to its performance to make promising films at low cost. Indeed, for the deposition by the plasma method, magnetron sputtering has been widely used for physically fabricating these films and coatings, with both direct current (DC) and radio frequency (RF) for generating the target power. In particular, DC magnetron sputtering is the most widely used because it provides higher deposition rates (e.g., ~ 1 μm per minute for Al metallization alloys) or alternatively, lower voltage operation than for simple DC sputtering [30].

2.2.1 Sputtering Process

Sputtering deposition processes are the deposition of metal vapour species by sputtering (momentum exchange) produced through bombardment of the target by positive ions. In this instance the transformation of the original material into a gaseous state does not involve an intermediate liquid phase as used in the conventional vacuum evaporation and ion plating [31]. The sputter process is illustrated schematically in Figure 2.3. Positive gas ions, which are usually argon ions produced in a glow discharge of either DC or RF, bombard the target material (cathode), dislodging groups of atoms which pass into the vapour phase and deposit onto the substrate. Since the solid-vapour phase transformation is direct in sputtering, the process is independent of the melting point of the material to be sputtered. Therefore, this technique is especially useful for the deposition of alloys, because the danger of decomposition of multi-component alloys is much less than that observed when other heating sources are employed [31].

Sputtering processes normally employ an argon atmosphere whose pressure is controlled between 5×10^{-4} and 10^{-1} mbar [32] in order to maintain the glow discharge. Compounds may be deposited in the presence of reactive gases such as N_2 , C_2H_2 and O_2 . The gas atoms react with the sputtered metal vapour to form compounds on both the substrate and the target. Hence, care must be taken to control poisoning of the target by the reactive gases [33]. Another way to form compound coatings is by direct sputtering a compound target. In this way, target poisoning is avoided, but the stoichiometry of the resultant coating may be slightly different from that of the target.

Figure 2.3 Basic sputtering process.

Historically, sputtering was used only for the deposition of very thin films on semiconductor devices due to its low deposition rate (10 nm/min.) [32]. However, high deposition rate can be achieved by enhancing the plasma density within the system to produce higher rates of target bombardment. This is achieved in the “magnetron sputtering” system, in which a crossed electric-magnetic field is generated in the chamber which can increase the ionization efficiency in the plasma [32]. This technique has been used to deposit successfully many refractory metal compounds, e.g. TiN [34-37], TiC [31], CrN and (TiAl)N [38] onto various substrates at temperatures ranging from 60°C to 500°C, with high deposition rates (0.15µm/min.).

Indeed, the development of sputtering sources with magnetic plasma confinement has greatly enhanced the capabilities of the sputtering process. Magnetron sputtering sources can be defined as diode devices in which magnetic fields are used in concert with the cathode surface to form electron traps which are so configured that the $\vec{E} \times \vec{B}$ electron drift currents can close on themselves. Ions are trapped electro-statically by the confined electrons. In the case of cylindrical magnetrons, an axial magnetic field, generated by magnetic field coils that are external to the vacuum system, is used to confine an intense plasma sheet over the outer surface of a cylindrical-post target or on the inner surface of a cylindrical hollow target. In the case of the very important planar magnetrons, a circular ring-shaped plasma is confined

over a planar target by the magnetic field which is generated by a system of permanent magnets or filed coils which are located in a water-cooled cavity behind the target. In addition, the target must keep cool enough to avoid inter-diffusion of the constituents and decomposition of the target.

In the magnetron sources, the electrons that maintain the discharge ionization are effectively confined in the vicinity of the target (cathode) surface until they diffuse away by engaging in energy exchange processes of the type that produce ionization. Consequently, ion production in magnetrons is very efficient, and high discharge currents, and hence high sputtering rates, can be achieved at relatively low discharge voltages. Magnetrons can be operated at such low pressures (0.1 to 0.5 Pa) that the sputtered atoms pass line of sight to the substrates. They can be scaled to large sizes that provide uniform deposition over very large areas.

2.2.2 Problems Encountered in Fabrication of TiB₂ Coatings

Although TiB₂ coatings have been widely studied by many researchers, their real applications have been very limited. This situation arises from the two main problems for TiB₂ coatings, as listed below.

1. Firstly, pure TiB₂ coatings exhibit a very high hardness, but they are too brittle for use as a wear-resistant or protective coating in both bulk and thin film forms. Furthermore, they are characterized by anisotropic properties caused by the strong [001] fibre texture of the growing columnar grains, with the grain boundaries perpendicular to the surface representing short crack paths that can also impair the toughness [39]. In addition, TiB₂ coatings normally develop very high compressive residual stresses after deposition [26], which can further impair its mechanical properties.
2. Another serious problem is that the adhesion of the TiB₂ coatings is poor for the coating-substrate system. The main reasons for this are that the TiB₂ coating deposited is very brittle and that it accommodates very high compressive residual stresses. This limits both the practical adhesion and the thickness of the TiB₂ coatings

[22]. Actually, the adhesion of the coating is the most critical aspect of the coating-substrate system and adhesion theories generally do not always provide guidelines on how to achieve good film or coating adhesion in practice. Conventional wisdom, for example, suggests using very clean substrates. However, this may not necessarily work for metal films on glass substrates because optimum adhesion appears to occur only when the metal contacts the substrate through an oxide bond [30].

2.2.3 Some Solutions

In order to overcome the above problems, three methods have been attempted, as discussed below.

(i) *The composite Ti-TiB₂*

By layering TiB₂ with another much tougher material e.g. titanium (Ti), it is convinced that a tougher composite coating can be obtained. Ti was chosen foremost as an interlayer for its similarity in crystal structure (hcp) and chemistry. Regarding Ti-TiB₂ multilayer coating, it is found that it can be used to increase fracture toughness, decrease residual stress and maintain relatively high hardness values [26, 40]. Furthermore, in the case of the residual stress in the coatings it has been indicated that the stress can be reduced if the stressed ceramic material is layered alternately with metallic material [41], e.g. TiB₂ layered with metallic Ti. However, some metallic materials, such as Al were used as an interlayer to improve adhesion for TiB₂ coatings [42].

(ii) *The multi-component coatings by introducing N₂ gas*

The multi-component coatings by introducing N₂ gas within the ternary system Ti-B-N are proposed [28, 29]. Ti-B-N coatings have attracted attention in recent years owing to their combination of high hardness and stiffness. The phase composition of a Ti-B-N system in thermodynamic equilibrium can be derived from the phase diagram of Novotny [43] as shown in Figure 2.4.

From Figure 2.4, it can be seen that the phase diagram is separated into five different regions labeled 1 to 5, corresponding to different combinations of co-existing phases. It is

interesting that there are no ternary phases existing in Ti-B-N system and there is only small boron solubility in TiN and a negligibly small solubility of nitrogen in the TiB_2 phases. Deng et al [25] found that the mechanical and tribological properties of TiB_2 coating can be significantly improved by introducing a small amount of N_2 gas because small N content causes (001) textured well-crystallised microstructure.

Figure 2.4: Simplified phase diagram of Ti-B-N [43].

(iii) Interface modification and doping of coatings

Compared to Ti- TiB_2 and Ti-B-N coatings, few investigations have been carried out interface modification and doping of coatings. For the doping of coatings, Mitterer et al [44] sputtered Ti-B-N system with additions of Al. All resultant TiAlBN coatings showed very dense structures and were mainly found to be only partially crystalline. For the interface modification, this may be an effective way to improve the adhesion since the interface is treated. However, the questions still remain as to what is the appropriate interface modification method or the doping system and what are the parameters for the introduction of gases for doping of coatings e.g. gas flow rate, working pressure, etc.

2.3 Structural Characterization of TiB_2 Coatings

2.3.1 The Structure Zone Model of PVD Ceramic Coatings

PVD processes usually involve three steps, namely the generation of metal or compound vapour, transportation of the vapour, and condensation of the coating atoms onto

the substrate surface [45]. The condensation of the coating atoms can be pictured as occurring in the following three steps [46];

- (1) incident atoms transfer kinetic energy to the lattice and become loosely bonded “adatoms”;
- (2) these adatoms diffuse over the surface, exchanging energy with the lattice and other adsorbed species until they become trapped at low energy lattice sites;
- (3) the incorporated atoms re-adjust their position within the lattice by bulk diffusion processes.

The most significant factors influencing the adatom surface mobility are the deposition temperature and the kinetic energy of the incident atoms. One can expect a dense and better microstructure at higher deposition temperature with incident atoms of greater kinetic energy.

Movchan and Demchishin [47] developed a structural zone model of deposited materials at different temperatures, which is based on the studies of thick coatings of Ti, Ni, W, ZrO and Al₂O₃ deposited by vacuum operation. The model describes the type of coating structure formed as a function of the ratio of deposition temperature (T) to the melting point of the deposited material (T_m), i.e. (T/T_m).

Zone I, (T/T_m) < 0.3, a low temperature zone, consists of tapered crystals with a domed surface appearance, as shown in Figure 2.5. It contains longitudinally oriented porosity between the tapered crystals. The internal structure of the crystals has a high dislocation density and is poorly defined. **Zone I** structures result when adatom diffusion is insufficient to overcome the effects of “shadowing” i.e. the high points of growing surface receiving more coating flux than the valleys do, resulting in open boundaries between crystals.

Figure 2.5 Structural zone model for coating growth proposed by Movchan and Demchishin [47].

Zone II, $0.3 < (T/T_m) < 0.5$, consists of columnar grains which are separated by distinct, dense, inter-crystalline boundaries (Figure 2.5). The surface has a smooth appearance. The dislocations are located primarily in boundary regions and grain size increases with (T/T_m) . This is the result of surface diffusion, which occurs during the deposition process, redistributing the coating flux and producing the coalescence of differently oriented islands with the formation of a more ordered surface with a preferred orientation.

Zone III, $(T/T_m) > 0.5$, a high temperature zone, consists of equiaxed grains with a bright surface. Bulk diffusion and recrystallization dominate in **zone III** and the structure and properties of the coating correspond to a fully annealed metal.

Thronton [46], in a study of the sputtered deposition of Ti, Cr, Fe, Cu, Mo and Al thick coatings, discovered that the working gas pressure (Ar) had a strong influence on the formation of **zone I** structure. He found that increasing gas pressure promoted the formation of **zone I** structure, and that a transition **zone T** existed between **zone I** and **zone II**. This transition zone consisted of a dense array of poorly defined fibrous grains without voided boundaries, as shown in Figure 2.6.

Figure 2.6 Structural zone model for coating growth proposed by Thornton [46].

The properties of the coating appear to depend essentially on the coating microstructure. It is seen that the hardness of pure metal and alloy coatings decreases with increasing deposition temperature [47, 48], whilst for compound materials, the hardness tends to increase with increasing deposition temperature. In general, as the coating structure changes from **zone I** through **zone II** to **zone III**, the hardness of the coating increases, with the maximum hardness being obtained for **zone III** structures [47,48]. This is due to the fact that the strength of ceramic materials is very adversely affected by flaws produced at low temperatures. At higher deposition temperatures the occurrence of these flaws is markedly reduced, producing a more “perfect” material which results in higher hardness.

2.3.2 Structure of TiB_2 Coatings

TiB_2 coatings exhibits a major tendency to form an extremely fine structure (nano-scale size), called nanostructured TiB_2 coatings, even forming amorphous structures when deposited at low temperatures due to the formation of strongly directional bonds [49]. This could be expected from its extremely low lattice diffusivity [10]. The fact is that the crystallinity of PVD-deposited coatings mostly depends on two parameters i.e. deposition temperature and ion bombardment energy. When the substrate was deposited at room temperature or lower temperatures by ion beam sputtering [50, 51], evaporation [52, 53] or

magnetron sputtering [54], the coating is amorphous in XRD and/or TEM examinations. Ion bombardment of the substrate at room temperature improves the crystallinity [50, 51].

For magnetron sputtered thicker coatings of more than 500 nm, they generally exhibit polycrystalline and (001)-textured, regardless of whether the substrate was nominally at room temperature [55, 56] or at elevated temperatures [22, 57, 58], although the coatings deposited at elevated temperature exhibit the more preferred (001) texture. Reports on the dependence of the morphology of TiB_2 coatings on the bias voltage are still inconclusive. Herr et al [59] suggested that the morphological change from texture to an amorphous appearance could take place with a higher bias voltage, associated with the decreased crystallinity. However, others argued that the amorphous morphology was independent of the bias [25, 42].

From the literature, few structural studies have been made to the thinner films. Chen and Bernard [60] found that the crystallinity of magnetron sputtered films decreased with film thickness over the range of 20-500 nm. The very strong (001) texture was observed by XRD in the film thickness of 500 nm, whilst the peak (001) decreased significantly with the reduced thickness, as shown in Figure 2.7. The loss of crystallinity in the thinner films may be due to reduced diffraction volumes.

Figure 2.7: XRD patterns for TiB_2 films at various thicknesses (angle of incidence = 5°) [60].

2.3.2 Residual Stress

Residual or internal stresses are present in coatings produced by both CVD and PVD processes. Indeed both tensile and compressive stresses could be found in coatings. It is generally accepted that residual stresses in thin coatings consist of two components [61];

- (1) intrinsic stress originating from the growth process as a result of in-grow defects or structural mismatch between the film and substrates. For example, it was found that the incorporation of Ar atoms in sputtered films can generate high compressive stress in the coating;
- (2) thermal stress originating from the differences in the thermal expansion coefficients of the coating and the substrate. Cooling down from the deposition temperature produces internal stress which is accommodated within the coating due to the relative thickness of the coating and substrate.

The internal stress in a coating can be expressed as;

$$\sigma_{\gamma} = \sigma_{th} + \sigma_i \quad (2.1)$$

where σ_{γ} is the total internal stress of the thin film, σ_{th} is the thermal stress and σ_i is the intrinsic stress. The component can be calculated by the following equation [62]:

$$\sigma_{th} = \frac{(\alpha_s - \alpha_c)(T_d - T_r)E_c}{1 - \nu_c} \quad (2.2)$$

Where α is the thermal expansion coefficient, T_d is the deposition temperature, T_r is the room temperature, E is the modulus of elasticity, ν_c is the Poisson's ratio, C denotes the coating and S denotes the substrate. Furthermore, it can be seen that in order to minimize the thermal stress, it is necessary to select coating and substrate materials which have similar coefficients of thermal expansion. If the coefficient of thermal expansion of the substrate is greater than that of the coating material, the tensile stresses which result are extremely detrimental to the adhesion.

For PVD TiB₂ coatings, although it has been recognized that high internal stress can be produced, very few measurements of the actual magnitude of this stress have been made. Deng et al [63] measured the internal stresses in TiB₂ coatings deposited on various substrates at room temperature and found that the residual stress strongly depends on the deposition pressure. There is a transition from compressive to tensile stress as a function of deposition parameters, such as deposition pressure and power. However, in comparison with pressure, the effect of deposition power on the stress is relatively small. Figure 2.8 is a stress transition contour map of TiB₂ deposition at room temperature, which illustrates the transition of the stresses from compressive to tensile or vice versa [25, 63]. For fixed deposition pressure and power the residual stress states of deposited TiB₂ coatings could be qualitatively estimated by this stress contour map. For example, for TiB₂ coatings was deposited at a fixed power of 400 W and a fixed total deposition pressure of 0.667 Pa (5 mTorr), the residual stress of all the films should be in compression, as marked in the Figure 2.8. This is in good agreement with the measurement results [25]. Indeed, this stress contour map can be used to predict an intrinsic stress (σ_i) formed in the coating during the growth process, as mentioned in section 2.3.2 and equation (2.1).

Recently, Berger et al. [64] reported that the residual stresses can be significantly reduced if the TiB₂ coatings are deposited by magnetron sputtering utilizing electrons to enhance adatom mobility on the growing film surface. This was done by switching the polarity of substrate bias from negative to positive. When the bias voltage changes from negative to positive the substrate bombardment by positive ions ceases. Instead, the necessary mobility of adatoms during growth is obtained through an increased thermal activity resulting from both resistive heating due to a high electron current through the substrate, and the energy released through electron bombardment.

Figure 2.8 Stress contour map of TiB₂ sputtered films [25].

Coatings deposited with electron assisted growth (positive bias voltage) displayed a significantly lowered compressive residual stress level compared to those produced with ion bombardment (negative bias voltage). This has also been shown by Logothetidis et al [65]. The thermal contribution to the residual stress originating from the cooling from deposition temperature to room temperature is estimated by using Eq. (2.2) to be -0.5 GPa, calculated with $E = 600$ GPa, $\Delta T = 500$ K and $\Delta\alpha = -1.44 \times 10^{-6}$ m/K⁻¹ (according to [66] the thermal expansion along the a -axis of TiB₂ is 3.56×10^{-6} m/K⁻¹). Consequently, since the thermal stress is close to the residual stress, the intrinsic stress generated during electron assisted growth is negligible. This means that films grow in a stress free state due to a high surface mobility. It is suggested that the difference in residual stress between the two categories of coatings is mainly a result of three effects, as follows:

- (1) The energetic ion bombardment contributes to the high stress level of negatively biased coatings. However, judging from the high compressive stress state of the coatings grown with floating potential, it is concluded that a reduced ion bombardment alone is not sufficient to reduce the stress level;
- (2) A contribution to the reduced stress of the positively biased coatings may also be given by an electron current enhanced surface mobility of adatoms [67]. However,

this effect is relatively unexplored and further studies are needed to confirm this mechanism;

- (3) The resistive heating of the substrates is increased with positive bias voltage. However, the resulting temperature increment (approximately 150 °C) is still low in terms of homologue temperature, which is not enough to alone explain the large difference in residual stresses [68].

Hence, the combination of a ceased ion bombardment, increased adatom mobility and bulk temperature during growth results in significantly reduced residual stresses for positively biased coatings as compared to coatings grown with conventional negative bias. In fact, the growth using positive bias is stress free and the resulting residual stress is a result of different thermal expansion between the substrate and coating. In addition, the beneficial effect of the reduction of compressive residual stresses is that it allows growth of thick TiB₂ coatings and coatings with an increased effective coating adhesion to substrate [69].

2.4 Mechanical Properties of TiB₂ Coatings

2.4.1 Hardness and Elastic Modulus

The diversity of the processing conditions is a significant factor in the often widely varying property values reported in the literature for polycrystalline TiB₂. The fact is that the elastic modulus and hardness of magnetron sputtered TiB₂ coatings depend on microstructure, such as texture, grain size, coating density, crystallinity, etc. So far, the limited reports of the elastic modulus covered a range of 300 GPa [25] to 600 GPa [22], with harder coatings generally showing higher moduli.

The hardness values ranged from that comparable to the bulk values of 33 GPa [15] to much higher values up to ~70 GPa [19]. Coatings with higher degrees of crystallinity and stronger (001) textures were generally harder [19, 22, 25]. With increasing (001) texture, the hardness could be improved significantly from 35 GPa [25] to 50 GPa [57] in DC magnetron sputtered coatings, whilst for the sputtered coatings using the unbalanced DC magnetron

mode with proper applications of external magnetic field and bias, the hardness could reach around 70 GPa [19].

It should be appreciated that the measurement of coating hardness requires a great deal of care, because the coating is very thin (less than 2 microns) and thus the measured value will be affected by the substrate when the applied load is relatively high. Under relatively low indentation loads, the indentation size is very small (in sub-micron scale). This leads to the difficulties in determining accurately the coating hardness or the intrinsic hardness of the coating. This might explain some of discrepancies between some values cited in the literature.

2.4.2 Adhesion of TiB₂ to Substrate

The adhesion of TiB₂ to substrate depends on the bond strength to other materials. Almond [70] suggested that good adhesion can form to weakly bonded materials, whilst poor wetting is expected by strongly bonded materials. It has also been proposed by Holleck [71] that the existence of metallic bonds within it contributes to formation of good adherence to metallic base materials.

2.5 Nanoindentation

2.5.1 Theory of Nanoindentation.

Nanoindentation or depth-sensing indentation (DSI) has become a common characterization tool for determining the mechanical properties of thin films and coatings of metals [72], ceramics [73], and polymers [74]. Conventional microhardness techniques require imaging of a residual indentation impression to estimate the projected contact area at peak load for hardness determination and the load divided by the area is called the hardness. However, to determine the mechanical properties of a film or coating from indentation experiments, the indentation depth must be at most a small fraction of the film or coating thickness [75]. This is difficult for thin films with the conventional hardness testing techniques, but becomes possible with the DSI or nanoindentation technique.

In nanoindentation, a prescribed load is applied to an indenter with pyramidal or spherical or other shapes in contact with the specimen surface. As load is applied to the indenter, the depth of penetration into the specimen is measured. A nanoindentation test instrument provides experimental results in the form of a load-displacement curve for the loading and the unloading parts of the indentation process. An analysis of the unloading data provides a value for the depth of contact at full load. The area of contact at full load is determined from the known angle or radius of the indenter. The hardness is found by dividing the load by the area of contact. The slope of the unloading curve provides a measure of elastic modulus [76].

The analysis method, however, requires careful calibration to determine the column compliance and indenter tip shape. A typical set of nanoindentation data is presented in Figure 2.9. The data were obtained by indenting fused silica with a Berkovich diamond indenter.

Figure 2.9 Nanoindentation load–displacement data for fused silica obtained with a Berkovich indenter during loading and unloading [77].

From Figure 2.9, it can be seen that there are the loading and unloading curves, where the loading curve responded when the load applied and then the indenter penetrated into fused silica, whilst unloading curve responded when the indenter distracted from fused silica. From Figure 2.9, it is noted that the maximum load used in this examination is 120 mN with the maximum penetration depth of 1,050 nm. The maximum load can be used for calculating the hardness, as elaborated in detail in the next session.

2.5.2 Load – Displacement (P-h) Data Analysis

The most popular technique for load – displacement data analysis is that of Oliver and Pharr [77] which is based on the elastic solution of Sneddon [78] for indentation by an axisymmetric body. Sneddon derived general relationships between load and displacement during the loading stage for many simple punch geometries written as;

$$P = K \cdot h_C^m \quad (2.3)$$

where P is the indentation load, h_C is the specimen displacement, and K and m are constants. Values of the exponent m for some common punch geometries are $m = 1$ for flat cylinders, $m = 2$ for cones, $m = 1.5$ for spheres and $m = 1.5$ for paraboloids. The proportional constant K is determined by materials properties and indenter geometry. Although during nanoindentation, plastic deformation occurs at the loading stage, Eq. (2.3), which is based on the elastic solution, can also be used to describe the loading behavior for most materials. Hainsworth et al [79] showed that, for the specified perfectly sharp indenter, K is mainly determined by Young's modulus and the hardness of the indenting material. Deviations from the behavior of Eq. (2.3) are sometimes observed at small depths due to rounding of the indenter tip, which destroys the geometric similarity or due to the indentation size effect (ISE) [80]. However, such deviations are significant only at small depths (typically less than a micrometer for tip rounding and of the order of a micrometer for the indentation size effect). For larger depths, the quadratic form of Eq. (2.3) is generally well-obeyed.

So far, experiments have shown that indentation loading curves obtained with Berkovich indenters ($m = 2$) are usually well-described by Eq. (2.3), as confirmed by several other investigators through experiments [81], FE calculation [82] and dimensional analysis [83]. During the unloading stage, elastic recovery occurs, and thus the relationship between the unloading curve and the elastic modulus of the material being tested can be described by elastic contact theory. Pharr, Oliver, and Brotzen [84] have shown that the compliance of the contact between any axisymmetric indenter and an elastically isotropic half-space is given by

$$\frac{1}{S} = C_s = \frac{dh}{dP} = \frac{\sqrt{\pi}}{2} \cdot \frac{1}{\sqrt{A}} \cdot \frac{1}{E_r} \quad (2.4)$$

$$\frac{1}{E_r} = \frac{(1 - \nu_s^2)}{E_s} + \frac{(1 - \nu_i^2)}{E_i} \quad (2.5)$$

where S is the experimentally measured stiffness of unloading data, A is the projected area of the contact, C_s is the specimen's compliance and P is the load on the indenter. E_r is reduced modulus owing to effects of elastic deformation of indenter (non-rigidity) and is the combined modulus of the indenter and the specimen. E_s , ν_s , E_i and ν_i are the elastic modulus and Poisson's ratio of the specimen and indenter, respectively. Eq. (2.4) has its origins in elastic contact theory and many investigators supported that it can be applied to any indenter that can be described as a body of revolution of a smooth function. In the usual way we define the hardness of the material, H , to be the mean pressure exerted by the indenter at maximum load, i.e.

$$H = \frac{P_{\max}}{A} \quad (2.6)$$

where $P_{\max}$ is the maximum load applied during the indentation and A is the projected area of contact between the indenter and the specimen. The measurements of indentation modulus and hardness depend on knowing the contact depth and then contact area of the indentations. The contact area is determined from a tip shape function, $A(h_s)$, that expresses the indenter's cross-sectional area in terms of the contact depth and must be determined for each indenter tip used in an experiment. Two models that have been widely used to determine the contact depth are those of Doerner and Nix [85] who model the indenter as a flat punch and assume initial unloading to be linear, and Oliver and Pharr [77], who treat the indenter as a paraboloid of revolution and describe the unloading curve by a power-law.

2.5.3 Oliver and Pharr's Method of Analysing Unloading Curve

The primary observations of the unloading curves suggested that unloading curves in some materials are linear, at least in the initial stages of loading. Doerner and Nix [85] reported linear unloading in metals over most of the unloading range and in silicon for at

least the first one-third of the unloading curve. The data they present as representative metallic behavior are that of aluminum. The data consisted of the unloading and loading curves on a single set of axes. On such a plot, the unloading curves were so steep that they gave the appearance of being linear even though they might not be.

Pharr and Bolshakov [86] did a series of experiments on a wide variety of materials including fused silica, soda-lime glass, and single crystals of aluminum, tungsten, and sapphire, and found that the unloading data could not be precisely fitted by a linear function, but could be well-described by the power-law relation [77]:

$$P = \alpha(h - h_f)^m \quad (2.7)$$

where h_f is the final displacement after complete unloading and α and m are material constants. Typical values of α and m determined from regression analyses of experimental data are included in Table 2.3, along with correlation coefficients for the curve fits [77]. The table shows not only that Eq. (2.7) provides a good description of the unloading data (correlation coefficients $R > 0.9999$) but also that the power-law exponents, m , while slightly material dependent, generally fall in the range 1.2–1.6. These exponents are consistent with neither the flat punch indenter geometry, for which $m = 1$ nor the conical geometry, for which $m = 2$ [78]. The flat punch geometry is important because it is sometimes invoked to model unloading behavior based on the assumption that the contact area remains constant, at least during the initial stages of unloading [85]. The conical geometry is important because it most closely approximates the self-similar geometry of the Berkovich indenter used to obtain the data. Curiously, an indenter with the geometry of a parabola of revolution, for which $m = 1.5$ [78] comes closest to predicting the experimental observations.

An explanation for the behaviour of the indentation unloading curves can be achieved by careful examination of the shape of the contact impression after unloading. As shown schematically in Figure 2.10, when a conical indenter is first pressed into a material, both elastic and plastic processes occur, with the contact impression conforming perfectly to the shape of the cone Figure 2.10 (a).

Table 2.3: Values of parameters characterizing unloading curves as observed in nanoindentation experiments with a Berkovich indenter. Data are from Ref. 77

Material	α (mN/nm ^m)	m	Correlation Coefficient, R
Aluminium	0.2650	1.38	0.999938
Soda-lime glass	0.0279	1.37	0.999997
Sapphire	0.0435	1.47	0.999998
Fused silica	0.0500	1.25	0.999997
Tungsten	0.1410	1.51	0.999986

Figure 2.10: Schematic representation of deformation processes during loading and unloading of a conical indenter [76].

However, during the initial unloading, elastic recovery causes the shape of the contact impression to change. The importance of the curvature follows by considering what happens when the contact impression is reloaded. From the geometries in Figs. 2.10 (b) and 2.10 (c), (where the curvature in Figure 2.10 (b) is grossly exaggerated for the sake of illustration), it is apparent that elastic reloading must occur with continuous increases in contact area until full contact is achieved at maximum load. However, because the unloading and reloading processes are elastic, what happens during reloading must be exactly the reverse of what happens during unloading. Thus, the unloading process must be characterized by a continuous decrease in contact area as the contact impression “peels away” from the indenter. Obviously, the contact depth does not remain constant in the early stage of unloading, which is the base of the linear unloading theory. Thus, unloading follows the power-law behavior (Eq.(2.7)).

Oliver and Pharr [77] proposed that the deformation pattern of a real elastic-plastic sample during and after indentation is shown schematically in Figure 2.11. It shows a cross section of an indentation and identifies the parameters used in the analysis. At any time during loading, the total measured displacement (h) is expressed as the sum of the contact depth or the specimen displacement (h_c) and the displacement of the surface at the perimeter of the contact (h_s). It then follows;

Figure 2.11: A schematic representation of a section through an indentation showing various quantities used in the analysis [77].

$$h = h_c + h_s \quad (2.8)$$

At peak load, the load and displacement are P_{max} and h_{max} , respectively, and the radius of the contact circle is a . Upon unloading, the elastic displacements are recovered, and when the indenter is fully withdrawn, the final depth of the residual hardness impression is h_f . The experiment parameters needed to determine stiffness (S) are shown in the schematic load-displacement data shown in Figure 2.12. The three key parameters are the peak load (P_{max}), the depth at peak load (h_{max}) and the initial unloading contact stiffness (S_{max}). It should be noted that the contact stiffness is measured only at peak load, and no restrictions are placed on the unloading data being linear during any portion of the unloading. The analysis begins by rewriting Eq. (2.4) as;

$$S = \frac{dP}{dh} = \frac{2 \cdot E_r \cdot \sqrt{A}}{\sqrt{\pi}} \quad (2.9)$$

To determine the contact depth (h_c) from the experiment data, it is noted that

$$h_c = h_{\max} - \varepsilon \frac{P_{\max}}{S} \quad (2.10)$$

where the geometric constant ε for the flat punch = 1, conical indenter = 0.72 and Berkovich = 0.75.

Figure 2.12: A schematic representation the load-displacement (P-h) curve showing quantities used in the analysis of the stiffness (S) as well as a graphical interpretation of the contact depth (h_c) [76].

2.5.4 Indentation Calibration

From the load-displacement curve, under either depth control or load control systems, the material properties can be obtained. Nevertheless, accurate determination of these properties always requires the indenter to be calibrated. Obvious calibration includes converting voltages from the capacitance probes to the appropriate force or length units. Moreover, calibration also requires knowledge of the compliance or stiffness of the machine in contrast to the sample stiffness and knowledge of the tip shape used to produce the indentation since all material properties rely on the contact area.

Load frame compliance (C_f) or machine compliance is very important because the measured displacements (h_t) are the sum of the displacements in the specimen (h) and the load frame (h_{fr}), and thus for accurately determining specimen displacements, the load frame compliance must be known with precision. This is especially important for large indentations made in materials with high modulus for which the load frame displacement can be a significant fraction of the total displacement, ie.

$$h_t = h + h_{fr} = h + PC_f \quad (2.11)$$

where C_f is the load frame compliance and P is the load on the indenter. Clearly, the penetration depth of the indenter into the specimen is less than the recorded total displacement. The real penetration depth can only be derived when the load frame compliance is properly calibrated for the instrument [77].

Oliver and Pharr's [77] also proposed a method to calibrate the load frame compliance by using unloading curves to derive the overall compliance of the specimen and the load frame for each depth. Based on the assumption that Young's modulus for the sample does not vary with depth, an iteration technique was then used to derive the C_f value for the load frame. The method followed by modeling the load frame and the specimen as two springs in series, in which case

$$C = C_s + C_f \quad (2.12)$$

where C is the total measured compliance and C_s is the compliance of the specimen. Since the specimen compliance during elastic contact is given by the inverse of the contact stiffness, S , Eqs. (2.9) and (2.11) combine to yield

$$C = \frac{\sqrt{\pi}}{2E_r} \cdot \frac{1}{\sqrt{A}} + C_f \quad (2.13)$$

It is thus seen that if the modulus is constant, a plot of C vs. $A^{-1/2}$ is linear for a given material, and the intercept of the plot is a direct measure of the load frame compliance. Furthermore, the best values of C_f are obtained when the first term on the right-hand side of Eq.(2.13) is small, i.e., for large indentations.

Sun et al [87] proposed a technique for the accurate and quick C_f calibration. Analyses of the obtained loading curves showed that the load frame compliance of the nanoindentation instrument can be determined from a single loading curve. In an actual indentation experiment, the obtained raw load-depth data during the loading stage can be described by the second-order polynomial dependence of depth on the square root of load, from which the C_f is determined. For a round tip indenter, it is obvious that Eq. (2.5) no longer holds true. Nevertheless, as proposed by Cheng and Cheng [83], if the correction depth ξ is taken into account, then Eq. (2.3) can also be used to describe approximately the loading curve of a round tip indenter indenting an elastic-perfectly plastic material for depths greater than d , the depth at which the sphere of the tip touches the cone, that is for $h_c > d$;

$$P = K(h + \xi)^2 \quad (2.14)$$

then,

$$P^{1/2} = K^{1/2} \cdot h + K^{1/2} \cdot \xi \quad (2.15)$$

where ξ is the difference in depth between the ideally sharp tip and the round tip of radius r . The schematic of the real geometry of indenter depicts in Figure 2.13.

Figure 2.13: Schematic diagram showing the geometry of a round tip indenter [87].

In real indentation experiments, the total depth from Eq. (2.11) is measured by the instrument. Hence, combining Eqs. (2.11) and (2.15) leads to (for $h > d$)

$$h_t = C_f \cdot P + K^{-1/2} \cdot P^{1/2} - \xi. \quad (2.16)$$

Clearly, a plot of the measured total depth h_t against the square root of the indentation load $P^{1/2}$ results in a second-order polynomial dependence of h_t on $P^{1/2}$. Figure 2.14 shows a typical curve of h against $P^{1/2}$ for silicon. Obviously, the first constant on the right hand side of the polynomial formula is a direct measure of C_f and the last term of polynomial equation is ξ .

Figure 2.14: Plots of h against $P^{1/2}$ plots for the experimentally measured loading data for silicon [87].

2.5.5 Area Function of Indenter Tip

To make accurate measurements by indentation experiments, the contact areas of the indentations must be precisely known. The area function is very important since computation of both the modulus and the hardness count on the contact areas through Eqs. (2.4) and (2.6). As noted above, it is a standard practice to assume that the area of contact for an indentation of a specified depth is the cross-sectional area of the diamond indenter tip at that depth. In this practice the geometry of the tip is described by an area function $A(h_c)$ and this function is used to determine the contact area of an indentation made to a prescribed depth. One method for determining the area function of a tip involves imaging the indentations. The calibration is made by fitting the imaged areas at known depths to an area function. However, optical imaging of submicron indentations is difficult, and SEM imaging does not provide sufficient contrast to discern the area of contact for shallow indentation [88].

Four procedures have been developed for determining area functions. Firstly, in the D & N's method, Doerner and Nix [85] described an indenter-tip calibration using transmission electron microscopy (TEM) images of indentation replicas, but this method is somewhat inconvenient, being both expensive and time-consuming.

Secondly, Oliver and Pharr [77] proposed the method for determining area function that required no imaging at all. The O&P method becomes one of the most popular methods for calibrating the shape of the indenter tip. The method is based on the assumption that the elastic modulus is independent of indentation depth and specific values for the modulus are not assumed. To find the area function the method takes the advantage of the fact that relatively large indentations can be made in aluminum because of its low hardness. Furthermore, for the largest indentations the area function for the ideal Berkovich geometry, $A(h_c) = 24.5h_c^2$, can be used to provide a first estimate of contact area. Initial estimates of C_f and E_f are thus obtained by plotting C vs. $A^{-1/2}$ for the two largest indentations in aluminum. Using these values, contact areas are computed for all indentation sizes by rewriting Eq. (2.13) as

$$A = \frac{\pi}{4} \cdot \frac{1}{E_r^2} \cdot \frac{1}{(C - C_f)^2} \quad (2.17)$$

from which an initial guess at the area function can be made by fitting the A vs. h_c data to the relationship

$$A(h_c) = 24.5h_c^2 + C_1h_c^1 + C_2h_c^{1/2} + C_3h_c^{1/4} + \dots + C_8h_c^{1/128} \quad (2.18)$$

where C_1 through C_8 are constants. The lead term describes a perfect Berkovich indenter; the others describe deviations from the Berkovich geometry due to blunting at the tip. However, this technique is time consuming and involves a series of indentation experiments from small depths to large depths.

The third interesting approach for indenter tip area function calibration, which is employed by the commercial instrument: Nano Test [89] is the modified O&P method which uses the first two terms of the O&P area function, i.e.

$$A = ah_c + bh_c^2 \quad (2.19)$$

where a and b are constants, which are determined experimentally by following the O&P procedure outline previously.

Finally, a quick method for calibrating the shape of the indenter tip is the one introduced by Sun et al [87] using the loading curve. They proposed a method to calibrate the indenter tip radius and load frame compliance by accounting the correction depth ξ in the ideal method as shown in Figure 2.13 and Eq. (2.20). For a round tip indenter, it is obvious that Eq. (2.3) no longer holds true due to the real geometry of a round tip indenter.

$$A = 24.5(h_c + \xi)^2 \quad (2.20)$$

The correction depth ξ can be found from the last term of the polynomial equation (Eq. 2.16) described in [87].

2.5.6 Thermal Drift

Thermal drift becomes particularly important for small indentations made over long periods of time. Although the system is thermally buffered from its surroundings and the room in which it is housed is temperature-controlled to within $\pm 1^\circ\text{C}$, small thermal fluctuations cause machine components to expand, and the expansion is manifested in the data as an apparent displacement in the specimen [77]. According to Oliver and Pharr [77], to account for thermal drift, the rate of displacement was measured during the last 80 seconds of the held period, and the displacement data were corrected by assuming that the displacements measured at the low load during the hold period are due mostly to thermal expansion rather than to time dependent plasticity in the specimen. Following the hold period, the specimen was loaded for a fourth and final time, with another 100 seconds hold period inserted at peak load to allow any final time dependent plastic effects to diminish, and the specimen was fully unloaded.

2.5.7 Nanoindentation Indenters

The most common indenter geometries used are the three-sided Berkovich indenter, the spherical indenter, and the four-sided Vickers indenter. These indenters have some degree of geometrical symmetry. A triangular pyramid has an area-to-depth relationship identical to that of the four-sided Vickers pyramid used commonly in micro-hardness testing. Because of the geometric self similarity of pyramidal indenters, it is often convenient to model their behavior by that of a cone with a half included angle that gives the same area-to-depth relationship. Furthermore, the equivalent cone for Berkovich indenter has the same area of contact for the same depth of penetration as a real Berkovich indenter [90].

The main requirements for the indenter are high elastic modulus, no plastic deformation, low-friction smooth surface and a well defined geometry that is capable of making a well defined indentation impression. For the reason of high elastic modulus, a diamond is chosen. For diamond, $E = 1,141 \text{ GPa}$ and $\nu = 0.07$ [91]. A well defined perfect tip

shape is difficult to achieve. Berkovich is a three-side pyramid, and provides a sharply pointed tip compared to the Vickers or Knoop indenters. Because any three nonparallel planes intersect at a single point, it is relatively easy to grind a sharp tip on an indenter if Berkovich geometry is used (Figure 2.15).

Figure 2.15: Schematics of the Berkovich indenter.

Many methods have been developed to correct for the tip shape. In calculation, it does need to turn the Berkovich indenter into an equivalent conical indenter for making the mathematics of the analysis easier. For the Berkovich and Vickers pyramids, the equivalent cone angle normally is 70.3° , and the area-to-depth relationship, also known as the area function [77], is derived in the area function of indenter section.

2.6 Adhesion of Coating/Substrate

2.6.1 Coating/Substrate Interface

The American Society for Testing and Materials (ASTM) (D907-70) [92] defines the adhesion as “the state in which two surfaces are held together by interfacial forces”. These bonding forces can be van der Waals forces, electrostatic forces or chemical bonds across the coating-substrate interface. A distinction must be made between basic adhesion (BA) which is the maximum possible attainable value of adhesion, and experimental adhesion (EA) which depends on other factors, for instance, the type of test, the residual stress levels in the film, and the interfacial flaw distribution, and thus as a result, $BA \gg EA$ (in reality). During service, the applied stresses on the coating surface are transmitted to the interface, where they can cause failure and stripping of the coating if they are of sufficient magnitude.

Adhesion between a coating and substrate depends mainly on the microstructure of the interface formed. Coating/substrate interfaces can be classified into the following manner [93, 94]:

- (1) Diffusion interface is characterized by a gradual change in the lattice parameter and composition in the coating/substrate transition region. This type of interface forms at high temperature when the coating material and substrate material have partial mutual solubility [94] and diffusion can occur. During CVD of ceramic coatings, which is carried out at high temperature, 800-1000 °C, diffusion between coating material and substrate material usually takes place. A diffusion interface can be formed, thus ensuring good adhesion between the coating and substrate.
- (2) Pseudo- diffusion interface is formed by implantation of high energy particles. It can be formed on material combinations that do not have mutual solubility. During sputtering deposition and ion plating of hard ceramic coatings, pseudo-diffusion interface layers are usually formed due to the high energy of the incident atoms and ion bombardment before the coating processes [93, 95].
- (3) Abrupt interface At low processing temperatures in system without any plasma assistance, it is not possible to form either diffusion interface or pseudo-diffusion interface. Under these circumstances, the coating/substrate interface is usually abrupt. Abrupt interfaces only have a constant chemical composition across several lattices or the transition region is only a monolayer. Coating/substrate bonding by such an interface is weak and therefore poor adhesion can be expected.
- (4) Mechanical interface When the substrate is rough and porous, the coating material will fill the pores and other morphologically advantageous places providing that there is sufficient surface mobility. This type of interface mechanically anchors the coating to the substrate [94].

2.6.2 Adhesion Measurement: Scratch Test

Nowadays, the scratch test is one of the approaches for measuring the adhesion. Indeed scratch test has been widely used to evaluate and analyze the adhesion strength of coating/substrate systems as well as to assess coating quality for tribological applications. Generally the test consists of applying a continuously increasing load on the coating surface by a Vickers or a Rockwell C (radius 200 μm) stylus whilst the sample is moved at a constant speed. The stylus causes increasing elastic and plastic deformation until damage takes place in the surface region. In practice, the film may not be removed entirely from the channel so it is convenient to address a critical load, L_c , which characterizes the mechanical adhesion strength of the coating/substrate systems. In addition, the critical load is a function of many parameters, such as coating thickness, interfacial stress, coefficient of friction, hardness, structure parameter, compressive stress, etc [96].

The advantage of this method is that it is quick and requires inexpensive equipment. However, it is difficult to obtain quantitative data since the complicated stress field imposed by the indenter is the obstacle to access the adhesion. In addition, mechanical properties of the substrate mostly affect the failure mechanism and the critical load thus making it impossible to compare the same coating which has been deposited on different substrates [97]. Samples within the data set also need to have the same coating thickness since the critical load also increases with coating thickness, as discussed in the next section.

2.6.3 Parameters Influencing on Critical Load

Critical load can be thought as a representative of the adhesion of coating to the substrate tested. However, one cannot directly compare the critical load values to check which gives better adhesion when the coating-substrate systems and test parameters are different. Thus, the use of critical load in the scratch test for comparison of coating quality and adhesion must be limited to systems with the same materials, properties, and test parameters only. This is because each parameter related to the testing conditions and to the coating-substrate system to be tested is affecting the value of the critical load observed.

Steinmann et al [98] stressed that the parameters such as scratching speed, loading rate, diamond tip radius, diamond wear, substrate and coating hardness, coating thickness, substrate and coating roughness, the coefficient of friction and frictional force genuinely affect the critical load value and showed how the relationship between each parameter and the critical load. The parameters could be categorized as intrinsic and extrinsic parameters, as follows:

(i) Intrinsic parameters

Intrinsic parameters associated with the scratch test are the parameters that directly related to the instrumentation or testing instrument and can therefore be chosen by the operator, such as loading rate and scratching speed, indenter tip radius and indenter tip wear, etc. Indeed, many of these intrinsic factors are instrument-specific and require a careful calibration if results are to be compared between instruments.

(ii) Extrinsic parameters

The extrinsic parameters influencing the scratch test are the parameters that depend directly on the coating-substrate system to be tested. It is of particular importance that this influence is known since these parameters are fixed and cannot be modified by the operator, such as substrate hardness, coating hardness, coating thickness, substrate and coating roughness and coefficient of friction, etc.

Many studies have been performed on different types of coating-substrate systems to examine what are the parameters that have an effect on the critical load value in the scratch test and in what manner that these parameters actually alter the data as shown in Table 2.4. However, one is still unable to express the adhesion of the coating quantitatively from these critical loads data and ranking the coating adhesion of different coating-substrate systems with different mechanical properties, conditions and parameters is still impossible.

Table 2.4: Factors affecting the critical load for coating failure [98].

Intrinsic parameters	Extrinsic parameters
Loading rate	Substrate properties (hardness, modulus)
Scratching speed	Coating properties (hardness, modulus)
Indenter tip radius	Coating thickness
Indenter tip wear	Substrate and coating roughness
Machine factors	Coefficient of friction

2.6.4 Models of Scratch Test

The critical load for coating failure as determined by scratch testing is often used to give some idea of the adhesion between the coating and the substrate and as a result, a number of models relating the critical load to the work of adhesion have been proposed. The work of adhesion, W_{AD} , is the amount of work required to break the bonds between coating and substrate atoms.

In 1950, Heavens [99] was the first to use the scratch test in his studies of adhesion of evaporated chromium films on glass. Ten years later, Benjamin and Weaver [100] used the same fundamental to study a number of metal films on glass substrate using the theory of plasticity. These attempts tried to link the critical normal force value to the critical interfacial shear stress. Unfortunately, their pioneered work was not able to fully explain the experimental data obtained, and Weaver [101] later suggested that an elastic-plastic approach was needed. Butler et al. [102] used the Benjamin and Weaver’s method to prove that brittle films and ductile films show differently to the test. In addition, observations showed that the process of scratch formation was generally very complex and varied with the film material, indicating that it is not possible to deduce absolute values of adhesion forces using a simple general theoretical model.

According to Weaver’s suggestion, Burnett and Rickerby [103] discussed the mechanics of the scratch test by extending the models for elastic-plastic indentation to the scratch test as shown in Figure 2.16. Their ideas consider the stresses responsible for coating loss in the scratch test to be the sum of three components: (i) an elastic- plastic indentation

stress field, (ii) an internal stress field and (iii) a frictional stress field. From their assumption, the first two components are relatively well defined, whilst the frictional stress is more difficult to determine. Furthermore, the ideas embodied in the volume-law-of-mixtures hardness model have also been applied to the scratch test, allowing estimates to be made of the interfacial shear strains present during testing since these contribute to the measured "critical load" L_c for coating failure.

There is an advantage to express all the stress contributions in terms of their effects on the friction coefficient when tangential force is measured experimentally during testing. The measured friction force is the linear sum of the components owing to ploughing (F_p), adhesion (F_a), and internal stress (F_s) as shown in Figure 2.16.

Figure 2.16: The scratch adhesion test represented as the sum of three contributions: an indentation term, an internal stress term and a friction term [103].

The friction force, F , can be transformed to the stress acting on the surface layer by being divided by cross sectional area of the track, A_l (Figure 2.17 (a)). Figure 2.17 (b) demonstrates that the surface is under a compressive stress, σ , given by:

$$\sigma_i = -\frac{F}{A_1} \quad (2.21)$$

which is applied parallel to the interface.

The tensile component responsible for coating detachment should be given by:

$$\sigma_t = \nu \frac{F}{A_1} \quad (2.22)$$

where ν is Poisson's ratio for the coating material.

Figure 2.17: (a) Schematic diagram of a scratch track showing an area of coating detached from substrate ahead of the indenter and the development of surface cracking from this failure, (b) Section through the center line of the scratch showing the stresses ahead of the indenter responsible for coating detachment [104].

However, the question of how stresses generated in the direction normal to the surface and exactly what stresses are relieved when the coating detaches remains unanswered. The analysis of Burnett and Rickerby was later extended and answered by Bull et al [104]. Each of the three stress components was then expressed in terms of their effects on the measured coefficient of friction. This is clearly advantageous when experimental measurements of the frictional force will be the linear sum of the components owing to ploughing, adhesion and internal stress.

It was also determined without any need for detailed theoretical calculations of any of the terms. The total friction, F_T , force is represented as:

$$F_T = A_1 P + A_2 \tau \quad (2.23)$$

where P is a compressive flow stress in the plane of the coating owing to ploughing adhesive friction, τ is a shear stress from the interaction of the indenter with a surface and A_2 is the contact area. In most contact situation, the adhesive term rules Eq. (2.23) and thus the measured frictional force cannot merely be divided by the projected area of the scratch track to get the compressive stress as same as Eq. (2.21) [104]. Using Laugier's energy balance method [105], the work of adhesion, W_{AD} , is related to the compressive and shear stresses as follows:

$$W_{AD} = \frac{\sigma^2 t}{2E} + \frac{\tau^2 t}{2G} \quad (2.24)$$

where G is the shear modulus and t is the thickness of the coating. In general, the applied shear stresses are small compared to the compressive flow stress, P , which mainly leads the stress relieved in the coating by detachment. Hence, the second term in Eq. (2.24) can be negligible and the equation can be rewritten as:

$$P = \frac{F_P}{A_1} = \left(\frac{2EW_{AD}}{t} \right)^2 \quad (2.25)$$

The assumption is made that during scratching, the compressive stress transferred by diamond point is supported by the front half of the indenter. Thus the compressive stress can be related to the normal applied load, L , given by:

$$L = \frac{8W}{\pi d^2} \quad (2.26)$$

where d is the scratch channel width (Figure 2.17(a)). At the critical load for the interface failure, $L = L_c$, the combination of Eqs (2.24) and (2.25) provides an expression for L_c in terms of the work of adhesion:

$$L_c = \frac{\pi d^2}{8} \left(\frac{2EW_{AD}}{t} \right)^{1/2} \quad (2.27)$$

Hence, a plot of L_c as a function of $d^2/t^{1/2}$ indicates a straight line of slope $(2EW_{AD})^{1/2} \pi/8$, from which W_{AD} can be calculated. The work of adhesion, W_{AD} , can be found if thickness and Young's modulus are known and track width and critical load, L_c , are measured experimentally. Furthermore, Bull et al [104] produced work of adhesion data for 3 μm TiN coatings on different steel substrate. The work of adhesion in this particular case (TiN/M2) was 125 J. m⁻².

2.6.5 Adhesion Scratch Test Failure Modes

Bull [106] is the first to define the scratch test failure modes determined by microscopic observations. They have been separated into three categories:

1. *Through-thickness cracking* - including tensile cracking behind the indenter, conformal cracking as the coating is bent into scratch tract, and Hertzian cracking.
2. *Spallation* - including compressive spallation ahead of the indenter, buckling spallation ahead of the indenter or elastic recovery induced spallation behind the indenter.

3. *Chipping of the coating.*

The type of failure investigated is mainly dependent on the coating hardness as well as the substrate hardness, as summarized in Figure 2.18. The TiB₂ coatings and the high speed steel substrate investigated in this work have high hardness values. Therefore, from Figure 2.18, the coatings deposited on high speed steel should fail as a result of spallation or chipping.

Dyrda [97] modified the failure modes from Bull’s categories to two general groups depending on whether the substrate behaves in a “brittle” or “ductile” manner during the test. Generally, brittle failure is related to hard ceramic materials while ductile failure takes place in a sample coated on a ductile material or substrate. In the brittle failure case, the damage area extended beyond the regions of the scratch track. On the other hand, in the ductile failure case, the damage area is small and confine within the track, as shown the summarized map of the main scratch test failure modes in Figure 2.18.

Figure 2.18: Map of the main scratch test failure modes in terms of substrate and coating hardness [106].

2.6.5.1 Brittle failure modes

A number of failure modes have been observed in the cases where the substrate is brittle. The main brittle failure modes are schematically shown in Figure 2.19. Large area spallation, Figure 2.19 (a), is common if the adhesion is poor or if the residual stress level in the coating is high. In this case, as the diamond contacts the coating, a crack is formed at the

coating-substrate interface which can propagate a distance of the track. This crack may nucleate at a large interfacial flaw or derive from through-thickness cracking [106]. A general failure is spallation in which the coating is detached to minimize the amount of elastic energy stored by the large compressive stresses ahead of the moving indenter tip. This means the relatively poor adhesion leads to semicircular crack, Figure 2.19 (b). This failure mode leads to chipping at the track side if the interfacial crack propagates outside on the scratching line before passing over it. When the indenter tip has reached the spalled region, it will either remove the chipping part or press the chipping back into the coating with the substrate.

Figure 2.19 (c) shows the recovery spallation which is not related to any delamination from indenter. This failure mode is associated with the elastic recovery which occurs behind the stylus as it travels over the coated surface and relies on the plastic deformation in the substrate and through- thickness cracking in the coating. After the stylus passes and the scratched region is unloaded, the elastic deformation in the coating/substrate system is relaxed. However, it is not possible to completely relax the substrate elastic deformation due to the plastic deformation, which result in the formation of the scratch track, so that the residual stress remains.

Figure 2.19: Brittle failure modes in the scratch test: (a) gross spallation, (b) compressive spallation, (c) recovery spallation behind the indenter, (d) Hertzian cracking and (e) tensile cracking [106].

Figure 2.19 (d) demonstrates a failure mode typical of very brittle substrates. The tensile radial stresses at the edge of the indenter tip contact generate a ring crack which propagates from the surface through the coating into the substrate (Hertzian cracking) [107].

As the indenter moves, several of these rings are formed which intersect and create a network along the edge of the crack. Figure 2.19 (e) shows the chipping occurred along the crack channel. These Hertzian cracks may provide the through-thickness cracking that initiates the elastic recovery cracking and also may occur from the cracks which form at the rear of the indenter tip contact resulted from the tensile stresses generated during sliding. If no scratch crack is formed, this seems identical to the Hertzian cracking. Once a crack channel is formed, the shape of the contact between the indenter and coating changes and the load is then mostly supported on the front half on the indenter. It will lead the crack to run perpendicular to the sliding direction with less curvature than in the Hertzian cracking case [106].

2.6.5.2 Ductile failure modes

The ductile failures are usually characterized by smaller crack areas, chipped or spalled regions and a larger number of failure events. Typical failure mode schematics are shown in Figure 2.20. The spallation and buckling failure modes, Figures 2.20 (a) and (b), are similar to the spallation mode for brittle failure except the magnitude of failure is smaller and is generally confined within the scratch track for thin coating.

Figure 2.20: Ductile failure modes in scratch test: (a) spallation, (b) buckling, (c) conformal cracking, and (d) tensile cracking [106].

Both of these failure modes take place ahead of the moving indenter. In general, spallation occurs where the adhesion is poor. However, elastic recovery spallation initiated behind the indenter is not usually observed for ductile failure [106]. Two other common modes of ductile failure are conformal cracking (Figure 2.20 (c)) and tensile cracking (Figure 2.20 (d)). The significant channel formation is observed for ductile materials since the load

on the indenter tip is transferred to the front half of the indenter once sliding starts. Since there is almost no load on the back of the indenter, the Hertzian cracking will not occur in this region. Two factors then contribute to the stress ahead of the indenter. Firstly the pile-up of materials ahead of and at the side of indenter causes bending of the coating, placing its surface to tension, and secondly the friction between the indenter tip and coating surface causes the maximum radial tensile stress at the side of indenter. This is supplemented by the tensile stress at the back of the contact area where the indenter moves pass the deformed material.

The tangential friction contributes compressive stresses ahead the indenter which lead to spallation and bucking failures. Tensile will then take place initially at the side of the indenter and this is marked by cracks at the track edge parallel to the scratch direction. Partial ring cracks can occur ahead of the indenter, which then pass over and push into the track. The coating can crack further on the indenter tip when it is bent into the scratch track. This leads to through-thickness cracking or conformal cracking, Figure 2.20 (c). Cracking can also take place at the back of the contact owing to the tensile stress generated on sliding as observed for the brittle materials, Figure 2.20 (d).

In summary of this chapter, the four main topics are discussed i.e. relevant properties of bulk TiB_2 , preparation of titanium diboride coatings, structural characterization of titanium diboride coatings, and mechanical properties of titanium diboride coatings. In addition, the measurement of mechanical properties was highlighted i.e. nanoindentation and microscratch test. Nanoindentation is the most widely used to measure the mechanical properties of materials on the micron or submicron scale in engineering. One of the great advantages of the technique is that many mechanical properties can be determined by analyses of the indentation load-displacement data alone, thereby avoiding the need to image the hardness impression and facilitating property measurement at the micro or sub-micron scale. In order to determine the coating adhesion, microscratch shows the possibility to extract it. However, it is difficult to obtain quantitative data since the complicated stress field imposed by the indenter is the obstacle to access the adhesion.

Chapter 3

Experimental Techniques

3.1 Substrate Materials and Preparation

High speed steel (HSS) was chosen as substrate in this study. The commercial HSS, SECO WKE45 (Sweden) was in a fully hardened and tempered condition. The tempering temperature of HSS was about 600 °C. The chemical composition (wt. %) of HSS substrate is shown in Table 3.1.

Table 3.1: Chemical composition (wt. %) of high speed steel.

Element	Content (wt.%)
C	1.4
Cr	4.2
W	9
Mo	3.5
V	3.5
Co	12.5
Fe	Balance

The HSS bar of 150×12×3 mm³ was cut into 12×12×3 mm³ pieces. The specimen's surface was manually ground by standard metallurgical silicon-carbide grinding papers, with grid size 180, 320, 800 and 1,000. This was followed by polishing with the diamond paste. The polished HSS sample has an average roughness of 0.1 micron as measured by atomic force microscopy, as shown in Figure 3.1. The HSS substrate was then ultrasonically cleaned with acetone at 20 °C for 10 minutes and cleaned with ethanol for another 10 minutes followed by blowing using a pressurised nitrogen gas before charging the deposition chamber. The initial hardness and elastic modulus of HSS were 11 GPa and 220 GPa, respectively as measured by nanoindentation.

Figure 3.1: AFM images showing the average surface finish of HSS substrate.

3.2 Coating Deposition Apparatus

3.2.1 Apparatus and General Deposition Set Up

In this study, the MSS3 type planar magnetron sputtering system, manufactured by Coaxial Power System Ltd. (United Kingdom), was used to deposit all TiB_2 -based coatings. A typical magnetron sputtering system is shown schematically in Figure 3.2. The system employs a simple chamber with two water-cooled 3-inch planar magnetron target holders. Sputtering can be performed in either DC (direct current) or RF (radio frequency) modes. Both DC and RF sputtering were used in this work by using DC power for the metallic targets, such as Ti and Cr, and RF power for the ceramic TiB_2 target as shown in Figure 3.3.

The MSS3 magnetron sputtering system has the ability to reach a base pressure of 10^{-5} Pa with the performance of the rotary pump and the turbo pump. The maximum DC and RF power that can be employed is 400 and 600 W, respectively. The system is also equipped with a substrate holder of 170 mm diameter made of Molybdenum, which can be rotated at 0 to 40 rpm. Below the substrate holder is a graphite heating element capable of heating the substrate up to 800 °C. A thermocouple, placed near to the substrate holder without directly contacting the samples, monitors the working temperature [108].

Figure 3.2: Schematic of a typical magnetron sputtering system [108].

In the present work, high-purity argon gas was introduced into the chamber after it was evacuated to below 5×10^{-4} Pa. The targets, i.e. TiB_2 and Ti, which were 75 mm in diameter and 5 mm in thickness, were located above the 170 mm diameter working table with an inclined angle of 30° with respect to the normal of the working table, as shown in Figure 3.3. Then the targets were pre-sputtered for 15 min with the target shutters closed. For the rotation case, the working table was rotating at 2 rpm during the deposition process.

The TiB_2 target was powered in the RF mode and the Ti target was powered in the DC mode. The substrates were positioned near to the edge of the working table below the TiB_2 target (see Figure 3.3). The substrate to target distance was held constant at 100 mm for DC target (Ti) and varied between 60-100 mm for the RF target (TiB_2). That means the shortest distance between the TiB_2 target and the substrate was 60 mm. Thus, as the table was rotated, the substrate-target distance varied from 60 mm to about 210 mm within one cycle of substrate rotation. All the experiments were conducted at a constant working pressure of 0.65 Pa and a total gas flow rate (Ar) of 20 sccm. The substrate temperature varied from RT to 400 °C and sputtering power (for both Ti and TiB_2 targets) varied from 150 to 350 W. Table 3.2 summarises the deposition conditions

employed in this work. Details of each set of experiments will be given in relevant sections in Chapter 5.

Figure 3.3: Schematic diagram showing the co-sputtering process.

Table 3.2: Deposition conditions	
Substrate temperature	RT to 400 °C
Substrate-to-target distance	
TiB ₂ Target (2 targets)	60-100 mm
Ti Target	100 mm
Gas	Ar
Total gas flow rate	20 sccm
Base pressure	5×10 ⁻⁴ Pa
Working pressure	0.65 Pa
Substrate rotation	Available
Sputter cleaning time	Available
DC sputtering power (Ti)	150-350 W
RF sputtering power (TiB ₂)	150-350 W (2 targets)

3.2.2 Substrate Biasing

In order to enhance the coating adhesion, substrate bias is practically applied during the sputtering deposition. The negative DC or RF electric fields are often applied to bias the substrate in order to vary the flux and energy of depositing charged species. The technique of applying bias has been utilized in all sputtering configurations, e.g. DC, Magnetron, RF, reactive [109]. Furthermore, substrate bias has been effective in

modifying a broad range of properties in the deposited films. Vossen and Kern [110] summarized the advantages of substrate biasing, as follows;

- (i) Improved film adhesion during initial stages of film formation
- (ii) Substantial improvement in step coverage
- (iii) Increased film density
- (iv) Significant reduction in resistivity of metal films
- (v) Change in film hardness and residual stress (either increase or decrease)
- (vi) Enhanced optical reflectivity
- (vii) Change in electrical properties of dielectric films (e.g. increase in resistivity, decrease in relative dielectric constant of SiO₂ films)
- (viii) Reduction in etch rate of silicon-nitride films
- (ix) Alteration of film morphology (e.g. columnar microstructure of Cr replaced by a compacted and fine-grained structure).

In addition, energetic-particle bombardment prior to and during film formation and growth promotes numerous changes and processes at a microscopic level. These include;

- (i) Removal of contaminants
- (ii) Alteration of surface chemistry
- (iii) Enhancement of nucleation and renucleation (owing to generation of nucleation sites via defects and implanted and recoil-implanted species)
- (iv) Higher surface mobility of adatoms
- (v) Elevated film temperatures with attendant acceleration of atomic reaction and interdiffusion rates.

Film properties are then modified through roughening of the surface, elimination of the interfacial voids and subsurface porosity, creation of finer, more isotropic grain morphology, and the elimination of columnar grains [109]. In the present work, a RF power biased to the substrate was used to provide substrate bias at different levels varied

the biasing power from 30 to 150 W with varied biasing time of 30 min to 180 min (throughout the deposition).

3.2.3 Substrate Cleaning (Plasma Cleaning)

For magnetron sputtering, the mechanism of substrate cleaning or plasma cleaning is similar to what happens at substrate by biasing during sputtering deposition. However, substrate cleaning or plasma cleaning is the pre-deposition treatment process using biasing to clean the substrate surfaces by removal of some contaminants or oxides at the nano or sub-micron scales (Figure 3.4). Since the substrate surface is treated, this could be beneficial tremendously for improving the coating-adhesion to substrate. In the present work, a RF power biased to the substrate was used to sputter clean the substrate surface at different levels by using sputter cleaning power of 150 W with varied sputter cleaning time of 20 min to 120 min.

Figure 3.4: Mechanism of substrate cleaning.

3.3 Post-deposition Treatment of Coatings

After deposition, some samples were annealed in a vacuum furnace at a pressure of 1.3×10^{-5} Pa at different temperatures, such as 450, 500 and 550 °C. The vacuum furnace was heated from room temperature to the desired temperature at the rate 10 °C per min. It was kept at the set temperature for two hours. The samples were then allowed to cool slowly in the furnace to room temperature. In addition, the annealing temperature was restricted by the tempering behaviour of the substrate materials (high speed steel). Thus, no

annealing experiments above 600 °C were attempted, since this will cause suffering of the HSS substrate.

3.4 Chemical Composition Analysis

When sputtering from compound targets, it is presumed that atomic species (i.e. Ti and B) leave the target (TiB₂), and it would be possible for the chamber walls to adsorb some of this species. Therefore, it was necessary to compare the composition of the targets with the coatings. X-ray photoelectron spectroscopy (XPS) measurements were carried out to analyse the chemical composition of selected coatings and to investigate chemistry bonding state by using a Kratos AXIS spectrometer (UK) with the monochromatic Al K α X-ray radiation at 1486.71 eV. The base vacuum in XPS analysis chamber was about 1.3×10^{-5} Pa.

3.5 Residual Stress

Measurements of the residual stress of the resultant coatings were carried out using the Tencor Stress Measurement System (Model FLX-2908). Figure 3.5 shows a schematic diagram of the Tencor Stress Measurement System [111] for films on a silicon substrate. The radius of curvature is the real value from measurement. The bare silicon wafer (100×100 mm²) and thin atop wafer are measured as before and after deposition. The average radius R_1 is obtained by measuring of the radius of curvature of bare substrate. $1/R_1$ equals half the slope obtained from the linear regression. After the film is deposited, the substrate deforms to a new radius R_2 .

Since the stress is proportional to $1/R_1$, it follows that

$$\frac{1}{R_{eff}} = \frac{1}{R_2} - \frac{1}{R_1} \quad (3.1)$$

or

$$R_{eff} = \frac{R_1 R_2}{R_1 - R_2} \quad (3.2)$$

The thin film stress is now determined by using the effective radius R_{eff} in the standard equation [112] described below:

$$\sigma_f = \frac{Et_s^2}{(1-\nu) 6R_{eff} t_f} \quad (3.3)$$

where $\frac{E}{1-\nu}$ is the biaxial elastic modulus of the substrate (1.805×10^{11} Pa for (100) silicon wafers), t_s is the substrate thickness (m), t_f is the film thickness (m), R is the substrate radius of curvature (m) and σ_f is the average film stress (Pa). It is also noted that Eq. 3.3 is valid when the substrate is much thicker than that of the deposited film, which is easily satisfied in this study.

Figure 3.5: A schematic diagram of the stress measurement.

However, Eq. 3.3 is used to calculate the stress on the silicon substrate, which visibly deflects. In the case of high-speed steel, the HSS substrate cannot be visibly deflected. Thus, it is impossible to measure the stress of the coating on the HSS substrate by Tencor Stress Measurement System. This indicates that the residual stress values

obtained from the Tencor Stress Measurement System cannot represent the real values of coating's residual stress onto HSS substrate.

3.6 Structural Characterization

The deposited TiB₂-based coatings were investigated by X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), scanning electron microscopy (SEM), ball cratering, atomic force microscopy (AFM) and the three-dimensional profilometer.

3.6.1 X-Ray Diffraction (XRD)

X-ray diffraction was used to measure the phase composition and orientation of the coatings. The samples for the present work were analyzed by an X-ray diffractometer (Rigaku Dmax 2200). Glancing-angle ($\theta/2\theta$ -standard) XRD spectra were obtained using Cu target at an incident angle of 2 degrees. The X-ray generator setting was 50 kV and 30 mA. The step-angle size was 0.02 degrees and the scanning speed was 2 degrees/minute. The scanning 2θ range was done from 20 to 80 degrees.

A detailed description of the X-ray diffraction theory has been given elsewhere [113-114]. Briefly, when a beam of X-rays strikes a single crystal, diffraction occurs only for certain definition of crystal such that the Bragg condition is satisfied.

$$n\lambda = 2d \sin \theta \quad (3.4)$$

When the orientation of any plane in the crystal is such that the glancing angle, θ , becomes equal to $\sin^{-1} (n\lambda/2d)$, then that plane reflects x-rays.

For the conventional $\theta/2\theta$ scanning method, the specimen is rotated so that the incident angle of the specimen and the X-ray is θ . The crystal plane that causes diffraction is parallel to the surface of the specimen. Therefore, for a specimen which has a certain lattice plane and is strongly oriented with respect to the surface of specimen, the peak from the crystal plane is very strong. On the other hand, a very weak-peak shows

that the crystal plane is not oriented (random) to the surface of specimen. Since sputtered coatings always have preferred-orientation, this approach is then valuable for studying the coating orientation.

3.6.2 Secondary Electron Imaging (SEI)

Scanning electron microscopy (SEM), (JEOL 5410LV), and field emission scanning electron microscopy (FESEM), (JEOL 6340F), were used to examine the morphology of the surfaces and fractured cross-sections of the films.

The SEM shows detailed 3-dimensional images at much higher magnifications than with a light microscope. The images created without light waves are rendered black and white. Samples need to be prepared carefully to withstand the vacuum inside the microscope. In the case of non-conductive samples, the SEM samples need to be coated with a very thin layer of gold by a machine called a sputter coater. During the analyzed procedure, the electron beam hits each spot on the sample; secondary electrons are knocked loose from its surface. A detector counts these electrons and sends the signals to an amplifier. The final image is built up from the number of electrons emitted from each spot on the sample [115].

Energy Dispersive Spectroscopy (EDS) analyses are also available using a JEOL 5410LV. A focused beam of electrons is scanned across a sample surface and synchronized with the raster of a cathode ray tube. The secondary electrons or backscattered electrons produced are detected and used to adapt the brightness of the cathode ray tube. The stored signal is then a detailed map of the sample surface. Since the electron beam also generates the emission of X-rays characteristic of the elements present, energy dispersive analysis of the X-rays provides a means of elemental identification.

In the case of FESEM, the brightness of the primary electron source is comparatively high, which avoids the necessity of using high accelerating voltages for improved lateral resolution as well as charging of poorly conducting samples [116]. In

the present work, the operating conditions for SEM and FESEM are summarized in Table 3.2.

Table 3.2: Summary of operating conditions for SEM and FESEM examinations.

Operating conditions	SEM	FESEM
Voltage	3-15 kV	5-10 kV
Magnification	Low	up to 100,000 x
Working distance	10 mm	7-8 mm

3.6.3 Atomic Force Microscopy (AFM)

AFM studies were conducted using a commercial Digital Instrument Nanoscope-III. The operation principle of AFM consists of a fine ceramic or semiconductor tip scanning the surface of the sample as shown schematically in Figure3.6. A silicon nitride tip with radius less than 10 nm (as claimed by the manufacturer) was used in the tapping mode at the scan size of 10 microns to obtain the three dimensional surface topography as well as average roughness (R_a) of the coatings. The tip is located at the end of a cantilever beam, which deflects according to the force of interaction with the surface. This force is measured by the deflection of a light beam that is reflected from the upper side of the cantilever beam and imprinting on a detector, which determines the position of the cantilever.

The fact that the tip is actually touching the surface makes the AFM a very reliable and accurate tool for estimating the surface topography. Typical transverse resolution for AFM goes down to within 0.1 nm and 1 μ m, and depth resolution has an average value of 0.5 nm. In spite of its high resolution, the AFM has been drawn back due to the relatively slow scan, very small space of probe to sample, difficulty to use in deep holes and easiness of damaging the tip during the test [117].

Figure 3.6: Schematics of the atomic force microscopy [117].

3.6.4 Ball Crater

The coating thickness was measured by making a ball-crater on the coating surface (Figure 3.7) using the Calotest machine manufactured by CSM (Switzerland). A stainless steel ball of 25.4 mm diameter was used for cratering with a speed of 500 rpm for 240 s. The equation to calculate the coating thickness is shown below [118].

$$\text{The total depth of penetration is: } T = R - \left(\frac{1}{2} \sqrt{4R^2 - D^2} \right) \quad (3.5)$$

where R is the ball radius and D is the diameter measured on the substrate.

$$\text{The depth of penetration in the substrate equals: } t = R - \left(\frac{1}{2} \sqrt{4R^2 - d^2} \right) \quad (3.6)$$

$$\text{The thickness of the coating is therefore: } s = T - t = \frac{1}{2} \left(\sqrt{4R^2 - d^2} - \sqrt{4R^2 - D^2} \right) \quad (3.7)$$

$$\text{Substitute } x - y = d \text{ and } x + y = D \text{ into Eq.3.7, then: } s = \frac{xy}{2R} \quad (3.8)$$

Figure 3.7: Ball crater calculation.

3.6.5 Three Dimensional Profilometer

Three dimensional profilometer (TALYSCAN 150, Taylor/Hobson Precision) was used for measuring the surface topography and profile across the wear track or groove resulted wear testing. This could help to understand the wear behaviour of coatings under the applied load. In addition, the wear volume or wear rate could also be calculated from the measured wear track volume.

3.7 Characterization of Properties

3.7.1 Ball-on-disc Tribometer Wear Test

A ball-on-disc tribometer (CSEM 15-208 Instruments, Neuchatel, Switzerland) was used to perform dry sliding friction and wear experiments on the film, as shown in Figure 3.8. The ball-on-disk test was performed on the coated sample by using a bearing

steel ball and an alumina ball (Al_2O_3) as the counterface slider, which has a diameter of 6 mm. The geometrical and mechanical properties of the balls are listed in Table 3.3.

Table 3.3: The geometrical and mechanical properties of the slider balls.

Materials	Ball Diameter (mm)	Composition (wt%)	Hardness (GPa)	Elastic Modulus (GPa)
Stainless Steel	6	1C, 16Cr, 1Mn, 1Si, 0.75 Mo	7	200
Alumina	6	99 Al_2O_3	18	370

Figure 3.8: Ball-on-disc tribometer equipment.

The available load of 1, 2, 5 or 10 N can be applied for the test. The sliding velocity and an accumulated sliding distance could be set in each test. In this dissertation, the ball-on-disk tests were conducted in ambient air conditions, at 23 °C and relative humidity of 50%. The operating conditions are listed in Table 3.4.

Table 3.4: Operating conditions for dry sliding wear test.

Load (N)	1, 2, 5, 10
Sliding speed (cm s^{-1})	2, 20
Sliding distance (m)	100, 200
Wear track radius (mm)	3, 4, 5
Temperature	Room temperature
Humidity	Ambient humidity

3.7.2 Nanoindentation Test

The indentation procedure is described here with reference to the NanoTest™ system (Micro Materials Ltd., Wrexham, United Kingdom). The NanoTest™ device measures the movement of a calibrated diamond indenter penetrating into a specimen surface at a controlled loading rate. The schematic diagram of the NanoTest™ system is shown in Figure 3.9. This device uses a pendulum pivoted on bearings which are essentially frictionless. A coil is mounted at the top of the pendulum so that when a coil current is present, the coil is attracted towards a permanent magnet, producing motion of the indenter towards the specimen and into the specimen surface. The displacement of the diamond is measured by means of a parallel plate capacitor, one plate of which is attached to the diamond holder; when the diamond moves, the capacitance changes, and this change is measured by means of a capacitance bridge [119].

The indenter used in this work is a Berkovich diamond, a three-sided pyramid, which is widely used for nanoindentation work because it can be machined down very accurately to a very sharp tip with a curvature radius of one half of a nanometer. The NanoTest™ device is capable of resolutions of the order of 0.1 μN and 0.1 nm for the load and displacement respectively, depending on the load and displacement ranges used. For the purpose of statistics and reliability, it is recommended to use ten loading/unloading curves in each experiment. The experiment then involved indenting the specimen to ten different peak depths and recording the load-displacement data during the loading and unloading stages. In the present work, the experimental conditions are listed in Table 3.5.

Table 3.5: Summary conditions of nanoindentation test.

Experimental conditions	Details
Mode	Depth controlled
Penetration depth	50 nm
Maximum load	10 mN
Loading/unloading rate	0.05 mN/s
Dwelling time	10 s
No. of indentations	10 times
Analysis techniques	Oliver and Pharr’s Method [77]
Indenter	Berkovich

Figure 3.9: Schematics of the NanoTest™ equipment [119].

3.7.3 Microscratch Adhesion Test

In this dissertation, the microscratch adhesion was performed using either the single-pass scratch test or the multi-pass wear test mode available in the NanoTest™ device with an indenter topped with a conical shape having spherical end form of $25\text{ }\mu\text{m}$ in radius. The stylus was moved tangential to the surface at desired speed ($\mu\text{m/s}$) over a desired length (μm). At the same time, the applied load was increased linearly at a desired rate (mN/s) until reaching the set load (mN). All scratch tests were performed at ambient temperature. Figure 3.10 shows a typical friction versus scratching distance curve measured during the single-pass microscratch test. The friction curve can be divided into three characteristic regimes: a smooth unload region (initial length A to B), followed by a smooth increase region (B to L_C), and a sudden increase and then a large fluctuating region (L_C to C). As confirmed by microscopic examination, the sudden change in friction during scratch test is due to coating adhesive failure, and the

corresponding load (L_C) is thus used as a measure of the adhesion strength of the TiB_2 coating to the HSS substrate. Table 3.6 summarises the typical conditions used for the single-pass microscratch test.

Figure 3.10: Schematic of the single-pass microscratch test, showing the scratch profile as confirmed by the SEM investigation.

Table 3.6: Summary conditions for single-pass microscratch test.

Scratch load (mN)	3,000
Scanning velocity ($\mu\text{m/s}$)	25
Scanning length (μm)	3,050
Initial length (μm)	50
Scan direction	-Z
Loading rate (mN/s)	25
Depth gain (%)	70

In addition, the multi-pass microscratch mode available in the NanoTestTM device was also used to test selected samples. This is a new test method employed in this work, as described by Xia et al [120] and detailed below with reference to Figure 3.11.

For each test, a set of surface profiles along the track was measured. Firstly, the initial track profile before scratch or surface topography (BS profile in Figure 3.11) was

measured by scanning across the full length of distance to be scratched with a small load of 0.25 mN. Then, the scanned length was scratched by applying a linearly increasing load at 5 mN/s after prescanning the initial 300 μm distance under a small initial load of 0.25 mN (from A to B in Figure 3.11). During scratching, the friction force on the indenter and the surface profile along the full length of the scratched track were measured continually, such that a friction force versus scratching distance (or load) curve and a during-scratch profile (DS profile in Figure 3.11) were obtained. The critical load for coating failure (L_C) was determined by the sudden change in friction force, which also led to a sudden change in the DS profile as schematically shown in Figure 3.8. After the scratch test, a third profile was measured with a small load of 0.25 mN along the full length to obtain an after-scratch profile of the track (AS profile in Figure 3.11). The difference between BS and DS profiles indicates the total scratch depth including elastic and plastic deformation and surface damage during the scratch process. The difference between BS and AS profiles represents the depth of the scratch groove remaining on the coating surface after the scratch test. Obviously, the difference between AS and DS profiles provides important information on elastic recovery of the coated surface after the scratch test.

The surface profiles obtained from the scratch test outlined above can thus be divided into several regions (Figure 3.11). Firstly, the region from point A to B is the pre-scan region under a small load of 0.25 mN, where no scratch damage occurred and the three profiles (BS, DS and AS) are the same. In the region from B to Y, DS profile increases with increasing load, but there is no plastic deformation or material loss in this region because the scratch depth is fully recovered after the scratch test, as evidenced by the same BS and AS profiles in this region. After point Y, plastic deformation or material loss starts, which leads to continually increased AS profile until point C, at which the DS and AS profiles change suddenly due to the failure of the coating. The load at point Y is hence crucial because it is a maximum scratch load that the coating can sustain without plastic deformation. This critical load is called the “Yield Load (L_Y)”. The critical load measured at point C (L_C) signifies the start of the failure of the coating and this is a measure of the adhesion strength of the TiB_2 coating to the HSS substrate.

Figure 3.11: Schematic of the multi-pass microscratch test, showing the before-scratch (BS) profile, the during-scratch (DS) profile, the linearly increasing load during scratch and the after-scratch (AS) profile.

Chapter 4

Modelling and Simulation of Nanoindentation and Microscratch Processes

In order to gain a better understanding of the nanoindentation procedure and microscratch processes, finite element modeling (FEM) was performed and discussed. All indentation and scratch modeling were performed with a commercial ABAQUS software programme at the Surface Engineering Laboratory, School of Materials Science and Engineering, Nanyang Technological University.

4.1 The ABAQUS Finite Element Software [121]

At present, ABAQUS software is one of the recognised software packages for advanced finite element analysis. The ABAQUS software package has a good reputation for technology, quality, and reliability. It has been adopted by many major corporations across all engineering disciplines as an integral part of their design process. ABAQUS software provides superior solutions for linear, nonlinear, explicit, and multi-body dynamics problems. The capability of ABAQUS software covers the following topics;

- Linear and nonlinear structural analysis
- Static, dynamic, and heat transfer analysis
- Material models: linear elasticity, hyper elasticity, and metal plasticity.
- Loads and constraints
- Modeling contact
- Selecting the appropriate elements for your problem
- Feature-based modeling, parts, and assemblies
- Working with CAD geometry and imported meshes
- Mesh generation techniques
- Creating, submitting, and monitoring analysis jobs
- Viewing simulation results
- Restarting an analysis.

4.2 Nanoindentation Simulation

Different numerical methods have been developed and can be used in indentation problems. Bhattachaya and Nix [122] used the finite element (FE) technique with a two-dimensional (2-D) model to solve the indentation problem with an axisymmetric conical indenter. This cone shape is constrained to have the same volume as a pyramid-shaped indenter for a given depth. Their FE hardness results compared well with experimental data. They also presented an elastoplastic analysis of axisymmetric conical indenter and showed that the shape of the plastic zone strongly relies on the indentation angle, Young's modulus and yield stress [123]. Sun et al [124-125] developed an axisymmetric FE model to simulate the indentation of coating-substrate systems using a conical indenter. The axisymmetric indenter is constrained to have the same projected area of the Berkovich indenter, as a function of the indentation depth. Three-dimensional (3-D) FE models have been developed to investigate the indentation response in coated systems and bulk materials by Licinchi et al [126], Wang and Bangret [127], and Knapp and Follstaedt [128], whilst Muliana used an artificial neural network (ANN) technique for nanoindentation processes simulation [129]. The complex deformation field is demonstrated by the 3-D model as well as the load and displacement curves. It was found that the load and displacement curves extracted from the 2-D model compares well to results from the 3-D model, showing that the 2-D model is computationally affordable [126].

Kennedy and Ling [130] used the FE method to analyze the indentation problem of a thin elastic-plastic coating deposited on different substrates. They showed that the indenter size, the contact pressure, the coating thickness, and the coating and substrate properties affect the yielding event. Komvopoulos [131] used elastic-plastic FE analysis to calculate the stress distribution of an indented ceramic coating on a metallic substrate. It was shown that the coating thickness and the mechanical properties of the coating and the substrate significantly affect the contact pressure profile on the contact surface. Also, it was found that yielding in the layered medium always initiates at the coating-substrate interface below the center of contact and the plastic zone does not grow toward the surface of the indented layered medium but is restricted to the boundary of the hard coating and the substrate. Similar FE analysis of a rigid indenter on an elastoplastic two-layered system has been

conducted by other investigators [132-134]. The Hertz theory and FEM have been combined by Djabella and Arnell [135] to analyze elastic stresses in single, double, and multilayer systems.

4.2.1 The Modelling Procedure

In this dissertation, all of the nanoindentation models and microscratch models were developed following the flowchart diagram shown in Figure 4.1, which was based on the FEM supported algorithm.

Figure 4.1: Flowchart of nanoindentation modeling.

Two models have been developed in this work i.e. the model of the single-layer ceramic coating with a Ti interlayer and the multilayer model by simulating the real coating/substrate condition such as coating thickness. In order to enhance the accuracy of the model, the indenter tip radius was modeled using the same geometry as the real tip radius in nanoindentation experiment (Figs. 2.13 and 2.14). The models have the ability to simulate the loading-unloading curves, study the influence of film structure and properties on indentation response, simulate the development of plastic deformation during indentation for the single-layer and multilayer systems, and extract intrinsic material property data from the test. These models are described in more details in following sections.

4.2.2 The Modelling Assumptions

All the nanoindentation models developed (both the single-layer model and the multilayer model) were based on the following assumptions.

- (1) There is no strain hardening of the materials used in the models.
- (2) All the coating and substrate materials were assumed to be isotropic (linear elastic-perfectly plastic materials).
- (3) There is a perfect interface between the indenter and the coating.
- (4) There is a perfect coating adhesion between coating and substrate.
- (5) The strain continuity condition is applied to the modeled specimen automatically in order to maintain the interface in each layer, so that the layer will not be debonded during indentation process.

4.2.3 Single Layer TiB₂ Coatings on High-Speed Steel Substrate with a Ti Interlayer

Since coatings have been fabricated by having an interlayer such as Ti, single layer TiB₂ coatings on high-speed steel substrate with a Ti Interlayer was developed instead of mere single-layer model. The indentation process under consideration involves a coating perfectly adherent to an interlayer and a substrate indented by a rigid indenter under the condition of frictionless contact. The indenter has a half-angle of 70.3°, and thus has the same projected area-depth function as the standard Berkovich indenter. The use of a conical indenter simplifies the analysis to a two dimension (2-D) axisymmetric problem.

Accordingly, the indentation process can be modelled with the finite element mesh shown in Figure 4.2 (a). A total of 1892 four-node axisymmetric reduced integration elements (CAX4R element type [121]) were used to model the semi-infinite layered medium. A very fine mesh was used in the coating and the substrate adjacent to the contact zone. The mesh was continuously coarsened further away from the contact area (Figure 4.2 (b)). Three element sets, one corresponding to the coating, one corresponding to the Ti-interlayer and the other to the substrate, were used to define separately the elastic and plastic properties of the coating, interlayer and the substrate materials.

Figure 4.2: The finite element mesh and boundary conditions (a) and the details of the mesh in the region near the tip of the indenter during the loading stage (b).

In order to detect the contact between the coating surface and the rigid indenter, the contact constraint was defined by choosing the indenter as the master surface and the coating surface as the slave surface, where only the master surface can penetrate into the slave surface. The contact or separation between the master surface and slave surface nodal points was automatically detected and monitored in the programme.

The boundary conditions of the present model are also illustrated in Figure 4.2(a). Roller boundary conditions were applied to the centreline and bottom surface nodes, whilst the outer right-hand side nodes were assumed traction-free. The validity of the described finite element model and programme has been tested by comparing the finite element results for the elastic contact between a half space and a rigid sphere, with the results of the analytical Hertz solution. Figure 4.3 indicates the normalized pressure distribution along the radius of the contact zone. It can be seen that very good agreement has been achieved between the FE and the analytical solutions [124]. The developed model has the ability to simulation the load-unload stages of the indentation process of any single-layer coating system, to study the plastic deformation behaviour in the coating on substrate and to extract mechanical properties from experimental indentation tests.

Figure 4.3: Pressure distribution in the contact zone obtained by the FE and the analytical solutions of elastic contact between the HSS halfspace and a rigid sphere (a , half contact width; r , distance from contact centre) [124].

For the purpose of using the developed model to extract the intrinsic mechanical properties of the coating system, several combinations of modulus (E_{TiB_2}) and yield strength (Y_{TiB_2}) of TiB_2 coating were used in the computation, as listed in Table 4.1, whilst the properties of Ti and HSS remained constant (Table 4.2). The hard coating and interlayer were perfectly adhered to the substrate and were indented by a rigid conical indenter. The set of E_{TiB_2} and Y_{TiB_2} that yields the best fit between the simulation load and unload curves and those of experiments is regarded as being the intrinsic properties of the TiB_2 coating.

Table 4.1: Material properties of TiB_2 used in the FE model.

No.	Young Modulus, E (GPa)	Yield Strength, Y (GPa)	Poisson Ratio
1	250	10	0.25
2	250	12	0.25
3	260	11	0.25
4	260	12	0.25
5	260	13	0.25
6	270	12	0.25
7	270	13	0.25
8	300	10	0.25

Table 4.2: Mechanical properties of Ti, TiB_2 , and HSS used in the FE model.

Material	Young’s Modulus, E (GPa)	Yield Strength, Y (GPa)	Poisson’s Ratio
Ti	200	0.5	0.30
TiB_2	250-300	10-13	0.25
HSS	225	4	0.30

For the experimental results, the Ti/ TiB_2 coating was deposited onto the HSS substrate experimentally, with a thickness of 0.15 μm and 1.25 μm for Ti and TiB_2 , respectively, as illustrated in Figure 4.4 (sample 1 in Table 5.7). Nanoindentation test was then performed using the NanoTestTM, with a Berkovich diamond indenter, to a depth of 50 nm.

Figure 4.4: The dimension of the Ti/TiB₂ coating, which follows the real coating dimension, used in this study.

In the calculation, the elastic deformation occurs in the beginning of the process. The Mises yield criterion is applied in the occurrence of the plastic deformation. The Mises stress equation is given by the expression

$$\sigma_{Mises} = \sqrt{\frac{(\sigma_1 - \sigma_2)^2 + (\sigma_2 - \sigma_3)^2 + (\sigma_3 - \sigma_1)^2}{2}} \quad (4.1)$$

where σ_1 , σ_2 and σ_3 are the three principle stresses. When the σ_{Mises} reaches the yield strength (Y), the specimen starts to deform plastically. There is no strain-hardening behaviour of the specimen considered in the model.

4.2.4 The Multilayer Ti/TiB₂ Models

At present, in the case of multilayer systems, very few FE models have been proposed in the literature for simulating the indentation process [133]. In this work, the multilayer systems have been proposed in order to overcome the problem of brittleness and the high residual stress of the TiB₂ coating, as mentioned in chapter 2. In practice, the uses of multilayer surface coatings offer suitable advantages when complimentary coating layers are chosen, for example, the use of alternate layers of ceramic and ductile materials to protect against erosion in gas turbine compressors [136] and the use in dry cutting applications [137-138]. The simulation modeling is significant for multilayer systems in order to gain a better understanding of its mechanical properties as well as deformation behaviour.

During the indentation process, the indenter or stresses may pass through several layers. This may cause errors and difficulties in interpretation because the values of the properties obtained will depend on the depth of indentation and the number of layers penetrated, as well as the substrate effect. In order to get a better understanding in this system, a six-layer coating were simulated by alternating the hard with the soft layers at the same dimensions as the experimental coatings. Figure 4.5 shows the model of the multilayer system of six layers by alternating the hard coatings (layer 2, 4, 6) with soft coatings (layers 1, 3, 5). The material properties used in the simulation for the multilayer systems in a case study are given in Table 4.3.

Table 4.3: Mechanical properties of Ti, TiB₂, and HSS used in the multilayer FE model.

Material	Young's Modulus E (GPa)	Yield Strength Y (GPa)	Poisson's Ratio
Ti	200	0.5	0.30
TiB ₂	350	10.0 to 15.0	0.25
HSS	225	4.0	0.30

Figure 4.5: Mesh of the specimen of multilayer system of six layers model.

The indentation process of the multilayer model involves the hard layers perfectly adherent to alternate soft layers and a substrate indented by a rigid indenter under the condition of frictionless contact. The indenter has a half-angle of 70.3° , and thus has the same projected area-depth function as the standard Berkovich indenter. The use of a conical indenter simplifies the analysis to a two dimension (2-D) axisymmetric problem. Accordingly, the indentation process can be modelled with the finite element mesh shown in Figure 4.6. A total of 2,453 four-node axisymmetric reduced integration elements (CAX4R element type) were used to model the semi-infinite layered medium. A very fine mesh was

used in the coating and the substrate adjacent to the contact zone. The mesh was continuously coarsened further away from the contact area (Figure 4.6). Three element sets, one corresponding to the hard layers, one corresponding to the soft layers and the other to the substrate, were used to define separately the elastic and plastic properties of the coating and the substrate materials.

Figure 4.6: The finite element mesh and boundary conditions and details of the mesh in the region near the tip of the indenter during the loading stage.

The boundary conditions of the present model are also illustrated in Figure 4.6. Roller boundary conditions were applied to the centre-line and bottom surface nodes, whilst the outer right-hand side nodes were assumed traction-free.

4.3 Microscratch Simulation

In order to gain a better understanding of the scratch behaviour during the test, attempts have also been made to simulate the scratch process of the coating-substrate system using the finite element (FE) method. The plastic deformation behaviour of the coating indented by a rigid conical indenter has been analysed to study the elastic-plastic behaviour and the stress-strain of the coating during the scratch process.

4.3.1 Finite Element Modelling of Microscratch Test

The scratch process was designed based on three steps i.e. loading (indentation), sliding and unloading. Although the scratch process which involves elastic-plastic deformation has been modelled and simulated for bulk materials using finite element method by some investigators [139-140], very few have modeled the scratch process of coating systems [141]. It is recognized that the scratch process in relative motion is a very complex system, and they are neither easy to understand nor easy to predict. In the present study, a three-dimensional (3-D) model has been developed by using the capacities of the ABAQUS finite element (FE) code [121].

The scratch process under consideration involves a hard coating (such as TiB_2) on a substrate (such as HSS) scratched by a rigid conical indenter. The conical has a spherical end form of 25 μm in radius, which is the same as the experimental indenter. Accordingly, the scratch process can be modelled with the finite element mesh shown in Figure 4.7. A very fine mesh was used in the coating and the substrate adjacent to the contact zone. The mesh was continuously coarsened further away from the contact area. Two element sets, one corresponding to the coating and the other to the substrate, were used to define separately the elastic and plastic properties of the coating and the substrate materials. Sample S2-1 (Table 5.3) with the coating thickness of 700 nm was used for modeling as a tested sample in this FE model (Figure 4.7).

In order to detect the contact between the coating surface and the rigid indenter, the contact constraint was defined by choosing the indenter as the master surface and the coating

surface as the slave surface, where only the master surface can penetrate into the slave surface. The contact or separation between the master surface and slave surface nodal points is automatically detected and monitored in the programme.

Figure 4.7: FE model of scratch process.

4.3.2 The Modelling Assumptions

Since strain-hardening was not considered in this work, all the coating and substrate materials were assumed to be isotropic, linear elastic-perfectly plastic materials. In addition, no coating residual stresses were considered in the model. For isotropic materials, elastic deformation ceases and yielding commences when the von Mises yield criterion is satisfied. To simplify the analysis, the adhesion between the stylus and the coating surface was ignored, such that the tangential force induced during sliding was caused only by the ploughing acting of the stylus. The Ti interlayer was negligible since the thickness of Ti interlayer is too small.

Table 4.4 lists all the material properties used in the FE calculation. Table 4.5 lists the micro-scratch conditions used in this FE model. Nevertheless, the above FE model is oversimplified the real scratch test, in that the real continuous test was simulated by a model

with step-wise process and frictionless interface. The results of simulation may only be compared qualitatively with experiments.

Table 4.4: The mechanical properties used in the FE model.

Material	Young's Modulus	Yield Strength	Poisson's ratio
	E (GPa)	Y (GPa)	
Coating (TiB ₂)	350	7	0.25
Substrate (HSS)	225	3	0.30

Table 4.5: Simulation test conditions.

Mode of scratch test	Constant applied load
Load	240 mN
Sliding distance	15 µm
Scratch indenter tip radius	25 µm

Chapter 5

Results and Interpretation

5.1 Single Layer TiB_2 Coatings on High-speed Steel Substrate with a Ti Interlayer

5.1.1 Introduction

Two sets of experiments were first conducted to study the effect of various parameters on the structure and properties of single layer TiB_2 coatings with a Ti interlayer (Figure 5.1). The purpose of depositing a thin Ti interfacial layer by sputtering a pure Ti target for a few minutes is to increase the adhesion between HSS substrate and TiB_2 coating. The first set was performed without substrate cleaning and biasing with the purpose to determine the best combination of other parameters in terms of structure and properties. The second set employed the optimized condition obtained from Set 1 and introduced substrate sputter cleaning and biasing during deposition to further enhance the structure and properties characteristics.

Figure 5.1: Schematic of single layer TiB_2 coating on HSS with a Ti interlayer.

Figure 5.2: FESEM image of fractured cross-section of samples S1-6.

5.1.2 Structural and Property Characterization of Set 1 Samples

Table 5.1 summarizes the deposition conditions and Table 5.2 summarizes the properties of Set 1 samples. Typical fractured cross-sectional morphology of selected coatings in this Set is given in Figure 5.2, which shows the columnar growth of the TiB_2 coatings and a thin Ti interlayer. Details of structural and properties features are given below.

Table 5.1: Summary of deposition conditions for TiB₂ coatings.

Sample	Substrate Temperature (°C)	Ti Power/Time	TiB ₂ Power/Time	TiB ₂ Target/ Substrate Distance
S1-1	RT	150 W/ 5 min	150 W/ 2 hours	100 mm
S1-2	100	150 W/ 5 min	150 W/ 2 hours	100 mm
S1-3	200	150 W/ 5 min	150 W/ 2 hours	100 mm
S1-4	300	150 W/ 5 min	150 W/ 2 hours	100 mm
S1-5	300	300 W/ 5 min	300 W/ 2 hours	100 mm
S1-6	400	350 W/ 20 min	350 W/ 3 hours	100 mm
S1-7	400	200 W/ 10 min	200 W/ 3 hours	60 mm

Table 5.2: Summary of the resultant coating properties.

Material	Coating Thickness (μm)		TiB ₂ Texture	Hardness (GPa)	Elastic Modulus (GPa)	Critical Load (mN)
	Ti	TiB ₂				
S1-1	0.05	0.35	(101)	8.2	166.6	20.8
S1-2	0.05	0.35	(101)	10.0	184.1	21.1
S1-3	0.05	0.35	(101)	8.1	171.7	26.5
S1-4	0.05	0.40	(101)	7.8	171.6	10.2
S1-5	0.10	0.65	(101)	11.1	189.5	18.1
S1-6	0.25	0.75	(101), (001)	17.1	208.5	65.0
S1-7	0.15	0.55	(001)	28.4	307.2	74.5

5.1.2.1 X-ray Diffraction Analysis

X-ray diffraction analysis shows that all the TiB₂ coatings produced with low TiB₂ target power (samples S1-1 to S1-4) exhibit a broad diffraction peak corresponding to the TiB₂ phase irrespective of deposition temperature (Figure 5.3). Small peaks of Ti were also found as expected. The presence of a single peak suggests a fiber texture with preferred (101) orientation in the TiB₂ coatings.

From the literature, most of the TiB₂ coatings reported display the patterns of the hexagonal phase with a preferred (001) orientation [22, 142-144] and the (001) oriented coatings yield the highest hardness [145]. The hexagonal TiB₂ phase in samples S1-1 to S1-4 did not demonstrate the preferred (001) orientation even with increased temperature to 300 °C. It is noted that since the (001) plane has the highest packing factor, energetic adatom are required to create such an orientation [19]. With this in mind, further

depositions were conducted by increasing the deposition power from 150 W to 300 W (sample S1-5). Unfortunately, this has little effect on the orientation of TiB_2 coating (Figure 5.3). Attempts were thus made to further increase the sputtering power to 350 W, substrate temperature to 400 °C and deposition time to 3 hours (sample S1-6). In this case, the (001) reflection appears in the diffraction pattern, indicating that the coating starts to orient in this direction. It thus appears that increasing sputtering power, substrate temperature and deposition time, favours the evolution of the (001) orientation.

Figure 5.3: XRD patterns generated from single layer TiB_2 coatings with a Ti interlayer in Set 1.

In order to enhance the development of the desired (001) orientations, another deposition was conducted by reducing the TiB_2 -target-substrate distance from 100 mm to 60 mm (sample S1-7). The sputtering power was reduced to 200 W because it was found that the TiB_2 target cracked after several depositions at 300 W. The XRD result shown in

Figure 5.3 reveals the development of a strong (001) texture in the coating. Thirteen depositions were thus conducted in Set 2 with this combination of parameters (S1-7).

5.1.2.2 Coating Properties

(a) Nanoindentation Test

Although nanoindentation has been carried out at various indentation depths, due to the small thickness of the coating (Table 5.2), the hardness and modulus values summarized in Table 5.2 were obtained from 50 nm depth, which is expected to minimize substrate effect. It can be seen that all the TiB_2 coatings with (101) orientations (samples S1-1 to S1-5) exhibit hardness and modulus values lower than those expected for bulk TiB_2 and those reported by other investigators [19-21]. This low hardness would be due to the poor orientation, small thickness and poor adhesion of the coating. Indeed, with increasing coating (001) orientation, the highest hardness of 28.4 GPa was obtained in sample S1-7, which is close to many reported values [21, 24, 27].

It is also worth to note the response of the coating to large indentation depth. Figure 5.4 shows the load-displacement curves of sample S1-6 produced at 300 nm depth. It is noted that pop-in event (arrow points at 1) occurs during loading, whilst pop-out event occurs during unloading (arrow points at 2) of some indentations. These non-linear phenomena were observed commonly in the single layer TiB_2 coatings (samples S1-1 to S1-7), and is associated with the brittleness of the coating and poor coating/substrate adhesion, which lead to coating cracking or debonding during the indentation process.

In order to gain a better understanding of the indentation deformation and cracking behaviour, selected indents produced at large depth were examined by SEM, as shown in Figure 5.5 for sample S1-6. Figure 5.5 (a) shows an indent at 500 nm depth, from which it is clearly seen that the sink-in effect takes place. However, the coating is cracked if the indentation is made at 1,500 nm in depth (the coating thickness of sample S1-6 is only 950 nm) as shown in Figure 5.5 (b).

Figure 5.4: Load-displacement curves of sample S1-6.

Figure 5.5: SEM images of sample S1-6 at indentation depth (a) 500 nm (b) 1,500 nm.

(b) Microscratch Test

Coating adhesion was assessed using the Microscratch mode of the NanoTestTM. The simplest method for evaluating the critical load for coating failure is to plot friction force vs load. Optical and scanning electron microscopic (SEM) examinations were also used to confirm the results from the friction curve. The results are summarized in Table 5.2.

As expected, since samples S1-1 to S1-5 have a very thin coating thickness, cohesive failure could not be detected, and only adhesive failure could be found. The critical load, L_C , for adhesive failure of these coatings was found to be very low, in the range between 16 mN to 30 mN (Table 5.2). No correlation has been found between L_C and substrate temperature and sputtering power. Figure 5.6 shows a typical plot of the friction force vs load (sample S1-5).

The critical load was measured to be 65 mN in sample S1-6, which also showed a higher hardness. Sample S1-7 showed the highest L_C value of 74.5 mN, which also exhibits the highest hardness and strongest (001) orientation (Table 5.2).

Figure 5.6: Plot of the friction force vs load of sample S1-5.

5.1.3 Set 2 Samples

The results of Set 1 experiments presented above demonstrated that sample S1-7 possesses the (001) texture, highest hardness and adhesion. However the coating hardness and adhesion achieved are still relatively low compared with those reported in the literature [19-22]. Set 2 experiments were thus conducted using the deposition conditions of sample S1-7, but with sputter-cleaning of the substrate during the initial stage, and substrate biasing during deposition. Table 5.3 summarizes the deposition condition for this set. It should be noted that the only variables in this Set are sputter-cleaning and substrate bias. The other parameters are kept constant (S1-7, Table 5.1).

Table 5.3: Summary of deposition conditions and properties conducted in Set 2.

Sample	Sputter-cleaning of substrate	Substrate bias (W)	Thickness (nm)	Coating Texture	Hardness (GPa)	Modulus (GPa)	Critical load L_c (mN)
S2-1 (S1-7)	No cleaning	No biasing	700	(001)	28.4	307.2	74.6
S2-2	rf 150 W, 20 min	30 W for 3 h	690	(101)	10.8	212.5	343.2
S2-3	rf 150 W, 20 min	60 W for 3 h	650	(101)	15.7	220.7	286.3
S2-4	rf 150 W, 20 min	90 W for 3 h	510	(101)	15.2	215.3	247.3
S2-5	rf 150 W, 20 min	120 W for 3 h	500	(101)	18.3	207.9	214.5
S2-6	rf 150 W, 20 min	No Biasing	780	(001)	29.2	297.1	96.4
S2-7	rf 150 W, 60 min	No Biasing	730	(001)	31.7	327.9	123.3
S2-8	No cleaning	30 W for the first hour only	650	(001)	19.2	235.5	529.1
S2-9	rf 150 W, 20 min	30 W for the first hour only	650	(001)	23.5	264.5	322.7
S2-10	rf 150 W, 30 min	30 W for the first hour only	650	(001)	20.8	242.5	595.4
S2-11	rf 150 W, 60 min	30 W for the first hour only	600	(001)	23.6	275.1	648.5
S2-12	rf 150 W, 90 min	30 W for the first hour only	550	(001)	26.4	283.2	875.5
S2-13	rf 150 W, 120 min	30 W for the first hour only	550	(001)	18.6	271.2	701.1

5.1.3.1 Structural Characteristics

XRD patterns are shown in Figure 5.7 for all samples of this Set. As discussed previously, for sample S1-7 (S2-1), the TiB_2 coating produced without sputter-cleaning of substrate and biasing has a hexagonal structure with strong (001) preferred orientation. (001) orientation was found in all the coatings produced without substrate biasing (samples S2-1, S2-6, S2-7) and with small biasing (30 W) for the first hour of deposition only, which was followed by 2 hours deposition without bias (sample S2-8 to S2-13). It can also be seen that sputter-cleaning of the substrate before deposition seems to reduce the degree of this orientation (compare sample S2-1 with sample S2-6 and S2-7). However, increasing the substrate sputter cleaning time from 20 min (sample S2-6) to 60 min (sample S2-7) slightly promoted the TiB_2 (001) orientation.

Figure 5.7: XRD patterns generated from TiB_2 coatings of sample S2-1 to S2-13.

With the introduction of substrate bias for the entire deposition of 3 h (S2-2 to S2-5), the orientation of the TiB_2 coating is significantly changed. From Figure 5.7, it can be seen that with increasing bias power, the evolution of the (001) orientation decreased and the orientation changed to (101), especially in samples S2-4 (bias 90 W) and S2-5 (bias 120 W). This is in agreement with the work of Weidemann and Oettel [146]. The change of orientation may account for the observed decrease in hardness as discussed later.

The morphology and thickness of the deposited coatings were examined under FESEM. The thickness values of the coatings are summarized in Table 5.3. A thickness between 700 nm to 800 nm is typical of the samples produced without substrate bias, while the thickness of the coatings decreases with applied substrate bias. FESEM images of coating morphology and fractured cross sections of selected samples are shown in Figure 5.8. The coatings produced without substrate bias exhibit a columnar structure in the cross section. The size of the grains is in nanometer scale, typically less than 50 nm on the surface. Many grains have well-defined boundaries with the others. Sample S2-6 (Figure 5.8 (b)) and S2-7 (Figure 5.8 (c)) consist of columnars with rounded morphology, which is understood to be due to the confinement of surrounding crystals during growth process. Microcracks were observed within the coating in sample S2-7.

Figure 5.8 (a) shows the morphology and fractured cross-section of the coating produced with substrate bias (sample S2-2). It is clear that most of rounded crystals are replaced by worm-like ones with porosity at grain boundaries. In the cross-section, the coating shows a denser and nearly featureless morphology. This indicates that with biasing, the morphology of the resultant coating is changed, which may result in the change in mechanical properties such as hardness and modulus.

Figure 5.9 shows the fractured cross-section of the coating produced with substrate cleaning and substrate biasing at the only first hour of whole 3 hours deposition (S2-8 to S2-13). Indeed, the effect of biasing of 1 hour can be seen clearly at the area near the interface between the TiB_2 top layer and the Ti interlayer. The affected area from biasing shows the similar thickness to the Ti interlayer (Figure 5.9).

However, the feature of this region could not be identified. It can also be seen that this region shows a different structure as compared to the columnar structure of TiB_2 top layer. From Figure 5.9, the Ti interlayer could be seen and the region produced by biasing can also be found in the TiB_2 coating. This indicates that biasing can significantly change the structure of the TiB_2 top layer, which may affect the coating properties, in particular the coating adhesion due to the modified structure at the interface. From Table 5.3, it can

be seen that the coating hardness slightly decreases, whilst the coating adhesion increases significantly. This shows that biasing can change the coating structure and helps to enhance the adhesion. However, it is noted that biasing during the whole deposition deteriorates both hardness and adhesion (Table 5.3). This can be concluded that substrate biasing for a short time during the whole deposition can help to improve the coating adhesion, and still maintain the high hardness.

Figure 5.8: FESEM images showing the surface morphology and fractured cross-section of coatings of samples S2-2, S2-6 and S2-7.

Figure 5.9: FESEM images showing the fractured cross-section of sample S2-10.

5.1.3.2 Nanoindentation Test

In order to assess the intrinsic mechanical properties of the coatings, i.e. hardness and modulus, all specimens were tested at 50 nm (less than 10% of coating thickness) penetration depth to minimize the effect from substrate. Figure 5.10 shows the typical load-displacement curves of samples S2-1, S2-2 and S2-8. The hardness and modulus values as measured by nanoindentation are summarised in Table 5.3.

It can be seen that the (101)-oriented coatings produced with substrate bias have relatively low hardness and modulus (Table 5.3) and experience significant plastic deformation during the indentation process (e.g. sample S2-2 in Figure 5.10). The (001)-oriented coatings produced without substrate bias experience significant elastic recovery during the unloading stage (e.g. sample S2-1 in Figure 5.10) and possess much higher hardness, around 30 GPa and higher modulus between 300-320 GPa. Substrate sputter cleaning before deposition seems to slightly increase the hardness of the coating, although the degree of (001) orientation is reduced. It is therefore clear that applying substrate bias during the whole deposition period (3 hours) causes a drop in coating hardness and modulus, in agreement with the observation of others [146]. In order to achieve reasonably high hardness and modulus, it is essential that the TiB_2 coating maintains its (001) preferred orientation. The effect of sputter cleaning time on TiB_2 coating hardness and modulus is shown in Figure 5.11. Sputter cleaning can slightly increase coating hardness and modulus. However, the hardness and modulus decrease when the sputter cleaning time is more than 90 min as illustrated in Figure 5.11.

Figure 5.10: Typical load-displacement curves of samples S2-1, S2-2 and S2-9 extracted at the penetration depth of 50 nm.

Figure 5.11: The effect of sputter-cleaning time on hardness and reduced modulus.

5.1.3.3 Microscratch Test

Table 5.3 also summarises the critical load (L_C) for coating failure during micro-scratch test. It can be seen that the coatings produced without substrate bias (samples S2-1, S2-6, S2-7), although exhibit high hardness, show low values of L_C , which indicate poor coating adhesion strength. In addition, it can be seen that substrate sputter cleaning helps to improve coating adhesion and with increasing sputter cleaning time, the L_C value increases. On the other hand, the coatings produced with substrate bias show high values of L_C , particularly with low bias power (30 W), although these coatings have low hardness.

Figure 5.12 demonstrates the typical scratch curves with linearly increasing load for a TiB_2 coating (Sample S2-2). It can be seen that DS profile during scratch increases linearly with increasing load. As mentioned in Chapter 3, the profiles in Figure 5.12 can be divided into several regions. Firstly, the region from A to B shows the pre-scan (300 μm) under the load of 0.25 mN, where no scratch damage occurred, since BS, DS and AS have the same profile. Secondly, in the region from B to C, DS profile increases almost

linearly with increasing load. However, there is no plastic deformation or material loss that has taken place during this period, which showed the elastic recovery of TiB_2 coating represented by having the same profile of AS and BS. It is noted that after point C, plastic deformation or material loss starts. From the region C to D, all profiles are relatively smooth until point D. It is obvious that there are fluctuations in DS profile and AS profile at point D. This indicates the damage of TiB_2 coating. Therefore, the scratch load at point D can be taken as the critical load (L_C) for coating failure (listed in Table 5.3). Furthermore, from the scratch results, the failure mode of coating could be observed. With biasing the failure mode is changed from compressive spallation (Figure 5.13 (a)) to micro-chipping (Figure 5.13 (b)), confirming the improvement of coating adhesion.

Figure 5.12: Microscratch curves of deposited TiB_2 coating under linearly increasing load.

In order to achieve both high hardness and good coating adhesion, samples S2-8 to S2-13 were produced under conditions of substrate sputter cleaning, substrate bias for the first hour of deposition and without substrate bias for the last 2 hours of deposition. From Table 5.3, it can be seen that a good combination of high coating hardness and adhesion is achieved. In addition, with increasing sputter cleaning time, the resultant coating exhibits a higher hardness and a high value of L_C . However, the L_C

decreases when the sputter cleaning time is more than 90 min. This is possibly due to the contamination or impurity layer originating from the deposition chamber, which is in an agreement with literature [147].

From these results, it is clear that TiB_2 coatings with high hardness and good adhesive strength can be produced with well-designed deposition parameters and process control. It is noted that sputter cleaning of the substrate is necessary prior to deposition and sputter cleaning time of 60 to 90 min gives very good results in coating adhesion, but the sputter cleaning time should not be longer than 90 min.

Figure 5.13: SEM images compared between (a) sample S2-7 (no bias applied) and (b) sample S2-2 (bias applied sample).

5.1.3.4 Summary

Based on the Set 1 and Set 2 experiments, the main results are summarized below.

- (1) It was found that in order to increase the hardness of the nanostructured TiB_2 coatings, the TiB_2 (001) preferred orientation should be promoted, and this can be achieved by reducing the target-to-substrate distance from 100 mm to 60 mm and increasing substrate temperature to 400 °C.
- (2) The hardness and elastic modulus of the TiB_2 coatings are affected by deposition conditions. The coatings exhibiting the enhanced (001) orientation possess the highest hardness.

- (3) The TiB_2 coatings produced without substrate bias are (001) oriented and have high hardness, but low adhesion with the substrate.
- (4) Sputtering cleaning of substrate helps to improve TiB_2 coating hardness and adhesion strength.
- (5) The TiB_2 coatings produced with substrate bias are (101) oriented and possess low hardness, but good adhesion with the substrate.
- (6) The deposition process can be controlled to produce a TiB_2 coating with both high hardness and good adhesion strength. This is achieved by introducing substrate sputter-cleaning and then biasing for the early stage of deposition, followed by deposition without biasing.

5.2 Effect of Substrate Rotation on Structure, Hardness and Adhesion of Nanostructured Ti/ TiB_2 Coatings

During sputter deposition, it is common practice that the substrate on the working table is rotating around its normal in order to achieve uniform deposition over the substrate surfaces to be coated. It is thus obvious that with substrate rotation, the substrate-target distance is not a constant but varies from the shortest to the longest within one cycle of rotation. Substrate-target distance is known to affect not only the deposition rate, but also the energy of the adatoms arriving the substrate surface [148]. Thus, the structure and properties of the coatings are expected to be influenced by substrate rotation. Indeed, a recent study on electron beam PVD deposition of ZrO_2 based coatings by Wada et al. [149] showed that substrate rotation has a strong effect on the structural development of the coating, in terms of morphology, grain structure and coating texture. However, very few detailed studies have been conducted to investigate the effects of substrate rotation on the structures and properties of sputter deposited coatings, in particular TiB_2 coatings [150]. For the purpose of studying the effect of substrate rotation on the structures and properties of sputter-deposited TiB_2 coatings, TiB_2 coatings were deposited onto stationary and rotating high speed steel substrates. Two TiB_2 targets with rf powers of 200 W each were used with similar geometry as shown in Figure 5.14. The purpose of this new arrangement was to increase the coating thickness.

Before deposition, the substrate was positioned near the edge of the working table below the TiB_2 target (see Figure 5.14). The shortest distance between the TiB_2 target and the substrate was 60 mm. Thus, as the table rotated, the substrate-target distance varied from 60 mm to about 210 mm within one cycle of substrate rotation. No sputter-cleaning of the substrate before deposition and no substrate biasing during deposition were used in this investigation.

Two sets of depositions were conducted for various times, one with the working table rotating at 2 rpm and the other without rotation of the working table, i.e. the substrates were stationary and the substrate-target distance was kept constant at 60 mm. The tested results are summarized in Table 5.4.

Figure 5.14: The deposition set up in this study.

Table 5.4: Summary of the TiB₂ coatings tested and the measured properties

Sample	Substrate Rotation	Deposition Time (min)	Coating Thickness (μm)	Hardness (GPa)	Reduced Modulus (GPa)	L _y (mN)	L _c (mN)
Sample 1	Rotating	180	1.4	23.6	301.5	161.7	528.3
Sample 2	Stationary	100	1.4	30.9	328.1	527.2	976.5
Sample 3	Rotating	300	2.5	20.4	297.9	362.2	880.2
Sample 4	Stationary	200	2.5	42.7	368.2	859.6	2,153.6

5.2.1 Deposition Rate

A series of experiments were first conducted to deposit TiB₂ coatings on the rotating and stationary substrates for various times. It was found that under the present experimental conditions the deposition rate was doubled with two TiB₂ targets (sample 1, Table 5.4) as compared to those with one target (sample S2-1, Table 5.3). More importantly, the deposition rate on stationary substrates (14 nm/min) was much higher than that on rotating substrates (8 nm/min). This is in line with general observations for sputter deposition that the deposition rate increases with decreasing substrate-target distance [149]. In the case of stationary substrates, the substrate-target distance was the shortest and kept constant, and thus the substrates received the largest and constant flux of adatoms from the sputtering target.

On the other hand, as the substrate was rotating, the substrate-target distance varied from 60 mm to 210 mm with decreasing flux of adatoms and thus reduced deposition rate. Therefore, for the same deposition time, the thickness of the TiB₂ coatings on stationary substrates is almost twice of that on the rotating substrates. To eliminate the possible influence of this thickness difference in the structural and property features of the coatings, structural and properties characterization were conducted on TiB₂ coatings with identical coating thicknesses of 1.4 μm and 2.5 μm on both stationary and rotating substrates (see Table 5.4). Longer deposition times were required to produce

these two sets of coatings on the rotating substrates than on the stationary substrates, as illustrated in Figure 5.15, for reasons discussed above.

Figure 5.15: Deposition time vs. coating thickness observed in this study.

5.2.2 Chemical Composition

The chemical composition of the coatings was analyzed by XPS. It was seen that the B/Ti ratio of sample 1 (rotating) is approximately stoichiometric ($B/Ti = 2.1$), but that of sample 2 (stationary) is significantly overstoichiometric ($B/Ti = 2.7$). From this result, it is noted that this is in agreement with the observation of other investigations that the B/Ti ratio varies with substrate-to-target distance during deposition and with decreasing substrate-to-target distance, the B/Ti ratio increases [12].

5.2.3 Structural Characteristics

Figure 5.16 shows the X-ray diffraction patterns recorded for the four coatings listed in Table 5.4. Each pattern reveals several broad reflection peaks corresponding to the hexagonal TiB_2 structure. The broadness of the reflection peaks indicates the nanocrystalline nature of the coating structure, as further confirmed by FESEM examination (Figure 5.17). The most interesting observation that can be made from Figure 5.16 is that the TiB_2 coatings deposited on rotating substrates (sample 1 and 3) did

not show any preferred orientation, whilst the coatings on stationary substrates (sample 2 and 4) showed strong (001) orientation, with the basal plane parallel to the substrate surface. It is also noted that preferred orientation of the coating produced with substrate rotation in this set is different from that produced with one TiB_2 target, which shows (001) texture (Figure 5.7). The reason for this change will be discussed in Chapter 6.

Figure 5.16: XRD patterns recorded for the coatings studied.

The morphologies of the as-deposited coating surfaces and fractured cross-sections were examined under FESEM, as shown in Figure 5.17 for sample 1 and 2. No significant differences were observed in surface morphology between the coatings on rotating substrates and those on stationary substrates. In all cases, the coating surface is populated with granular grains with typical size less than 30 nm. The grains have well-defined boundaries with the others. Some pores of less than 10 nm size could be observed at grain boundaries. The grain size distribution in the coating on the rotating substrate is not as uniform as that on the stationary substrate, as some excessively larger grains are observed in the former.

Figure 5.17: FESEM images showing the surface morphology and fractured cross-sectional morphology of TiB₂ coatings: (a) and (b) sample 1 (rotating substrate); (c) and (d) sample 2 (stationary substrate).

Although the TiB₂ coatings on both stationary and rotating substrates showed similar surface morphology, significant difference in the fractured cross sectional morphology was observed from Figure 5.17. The coatings on rotating substrates exhibited a columnar structure typical of sputter deposition at relatively low temperatures, with low adatom energies and limited mobility. However, the coatings on the stationary substrates exhibited a dense and almost featureless microstructure. This structure can be regarded as a transition zone (zone T) in the well-known Thornton diagram [46].

5.2.4 Residual Stress

Residual stress of deposited TiB₂ sample 1 (rotated sample) and sample 2 (stationary) presented is 230 and 270 MPa, respectively ($R_{eff} = 24.2$ and 12.3 m). The

residual stress was calculated from Eq. 3.3 (section 3.5) by using the measured R_{eff} from the silicon substrate. Figure 5.18 shows the curvature of the silicon wafer deposited with these two coatings, from which it can be seen that the coating has a residual tensile stress. It is thus clear that deposition of TiB_2 coating on stationary substrate (sample 2) generates a higher residual stress than deposition on rotating substrate (sample 1).

Figure 5.18: (a) the curvature of resultant coating and (b) the effective radius of curvature of sample 1 (rotation) and sample 2 (stationary).

5.2.5 Coating Hardness

Figure 5.19 shows the typical load-displacement curves recorded for all samples. The hardness and modulus values measured by nanoindentation of all samples are summarized in Table 5.4. The indentation responses are typical of a hard material, with significant elastic recovery. A comparison of the indentation response of the coatings with the same thickness on rotating substrates (sample 1 and 3) and stationary substrates

(sample 2 and 4) revealed that elastic recovery is more significant in the coatings on stationary substrates. This is particularly so in the 2.5 μm thick coating deposited on the stationary substrate (sample 4), where nearly complete elastic recovery is observed after indentation to a depth of 50 nm.

From the results shown in Table 5.4, it can be seen that the randomly-oriented coatings produced on rotating substrates have relatively low hardness and reduced modulus values. On the other hand, the (001)-oriented coatings produced on stationary substrates possess much higher hardness and modulus values. For example, the hardness of the (001)-oriented coating in sample 4 is more than twice that of the randomly oriented coating in sample 3, both having the same thickness of 2.5 μm . It is thus clear that substrate rotation during the deposition period has detrimental effects on the mechanical properties of the resultant TiB_2 coating. The enhanced hardness and elastic behaviour of the coatings on stationary substrates can be understood from the observed denser structure and (001) orientation of the coatings.

5.2.6 Coating-substrate Adhesion

Substrate rotation also has a significant effect on the adhesion strength of the coating to the substrate. Table 5.4 summarizes the two critical loads, i.e. L_Y and L_C , measured for the coatings by the multi-pass micro-scratch test described in Section 3.5.3. It can be seen that for the same coating thickness, the coatings deposited on stationary substrates not only possess higher coating-substrate adhesion (represented by the larger L_C values), but also exhibit much better resistance to plastic deformation and scratch damage as derived from the higher “yield load” (L_Y) values. This improved L_Y load can be attributed to the enhanced coating hardness which could provide more resistance to plastic deformation and to abrasion by the diamond stylus during the scratching process.

Figure 5.19: Nanoindentation load-displacement curves extracted at the penetration depth of 50 nm for the four samples listed in Table 5.7.

The enhancement in coating-substrate adhesion strength by keeping the substrate stationary during deposition was further demonstrated by examining the recorded friction curves and the scratch tracks. Figure 5.20 shows the typical scratch friction force curves recorded for sample 3 (with substrate rotation) and sample 4 (without substrate rotation). Each friction curve is characterized by an initial smooth region which increases with increasing load, followed by a region with large fluctuation. The critical load at the transition between these two regions coincides with that measured by the surface profile and microscopic examination (Figure 5.21), and thus corresponds to the critical load for

coating adhesive failure (L_c). Clearly, the coatings on stationary substrates possess much higher critical loads than those on rotating substrates (Table 5.4).

Figure 5.20: Friction force curves recorded during microscratch test for sample 3 and sample 4.

Microscopic examination (Figure 5.21) revealed that compressive spallation is the dominant coating failure mode in all samples. However, after the critical load (L_c) for each coating, the damaged area is larger on the coatings deposited on rotating substrates than those on stationary substrates. This is because some parts of the coating on stationary substrates still remain at the side of the scratch track, as can be clearly seen in Figure 5.21 (b) and Figure 5.21 (d). In order to further confirm the failure mode of the coatings, EDS elemental mapping of the scratch tracks was acquired. Figure 5.22 shows the mapping images for sample 4. It can be deduced that coating failure is of the adhesive type and occurred at the interface between the titanium interlayer and the HSS substrate since no titanium was detected within the track after failure of the coating.

Figure 5.21: SEM images showing the scratch tracks and the failure of the coatings at loads above the L_C values. (a) sample 1, (b) sample 2, (c) sample 3 and (d) sample 4.

5.2.7 Summary

Under the present deposition conditions, the main results are summarized below.

- (1) Substrate rotation has a significant effect on the structure, orientation, hardness and adhesion strength of non-reactive magnetron sputtered TiB_2 coatings.
- (2) The TiB_2 coatings deposited on rotating substrates are characterized by random orientation, columnar growth, relatively low hardness and adhesion strength. On the other hand, without substrate rotation, the resultant coatings exhibit the beneficial (001) orientation, dense and equiaxed grain structure, and enhanced hardness and adhesion strength.
- (3) These structural and properties difference between rotation and stationary substrate will be discussed in more details in Chapter 6.

Figure 5.22: SEM image (a) and EDS elemental mapping of Ti (b) and Fe (c) of the damage region in the scratch track on sample 4.

5.3 Post-deposition Heat Treatment of Single Layer TiB_2 Coatings with a Ti Interlayer

Attempts to enhance the hardness and coating adhesion of the TiB_2 -based nanostructured coatings by annealing after deposition are presented in this section. A new set of samples was prepared by using two TiB_2 targets with similar geometry and orientation as shown in Figure 5.14. The Ti interlayer thickness is about 150 nm (deposition 30 min) and the TiB_2 coating thickness is about 2 μm (3 h). The samples were then annealed in vacuum at 450 °C, 500 °C and 550 °C for 2 hours. The annealing temperature was restricted by the tempering behaviour of the HSS substrate materials. The tested results are summarized in Table 5.5.

Table 5.5: Summary of properties of studied samples.

Samples	Annealing Temperature (°C)	Coating Thickness (µm)	Ra*	Hardness (GPa)	Reduced Modulus (GPa)	Critical Load L _C (mN)
No.1	as-deposited	1.98	6.95	31.6	321.3	1,089
No.2	450	1.83	6.43	41.9	338.3	2,596
No.3	500	1.67	8.12	38.8	326.6	1,880
No.4	550	1.67	7.13	38.7	305.8	1,653

* Ra = average roughness

5.3.1 Structural Characterization

Figure 5.23 shows the X-ray diffraction patterns of as-deposited and annealed coatings. It is noticed that all annealed samples retain the (001) TiB₂ peak achieved in the as-deposited samples. Moreover, with increasing annealing temperature from 450 to 550 °C, the intensity of peak (001) increases, suggesting increased degree of (001) texture by annealing. This may account for the increased hardness as compared to as-deposited sample (Table 5.5).

FESEM images of fractured cross sections of all samples are shown in Figure 5.24. Obviously, all coatings (both deposited and annealed at different temperatures) exhibit a columnar structure in the cross-section. Voids were observed in the as-deposited coating. After annealing, such voids were hardly observed.

From this study, it seems that after annealing the coating structure and quality could be improved, especially with annealing temperature of 450 °C. These benefits could be associated with the densification of the coating after annealing, as evident from the reduced coating thickness (Table 5.5) and the reduction of voids in the cross-section in Figure 5.24.

Figure 5.23: XRD patterns generated from deposited and annealed TiB₂ coatings.

The surface morphology and roughness values were measured by atomic force microscopy (AFM) (Figure 5.25 and Table 5.5). AFM reveals that all coatings exhibit similar surface morphological features, characterized by the densely populated conical projections. But the number and individual size of these conical projections vary with annealing temperature. From Figure 5.25 (b), it can be seen that after annealing at 450 °C, the number of projections increases and the size of individual projects decreases, which result in the reduction of R_a (Table 5.5). After annealing at 500 °C, the number of projections increases and the size of individual projects decreases, but the coating morphology becomes non-uniform, with clusters of asperities with significant height. The lack of uniformity may be due to the reconstruction of structure taking place at higher temperature (500 °C). This results in the increase of R_a for sample 3.

Figure 5.24: FESEM images showing the fractured cross-section of the as-deposited and annealed coatings.

Interestingly, after annealing at 550 °C, the surface asperities start to grow in size (Figure 5.25 (d)), which result in the increase of R_a as compared to the as-deposited sample (sample 1).

5.3.2 Mechanical Properties Characterization

Table 5.5 shows that after annealing, the hardness of all tested samples is increased, as expected from the coating structural improvement (higher coating density). In particular, the hardness of the sample annealed at 450 °C is increased most significantly. However, annealing does not seem to affect coating modulus too much. However, from Table 5.5, it can be seen that the TiB₂ coating thickness decreases with increasing annealing temperature. This is probably due to the stress relaxation and

densification of the coating. Micro-voids could be found in the as-deposited sample (sample no.1), whilst the micro-void decreases in sample 2 (annealed at 450 °C). This may be due to the denser structure of coating. In addition, it is noticed that the size of columnar structure of TiB_2 texture enhances with increased annealing temperature.

From Figure 5.24, it is noted that the Ti inter-layer can be seen clearly in all samples. It can be seen that the thickness of Ti interlayer seems to increase with the increase of annealing temperature. Such increment of Ti interlayer may be due to the lattice expansion of α -Ti (O) phase. During annealing, the native oxide film on HSS surface decomposed and the oxygen atoms diffused into the Ti interlayer and formed solid solution in α -Ti (O) phase. This caused lattice expansion and Ti interlayer thickness increment.

Figure 5.25: AFM images showing the surface roughness of as-deposited (a) and annealed TiB_2 samples at 450 °C (b), 500 °C (c) and 550 °C (d).

Figure 5.26 shows the typical single-pass micro-scratch curves with linearly increasing load for all samples. Clearly, the coatings with annealing possess much higher critical loads (L_C) than those without annealing (Table 5.5 and Figure 5.26).

Figure 5.26: Microscratch curves of as-deposited and annealed TiB₂ coatings.

SEM examination (Figure 5.27) reveals the difference in the scratch failure mode between the deposited and annealed samples. Indeed, it can be seen that the compressive gross spallation failure mode is dominant in all samples, which is usually associated with high residual stress within the coating. However, after coating failure some coatings still remain at the side of the scratch track on the annealed sample. This is an overlap of the two modes of failure (gross spallation and wedge spallation), which is typical of hard coatings with good adhesion. Interestingly, it is noted that coating failure in the annealed samples took place by cracking with through-thickness cracks (arrow indicated in Figure 5.27).

5.3.3 Summary

- (1) Annealing helps to promote the (001) orientation of the TiB₂ coating and improve its hardness.
- (2) Coating adhesion strength is enhanced significantly by annealing.

(3) It was found that annealing at optimum temperature of 450 °C shows the most improvement of mechanical properties (hardness, elastic modulus and adhesion) and the reduction of surface roughness, which is beneficial for many tribological applications.

Figure 5.27: SEM images showing the scratch tracks between as deposited (a) and annealed samples (b)-(d).

5.4 Effect of Nitrogen Doping Titanium Interlayer on Adhesion of Nanostructured Ti/TiB₂ Coatings

In all the depositions so far, a thin pure Ti interlayer has been used to enhance the coating TiB₂-HSS adhesion. This is a common practice for many ceramic coating-substrate systems [151]. But there is a speculation that the soft pure Ti interlayer may not be able to give the best match between the hard TiB₂ coating and the hard HSS substrate. Attempts have been made to increase the strength of the Ti interlayer by doping it with nitrogen in argon-nitrogen gas mixtures.

The details of deposition conditions are summarized in Table 3.2 (section 3.2.1). Before TiB₂ deposition, a thin Ti interlayer was deposited by sputtering the Ti target for 30 min in pure argon gas and various argon-nitrogen gas mixtures. Before deposition, the substrates were sputter-cleaned for 60 min to remove oxide layers or contaminants at the substrate surface. In addition, in order to avoid the formation of TiN compound during deposition of nitrogen-doped Ti interlayer, no substrate biasing during deposition was applied for all depositions. Table 5.6 summarizes the deposition details of Ti interlayer in this study.

Table 5.6 Deposition conditions of Ti interlayer.

Materials	Substrate cleaning power/time	Ti power/time	% N ₂ in sputtering gas
Sample 1	150 W/ 60 min	Ti 200 W/ 30 min	0
Sample 2	150 W/ 60 min	Ti 200 W/ 30 min	10
Sample 3	150 W/ 60 min	Ti 200 W/ 30 min	20
Sample 4	150 W/ 60 min	Ti 200 W/ 30 min	33
Sample 5	150 W/ 60 min	Ti 200 W/ 30 min	50

5.4.1 Structural Characterization of Resultant Coatings

Figure 5.28 shows the X-ray diffraction patterns recorded for all five samples listed in Table 5.6. Each pattern shows several broad reflection peaks corresponding to the hexagonal TiB₂ structure. The dominant peak is (001), which indicates that the basal plane of TiB₂ is preferentially oriented parallel to the substrate surface in all samples. The

degree of such preferred orientation seems to increase with increasing degree of nitrogen doping in the Ti interlayer, as evident from the increased relative intensity of the (001) peak. The broadness of the reflection peaks indicates the nanocrystalline nature of the coating structure, as further confirmed by FESEM examination (Figure 5.29).

Figure 5.28: XRD patterns of all samples.

The morphologies of the as-deposited coating surfaces and fractured cross-sections were examined under FESEM, as illustrated in Figure 5.29. Similar morphological features were also observed for other coatings. In all cases, the coating surface is populated with granular grains with typical size less than 30 nm. The virtual grains are formed from many nanoclusters and they have well-defined boundaries with the others. Some pores of less than 10 nm size could be observed at boundaries of virtual grain.

Regarding the fractured cross-section (Figure 5.29 (b)-(d)), a thin Ti interlayer could be observed in all samples. It can also be seen that the coatings exhibit a columnar structure, which is typical of sputter deposition at relatively low adatom energies and limited mobility.

5.4.2 Surface Roughness

The surface morphology and roughness values were measured by AFM (Figure 5.30, Table 5.7). It can be clearly seen from Table 5.7 that nitrogen-doping of the Ti interlayer is very effective in reducing the surface roughness of the subsequent TiB_2 coating. For example, the R_a value of TiB_2 coating surface was reduced from 6.95 nm to 1.87 nm and further to 0.81 nm with increasing nitrogen-doping. This demonstrates the beneficial effect of nitrogen doping the interlayer in maintaining the smoothness of the substrate surface, which is important for many practical applications.

Figure 5.29: FESEM images showing the surface morphology of sample 1 (a) and fractured cross-sectional morphology of sample 1 (b), sample 2 (c) and sample 3 (d).

Table 5.7: Properties of resultant coatings.

Samples	Percentage of N ₂	Coating Thickness (micron)	R _a (nm)	Hardness (GPa)	Reduced modulus (GPa)	Critical load L _c (mN)
No.1	0	1.98	6.95	31.6	321.3	1,089.1
No.2	10	1.85	1.87	35.6	316.2	1,784.5
No.3	20	1.87	1.62	33.3	355.8	1,352.4
No.4	33	1.89	1.51	33.2	332.7	1,446.1
No.5	50	1.92	0.81	29.9	310.5	1,387.5

Figure 5.30 shows the AFM images recorded for all the coating surfaces. All coatings exhibit similar surface morphological features, characterized by the densely populated conical projections. But the number and individual size of these conical projections vary with the degree of nitrogen-doping into the interlayer. With increasing nitrogen doping, the number of projections increases and the size of individual projects decreases. These are in good agreement with the R_a roughness values measured for the coating surfaces.

Figure 5.30: AFM images showing the average surface roughness (R_a) of all tested samples.

5.4.3 Coating Hardness

The hardness and reduced modulus values of all TiB_2 coatings, measured by nanoindentation, are summarized in Table 5.7. Figure 5.31 shows the relationship between coating hardness and degree of nitrogen doping into the Ti interlayer (represented by N_2 % in the sputtering atmosphere). The hardness values of the Ti interlayers were also measured as a function of nitrogen doping. This was done on a separate series of samples deposited with Ti interlayers only without the subsequent TiB_2 coating deposition. An important observation that can be made from Figure 5.31 is that without nitrogen doping, the pure Ti interlayer is very soft, with a hardness value around 2.5 GPa, and nitrogen doping is effective in enhancing the hardness and strength of the interlayer. There is a general trend that the hardness of the Ti interlayer increases with increasing degree of nitrogen doping. This is possible for the formation of TiN at Ti interlayer. Such an increased interlayer strength may account for the observed enhancement in TiB_2 -substrate adhesion as discussed later.

Figure 5.31: The relationship between the coating hardness and percentage of nitrogen.

From Figure 5.31, it can also be seen that the hardness of the TiB_2 coating first increases with increasing nitrogen doping into Ti interlayer, and then decreases with further increased doping.

5.4.4 Coating-substrate Adhesion

Figure 5.32 shows typical friction versus scratching load curves measured during the microscratch test. Table 5.7 also summarises the L_C values for all the coatings studied in this work. Clearly, nitrogen doping into the Ti interlayer can significantly enhance the TiB_2 -HSS adhesion, with doping in 10% N_2 being the most effective. This is another important observation made in this work, since coating-substrate adhesion is critical in many practical applications.

Figure 5.32: Friction versus load curves for selected coatings.

5.4.5 Summary

From the experimental results under the present deposition conditions, it can be concluded that doping the Ti interlayer with nitrogen has the following beneficial effects on the structures and properties on sputtered TiB_2 coatings:

- (1) It can increase the hardness and strength of the interlayer due to nitrogen dissolution in the α -Ti lattice.
- (2) It can enhance the (001) preferred orientation of the subsequent TiB_2 coating.
- (3) It is effective in reducing the surface roughness of the TiB_2 coating.
- (4) It can significantly enhance the TiB_2 coating-HSS substrate adhesion strength, with doping in 10% N_2 showing the optimum enhancement.

5.5 Improvement in Adhesion of Sputtered TiB_2 Coatings by a Chromium Interlayer

To enhance the adhesion of a ceramic coating onto a metallic substrate, it is a common practice that a thin titanium interlayer is used between the coating and the substrate. However, Berger and Larson [26] addressed that the yield strength and fracture strength of titanium interlayers were insufficient to accommodate the level of stresses generated in TiB_2 coatings during deposition and during application. In the present attempt to further improve the adhesion strength of sputtered TiB_2 coatings onto HSS substrates, chromium was used as the interlayer material. Table 5.8 lists the two sets of coatings produced at 400 °C with two TiB_2 targets (Figure5.14) with rf power of 200 W each. One set was deposited with a Cr interlayer, the other with a Ti interlayer of identical thickness.

Table 5.8: Properties of resultant TiB_2 coatings.

Interlayer/Coating	Thickness (μm)			Hardness (GPa)	Reduced Modulus (GPa)	Critical Load, L_C (mN)
	Interlayer	TiB_2	Total			
Ti/ TiB_2	0.30	1.45	1.75	34.3	329.5	1,240
Cr/ TiB_2	0.35	1.35	1.70	36.3	303.1	2,034

5.5.1 Structural Characterization

X-ray diffraction analysis (Figure 5.33) shows that both TiB_2 coatings shown in Table 5.8 have a similar hexagonal crystal structure, with strong (001) preferred orientation. This is a desired texture since TiB_2 coatings with the basal plane (001)

parallel to the surface is known to possess the highest hardness as compared to TiB_2 coatings with other orientations.

Figure 5.33: X-ray diffraction patterns recorded from the TiB_2 coatings.

Figure 5.34 (a) shows the typical fractured cross-sectional morphology of the TiB_2 coating with a Cr interlayer. It can be seen that the Cr interlayer exhibits a columnar growth mode, whilst the TiB_2 coating has a dense and nearly equiaxed structure. Similar morphological features have also been observed for the TiB_2 coating with a conventional Ti interlayer. As discussed earlier, surface morphological examination by AFM (Figure 5.34 (b)) also revealed that the two TiB_2 coatings have a similar topographic feature, which is characterized by the densely populated conical projections typical of sputter-deposited coatings. The average surface roughness (R_a) of the two coatings has a similar value of around 3.0 nm.

Figure 5.34: FESEM image showing the fractured cross-section (a) and AFM image showing the surface topography (b) of TiB₂ coating with a Cr interlayer.

5.5.2 Mechanical Characterization

The above structural analyses demonstrate that the change in the interlayer material between Cr and Ti does not significantly affect the structure and morphology of the subsequent TiB₂ coating. However, the interlayer considerably affects the mechanical properties and integrity of the coating. Figure 5.35 shows typical nanoindentation load-unload curves recorded for the two coating systems. The average hardness and reduced modulus derived from 10 measurements for each coating are summarized in Table 5.8. It can be seen that the use of a Cr interlayer results in higher hardness and smaller reduced modulus of the TiB₂ coating. These are also reflected in the load-unload curves shown in Figure 5.36, which show that the TiB₂ coating with a Cr interlayer exhibits greater resistance to indentation and larger elastic recovery during the unloading stage.

The adhesion strength of the TiB₂ coating to the substrate was evaluated by micro-scratch testing, as discussed in section 3.7.3. The recorded friction force versus applied normal load curves are given in Figure 5.36. Table 5.10 also summarizes the L_C values for the two coatings studied in this work. It thus confirms that a Cr interlayer is more beneficial in further enhancing the adhesion of TiB₂ coating onto HSS substrate.

Figure 5.35: Typical nanoindentation load-unload curves recorded from the TiB_2 coatings.

Figure 5.36: Recorded friction force versus load curves for the TiB_2 coatings during microscratch test with linearly increasing load.

Microscopic examination and energy dispersive spectroscopy (EDS) X-ray elemental mapping reveal that compressive spallation is the dominant adhesive failure mode in both coatings, with coating debonding at the interlayer-substrate interface (Figure 5.37). It thus appears that the adhesion of the interlayer onto the HSS substrate

plays the most important role in determining the mechanical integrity of the coating-substrate system.

5.5.3 Summary

This work demonstrates that changing the interlayer material from HCP-Ti to BCC-Cr does not significantly affect the structure and morphology of the subsequent TiB_2 coating, but results in higher hardness of the interlayer and the TiB_2 coating. More importantly, the adhesion of the TiB_2 coating to the HSS steel substrate can be significantly enhanced by the Cr interlayer. Possible reasons for such an enhancement would be discussed in Chapter 6.

Figure 5.37: SEM images and EDS elemental mapping of the scratch tracks: (a) TiB_2 with Ti interlayer; (b) TiB_2 with Cr interlayer.

5.6 Multilayer of Nanostructured Ti/TiB₂ Coatings

In this work, the multilayer systems have been proposed in order to overcome the problem of brittleness and the high residual stress of the TiB₂ coating. This also includes enhancing of coating adhesion and retaining high hardness. Highly stressed TiB₂ coatings were layered with a ductile Ti layer. There are several reasons for choosing ductile Ti for multilayer structure. Firstly, Ti has similar crystal structure (hcp) and chemistry to TiB₂, which shows the material compatibility [26]. Secondly, Ti is mostly used to be an interlayer media between two materials owing to its strong adhesion to other materials [40, 151]. Thirdly, Ti is a good metallic material to accommodate stress from ceramic materials [41].

In this study, the multilayer coatings were deposited using magnetron sputtering with Ti and TiB₂ targets. Therefore, four types of TiB₂-based nanostructured coatings have been fabricated using the conditions listed in Table 5.9. These include:

- (1) Conventional two layer Ti-TiB₂ coating, by depositing a thin Ti interfacial layer at the interface followed by a TiB₂ layer on top.
- (2) Four layer Ti-TiB₂ coating, by depositing 4 alternate Ti and TiB₂ layers.
- (3) Six layer Ti-TiB₂ coating, by depositing 6 alternate Ti and TiB₂ layers
- (4) Twelve layer Ti-TiB₂ coating, by depositing 12 alternate Ti and TiB₂ layers.

The total deposition time for TiB₂ was fixed at 3 h in all depositions. Thus, the overall thickness of TiB₂ is similar for all samples. The details of deposition are summarized in Table 5.9. The results of coating properties are listed in Table 5.10.

Table 5.9: Deposition conditions of multilayer Ti/TiB₂ coatings.

Materials	Mode	Conditions
Sample 1	Conventional 2 layers Ti/TiB ₂	Ti 20 min + TiB ₂ 180 min
Sample 2	4 layers Ti/TiB ₂	2×(Ti 20 min + TiB ₂ 90 min)
Sample 3	6 layers Ti/TiB ₂	3×(Ti 20 min + TiB ₂ 60 min)
Sample 4	12 layers Ti/TiB ₂	6×(Ti 20 min + TiB ₂ 30 min)

Table 5.10: Properties of resultant coatings.

Samples	Mode	Coating thickness (micron)	Average roughness, R_a (nm)	Hardness (GPa) (at 50 nm)	Reduced modulus (GPa)	Critical load L_c (mN)
No.1	2 layers	1.75	2.33	34.3 ± 1.2	329.5 ± 4.2	1,240
No.2	4 layers	2.52	15.49	33.4 ± 0.9	340.2 ± 5.2	1,855
No.3	6 layers	3.15	18.18	35.6 ± 2.2	365.4 ± 7.2	1,995
No.4	12 layers	3.42	20.61	20.1 ± 5.9	126.4 ± 23.5	1,650

5.6.1 Structural Characteristics

Figure 5.38 shows the X-ray diffraction patterns recorded for the four coatings listed in Table 5.10. Each pattern shows several broad reflection peaks corresponding to the hexagonal TiB_2 structure and some minor peaks from the Ti layers. The broadness of the reflected peaks indicates the nanocrystalline nature of the coating structure, as confirmed by FESEM examination (Figure 5.39). It is interesting to note that the conventional TiB_2 coating (sample 1) exhibits a very strong (001) preferred orientation, and such a fiber texture, to a lesser extent, is retained in the 4-layer coating (sample 2). But the TiB_2 phase is randomly oriented in the 6-layer and the 12-layer coatings. Another interesting observation is that with increasing number of layers, the crystallinity of the TiB_2 phase decreases, as evidenced by the decreased XRD intensity and increased broadness of the reflected peaks. These observations suggest that the TiB_2 layer needs sufficient time (at least 90 min in the case of sample 2) to develop into a well crystalline structure with preferred (001) orientation. The limited growth time of 60 min (sample 3) and 30 min (sample 4) for each individual TiB_2 layer was obviously not enough for the development of the (001) fiber texture.

Since TiB_2 coatings with (001) orientation is known to yield the highest hardness as compared with TiB_2 coatings with other orientation, it is believed that sample 1 with the highest (001) peak may show the highest hardness. In this study, however, the multilayer Ti/ TiB_2 coating with 6 alternate Ti and TiB_2 layers (sample 3) shows the

highest hardness value around 36 GPa despite showing a less dominant (001) orientation compared to samples 1 and 2.

Figure 5.38: XRD patterns of multilayer TiB₂ coatings.

Figure 5.39 shows the fractured cross-sections of all samples studied in this work, from which the alternate Ti/TiB₂ layered structures can be clearly seen. The total thickness and other structural and property features of each coating are listed in Table 5.10. Since the total sputtering time for the TiB₂ target was the same for all coatings, it is obvious that with increasing number of alternate layers, the thickness of each individual TiB₂ layer decreases due to the shorter sputtering time for each layer and the total coating thickness increase due to the introduction of more Ti layers.

Figure 5.39: FESEM images showing the fractured cross-section of (a) sample 1, (b) sample 2 and (c) sample 3 and (d) sample 4.

From Figure 5.39, it can be seen that the conventional TiB_2 coating (sample 1) exhibits a dense and nearly equiaxed grain structure (Figure 5.39 (a)), whilst the multilayer coatings (samples 2-4) show a columnar structure, which is typical of sputter deposition at relatively low adatom energies and limited mobility. This observation indicates that sufficient time is required for the TiB_2 layer to develop into a dense and equiaxed structure, and interrupting the growth of the TiB_2 layer with a Ti layer obstructs the development of such a structure and favours the columnar growth of TiB_2 .

The coating morphology was also revealed (see Table 5.10) by making a ball-crater on the coating surface using the Calotest machine. A stainless steel ball of 25.4 mm diameter was used for cratering with a speed of 700 rpm for 360 s. Figure 5.40 shows the

ball-crater images of sample 4 (12 layers), from which the alternated layers between TiB_2 layers and Ti layers can be clearly identified.

Figure 5.40: SEM image showing the ball-crater images of sample 4 (12 layers).

5.6.2 Residual Stress

Residual stresses present in the coating on sample 1, sample 2 and sample 3 are 312.1 MPa (tensile), 23.9 MPa (tensile) and -70.1 MPa (compressive), respectively. The R_{eff} of sample 1, sample 2 and sample 3 are 15.3, 96.8 and -43.2 m, respectively. It can be seen from Figure 5.41 that the coating sample 1 and 2 demonstrates tensile stress, whilst sample 3 indicates compressive stress. It is noted that with increasing multilayer the

residual stress decreases [26] and changes mode from tensile stress to compressive stress when the multilayer reaches at alternated 6 layers (sample 3).

Figure 5.41 Curvature profiles of sample 1, sample 2 and sample 3.

5.6.3 Surface Roughness

Figure 5.42 shows typical AFM images taken from the surfaces of all samples. The coating surface is densely populated with conical projections of varying sizes. Such a surface topography is typical of sputter deposited coatings. The density and sizes of the conical projections vary with the number of multilayers in the coating. As can be seen from Figure 5.42, the size of individual projections is much larger on the multilayer coatings than on the conventional two layer coating. This is also reflected in the measured average roughness (R_a) values summarized in Table 5.10. The relationship between the number of coating layers and the average surface roughness is more clearly shown in Figure 5.43. It can be seen that surface roughness increases considerably with increasing number of layers. Such an increase is more dramatic when the number of layers is increased from 2 to 4, and becomes more gradual with further increased of layers from 6 to 12. The increased surface roughness on multilayer coatings is most likely due to the increased number of Ti layers which promotes the development of a columnar

structure as discussed in the previous section. A coating with columnar structure is likely to have a rougher surface than a coating with dense and equiaxed structure due to the characteristic columnar growth mode.

Figure 5.42: AFM showing the surface roughness of all multilayer samples.

Figure 5.43: The relationship between the number of coating layers and the average surface roughness.

5.6.4 Hardness Test

The hardness and reduced modulus values measured by nanoindentation of all samples are summarized in Table 5.10. It can be seen that all samples, which were measured at 50 nm depth, show high hardness (above 30 GPa) and reduced modulus (above 300 GPa) except for sample 4 with 12 alternate layers. The relatively low hardness of this coating is due to the small thickness of the top TiB₂ layer and the effect of underlying soft Ti interlayer. This indicates that the thickness of top TiB₂ layer mainly determines the measured hardness value at 50 nm indentation depth. Indeed, the other three samples with a top TiB₂ layer thicker than 500 nm possess similar hardness of around 35 GPa. Attempts have been made to measure the hardness and modulus at different penetration depths varying from 100 nm to 1,000 nm (Figure 5.44). It was found that at penetration depth less than 100 nm, the measured hardness is very high for samples 1, 2 and 3. But only sample 1, which has the thickest top TiB₂ layer, shows stable hardness up to an indentation depth of 300 nm. For sample 2 and 3, the hardness drops significantly at depth above 100 nm, obviously due to the contribution of the soft

Ti layers. This is followed by another abrupt drop at depth of 400 nm, obviously due to the effect of substrate.

Figure 5.44: Hardness of resultant coatings at various penetration depths.

5.6.5 Coating-Substrate Adhesion

Figure 5.45 shows the scratch friction force curves recorded for all samples. Each friction curve is characterized by an initial smooth region which increases with increasing load, followed by a region with large fluctuation. The critical load at the transition between these two regions coincides with that measured by the surface profile and microscopic examination (Figure 5.46), and thus corresponds to the critical load for coating adhesive failure (L_C). Clearly, the multilayer Ti/TiB₂ coatings (samples 2, 3 and 4) possess much higher critical loads than the conventional two-layer coating (sample 1) as shown in Table 5.10 and Figure 5.45. The critical load initially increases with increasing number of layers, reaching a maximum with the 6-layer coating, and then decreases with further increase in the number of layers to 12. Thus, there exists an optimum combination of alternate layers that gives the optimal enhancement in coating adhesion.

Figure 5.45: Friction force curves of deposited TiB_2 coating under linearly increasing load.

In order to investigate the coating failure mode at the L_c point and the effect of multilayer on coating failure, Figure 5.46 shows the SEM and EDS elemental mapping of Ti and Fe of selected samples. Microscopic examination revealed that spallation is the dominant coating failure mode in all samples. However, after the critical load (L_c) for each coating, the damaged area is larger on the two layer Ti/TiB₂ coating (sample 1) than on the multilayer Ti/TiB₂ coatings (samples 2 and 3), because some parts of the coating of multilayer Ti/TiB₂ coatings still remain in the scratch track (arrow), as can be clearly seen in Figure 5.46 (d) and (g). This clearly shows the beneficial effect of multilayer in enhancing the coating adhesion for TiB₂ coatings. In order to further confirm the failure mode of the coatings, EDS elemental mapping of the scratch tracks was acquired. Figures. 5.46 (b), (e) and (h) show the mapping images for Ti element of these selected samples. It is noted that coating failure is of the adhesive type and occurred at the interface between all titanium layer/interlayer and the HSS substrate since no titanium was detected within the track after failure of the coating.

Figure 5.46: SEM of damage region and EDS of the damage area illustrating sample 1 ((a) to (c)), sample 2 ((d) to (f)), and sample 3 ((g) to (i)).

5.6.6 Summary

From the experimental results, it can be concluded that under the present deposition conditions, magnetron sputtering of Ti and TiB_2 can be used to produce multilayer coatings with increased coating adhesion and relatively high hardness. There exists an optimum combination of alternate layers that gives the optimal enhancement in coating adhesion. In the present case, the 6-layer coating gives the best results in terms of coating hardness and adhesion strength. In addition, the development of multilayer Ti/TiB₂ structure significantly affects the structure, texture, morphology and surface roughness of the coating.

5.7 Tribological Behaviour of Nanostructured Ti/TiB₂ Coatings for being Protective Coatings

In the present investigation, two sets of experiments were conducted to determine the tribological properties of TiB₂ coatings. In the first set (Set 1), experiments have been carried out by selecting the best sample achieved with highest hardness (42 GPa) and critical load (2,153 mN) to study the sliding wear and friction behaviour of TiB₂ coating against steel and alumina under unlubricated condition, employing various sliding speeds and applied loads. In Set 2, experiments have been carried out by selecting the best samples from each respective section to study the sliding wear and friction behaviour of TiB₂ coating against alumina under unlubricated condition, employing various sliding speeds and applied loads.

5.7.1 Experiments of Set 1

The selected sample in Set 1 was sample 4 in Table 5.7. It has a single TiB₂ layer with a Ti interlayer, and shows the highest hardness and very good coating adhesion achieved so far. This coating has a dense, fine structure and a high hardness of 42.7 ± 1.2 GPa. This sample will be addressed as a sample 1 in this set.

From Section 5.3, it was found that annealing at optimum temperature of 450 °C shows the most improvement on mechanical properties of TiB₂ coatings. From these results, the sample 1 in this set or sample 4 in Table 5.7 was annealed in the vacuum furnace at a pressure of 10^{-7} Pa at 450 °C for 2 hours and this annealed sample was named “sample 2” in this set. Table 5.11 lists some relevant properties of sample 1 and sample 2.

Table 5.11: Properties of resultant TiB₂ coatings of Set 1.

Ti/TiB₂ Coatings	Thickness (μm)	Hardness (GPa)	Reduced Modulus (GPa)	Critical Load, L_c (mN)
Sample 1	2.50	42.7 ± 1.2	368.2 ± 8.2	2,153.6
Sample 2	2.40	48.5 ± 2.7	310.7 ± 12.7	3,012.5

From Table 5.11, it is noted that the hardness and modulus of sample 2 is higher than sample 1, as expected from annealing (section 5.3). Sample 2 shows slightly reduction of coating thickness due to coating densification during annealing. It is well-known that wear resistance of the coating is related to the properties of the coatings. The wear rate of the coatings decreases with increasing hardness of the coating [36]. Since both coatings have a high hardness and good adhesion (high L_c values), the test samples should possess good tribological properties such as wear resistance, as discussed later.

5.7.1.1 Dry Sliding Wear against a Bearing Steel Ball of Set 1

The friction tests were performed using a ball-on-disc friction testing machine, as described in section 3.5.1. The slider used in this study was bearing steel ball of 6 mm in diameter. The applied loads were 1, 5 and 10 N and sliding speed was 2 cm/s.

Typical curves of friction coefficient versus sliding distance, obtained under a load of 1 N are shown in Figure 5.47. All the friction curves demonstrate a similar pattern, which can be characterized by the initial transient state followed by a steady state. Under the testing condition, at the start of the test, the friction coefficient of samples 1 and 2 increased rapidly with increasing sliding distance until steady state was reached after about 10 m and 30 m of sliding distance for sample 1 and sample 2, respectively. The transient state is longer for the HSS substrate. It can be seen that the friction coefficient of sample 1 reaches the steady state faster than sample 2. The values of friction coefficient of sample 1 and 2 are similar, but are slightly higher than that of HSS substrate.

Figure 5.47: Typical friction coefficient curves for HSS substrate and resultant coatings sliding against a bearing steel slider.

During the sliding process, a circular wear scar or wear track was produced on the tested samples. In order to study the wear track and confirm that the coating was not removed from the substrate during the test, SEM was used. SEM revealed that the coating had not been worn after test termination. Instead, only the steel ball (slider) was worn and its material was transferred to the coating surface (arrow), as shown in Figure 5.48 (a) (at 1 N) and Figure 5.48 (b) (at 5 N). This is because the ceramic coating is much harder than the steel slider. This result demonstrates that the coating of ceramic TiB_2 onto the steel substrate is beneficial as a protective coating against wear.

From Figure 5.48 (a) and (b), it is noted that with increasing applied load from 1 N to 5 N, the slider material gradually accumulated increasingly on the coating surface. This is further confirmed by 3-D profilometre, as shown in Figure 5.49. No measurable wear and damage to the coating were detected on the coated sample.

(a)

(b)

Figure 5.48: SEM images of sample 1 showing of a circular wear track with material transferred (from the steel slider) for tested load of 1 N (a) and for tested load of 5 N (b).

Figure 5.49: Three-dimensional profilometer showing wear track of sample 1 tested under load of 5 N and 1 N.

5.7.1.2 Dry Sliding Wear against an Alumina Ball of Set 1

Attempts to study tribological properties of Ti/TiB₂ coating were made by changing the slider material from steel to hard alumina (Al₂O₃). To increase the severity of the test, the sliding speed was increased to 20 cm/s and the load employed was 5 N and 10 N.

Typical curves of friction coefficient versus sliding distance, for the HSS substrate, sample 1 and sample 2 against an alumina slider (ball) are illustrated in Figure 5.50, from which it can be seen that sample 1 and sample 2 have different friction pattern. Under the testing condition, the friction curve of sample 1 can be characterized in four steps, i.e. the initial transient state, the first steady state, rapidly transient state and second steady state. At the beginning of the test, the friction coefficient of samples 1 increased rapidly with increasing sliding distance (initial transient state) until the first steady state at friction coefficient of 0.16 was reached after about 2 m of sliding distance. However, after sliding distance of 10 m, the friction coefficient of sample 1 increased rapidly (transient state) until the second steady state at friction coefficient of 0.32 was reached after about 30 m of sliding distance.

Figure 5.50: Typical friction coefficient curves for HSS substrate and resultant coatings sliding against an alumina slider (load applied of 5 N).

It is noted that the friction coefficient of 0.16 at the first steady state was the friction coefficient of the TiB_2 coating (sample 1) until a sliding distance of 10 m. The sudden change of friction coefficient in the rapidly transient state was due to the failure of the coating (arrow). The friction coefficient of 0.32 at the second steady state was the friction coefficient value of the HSS substrate.

From Figure 5.50, it can also be seen that under the testing condition, the friction curve of sample 2 can be characterized in two steps, i.e. the initial transient state and the steady state. In the beginning of the test, the friction coefficient of samples 2 increased rapidly with increasing sliding distance (transient state), until the steady state at friction coefficient of 0.23 was reached after about 18 m of sliding distance. Since there is no sudden change of friction coefficient during steady state, it seems that the coating still remains and there is no coating failure in sample 2 for a sliding distance of 100 m.

Figure 5.51 shows the friction coefficient curves versus sliding distance, obtained under a higher load (10 N). In this case, the friction curves of sample 1 and sample 2 have a similar pattern. Under the testing condition of 10 N load, the friction curve of both samples 1 and 2 can be characterized in four steps, i.e. the initial transient state, the first steady state, rapidly transient state and second steady state. At the beginning of the test,

the friction coefficient of samples 1 increased rapidly with increasing sliding distance (initial transient state) until the first steady state at friction coefficient of 0.27 was reached. However, after a sliding distance of 2.5 m, the friction coefficient of sample 1 increased rapidly (transient state) until the second steady state at friction coefficient of 0.35 was reached after about 5 m of sliding distance. Again, it is noted that friction coefficient of 0.27 at the first steady state was the friction coefficient of the coating (sample 1) and the friction coefficient of 0.35 in the second steady state was the friction coefficient value of the HSS substrate.

Figure 5.51: Typical friction coefficient curves of resultant coatings sliding against an alumina slider (load applied of 10 N).

However, sample 2 shows a longer period of the first steady state until the sliding distance of 12 m, at which the sudden change of friction coefficient occurs, indicating the failure of coating. Clearly, under the same testing conditions, sample 2 lasts longer and possesses a better wear resistance than sample 1.

During the sliding process, a circular wear track was produced on the tested samples. Under the testing conditions of load 5 and 10 N, wear of the untreated sample (HSS) occurred in a severe mode, resulting in a very rough metallic surface and plate-like

metallic wear debris, in particular under load 10 N (Figure 5.52). These are typical of the result of adhesive wear [152].

Figure 5.52: SEM image of worn surface after wear sliding testing of HSS under 10 N.

SEM images of sample 1 (Figure 5.53 (a)) and sample 2 (Figure 5.53(b)) show circular wear tracks tested under applied load of 5 and 10 N. It is noted that the worn surface produced by the alumina slider is microscopically smoother and is not so heavily scored. As the wear test proceeds, the original contact areas are enlarged and more asperities brought into the contact. During this process, the thickness of the tested coating in contact area is progressively reduced due to material loss. There is evidence that material loss from the coating is caused by polishing and abrasion actions of the hard Al_2O_3 ball. Abrasive grooves have been observed on the contact area of the TiB_2 coating (Figure 5.53 (a) and Figure 5.53(b)).

From Figure 5.53 (b), under 5 N applied load, it is noted that the abrasive groove can not be observed on the contact area of sample 2. Since the hardness and L_C of sample 2 are higher than sample 1, it is thus expected that the increase in hardness and L_C will reduce the wear rate of the coating. Accordingly, increasing the coating hardness and L_C is effective in increasing the wear resistance.

Figure 5.53: SEM image of worn surface after wear testing (sliding) under applied load of 5 and 10 N, revealing severe plastic deformation in the substrate (a) sample 1 and (b) sample 2.

EDX mapping was used to identify the Ti element on the wear track. Figure 5.54 and Figure 5.55 show the results of EDX mapping. For sample 1 (Figure 5.54), under testing loads of 5 and 10 N, the coating is permanently worn out from the substrate in the wear track. The Ti element could not be evidently detected at the wear track. However,

the Ti element could be found at the wear track produced on sample 2 under 5 N load. This evidently remarks that the coating (sample 2) has not been worn out under 5 N load after sliding distance of 100 m, as confirmed by Figure 5.56. However, at the applied load of 10 N, the coating was permanently worn out from the substrate in the wear track of sample 2 (Figure 5.55).

Figure 5.54: SEM of abrasive grooves and EDS images illustrating of sample 1 under testing load of 10 N ((a) and (b)) and under testing load of 5 N ((c) and (d)).

Figure 5.55: SEM of abrasive grooves and EDS images illustrating of sample 2 under testing load of 10 N ((a) and (b)) and under testing load of 5 N ((c) and (d)).

Figure 5.56 shows the 3-D profilometre of both tested samples, where the wear tracks could be clearly seen. At the same applied load, it can be seen that wear rate is higher in sample 1 (Figure 5.56 (a)) compared to sample 2 (Figure 5.56 (b)). In particular, the wear rate of sample 2 under 5 N is immeasurably small. This evidently supports the results from the friction curves and EDS tests that the increase in hardness and L_C will reduce the wear rate of the coating. Accordingly, increasing the coating hardness and L_C is effective in increasing the wear resistance.

Figure 5.56: Three-dimensional profilometer showing abrasive grooves of sample 1 (a) and sample 2 (b) tested under load of 5 N and 10 N.

5.7.2 Tribological Experiments of Set 2

Five samples i.e. the three best samples in terms of hardness and L_c in sections 5.4, 5.5, 5.6 and the two newly deposited samples were selected as Set 2 samples for tribological test. These include:

1. Sample 1 selected from sample 2 in section 5.4 in Table 5.7,
2. Sample 2 selected from sample 2 in section 5.5 in Table 5.8,
3. Sample 3 selected from sample 3 in section 5.6 in Table 5.10,
4. Sample 4 selected from sample 1 in section 5.4 in Table 5.6 with Ti interlayer at 10 min and applied biasing for the first 30 min only,

5. Sample 5 selected from sample 1 in section 5.4 in Table 5.6 with Ti interlayer at 10 min and deposited TiB₂ top layer for 300 min (5 h).

Table 5.12 summarizes the details and some properties of the selected coatings. It is noted that all samples were deposited using the deposition time of TiB₂ coating for 180 min (3 h) in total, except sample 5 deposited for 300 min (5 h).

Table 5.12: Summary of samples used in this Set 2.

Sample	Sections	Details	R _a (nm)	Coating thickness (μm)	Hardness (GPa)	L _C (mN)
Sample 1	5.4	Ti (N)/TiB ₂	1.9	1.85	35.6	1,784.5
Sample 2	5.5	Cr/TiB ₂	2.8	1.70	36.3	2,034.1
Sample 3	5.6	Multilayer Ti/TiB ₂	18.2	3.15	35.6	1,995.0
Sample 4	-	Ti/TiB ₂ with biasing	4.6	1.75	38.5	2,012.4
Sample 5	-	Thick Ti/TiB ₂	6.3	2.90	44.1	4,203.2

According to the dry sliding wear against an alumina ball of Set 2, typical curves of friction coefficient versus sliding distance are illustrated in Figure 5.57, which were obtained at a sliding speed of 20 cm/s and applied load of 5 N (Figure 5.57 (a)) and 10 N (Figure 5.57 (b)) under unlubricated conditions.

From Figure 5.57 (a), it can be seen that the friction coefficient of all samples initially increases with sliding distance until a peak value is reached, then it decreases with sliding distance and gradually approaches the steady state after about 78 m, 60 m, 20 m, 105 m and 84 m sliding for samples 1, 2, 3, 4 and 5, respectively. The friction curves of sample 1 and sample 2 show a similar pattern with similar friction coefficient of 0.7 at steady state, whilst samples 3 to 5 show a friction coefficient of 0.55 at steady state. It is well-known that the friction coefficient increases with increasing surface roughness (R_a). However, under the present conditions, it can be seen that the R_a of samples 1 and 2 is much smaller than that of samples 3 to 5 (Table 5.12). The fact that sample 1 and 2

exhibit higher friction coefficient suggests that roughness do not play a significant role here, but rather structural factors are more dominant.

Figure 5.57: Typical friction coefficient curves for the deposited samples sliding against alumina ball (a) under load 5 N applied and (b) under load 10 N applied.

Figure 5.57 (b) shows the friction coefficient of all samples tested under 10 N load. The curves under 10 N show a lower scatter and less fluctuation of the obtained

values. It can be seen that the friction curves of all samples initially increases with sliding distance until a peak value is reached, then it decreases with sliding distance and gradually approaches the steady state with the similar friction coefficient of 0.65 after about 75 m, 20 m, 20 m, 90 m and 80 m sliding for samples 1, 2, 3, 4 and 5, respectively. The critical distances in which the friction curves show sudden change are plotted in Figure 5.58. It can be seen that sample 4 demonstrates the best results by having the highest critical distance under both 5 N and 10 N load which resulted in the best wear resistance among all the tested samples.

Figure 5.58: The plotted curves of critical distance of all samples.

In order to study the failure behaviour and to confirm that the coating had been worn out from the substrate, SEM and EDX were carried out. Figure 5.59 shows the SEM image and results of EDX mapping of sample 1. It can be seen that the worn surface produced by the alumina slider is microscopically smoother and is not so heavily scored as compared to uncoated HSS substrate (Figure 5.52). Microscopically, large valley of wear groove was formed with larger applied load. It is noted that for sample 1, under testing loads of 5 and 10 N, the coating had been permanently worn out from the substrate in the wear track since Ti element could not be evidently detected at the wear track.

Figure 5.59: SEM image of abrasive grooves and EDS images of sample 1.

Figure 5.60: Three-dimensional profilometer showing abrasive grooves of sample Set 2 by testing under load 5 N (left grooves) and under 10 N (right grooves).

Figure 5.60 shows the three-dimensional profilometry view of the wear tracks of all samples in Set 2 tested under 5 N (left grooves) and under 10 N (right grooves). The wear volume from each track was measured and summarized in Figure 5.61. It can be seen that under unlubricated sliding against an alumina ball, the TiB₂ based coatings produced under various deposition conditions increases the wear resistance of high speed steel by more than three times (compared to sample 4). It is noted that all samples can improve the wear resistance of HSS. It is interesting to note that the coating thickness has no significant influence in the wear volume, which is in agreement with reports for nitrided coatings [5-15]. Although sample 4 (1.75 micron thick) is much thinner than sample 3 (3.75 micron thick), it can provide much improved wear resistance.

Figure 5.61: Wear volumes produced from various samples by an alumina ball slider under unlubricated conditions.

5.8 Finite Element (FE) Analysis of Nanoindentation of Single Layer TiB₂ Coatings with a Ti Interlayer

The nanoindentation technique has been used throughout this project as a powerful experimental tool to evaluate the hardness and Young’s modulus of the TiB₂ coatings. Although in order to measure the intrinsic properties of the coating, the “rule of thumb”,

has been followed by using an indentation depth of 50 nm, which is less than one-tenth of the TiB_2 coating thickness. There are still uncertainty about the measured properties and the response of the TiB_2 coating, the interlayer and the substrate to indentation process. In order to gain a better understanding of the load-displacement behaviour, deformation behaviour of single layer and multilayer systems, several finite element (FE) models have been developed in this work, as detailed in Chapter 4. This section discusses the computation results and their comparison with the experimental work for the single layer TiB_2 coating with a Ti interlayer. The computation results for the multilayer systems and micro-scratch test are presented in the following sections.

5.8.1 The Load-displacement Curves and Material Sink-in

The typical loading and unloading curve of the experimental nanoindentation test (sample 1 in Table 5.4, section 5.2) was plotted, as shown in Figure 5.62. This experimental load-displacement curve was used to compare with the simulation results to find out the best fit between FE and experimental results. Since the best fit was found, the important coating properties could be predicted by the FE model such as the yield stress (Y) and elastic modulus (E).

Figure 5.62: Experimental loading and unloading curve of Ti/ TiB_2 coating (sample 1 in Table 5.4, section 5.2).

Load-displacement curves calculated by the FE model with different coating properties were plotted and compared with the experimental curve (Figure 5.63 (a)-(h)).

The properties of the HSS substrate and Ti interlayer used in the models were fixed as shown in Table 4.2, whilst the properties of TiB_2 coating were varied (Table 4.1). Figure 5.63 (e) shows the best fit of the FE curve to the experimental curve. Hence, it can be assumed that the mechanical properties of this TiB_2 coating are: Young's modulus = 260 GPa and yield strength = 13 GPa. From this result, it is clear that with the FE technique, the properties of the coating could be derived, in particular the yield strength, which could not be extracted from experimental nanoindentation.

In order to extract the intrinsic mechanical properties such as hardness of TiB_2 coating by using the FE model, the model was inputted with the above mechanical properties i.e. $E = 260$ GPa and $Y = 13$ GPa and then the nanoindentation processes were simulated. Figure 5.64 shows the indentation profiles simulated for the HSS substrate alone, the coating material alone and the coating-substrate system at the same indentation depth of 500 nm. It can be seen that indentation of the substrate halfspace alone and the coating halfspace results in material sink-in as expected from the material properties of the hard materials [153]. The coating-substrate system experiences material sink-in, which is greater than the HSS substrate halfspace.

Figure 5.63: Comparison load-displacement curves between experiments and FE results to find the best fit of both curves.

Figure 5.64: Surface profiles of the indented coating/substrate system (TiB_2 coating) and the corresponding substrate and coating halfspace, showing sink-in in the coating/substrate system.

To further demonstrate the phenomenon of material sink-in in the coating-substrate system, Figure 5.65 compares the sink-in depth (i.e. the depth of the sink-in material with reference to the original surface of the coating) of the coating/substrate system with those of the corresponding coating halfspace.

Figure 5.65: Comparison of sink-in depth in the coating/substrate system and in the corresponding coating halfspace, showing enhanced sink-in in the coating/substrate system after certain critical penetration depth.

From Figure 5.65, it can be seen that at indentation depth below $0.2\ \mu\text{m}$ (arrow), there is no difference in sink-in behaviour between the coating halfspace and the coating-substrate system, indicating insignificant substrate effect. The sink-in effect in different penetration depth is further illustrated in Figure 5.66 as obtained by the FE model. It can be seen that the sink-in depth increases as penetration depth increases.

Figure 5.66: The sink-in effect in different penetration depth.

From such indentation profiles, the true contact area could be derived by measuring the area where the indenter tip made contact with the coating (arrow in Figure 5.66). This is regarded as the true contact area. The hardness calculated (using Eq. 2.6) from the true area at 50 nm depth with the calculated maximum load of 2.6 mN is 24.48 GPa, which is in very good agreement with the experiment (sample 1 in Table 5.4, section 5.2). Further investigation was conducted to calculate the true hardness of TiB_2 coating at different penetration depths i.e. 100 nm, 200 nm, 300 nm, 400 nm and 500 nm.

Table 5.13 summarizes the calculated true hardness of TiB₂ coating at different depth by FE modeling.

Table 5.13: Calculated true hardness of TiB₂ coating at different depth.

Penetration Depth (nm)	Calculated Hardness (GPa)
50	24.48
100	24.16
200	23.48
300	22.20
400	19.15
500	17.50

Table 5.13 shows that the calculated hardness decreases with the increase in the penetration depth due to the substrate effect, which will be discuss later. The results of FE calculation and experimental measurements are compared in Figure 5.67. Good agreement is evident from the figure.

Figure 5.67: The comparison between FE calculation and experimental results at different penetration depth.

Figure 5.68 shows the propagation of the plastic deformation zone in the TiB₂ coating (with Ti interlayer) and the HSS substrate during the nanoindentation process. At

small indentation depths, plastic deformation occurs in the coating only, which propagates both vertically and laterally (Figure 5.68 (a) and (b)). At larger depths, the plastic zone in the coating reaches the coating/substrate interface, and then is constrained vertically, such that the zone only propagates along the lateral direction (Figure 5.68 (c) and (d)). A further increase in depth results in the further lateral propagation of the plastic zone in the coating, until a certain critical depth, at which plastic deformation in the substrate at the interface is initiated and then propagated (Figure 5.68 (e)). The plastic deformation occurred in the substrate will affect the measurement of the coating properties. The propagation of the plastic deformation zone in the Ti interlayer could not be shown in Figure 5.68 because the Ti interlayer can be deformed easily due to its low yield strength. Once the indentation penetrated into the coating (at 50 nm), the plastic deformation zone in the Ti interlayer started immediately. This means that the plastic deformation zone in the Ti interlayer only propagates along the lateral direction.

Figure 5.68 (a)-(d) shows that the HSS substrate is free from plastic deformation (yield strength of the HSS substrate is 4 GPa). However, a plastic zone started to form in the substrate when the indentation depth reached 365 nm (arrow in Figure 5.68 (e)). Therefore, it is necessary to avoid indenting above this depth in order to prevent the substrate from undergoing plastic deformation.

However, this result of critical indentation depth of 365 nm was over-calculated due to the influence of the soft Ti interlayer, which helps to accommodate the stress before it goes through the substrate [41]. This also proves the benefit of the thin interlayer to the stress accommodation, which results in enhanced coating properties. The critical depth due to the effect of substrate will be studied in the next section.

5.8.2 The Critical Depth to Coating Thickness at which the Contribution of the Substrate is Negligible.

It is a well known fact that in order to measure the hardness of a coating on a substrate by indentation, the penetration depth must be less than a critical value, which is a small fraction of the thickness of the coating. The frequently used one-tenth rule suggests that if a coating has a thickness of ten times the indentation depth, then the measured hardness is very close to the true hardness of the coating [154]. Therefore, a large penetration depth is not desirable as it will introduce substrate effect into coating property measurement. Indeed, the penetration depth genuinely does affect the measured hardness as shown in Figure 5.67.

Therefore, the halfspace method was developed in order to find out the critical penetration depth above which the substrate starts to affect the load-displacement behaviour of the coating. Figure 5.69 shows the load-displacement curves of the coating-substrate system and the coating halfspace. It can be seen that there is no substrate effect when the penetration depth is 50 nm, since the loading-displacement curve of the coating-substrate system coincides well with that of the coating halfspace. But the load-displacement curves of coating halfspace start to deviate from the curves of coating-substrate system at increasing penetration depth. The penetration depth at which the deviation starts to take place (arrow) can be considered as the critical depth for the substrate to take effect. From Figure 5.69, the critical depth is found to be around 92 nm, which agrees with the results shown in Figure 5.67. It should be noted that the TiB_2 coating thickness is 1.4 μm . The critical depth of 92 nm corresponds to a depth-to-coating thickness ratio of 0.07, i.e. in order to avoid substrate effect in TiB_2 coating hardness measurement, the indentation depth should not exceed about 7% of the coating thickness. This is in agreement with Sun et al's work [155] and is in an approximation with the well known "one-tenth" rule.

Figure 5.69: Load-displacement curves of coating-substrate systems and the corresponding coating halfspaces at different indentation depths: (a) 50 nm, (b) 100 nm, (c) 200 nm, (d) 300 nm, (e) 400 nm, (f) 500 nm.

5.9 Finite Element Modeling of Multilayer Ti/TiB₂ Coatings

The nanoindentation load-displacement behaviour of multilayer systems was simulated by the multilayer model described in Section 4.2.4. The FE results of load-displacement curves calculated using the material properties given in Table 4.4 are plotted in Figure

5.70. It can be seen that with Young's modulus of 350 GPa and yield strength of 15 GPa for the TiB₂ coating, the best fit to the experimental curve was achieved.

Figure 5.70: Comparison of simulated results with experimental data of multilayer system.

5.9.1 Development of Plastic Deformation Zone in Multilayer System

The plastic deformation behaviour in the multilayer Ti-TiB₂ system as the indentation depth is increased was also simulated by the FE model. Figure 5.71 shows the propagation of the plastic deformation zone in the sample at different stages and depths, i.e. (a) initial stage, (b) 50 nm, (c) 300 nm and (d) 500 nm.

From Figure 5.71, it is noted that at small indentation depth of 50 nm, the indenter penetrates the top layer, i.e. the hard TiB₂ layer, and plastic deformation occurs around indenter tip region, which propagates both vertically and laterally as round shape, not only in the first top layer (the hard coating, TiB₂), but also in the underlying second layer (soft coating, Ti) and the third layer (the hard coating, TiB₂) (Figure 5.71 (b)). At larger depth (Figure 5.71 (c) the plastic deformation propagates further below the surface, to the

third layer (the hard coating, TiB_2). At the maximum penetration depth of 500 nm (maximum load applied), the plastic deformation propagates further below the surface, to all layers as shown in Figure 5.71 (d). It is interesting to note that plastic deformation is initiated from the bottom of the third and fifth layers (the hard coating, TiB_2) so that for the multilayer, the plastic deformation does not start around indenter tip region except for the first top layer. The detail of this phenomenon needs further investigation.

Figure 5.71: Development of plastic zone in multilayer system as the indentation depth is increased: (a) initial stage, (b) at 50 nm, (c) at 300 nm and (d) at 500 nm.

5.9.2 The Load-displacement Curves and Hardness as a Function of Penetration Depth in Multilayer System

From the FE results of multilayer coatings, six load-displacement curves calculated at indentation depth of 50 nm, 100 nm, 200 nm, 300nm, 400 nm and 500 nm are plotted as shown in Figure 5.72. Figure 5.73 shows the hardness and reduced modulus versus depth of penetration computed by FE simulation and measured by experiments.

Figure 5.72: Load-displacement curves of the multilayer systems at different penetration depth.

From Figure 5.73, it is noted that the hardness decreases with increasing penetration depth due to the substrate and interlayer effect. It can be seen that the hardness values calculated by FE modeling is slightly lower than those measured by experimental nanoindentation. The value of hardness calculated from a penetration depth of 50 nm is 31 GPa, which is lower than the measured hardness (36.5 GPa). This is probably due to by an indentation size effect [77], which is the error associated with the area function of the indenter, in particular at very small values of penetration depth. In general, the indentation hardness of materials is observed to increase with decreasing size of indentation owing to the nucleation of dislocation within the plastic zone. The

presence of dislocations serves to increase the effective yield strength of material and this in turn means an increase in hardness [76].

Figure 5.73: The comparison of hardness between FE calculation and experimental results at different penetration depth.

5.9.3 Effect of Sink-in Phenomena in Multilayer System

Figure 5.74 shows the sink-in behaviour when the multilayer model is indented at 50 nm, 100 nm, 200 nm, 300 nm, 400 nm and 500 nm. From the FE results, it is noted that sink-in is dominant at all penetration depth and the degree of sink-in increases with increasing penetration depth.

Figure 5.74: The effect of sink-in when the multilayer model was indented at 50 nm, 100 nm, 200 nm, 300 nm, 400 nm and 500 nm.

5.10 Finite Element Modeling of Micro-Scratch Test

In order to gain a better understanding of the scratch behaviour during the testing process, FE simulation has been employed. To simplify the problem, the scratch process was simulated with constant applied load (normal load) mode. Sample S2-1 (Table 5.3) with coating thickness of 700 nm was used for modeling as a test sample in this FE model (Figure 4.8) as described in section 4.3.

Figure 5.75 shows the von Mises stress contours calculated in the TiB₂ coating/HSS substrate system during the scratch process. Figure 5.75 (a) shows the step of indentation into the coating, in which there is no sliding movement but only a normal load applied by the indenter. At small indentation depth of 0.1 μm at the loading stage (Figure 5.75 (a)), plastic deformation occurs around the indenter tip region, which propagates both vertically and laterally as round shape. It is noted that plastic

deformation occurs at the indenter tip region, not only in the top layer (stress level of 7 GPa), but also propagates to the substrate (stress level of 3 GPa). With increasing penetration depth, plastic deformation propagates further below the surface and at the substrate. Plastic deformation also propagates both vertically and laterally both in the coating and the substrate. The interface between the coating and substrate can be identified clearly by the different level of stresses (as shown in the figure in different colours), arising from the difference in material properties.

Figure 5.75 (b) shows the early stage of scratching process. The indenter slides on the surface under the applied normal load. This results in the ploughing of the material, and a tangential force due to this ploughing action. As the stylus is moving, the plastic deformation zone is moving in the same direction but the plastic deformation zone is no longer located in the center of the indenter tip region. It is moved towards the leading edge of the indenter, which can be clearly seen from the top view as shown in Figure 5.76 (a). When the scratch test finishes, the stylus moves away from the coating as unloading step. It can be seen that compressive residual stresses are present within the groove and material pile-up is identified (Figure 5.76 (b)).

Figure 5.75: Development of plastic zone in the scratch process (transverse section view): (a) loading process at penetration depth of $0.1\text{ }\mu\text{m}$, (b) during scratch process.

Figure 5.76: (a) 3-D stress contours during scratch process, and (b) scratch track after unloading step.

Figure 5.77 shows the top view of the scratch process i.e. loading stage (Figure 5.77 (a)), sliding (Figure 5.77 (b) to (e)) and unloading stage (Figure 5.77 (f)). It can be seen that the plastic deformation zone is moving towards the leading edge of the indenter during the scratch test (Figure 5.77 (b) to (e)).

Figure 5.77: The top view of the scratch process.

In order to compare the simulation results with the experiment ones, constant load scratch test was conducted at a load of 240 mN. Figure 5.78 compares the measured tangential (friction) force with that from FE simulation. It can be seen that the friction

force from the experiment is higher than the calculated one. The reason for this is discussed in Chapter 6.

Figure 5.78: Comparison of simulated tangential force with experimental results at constant load of 240 mN and scratch distance 15 μm.

Chapter 6

Discussion

The experimental and finite element analysis results, together with some interpretation of the results, have been presented in the last chapter. Several important observations that arose from the experimental and analysis work deserve further discussion in this chapter. These include the factors that affect the preferred orientation, hardness, adhesion and overall quality of TiB_2 based coatings, and some phenomena observed during tribological testing and FEA simulation.

6.1 Factors Affecting Preferred Orientation of TiB_2 Coating

In physical vapour deposition processes, coatings grown from the vapour phase usually reveal preferred orientation. From the experimental results presented in the last chapter, it can be seen that the TiB_2 coatings produced under the conditions of optimum substrate temperature and deposition time, stationary substrate, sputter-cleaning the substrate and annealing, tend to develop a texture with a (001) preferred orientation, whilst substrate biasing and multilayers tend to decrease the (001) preferred orientation as discussed in more detail below.

6.1.1 Substrate Temperature and Deposition Time

The first deposition parameter that needs to be optimized is the substrate temperature. Varying the substrate temperature can have a significant effect on the preferred orientation of TiB_2 coating. The hexagonal TiB_2 phase in samples deposited at room temperature up to 300 °C did not demonstrate the preferred (001) orientation as shown in Figure 5.3. The (001) reflection appears in the diffraction pattern at deposition temperature of 400 °C, indicating that the coating starts to orient in (001) direction at this temperature. This could be explained by the fact that with increasing temperature, the surface diffusion of adatoms is increased, which results in the development of the preferred (001) orientation.

Experimental results given in section 5.1.2.1 and section 5.6.1 show that the preferred orientation of TiB_2 coating is a function of deposition time. For deposition of TiB_2 with one TiB_2 target, the preferred (001) orientation did not develop at deposition time of 2 h, although the power was increased from 150 W (sample S1-4) to 300 W (sample S1-5) (Table 5.1). The preferred (001) orientation developed evidently at deposition time of 3 h (sample S1-6). For deposition of TiB_2 with two TiB_2 targets, the observed results suggest that the TiB_2 layer needs a deposition time at least 90 min to develop into a well crystallized structure with preferred (001) orientation (Figure 5.38). It can thus be concluded that the texture evolves from random orientation in initial deposition to preferred orientation as the coating thickens further. This is beneficial for the multilayer system. From the XRD results (Figure 5.38), it is clear that with increasing number of multilayers, TiB_2 layers exhibit more random orientation, whilst the two-layer coating produced under the same conditions shows strong (001) orientation. Therefore, in order to deposit TiB_2 multilayer coatings with a strong (001) texture, the TiB_2 layer needs sufficient time to develop such a well crystallized structure with preferred (001) orientation, which is 90 min in this study.

6.1.2 Substrate State during Deposition

From Figure 5.16, it is noted that preferred orientation of the coating produced with substrate rotation in this set is different from that produced with one TiB_2 target (the substrate-to-target is 60 mm), which showed (001) texture (sample S1-7 in Figure 5.3). The reason for this is that for one target during substrate rotating the deposition rate is reduced because of reduced distance between substrate and target and thus reduced flux of adatoms. This would allow more time for the surface species to diffuse and thus would help to develop the (001) texture. However, in the case of two TiB_2 targets, during substrate rotation the flux of adatoms is not reduced between substrate and target, which resulted in the random orientation of the resultant coatings due to the lack of time to grow the (001) texture.

From the XRD examinations (Figure 5.16), it is clear that the TiB_2 coatings deposited on rotating substrates have a random orientation whilst the coatings produced

under the same conditions on stationary substrates show strong (001). The effect of substrate rotation on (001) texture development can be considered to be three-fold. First, as the substrate rotates, the deposition rate is reduced as a result of reduced flux of adatoms. This would allow more time for the surface species to diffuse and thus would favor the formation of the development of the (001) texture, as observed by Lee et. al [150] for TiB_2/TC multilayer coatings. However, in the present work, a (001) textured TiB_2 coating was formed on the stationary substrate rather than on the expected rotating substrate. This can be explained by the second effect of substrate rotation, which lies in the energy of the sputtered species arriving on the substrate surface. It is known that the energy of the sputtered species decreases with increasing substrate-target distance due to increased collisions between the sputtered species and the gas molecules in the sputtering atmosphere [148]. The energy of the sputtered species arriving at the stationary substrates is thus higher than that arriving on the rotating substrates, and this would lead to increased adatom mobility and development of the (001) orientation in the coating. It is obvious that the second effect played a more crucial role than the first effect in the present case.

The third effect of substrate rotation lies in the influence of the different scattering probabilities of Ti and B atoms in the discharge. This was used to explain the overstoichiometry of the sputtered TiB_2 coating [49, 156]. In short, generally in nonreactive sputtering process, stoichiometric deviations of the coating from the target composition attribute to interactions of the sputtered target atoms with the plasma discharge in the transport phase and at the surface of the growing film. Considering B atoms having the low particle radius and therefore low collision cross section, B atoms possess a higher mobility within the discharge compared to Ti atoms. B atoms could arrive to the substrate easily causing an excess of B in the coating (overstoichiometry).

Further study showed that at a higher ratio of B/Ti, the preferred orientation of the coating changes from (101) to (001) and the intensity of the (001) reflections is strongly increased, whilst the broadness of the XRD reflections decreases [157]. This is in agreement with the XRD results in this study, as shown in Figure 5.16.

6.1.3 Sputter-cleaning the Substrate

From Figure 5.7 (section 5.1.3.1), the TiB_2 coating (sample S2-1) produced without sputter-cleaning of substrate has a hexagonal structure with strong (001) preferred orientation. It can be seen that sputter-cleaning of the substrate before deposition seems to reduce the degree of this orientation (compare sample S2-1 with sample S2-6 and S2-7 in Figure 5.7). However, increasing the substrate sputter-cleaning time from 20 min (sample S2-6) to 60 min (sample S2-7) slightly promoted the TiB_2 (001) orientation (Figure 5.7). This is possible to explain that the increase of sputter-cleaning time will increase the surface roughness owing to an increased amount of droplets. This may be associated with the enhancement of nucleation and re-nucleation (owing to generation of nucleation sites via defects and implanted), resulting in the development of the (001) texture. Nevertheless, no clear correlation between sputter cleaning and texture development has been developed in this work

6.1.4 Annealing

It is a widely known fact that the texture may develop or change as a result of annealing [30]. From Figure 5.23, it can be seen that with annealing the (001) texture could be retained and even increased as compared to the as-deposited sample. Moreover, with increasing annealing temperature, the intensity of peak (001) increases, suggesting increased degree of (001) texture by annealing. A possible reason is that at elevated temperatures where low-strain growth takes place, surface and interfacial-energy minimization dominates grain growth. Under these condition, close-packed plane texture (the preferred growth plane) evolves.

6.1.5 Substrate Biasing

An important parameter that can affect the orientation during growing coating is the application of a substrate biasing. Experimental results revealed that the TiB_2 coating produced without biasing has a hexagonal structure with strong (001) preferred orientation (Figure 5.7). The (001) texture could also be found in the coatings produced with small biasing for a short period of whole deposition. However, increasing substrate

biasing seems to reduce the degree of (001) texture (compare sample S2-1 with samples S2-6 and S2-7).

With the introduction of substrate biasing for the entire deposition of 3 h (S2-2 to S2-5 in Figure 5.7), the orientation of the TiB_2 coating is significantly changed. From Figure 5.7, it can be seen that with increasing bias power, the evolution of the (001) orientation was decreased and the orientation is changed to (101), particularly in sample with high biasing energy. Indeed, by applying a negative bias to the substrate, ions are extracted from the plasma and accelerated towards the depositing coating. This bombardment suppresses the formation of microstructure of the coating.

6.2 Factors Affecting Hardness of TiB_2 Coating

Since TiB_2 coatings with (001) orientation is known to yield the highest hardness as compared to TiB_2 coatings with other orientations [145], the factors that enhance the (001) texture mentioned in section 6.1 should be firstly investigated in association with the hardness of TiB_2 coatings.

6.2.1 Substrate Stationary during Deposition

As mentioned in section 6.1.2 that during sputtering process, the energy of the sputtered species arriving on the stationary substrates is higher than that arriving on the rotating substrates, and this would lead to increased adatom mobility and higher ion bombardment during deposition, resulting in the development of a denser structure in the coating (Figure 5.17). This coating with a higher densification and higher compactness could improve the coating hardness.

6.2.2 Sputter-Cleaning the Substrate

As in the case of coating texture development, the effect of sputter cleaning time on TiB_2 coating hardness was found to be complex and inconclusive (Figure 5.11). The coating hardness initially increases with sputtering time, but it would decrease when the sputter cleaning time is too long, probably owing to the contamination from the

deposition chamber. The optimum sputter cleaning time was 90 min in order to achieve a higher hardness and coating adhesion.

6.2.3 Annealing

The increased hardness of annealed samples may be mainly due to the increased coating density and refinement of grain size. Yet, the increased hardness of annealed samples should take into account of the combined effect of coating densification, grain refinement and the solid solution hardening of the α -Ti(O) phase in the interlayer. The solid solution hardening took place during annealing since the oxygen atoms from the oxide film located on the HSS surface was decomposed, causing increased kinetic energy of oxygen atoms. The oxygen atoms then moved from the oxide film by diffusing into the Ti inter-layer and then form solid solution in α -Ti (O) phase. This may help to improve the hardness of the interlayer and coating adhesion to the substrate. In addition, from the experimental results, annealing seems to help in improving coating quality, which could be seen in the minimization of micro-voids by the change of coating structure with the elevated temperature as shown in Figure 5.24. This is beneficial to minimize coating defects (micro-voids) which could significantly impair the coating properties such as hardness and coating adhesion.

6.2.4 Substrate Biasing

From experimental results given in section 5.1.3, it is noted that coating hardness decreases with higher bias power. The reason for this behaviour may be due to the different microstructure of the coatings [146]. The microstructure of the growing coatings is significantly affected by the application of substrate biasing. For sputtering at low bias power, the coatings showed a strong (001) fiber texture [146]. By applying a negative biasing to the substrate, ions are extracted from the plasma and accelerated towards the depositing film [158]. This bombardment suppresses the formation of an open structure (Zone I). With increasing negative energy of the bombarding ions, the surface mobility is enhanced, which resulted in shifting the Zone I and Zone T boundary to a lower homologous temperature. It is noted that the structure has been significantly changed by biasing from Zone I which contained longitudinally oriented porosity between its tapered

crystals to Zone T which consisting of a dense array of poorly defined fibrous grains without voided boundaries. In addition, the increased hardness of coating may be related to the increase of structural bonding state [159].

6.2.5 TiB₂ Coating with Cr Interlayer

Although the XRD results detected from TiB₂ coating with Ti and Cr interlayers did show similar patterns with high (001) texture as shown in Figure 5.33 , it was observed experimentally that the Cr interlayer helps to slightly enhance the hardness of the TiB₂ top layer. The increased hardness of the TiB₂ coating with Cr interlayer may be related to the higher strength of the Cr interlayer as compared to that of the Ti interlayer. Indeed, nanoindentation tests of the interlayers on separate samples without subsequent deposition of TiB₂ coatings revealed that the Cr interlayer has a hardness of 4.5 GPa, as compared to the Ti interlayer which has a hardness of as low as 2.5 GPa.

6.2.6 Effect of Doping the Ti Interlayer with Nitrogen

The hardness peaking at doping the Ti interlayer with 10% N₂ may be attributed to the increased hardness of the Ti interlayer and the enhanced (001) preferred orientation of the TiB₂ coating (Figure 5.29), as TiB₂ coating with (001) orientation is known to yield the highest hardness as compared with TiB₂ coatings with other orientations. This is obviously due to the dissolution of nitrogen in the α -Ti lattice, causing solid solution hardening in the interlayer. Such an increased interlayer strength may account for the observed enhancement in hardness and enhanced (001) orientation. However, the reasons associated with the decrease in TiB₂ hardness with further increased nitrogen doping are not fully understood. It may arise from the embrittlement of the interlayer resulting from too much nitrogen incorporation.

6.3 Factors Affecting Adhesion of TiB₂ Coating

6.3.1 Substrate Stationary during Deposition

The higher adhesion strength found for the coatings on stationary substrates could be explained by the higher adatom energy as a result of the shorter substrate-target

distance. This would enhance adatom mobility in the growing coating and lead to improved coating-substrate interaction during the deposition process. The improved coating density and hardness also help to increase the critical load for coating failure during the scratch test. It is noted that since no substrate pretreatment was used, the micro-scratch test evaluates mainly the substrate adhesion and the coating structure plays only a minor role.

6.3.2 Sputter-cleaning the substrate

It is well known that sputter-cleaning the substrate is beneficial for improving the coating adhesion to substrate. The sputtering plasma can clean the substrate surfaces before starting deposition by removal of some contaminants or native oxides at the nano or sub-micron scales. This is a common technique used for enhancing the coating adhesion. In addition, after removing the native oxides on the substrate's surface, the sputtering plasma may cause the roughening of the surface which helps to improve the adhesion with coating by micro/nano-mechanical interlocking. However, from the experimental results, sputter cleaning for too long could impair the coating adhesion, probably due to the contamination from the chamber.

6.3.3 Substrate biasing

In the present work, the negative RF electric field was applied to bias the substrate in order to vary the flux and energy of depositing charged species. Due to the charge-exchange processes in the anode dark space, very few discharge ions strike the substrate with full bias voltage. Rather, a broad low energy distribution of ions and neutrals bombards the growing film. Indeed, substrate bias has been effective in modifying a broad range of properties in the deposited coatings including the improved coating adhesion since an enhancement of ions energy increases the surface mobility.

6.3.4 Multilayer TiB₂ coating

From the experimental results, it was found that an optimum combination of alternate layers gave the optimal enhancement in coating adhesion. This could be concluded in two-fold. First, during the scratch test, Ti is a good metallic material to

accommodate the stress from ceramic materials such as the highly stressed TiB₂ coatings [41]. This could help in enhancing coating adhesion. Another aspect is the decrease of residual stress by multilayer, because the soft Ti layers act as compliance layers to accommodate the residual stresses evolved in the TiB₂ layer, and thus help to reduce the overall residual stress level. Therefore, reducing the internal stress without sacrificing the hardness is a key point to obtaining good-quality coating.

6.3.5 Enhancing the strength of the interlayer materials

It has been a common practice that in the deposition of a ceramic coating onto a substrate, a thin titanium interlayer is used to improve the adhesion between the coating and the substrate. The roles of the metallic interlayer have been reported to be two-fold [160]. Firstly, the titanium interlayer acts as an oxygen-getter to dissolve the native oxide film on the substrate surface. Secondly, the soft interlayer acts as a compliance layer by plastic deformation under mechanical loading to reduce the stresses at the coating-substrate interface region. Similar techniques have been used to enhance the adhesion of TiB₂ coating onto steel substrates [161-162]. However, it seems that the yield strength of titanium interlayer was insufficient to accommodate the level of stresses generated in TiB₂ coatings during deposition and during application [26]. Some techniques were investigated to further improve the adhesion strength of sputtered TiB₂ coatings onto high speed steel (HSS) substrates, i.e. annealing the Ti/TiB₂ coating, nitrogen doping the Ti interlayer and using Cr as an interlayer material.

6.3.5.1 Annealing

As mentioned in section 6.2.3, the annealing could help to improve the coating adhesion to substrate since the oxygen atoms were moved from the oxide film due to the elevated temperature by diffusing into the Ti interlayer and then form the solid solution in α -Ti (O) phase. This could help to enhance the strength of Ti interlayer, resulted in the enhanced coating adhesion.

6.3.5.2 The nitrogen doped Ti interlayer of TiB₂ coating

The observed enhancement in adhesion strength can be attributed to the increased strength of the nitrogen doped Ti interlayer. As discussed previously, the titanium interlayer serves as an oxygen getter to decompose the native oxide film on the substrate surface, thus promoting adhesion between the coating and the substrate. Doping the Ti interlayer with nitrogen does not significantly change the chemical nature of α -Ti, because no TiN compound is formed and nitrogen is dissolved in the α -Ti lattice. It is thus expected that the doped Ti interlayer also plays a similar role as an oxygen getter. In addition, the interlayer also provides compliance for the hard and brittle TiB₂ coating and helps to accommodate interfacial stresses through plastic deformation. However, if the interlayer is too soft, such as a pure Ti interlayer, it will deform too easily and provide less support to the TiB₂ coating. With nitrogen doping, the Ti interlayer becomes stronger and thus can provide increased support to the TiB₂ coating, leading to enhanced adhesion strength. But, with further increasing nitrogen doping, the interlayer becomes too strong and brittle to accommodate the interfacial stresses, leading to the observed reduction in adhesion strength. In this study, doping the interlayer in 10% N₂ seems to produce the optimum combination of strength and compliance for adhesion enhancement in the present deposition conditions.

6.3.5.3 TiB₂ coating with Cr interlayer

The enhanced coating adhesion with a Cr interlayer could be derived from not only the higher strength of the interlayer, but also the better structural match or a better materials compatibility between Cr and the HSS substrate. It is noted that both Cr and HSS have the same body centered cubic (BCC) structure as compared to Ti which has a hexagonal close packed (HCP) structure.

6.4 Adhesion Critical Load vs. Indenter Radius

For scratch measurements, it has been established that the critical load (L_c) value increase as a function of indenter tip radius, as mentioned in section 2.6.3. This can be explained simply by considering that the smaller the tip radius, the higher the contact

pressure, and thus the lower the load required to cause failure in the coating. However, it is noted that the L_c depends not only on the indenter radius, but also on the loading rate and the scratch speed (section 2.6.3).

From the literature, most of the L_c values were obtained experimentally with scratch indenter tip radius of 200 μm as summarized in Table 2.2. In the present investigation, all micro-scratch experiments were carried out with the scratch indenter tip radius of 25 μm . Therefore, the values of experimental results show lower values as compared to those obtained with the tip radius of 200 μm . So far, experience in the scratch testing field has shown that different radii of diamond indenter are often required in order to adequately characterize the adhesion of modern coatings. In particular, ultra-thin films require even a smaller tip radius such as that used in nanoscratch measurement. However, there is no exact equations to show the correlation between the scratch tip radius and L_c . This needs to include the effect of coating thickness and its properties, interlayer and substrate.

Ahn et al [163] reported that the average pressure, P_m , applied by a spherical point at the moment the critical load is reached is related to the plastic deformation in the substrate and can be approximated to the substrate hardness, H , by the equation:

$$P_m \approx H = \frac{2L_c}{\pi b^2} \quad (6.1)$$

where b is the half-width of the scratch. Because b is proportional to the indenter tip radius, R . Eq. 6.1 shows that the critical load must be proportional to R^2 . Steinmann et al. [164] showed experimentally that the critical load variation is not proportional to R^2 , but varies from $R^{0.85}$ to $R^{1.10}$, depending on the value of dL/dx (the ratio between the loading rate, dL/dt , and the scratching speed, dx/dt). It is interesting to note that if the ratio dL/dx remains constant then the critical load is independent of the loading rate and the scratching speed.

In order to estimate the comparative L_c between tip radius of 25 μm and 200 μm , Randell et al [165] reported that the tip radius did affect the measured L_c tremendously as shown in Figure 6.1 (a) for TiN coatings and Figure 6.1 (b) for W coatings. The evolution of critical load as a function of indenter radius of 20 μm , 50 μm , 100 μm , and 200 μm is shown graphically for each tested material in both figures. It can be seen that the measured critical load (L_{c3} in the figure) increases dramatically with the increase of the indenter radius. The critical load increases about five times for TiN (Figure 6.1 (a)) and more than ten times for W coatings (Figure 6.1 (b)) when the tip radius increases from 20 μm to 200 μm . From these results, it is noted that the measured critical load values of the TiB_2 coatings using an indenter tip radius of 25 μm addressed in this work should be increased for five to ten (or more) times if a conventional tip radius of 200 μm was used. Indeed, by comparing the hardness between TiB_2 coating and TiN and W coatings, it is noted that the TiB_2 coating shows a similar hardness value to the W coating or even higher. Thus, this indicates that the measured critical load of TiB_2 coating with 25 μm tip radius should be increased at least ten times if a conventional tip radius of 200 μm was used.

For comparison purpose, the critical load values of TiB_2 coatings reported in the literature (see Table 2.2) tested under a conventional indenter tip radius of 200 μm should be examined carefully. Values in the range of 6 to 45 N for the various thicknesses up to 4 μm were found by other investigators. In extreme cases, critical load up to 70 N was obtained for coating thickness of 60 μm (Table 2.2). In this experimental work with a 25 μm tip radius, the critical load values are in the range of 1 to 4.2 N (thickness is less than 3 μm). It can be reasonably estimated that if the conventional tip radius of 200 μm were used, the critical load could have been at least in the range of 10 to 42 N, which is in agreement with the literature and is acceptable for tribological applications.

Figure 6.1: Variation in the critical load (indicating in L_{c3} in the figure) as a function of different indenter radii on (a) TiN and (b) W [165].

6.5 Residual Stresses

In section 2.3.2, the stress contour map (Figure 2.8) was drawn to study the effect of sputtering power and the working pressure on the residual stress of resultant coatings deposited at room temperature. It is noted that this stress contour map can be used to estimate the intrinsic stress (σ_i) developed in the resultant coating if the same TiB_2 target size with diameter of 10 mm is used. It can be seen from Figure 6.2 that at a fixed power of 400 W and a fixed total deposition pressure of 0.667 Pa (5 mTorr), the TiB_2 coatings produced in this work should show a residual stress value of -300 MPa, as marked in Figure 6.2. It is noted that there is no Ti interlayer used in this stress contour map (Figure 6.2).

Figure 6.2: Intrinsic stress contour map of TiB₂ coating at room temperature [25].

It is also noted that another crucial factor causing the residual stress is the thermal stress. The thermal contribution to the residual stress originating from the cooling from deposition temperature of 400 °C to room temperature is estimated by using Eq. (2.2) to be -910 MPa, calculated (from Table 2.1) with $E = 551 \text{ GPa}$, Poisson's ratio = 0.104, thermal expansion coefficient of $\text{TiB}_2 = 8.65 \times 10^{-6} \text{ m/K}^{-1}$, thermal expansion coefficient of HSS = $12.6 \times 10^{-6} \text{ m/K}^{-1}$ ($\Delta\alpha = -3.95 \times 10^{-6} \text{ m/K}^{-1}$). The calculated thermal stress of TiB_2 coating on HSS substrate is shown in Figure 6.3.

Figure 6.3: The calculated thermal stress of TiB₂ coating on HSS substrate.

It can be seen that the intrinsic stress (-300 MPa) is smaller than the thermal stress (-910 MPa). Hence, the residual stress in the resultant coating is dominantly (more than 75 %) generated from the thermal stress. This estimated residual stress is in a good agreement with those reported in the literature [21].

According to the atomic peening mechanism reported by Thornton and Hoffman [166], neutral working gas atoms rebounding from the target can bombard the growing film and modify the film structure and create the compressive stress. This mechanism can be applied to explain the existence of compressive stresses in sputtered TiB₂ coating [60]. It is suggested that compressive stresses in deposited TiB₂ coating accumulates during sputtering process. However, under similar deposition conditions the compressive stress could not be found in pure Ti coatings [26, 167]. It is believed that the compressive stress observed in TiB₂ coatings is associated with its high melting point. Relaxation of stress during growth by elimination of defects is not effective if the ratio of T_s/T_m is low and adatom mobility is low (T_s is deposition temperature and T_m is melting temperature). This macro-stress generated by ion bombardment could not be relaxed because the experiments were carried out at relatively low deposition temperature i.e. $T_s/T_m = 0.19$ for $T_s = 400$ °C and $T_m = 3,225$ °C.

However, the measured residual stress (section 5.3.4) is much lower than the estimated and those reported in the literature. The cause of the lower residual stress is probably considered to be two-fold. First, the effect of Ti interlayer used in all TiB₂ coatings in this work should be considered. It is believed that the ductile Ti interlayer could help to absorb the stress during the development of TiB₂ top coating [26]. Berger and Larsson [26] addressed that by alternating deposits of a highly stressed TiB₂ with the ductile Ti in a multilayer structure, the residual stresses in the former can be reduced. Second, the residual stress measured in this study was performed by using silicon wafer as a substrate material, whose property is very different as compared to the actual substrate of HSS. This shows that the residual stress measured from silicon wafer substrate could not be used to indicate the exact value. However, the value can be used for comparison purpose.

From section 5.6.2, it can be seen that the measured residual stress of multilayer TiB₂ coatings (sample 2) is much lower than the single TiB₂ layer with Ti interlayer (sample 1). This is in a good agreement with literature in multilayer Ti/TiB₂ coatings reported by Berger and Larsson [26]. By alternating deposits of a highly stressed TiB₂ with the ductile Ti in a multilayer structure, the residual stresses in the former can be reduced. This is due to the ability of a soft interlayer to accommodate the coating stress and the Ti interlayer plays the role by interrupting the development of the growing TiB₂ layer with the dense structure, resulted in the change of coating texture to the columnar structure as confirmed by XRD results.

6.6 Wear Mechanism and Factors Affecting Wear

6.6.1 Dry Sliding Wear against a Bearing Steel Ball

From Figure 5.49, under load 1 N, the friction coefficient of HSS substrate increased slowly with increasing sliding distance until 18 m of sliding distance and then increased rapidly with increasing sliding distance until the steady state was reached after about 30 m of sliding distance. This initial low friction of the HSS substrate may be due to the smoothness of polished surface and the native oxide film on the surface. The

gradual increase in friction coefficient to reach the steady state is due to the penetration of the steel ball through the smooth surface. With further sliding up to 100 m, the friction coefficient increased only slightly with sliding distance, which may be due to the interaction between the slider and the third body material either worn out from steel ball or HSS (or both).

From Figure 5.51, it can be seen that the material was transferred from the steel slider to the TiB_2 coating surface with increasing load. This is because with increasing load, the contact pressure and contact area between the coating surface and the steel ball increased, which resulted in the increased wear rate of slider material. Figure 6.4 illustrates the wear process of steel ball slider during testing of the TiB_2 coating (with a Ti-interlayer), where wear debris is generated from the steel ball and some transferred onto the coating surfaces, resulting in the formation of a transferred film on the TiB_2 coating surface. No damage to the TiB_2 coatings was observed, and thus the TiB_2 coatings have proven effective as wear resistant coatings on HSS.

Figure 6.4: Schematic illustration of wear process of the Ti/TiB₂ coating against bearing steel slider.

6.6.2 Dry Sliding Wear against an Alumina Ball

Figure 6.5 shows the wear process of the TiB_2 coating against an alumina ball, which undergoes three stages i.e. the wear of TiB_2 top layer (b); the wear of Ti interlayer (c); and the wear of the substrate (HSS) through the test process (d).

Figure 6.5: Schematic illustration of wear process of the Ti/TiB₂ coating against alumina ball.

However, significant amount of wear was also produced from both the TiB₂ coating surface and the alumina ball slider. The wear of alumina ball slider is shown in Figure 6.6. It is believed that during the wear process, certain chemical reactions took place at the contact surfaces, probably through the diffusion of oxygen from alumina to the TiB₂ coating surface, resulting in the decomposition of alumina (Figure 6.6 (b)) and formation of titanium oxide (Figure 6.6 (c)). A diffusion couple was thus formed at the contact surfaces, resulting in accelerated wear of both encountered surfaces. This is a situation where diffusion wear prevails, which has been investigated in the titanium-alumina tribosystem, which is characterized by high wear rates of both contact surfaces

[168]. In addition, during the wear process, frictional heating of the contact areas and asperity plastic deformation are produced, which may change the system energy and activate the coating surface. This may also promote the diffusion of oxygen from alumina to the TiB_2 coatings surfaces.

Figure 6.6: Wear of alumina ball slider against TiB_2 coatings.

A comparison of the wear volumes of HSS after various treatments given in Figure 5.61 clearly shows that the wear behaviour of the HSS was improved by the TiB_2 coatings. It has been shown that the sliding wear volumes of the HSS is reduced by up to four times by the TiB_2 coatings (sample 4), although the TiB_2 coatings exhibit relatively high friction (Figure 5.57). Before the breakdown of the TiB_2 coatings, wear is obviously characteristic of the coating against the slider (alumina). Thus the variation of the wear behaviour with different TiB_2 coatings is related to the properties of the coatings. Further

examination of Figure 5.61 and Table 5.12 reveals that the wear rate of the coatings decreases with increasing hardness of the coating. If the wear resistance of the HSS substrate is taken to be unity, the relative wear resistance of a TiB₂ coating can be expressed as follows:

$$\text{Relative wear resistance} = \frac{\text{amount of wear of HSS}}{\text{amount of wear of TiB}_2 \text{ coating}}$$

Figure 6.7 is a plot of the relative wear resistance of the TiB₂ coatings against the hardness of the coatings. There is an approximate relationship, i.e. the relative wear resistance of the TiB₂ coating initially increases with the increase in the hardness of the coating until an optimal is reached at about 39 GPa coating hardness, above which the coating wear resistance decreases. Although the initial increase in wear resistance with coating hardness is expected according to both the abrasive wear law [169] and the adhesive law (Archard's equation) [170], the drop in wear resistance for the superhard coating cannot be explained by these two laws. This is probably associated with the brittleness and high residual stresses in superhard coatings.

Figure 6.7: Relative wear resistance of TiB₂ coatings as a function of coating hardness, sliding against an Al₂O₃ ball under 10 N for 200 m.

It is well known that the wear resistance of hard ceramic coatings is mainly imparted by their ultra high hardness [171]. However, it can be seen that coating hardness is not the only factor that can affect the wear resistance, but other factors also should be taken into account. This is indicated evidently in sample 5 (Table 5.12) which has the highest hardness of 44 GPa (deposition for 5 h, high residual stress) but shows a lower wear resistance than sample 4 (hardness of 38 GPa). This observation of an optimal TiB_2 hardness for best wear resistance obviously has significance for TiB_2 coating process optimization in real application situations.

6.7 Optimisation of TiB_2 -HSS System

From Chapter 5, it can be concluded that the TiB_2 coating deposited onto HSS with good mechanical properties such as high hardness, high coating adhesion as well as good tribological properties can be achieved by controlling the deposition processes, using the techniques of multilayer and heat treatments, and manipulating and modifying the interlayer material by doping nitrogen gas. However, there is the quest to find out the optimum conditions to produce the best coating properties for TiB_2 -HSS system. Based on the experimental results, it is noted that in order to achieve hard and good adhesion coatings with good tribological properties, the optimisation of TiB_2 -HSS system should be made as follows:

1. The substrate-to-target distance should be around 60 mm for TiB_2 targets in order to enhance the ions energy and mobility during the deposition process.
2. Substrate temperature should be around 400 °C to promote the preferred orientation of the TiB_2 coatings.
3. For the heat treatment, the hardness of annealed sample at optimum temperature of 450 °C is increased most significantly as expected from the coating structural improvement (higher coating density).

4. Doping the interlayer in 10% N₂ seems to produce the optimum combination of strength and compliance for adhesion enhancement in the present deposition conditions, whilst too much nitrogen doping causes interlayer embrittlement.
5. The development of multilayer Ti/TiB₂ coatings significantly affects the structure, texture, morphology and surface roughness compared to a conventional single layer TiB₂ coating with a Ti interlayer. It was found that the 6-layer coating gave the best results in terms of coating hardness and adhesion strength. This is due to the existence of an optimum combination of alternate layers that gives the optimal enhancement in coating adhesion.

6.8 Finite Element (FE) Analysis as a Tool for Understanding the Indentation and Scratch Processes

The nanoindentation and micro-scratch tests have proven useful and effective in evaluating the properties and quality of the TiB₂ coatings. In order to gain further insights into the stress distribution and deformation behaviour during indentation and scratch processes, several finite element models have been developed in this work as discussed in sections 4.2 and 4.3. Some important issues relating to the FE model and simulation deserve further discussion in this section.

6.8.1 Nanoindentation of Single Layer TiB₂ Coating with a Ti Interlayer

6.8.1.1. Sink-in effects

From Figure 5.69, it can be seen that the existence of a hard coating on a soft substrate promotes sink-in of the coating material around the indenter during nanoindentation. This observed sink-in is expected for materials with a low value of E/Y (e.g., some glasses and ceramics). The plastic zone is typically contained within the boundary of the circle of contact and the elastic deformations that accommodate the volume of the indentation are spread at a greater distance from the indenter [76]. It can also be seen that the sink-in height increases when the penetration depth increases. But

the sink-in height of coating/substrate system is less than those from coating halfspace when the penetration depth is above 0.2 μm due to the substrate effect.

6.8.1.2. Properties extraction

FE analysis of contact in which sink-in takes place has shown that the true contact area can be significantly smaller than that calculated from the conventional O&P method [77] (measured penetration depth and the assumed elastic unloading response). It is noted that the true properties such as true hardness and modulus can be extracted by using the true contact area obtained from the FE analysis. Since the true contact area calculated from FE analysis is smaller than the measured one, the hardness calculated from the true contact area should be larger than the value obtained from experiment. This is the reason why the hardness values calculated by FE calculation (true hardness) are slightly higher than the experimental ones (Figure 5.67) at various penetration depths.

On the other hand, if pile-up occurs, the true contact area can be significantly greater than that calculated using the conventional method, resulting in the lower hardness values from the true hardness calculation. In addition, the effect of sink-in and pile-up on the contact area can cause the errors in contact area of up to 60% [172]. Thus, sink-in and pile-up can have detrimental effect on the determination of the area function of the indenter if the specimen used for the examination of the area function behaves differently [76]. With the use of the FE technique, the determination of the true mechanical properties can be obtained.

6.8.1.3. Plastic zone deformation

From Figure 5.68, it can be seen that substrate effect starts once the plastic zone in the coating reaches the interface and thus before substrate deformation is actually initiated. The vertical constraint of the plastic zone at the interface is accommodated by the lateral development of the zone, which results in further material sink-in around the indenter.

6.8.1.4. Critical Depth

From the present model, the critical indentation depth to coating thickness ratio at which the contribution of the substrate is negligible could be found. This is beneficial to extract the intrinsic mechanical properties of the coating without the effect from the substrate. From Figure 5.69, the critical depth is found to be around 92 nm. It should be noted that the TiB_2 coating thickness in the model is 1.4 μm . The critical depth of 92 nm corresponds to a depth-to-coating thickness ratio of 0.07, i.e. in order to avoid substrate effect in TiB_2 coating hardness measurement, the indentation depth should not exceed about 7% of the coating thickness. This is in agreement with Sun et al's work [155]. In addition, it should be pointed out that the frequently used one-tenth "rule of thumb" does not apply for TiB_2 coating property measurement (ultrahard coating). For the wide range of coatings investigated, the coating hardness can be safely measured if the indentation depth is less than 7% of the coating thickness.

6.8.2 Nanoindentation of Multilayer Ti/TiB₂ Coating

The degree of pile-up or sink-in depends upon the ratio E/Y , where E is the elastic modulus, and Y is the yield strength [76]. But for the multilayer system, the pile-up or sink-in behaviour cannot be predicted by such a ratio. For non-strain-hardening materials with a large value of E/Y (or soft coating), pile-up is expected since plastic deformation occurs in the indenter's vicinity. On the other hand, sink-in occurs mostly for materials with a low value of E/Y (hard coatings). Based on the FE results under the present conditions of multilayer system, it is noted that the sink-in is dominant at all penetration depths. This is due to the plastic zone near the indenter is contained within the boundary of the circle of contact, and the multilayer coating behaves like a "soft" coating rather than a "hard" coating despite its overall high hardness of around 30 GPa.

6.8.3 Modeling of Micro-scratch Processes

Although the FE model for the microscratch process was based on some simplified assumptions such as step-wise loading and scratch, and frictionless interface between the stylus and the coating surface, the calculation results give some insight into the stress field and deformation behaviour around the stylus during the scratch process. In

particular, the adhesion force between the stylus and the coating surface could be estimated by comparing the measured tangential (friction) force with that from FE simulation. From Figure 5.85, it can be seen that the friction force from the experiment is higher than the calculated one. It arises from the fact that the measured friction force is the combined effect of the ploughing action of the stylus and the adhesion between the stylus and the coating surface, whilst the calculation tangential force is the result of the ploughing action alone, since stylus-coating adhesion was not considered in the FE model. Thus, the difference between the measured value and calculated value should be the adhesion force between the stylus and the coating surface, which is difficult to measure by experiment, but can be estimated through simulation using the present model. For example, in this case study, the experiment shows the average friction force value of 48.41 mN, whilst the FE model calculates the average tangential force value of 22.39 mN. The adhesion force between the stylus and the coating surface should be around 26.02 mN.

Chapter 7

Conclusions

Based on the experimental results and finite elemental analysis conducted throughout this work, the following conclusions can be drawn regarding the fabrication, structural and properties characteristics of TiB₂ based coating by magnetron sputtering

1. In order to increase the hardness of the nanostructured TiB₂ coatings, the TiB₂ preferred orientation (001) should be promoted. This can be achieved by using a substrate-to-target distance of around 60 mm for TiB₂ targets in order to enhance the ions energy and mobility during the deposition process.
2. Substrate temperature should be around 400 °C to promote the preferred orientation of the TiB₂ coatings.
3. Sputter cleaning of substrate helps to improve TiB₂ coating hardness and adhesion strength.
4. Substrate biasing during deposition helps to significantly enhance TiB₂ coating adhesion, but at the expense of coating hardness.
5. Substrate rotation has a significant effect on the structure, orientation, hardness and adhesion strength of non-reactive magnetron sputtered TiB₂ coatings. The TiB₂ coatings deposited on rotating substrates are characterized by random orientation, columnar growth, relatively low hardness and adhesion strength. On the other hand, without substrate rotation, the resultant coatings exhibit the beneficial (001) orientation, dense and equiaxed grain structure, and enhanced hardness and adhesion strength.

6. Proper annealing in vacuum can further improve TiB₂ coating quality. Annealing at 450 °C was found to be the most effective in enhancing coating hardness and adhesion strength.
7. Doping the Ti interlayer with nitrogen in a gas mixture containing 10% N₂ seems to produce the optimum combination of strength and compliance for adhesion enhancement in the present deposition conditions.
8. The adhesion of the TiB₂ coating to the HSS steel substrate can be significantly enhanced by the Cr interlayer due to the material compatibility.
9. The development of multilayer Ti/TiB₂ coatings significantly affects the structure, texture, morphology and surface roughness compared to a conventional single layer TiB₂ coating with a Ti interlayer. It was found that the 6-layer coating gave the best results in terms of coating hardness and adhesion strength. This is due to the existence of an optimum combination of alternate layers that gives the optimal enhancement in coating adhesion.
10. Under unlubricated sliding against an alumina ball, the TiB₂ based coatings produced under various deposition conditions increase the wear resistance of high speed steel by more than three times. It is noted that all samples can improve the wear resistance of HSS. The TiB₂ based coating provides a hard layer to resist plastic deformation and eliminate adhesion between the test surface and the ball slider, which are the main reasons of severe wear of untreated HSS.
11. Finite element models have been developed to simulate the nanoindentation response of the coating and multilayer systems. The models have the ability to simulate the loading and unloading stages, the plastic deformation behaviour of the coating and the substrate, extract the mechanical properties of the coating, and simulate the complicated coating behaviour during indentation such as sink-in effect.

12. The developed models have been successfully used together with the nanoindentation experiments to extract intrinsic yield strength value for selected TiB_2 -based coatings.
13. In order to avoid substrate effect in TiB_2 coating hardness measurement, the indentation depth should not exceed about 7% of the coating thickness.
14. A FE model has been developed to study and simulate the scratch process. The model is applied under the assumption of step-wise loading, and scratch, and can be used to simulate the loading, scratching and unloading stages, the plastic deformation behaviour of the coating and the substrate during the scratch test.
15. The present model can be used for the estimation of the adhesion force between the stylus and the coating surface which is difficult to measure by experiment.

Chapter 8

Future Work

TiB₂-based nanostructured coatings have successfully been fabricated using magnetron sputtering under various sputtering conditions onto high speed steel substrates which allow for the evaluation of the effects of sputter target power, substrate temperature, substrate rotation, sputter cleaning and sputtering time, on the structures and properties of the resultant coatings. FE models have also been developed to simulate the nanoindentation response of single-layer with interlayer and multilayer systems. The models have the ability to simulate the loading and unloading processes, the plastic deformation behaviour of the coating and the substrate. Mechanical properties, such as hardness and yield strength, can be extracted from the FE results.

The FE models have also been developed for the micro-scratch systems. The scratching processes could be simulated to investigate the plastic deformation behaviour of the coating and the substrate. In addition, the estimation of the adhesion force between the stylus and the coating surface could be obtained by this developed model. Indeed, this is very difficult to measure by experiment, but can be estimated through simulation using the present model. Future research may include the following:

8.1 Fabrication of Multilayer Cr/TiB₂-based Nanostructured Coatings

Since residual stresses in the TiB₂ coating not only deteriorate the coating adhesion, but also limits coating thickness, it is important to control and reduce the very high compressive stresses which develop during coating growth. Multilayer system then becomes a possible way to obtain the lower stress levels as proven in section 5.6. It is noted that multilayer system can help to improve the coating adhesion and maintaining high coating hardness.

From the section 5.5, it can be concluded that the adhesion of the TiB₂ coating to the HSS steel substrate can be significantly enhanced by the Cr interlayer. Therefore, by using Cr

as an interlayer material for the multilayer systems may help to improve even greater than using Ti interlayer. It would be interesting to investigate the optimum conditions and feasibility to obtain the ultra-hard with an excellent coating adhesion of the multilayer Cr/TiB₂ coatings.

8.2 Characterisation of TiB₂-based Nanostructured Coatings by TEM

Transmission electron microscopy, TEM, is a powerful tool to investigate how the microstructure relates to deposition parameters. The characteristics of the resultant coating can be revealed by TEM, such as the crystallinity of the coatings, coating density, grain boundaries, porosity or voids as well as the identified phase orientations.

8.3 Wear Test Simulation

In order to gain a better understanding of wear processes and the relationships between damage development and the wear process parameters, simulation method can be used as an effective tool. At present, the knowledge of FE analysis of wear test is extremely limited. So this future work may become one of the few reports concerning the model of the wear process for TiB₂-based nanostructured coatings or the coating/substrate systems.

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Appendix

A: Book Chapter

Nurot Panich and Sun Yong (Chapter 10): Mechanical Characterization of Nanostructured TiB₂ Coatings Using Microscratch Techniques, Scratching of Materials and Applications, Tribology and Interface Engineering Series edited by Professor Brian J. Briscoe, Elsevier, Amsterdam, 2006, pages 208-220.

B: International Published Papers

1. **N. Panich**, S.R. Kappaganthu and Y. Sun, *Polytetrafluoroethylene Doped MoS₂ Films for Precision Engineering Applications*, Proceedings the International Conference on Precision Engineering 2003/04 (ICoPE2003/04): New Frontiers in Precision Engineering; Singapore (2004) pages 564-570.
2. **N. Panich** and Y. Sun, *Effect of Penetration Depth on Indentation Response of Soft Coatings on Hard Substrates: A Finite Element Analysis*, Surface and Coatings Technology, Vol.182 (2004) pages 342-350. ✓
3. **N. Panich**, and Y. Sun, *Fabrication and characterisation of superhard nanostructured coating*, Proceedings the 3rd Thailand Materials Science and Technology Conference; Bangkok, Thailand, (2004) pages 178-180.
4. **N. Panich** and Y. Sun, *Improved Anti-wear Performance of Nano-structured TiB₂ Coatings*, Proceedings the International Conference on Smart Materials (SmartMat-'04), Chiang Mai, Thailand (2004) pages 307-311.
5. **N. Panich** and Y. Sun, *Microscratch and Nanoindentation of Deposited and Annealed Nanostructured TiB₂ Based Coatings*, Proceedings the 1st International Conference on Advanced Tribology 2004 (iCAT 2004): Recent Progress and New Directions; Singapore.

6. **N. Panich** and Y. Sun, *Mechanical Properties of TiB₂ Based Nanostructured Coatings*, Surface and Coatings Technology, Vol.198 (2005) pages 14-19. ✓

7. **Nurot Panich** and Sun Yong, “Techniques to improve coating adhesion of magnetron sputtered TiB₂ Coatings on High Speed Steel”, Proceeding the 3rd Asian Conference on Heat Treatment of Materials, Gyeongju, Korea pages 189-191 (2005).

8. **N. Panich**, S. Hannongbua and Y. Sun, *Structure, Hardness and Adhesion Studies of Multilayer Ti/TiB₂ Coatings on High Speed Steel*, Proceeding the 2nd MRS-S Conference on Advanced Materials, Singapore (2006).

9. **N. Panich** and Y. Sun, *Mechanical Characterization of Nanostructured TiB₂ Coatings Using Microscratch Techniques*, Tribology International, Vol.39 (2006) pages 138-145. ✓

10. **N. Panich** and Y. Sun, *Effect of Substrate Rotation on Structure, Hardness and Adhesion of Magnetron Sputtered TiB₂ Coating on High Speed Steel*, Thin Solid Films, Vol. 500 (2006) pages 190-196. ✓

11. **N. Panich** and Y. Sun, “Structural and Property Studies of Multilayer Ti/TiB₂ Coatings”, Transactions of Materials & Heat Treatment, Vol. 27 (2), (2006) pages 88-93. ✓

12. **N. Panich** and Y. Sun, *Effect of Nitrogen Doping Ti Interlayer on Adhesion of TiB₂ Coatings on High Speed Steel*, Proceedings the 3rd International Conference on Materials for Advanced Technologies (ICMAT 2005), Republic of Singapore.

13. **N. Panich** and Y. Sun, *Improvement in Adhesion of Sputtered TiB₂ Coating onto High Speed Steel by a Chromium Interlayer*, Journal of Materials Science Letters, ✓ submitted.

C: Biography

Mr. Nurot Panich was born in Chonburi Province, Thailand, in 1975. Graduated from Mahidol University, Thailand, in 1997 with B.Eng in Mechanical Engineering and then was working as a lecturer at Department of Mechanical Engineering, Mahidol University for a year. Received a M.Eng (Metallurgical Engineering) from Chulalongkorn University, Thailand, in 2000 with the training programme at R&D department of NKK corporation, Japan. After working as a lecturer at Department of Mechanical Engineering, Rajapark College, Thailand, for a year, received a scholarship to study in Singapore by Nanyang Technological University in 2002 as a Ph.D research student.