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Dangeti, Siva Rama Krishna

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FABRICATION AND CHARACTERISATION OF RUTILE BASED HYBRID THIN FILMS

DANGETI SIVA RAMA KRISHNA

**SCHOOL OF MATERIALS SCIENCE AND
ENGINEERING**

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**A Thesis submitted to Nanyang Technological University in
fulfillment of the requirement for the degree of Doctor in Philosophy**

2010

*Dedicated
to
My Respected Teachers
and
Beloved Family Members*

PREAMBLE

This thesis is submitted for the degree of Doctor of Philosophy (Ph.D) in the Department of Materials Science and Engineering, Nanyang Technological University (NTU) of Singapore under the supervision of **Assoc. Prof. Chen Zhong**. No part of this thesis has been submitted for any degree or diploma at any other University or Institution. To the best of the author's knowledge, all work in this thesis is original unless reference is made to other work. Part of this thesis has been published/ under review for publication as listed below:

List of Journal Publications:

1. D. Siva Rama Krishna and Y. Sun, Thermally oxidised rutile -TiO₂ coating on stainless steel for tribological properties and corrosion resistance enhancement, *Applied Surface Science*, 252, 4 (2005), 1107-1116.
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3. D. Siva Rama Krishna, Y. L. Brama and Y. Sun, Thick rutile layer on titanium for tribological applications, *Tribology International*, 40 (2007) 329-334.
4. Y.L. Brama, Y. Sun, S.R.K. Dangeti and M. Mujahid, Response of sputtered titanium films on silicon to thermal oxidation, *Surface and Coatings Technology*, 195, 2-3, (2005)189-197.
5. Y. Sun and D. Siva Rama Krishna, Fabrication and Characterization of Rutile-TiO₂ Coatings on Metallic Alloy Substrates, *Transactions of Materials and Heat Treatment* (China), vol.25 (5) , 2004.
6. D. Siva Rama Krishna, Y. Sun and Z. Chen, Magnetron Sputtered TiO₂ Films on Stainless Steel Substrate: Selective Rutile Phase Formation and Its Tribological and Anti-corrosion Performance, (*Thin Solid Films*, Under review)

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ABSTRACT

Titanium dioxide (TiO_2) with a rutile structure is known for its useful physical, chemical, mechanical and biomedical properties. Increasing efforts have been made to fabricate this material in the form of thin films for various applications, like chemical catalysts, optical devices and electromagnetic devices. More recently, it has been discovered that rutile has good biocompatibility and is a potential friction-reducing and wear resistant material, and thus it has a great potential for applications in human implants, medical devices and other tribological applications.

In the present work, efforts have been made to produce protective rutile- TiO_2 films. This has been achieved by three routes: 1) thermal oxidation of bulk titanium 2) thermal oxidation of titanium film and 3) sputter deposition of rutile- TiO_2 with the aid of Ti underlayers.

In order to understand the thermal oxidation mechanism and kinetics, a systematic study was carried out on bulk titanium. The effect of cooling rate on the adhesion of the oxide layer on titanium has been investigated.

Efforts have been made to deposit titanium films onto AISI 316L stainless steel by magnetron sputtering, and then to partially convert the titanium films to titanium oxide by thermal oxidation. The resultant coating has a layered structure, comprising of rutile- TiO_2 layer at the top, an oxygen and nitrogen containing α -Ti layer in the middle and a diffuse-type interface. Such a hybrid coating system showed good adhesion with the substrate, improved corrosion resistance, and significantly enhanced surface hardness and tribological properties compared to stainless steel in terms of much reduced friction coefficient and increased wear resistance.

Attempts have been made to fabricate TiO_2 films on 316L stainless steel by non-reactive magnetron sputtering of a rutile TiO_2 target, with and without a titanium underlayer. The effect of titanium underlayer thickness has been investigated in terms of phase evolution, film morphology, corrosion resistance, adhesion strength, hardness and tribological characteristics. Results showed that a titanium underlayer has a significant effect on the phase evolution in the TiO_2 film. Without this underlayer, an anatase- TiO_2 film is produced, in consistence with many other investigations. However, it is found for the first time that with a titanium underlayer, a rutile- TiO_2 film can be formed on the

substrate. The underlayer characteristics play vital role in oxide film phase formations. The resultant rutile films show much improved friction, wear and corrosion properties, which vary with the thickness of the titanium underlayer.

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NOMENCLATURE

AFM	Atom force microscope
at.	Atomic
Ar	Argon
Bcc	Body centered cubic
C	Carbon
At.% N	Concentration of nitrogen
Cr	Chromium
d	Crystal lattice spacing
Fcc	Face centered cubic
Fe	Iron
G	Gauss
GDS	Glow discharge spectroscopy
GIXD	grazing incidence X-ray diffraction
k	Boltzman constant
Mg	Magnesium
mTorr	Milli Torr
N	Nitrogen
Ni	Nickel
nm	Nanometer
O	Oxygen
ODT	Oxygen diffused titanium

Pa	Pascal
RF	Radio frequency
RT	Room temperature
Sccm	Standard cubic centimeter per minute
SEM	Scanning electron microscope
SS	Stainless steel
Si	Silicon
Ta	Tantalum
T _e	Electron temperature
Ti	Titanium
TiO ₂	Titanium dioxide
TEM	Transmission electron microscope
T _{sub}	Substrate temperature
W	Watt
XRD	X-ray diffraction
θ	Angle of incidence of X-ray
γ	Surface energy
μm	Micro meter (10^{-6} M)
°C	Degree centigrade
%	Percentage

CHAPTER 1 INTRODUCTION

1.1 BACKGROUND AND MOTIVATION

Titanium dioxide (TiO_2) is the most widely investigated crystalline material in the surface science of metal oxides [Diebold, 2003]. TiO_2 with a rutile structure has many useful physical, chemical, and mechanical properties. In recent years, increasing efforts have been made to fabricate this material in the form of thin films for applications like chemical catalysts, optical, dielectrical, insulating, electromagnetic and biomedical devices [Diebold, 2003]. More recently, it was discovered that rutile has extremely good biocompatibility and excellent friction reducing ability along with excellent wear resistance, thus having great potential for applications in industrial, marine and medical devices [Brunette, 2001]. So far, very few efforts have been made to apply rutile- TiO_2 on materials other than titanium for tribological and biomedical applications.

On the other hand, the family of stainless steels is arguably unique as engineering materials by virtue of their properties and general resistance to environmental conditions [Pickering, 1984; Bell, 2002]. The austenitic stainless steels are by far the most widely used stainless steels comprising of 70-80 % of stainless steel production [Pickering, 1984], whose applications include chemical, food, paper, mining, pharmaceutical, petroleum industries and biomedical devices and human body implants [Brunette 2001, Oh 1998, Olivares 2003]. Despite these superior properties of the austenitic stainless steels, it possesses modest wear resistance. It suffers from severe metallic wear when in contact with itself or other materials due to the formation of strong adhesion junctions between the contact surfaces and severe surface/subsurface plastic deformation [Sun, 2002]. In order to improve the tribological properties, surface modification techniques like Nitriding and Carburising have been developed. But from significant reduction in the corrosion resistance by Nitriding [Sun, 1998], metal dusting by Carburising [Tabet, 2003] and requirement for a biocompatible surface [Chu 2002, Sridhar 2003] arises the need for some suitable processes. In this situation it is worth realizing the potential of rutile- TiO_2 surface-modified austenitic stainless steels.

Fabrication of pure rutile films has presented a challenge due to the existence of several forms of TiO_2 depending on the thermodynamic conditions. TiO_2 with good tribological properties and corrosion resistance can also be produced by thermal oxidation of titanium [Dong, 1999]. Thermal oxidation renders well-adhered oxide layer especially on titanium surface due to the longer range of diffusion zone across the Ti/ TiO_2 interface.

Limitations on the adhesion of TiO_2 films by conventional deposition techniques and the potential of hybrid films in yielding superior adhesion led to the choice of thermal oxidation for Ti film on SS substrate. The idea of using hybrid TiO_2 film deposition over stainless steel substrate is indeed a novel approach to improve the tribological properties and the novelty also lies in the two techniques followed to meet the goal, which are Thermal Oxidation of Ti film and Direct Sputter Deposition of TiO_2 with the aid of Ti underlayer.

The hybrid TiO_2 film can be achieved by controlled thermal oxidation of as-deposited Ti film on the austenitic stainless steel substrate, bonding between which has been demonstrated to be good [Mudali, 2003; Ghosh, 2002 & 2003]. Sputter deposited TiO_2 films also have considerable importance for various applications such as high dielectric constant, refractive index, hardness and photocatalysis. The properties of the TiO_2 films are determined by the phase present in it. TiO_2 films deposited at lower temperatures results amorphous phase and higher temperatures are needed for crystalline phases. Obtaining a complete rutile film, even from a rutile target, on any substrate requires tedious post heat treatments to transform it from the thermodynamically stable phases, anatase/amorphous phases, which have poorer tribological properties than rutile. Also, rutile with good wear resistance and friction can not be directly deposited on metallic substrates due to the limitation of poor adhesion. The presence of underlayer/ interlayer increases adhesion and load bearing capacity of the oxide films.

1.2 OBJECTIVES

The main goal of this research was to obtain engineered rutile- TiO_2 based hybrid surface coatings, with optimal wear, friction and adhesion properties. In order to achieve this goal, the work has been divided into following tasks:

- To understand bulk-Titanium thermal oxidation mechanism and kinetics
- To fabricate and modify Ti surface on 316L substrate through process study

- To optimize the thermal oxidation conditions in order to obtain the desired properties of rutile based hybrid films
- To optimize process conditions for obtaining rutile based hybrid films by sputter deposition using TiO₂ target
- To understand the effect of underlayer on the oxide phase formation

1.3 THESIS ORGANISATION

Introduction chapter provides the basic background, motivation and objectives of the research. Review of stainless steels, titanium and its oxides, rutile films and thermal oxidation, tribological testing methods and adhesion scratch test is presented in chapter 2. Experimental procedures, structural characterization techniques and mechanical, tribological, corrosion and biocompatibility evaluation methods are discussed in chapter 3. Experimental results and discussions of thermal oxidation of CP-Ti and Ti film are elucidated in chapters 4 and 5 respectively. Chapter 6 covers results and discussion of sputter deposited TiO₂ films, Ti underlayer effect and substrate surface impact on oxide layer phase formations. Findings of the current study have been summarized in chapter 7.

CHAPTER 2

LITERATURE REVIEW

2.1 STAINLESS STEELS

Ferrous materials occupy 85% of the total production of metals. Stainless-steels are superior among the ferrous materials because of their excellent properties in corrosion resistance, formability, toughness etc. The term “Stainless” implies a resistance to staining, rusting, and pitting in moist and polluted air, and generally defines chromium content of 11% - 30% and very low carbon content [Lula, 1985].

Although various specifying bodies categorize stainless steels according to chemical composition and other properties, they classified it into six major classes that represent three types of alloy constitution, or structure. These are ferritic, martensitic, austenitic, duplex, austenitic-ferritic and precipitation hardened [Lula, 1985]. Of all these, austenitic stainless steels are the most popular for their high corrosion resistance due to the presence of nickel (8%) and chromium (18%).

Table 2.1: Properties of 316L stainless steel [Lula, 1985]

Property	Value
Tensile strength	558 MPa
Proof stress (0.2% off set)	290 MPa
Elongation (% in 2")	50
Hardness (Rockwell B)	79
Density	7.99 g/cm ³
Thermal Conductivity (at 100° C)	16.2 W·K ⁻¹ ·m ⁻¹
Coefficient of Thermal Expansion (20°C to 100°C)	16 µm.m ⁻¹ ·C ⁻¹
Specific Heat (0° C to 100° C)	0.46 KJ .Kg ⁻¹ .°C ⁻¹

316L, an austenitic stainless steel with carbon content of less than 0.03% has been used for its superior corrosion resistance. Table 2.1 shows the properties of 316L, whose applications include chemical, food, paper, mining, pharmaceutical, petroleum industries and biomedical devices and human body implants [Brunette,2001; Oh,1998; Olivares, 2003]. Despite these superior properties of the austenitic stainless steels, it possesses modest wear resistance. It suffers from severe metallic wear when in contact

with itself or other materials due to the formation of strong adhesion junctions between the contact surfaces and severe surface/subsurface plastic deformation [Sun, 2002]. Biocompatibility of the 316L austenitic stainless steel and its poor wear resistance together demand a biocompatible modified surface [Chu, 2002; Sridhar, 2003].

2.2 TITANIUM AND ITS OXIDES

2.2.1 Titanium in General

Titanium (Ti), the fourth most common metal after aluminium, iron, and magnesium and the ninth most abundant element on Earth, is a gray metal that is lighter and stronger than steel and highly resistant to decay. It is occasionally referred to as the “wonder metal” and has been utilized in a growing list of specialized applications, since the Kroll process made the winning of this material from ores a commercial possibility in 1936 [Brunette, 2001]. Ti and its alloys have wide range of applications in the fields of aerospace, chemical industry, marine and biomedical devices because of their combination of outstanding properties in terms of high strength to weight ratio, exceptional resistance to corrosion, and excellent biocompatibility [Lund, 1990; Dong, 2000].

Titanium and its alloys show polymorphism, i.e., can exist in three microstructural forms namely Alpha titanium (α -Ti), Beta titanium (β -Ti), and Alpha-Beta titanium (α - β -Ti) [Donachie, 1988]. α -Ti exists at room temperature with hexagonal close packed crystal structure (HCP) having lattice parameters $a = 2.95 \text{ \AA}$ and $c = 4.686 \text{ \AA}$ (JCPDS, 5-0682). It transforms to β phase at 883°C which has a body-centred cubic (BCC) crystal structure with lattice parameter $a = 3.3065 \text{ \AA}$ (JCPDS, 44-1288). The c/a ratio for pure α -Ti is 1.587, smaller than the ideal ratio of 1.633 for the hexagonal close-packed crystal structure.

β -Ti phase has six most densely packed $\{110\}$ lattice planes and the close-packed directions are the four $\langle 111 \rangle$ directions (Fig. 2.1b).

The main slip directions of α -Ti are the three closely-packed directions of type $\langle 11\bar{2}0 \rangle$. The slip planes containing this type of Burgers vector are the (0002) plane, the three $\{10\bar{1}0\}$ planes, and the six $\{10\bar{1}1\}$ planes (Fig. 2.1c). Among these three different types of slip planes together with the possible slip directions there are a total of 12 slip systems (Table 2.2). These can be reduced to nominally 8 independent

Fig. 2.1: Crystal structure of (a) α -Ti (HCP) (b) β - Ti (BCC) and (c) Slip systems of Hexagonal crystal lattices [Peters, 2003]

Table 2.2: Slip Systems in the hexagonal α phase [Lutjering, 2003].

Slip system type	Burgers vector type	Slip direction	Slip plane	No. of slip systems	
				Total	Independent
1	$\vec{a}$	$\langle 11\bar{2}0 \rangle$	(0002)	3	2
2	$\vec{a}$	$\langle 11\bar{2}0 \rangle$	{ 10 $\bar{1}0$ }	3	2
3	$\vec{a}$	$\langle 11\bar{2}0 \rangle$	{ 10 $\bar{1}1$ }	6	4
4	$\vec{c} + \vec{a}$	$\langle 11\bar{2}3 \rangle$	{ 11 $\bar{2}2$ }	6	5

slip systems. However, this is further reduced to only 4 independent slip systems because the shape changes that are produced by the combined action of slip system types 1 and 2 (Table 2.2) are identical to slip system type 3. Therefore, considering the Von Mises criterion [Dieter, 1988], which requires at least five independent slip systems for a homogenous plastic deformation of polycrystals, the operation of one of the slip systems with a so-called non-basal Burgers vector needs to be activated, either the $\vec{c}$ type with the slip direction $[0001]$ or the $\vec{c} + \vec{a}$ type with the slip direction $\langle 11\bar{2}3 \rangle$ (Fig. 2.1c and Table 2.2). The presence of $\vec{c} + \vec{a}$ type dislocations has been observed by TEM observations in a number of titanium alloys [Lutjering, 2003]. Assuming the critical resolved shear stresses (CRSS) are identical for both types of slip planes, then the slip system with a non-basal Burgers vector which is activated most likely in α - titanium is of the type $\langle 11\bar{2}3 \rangle$ $\{11\bar{2}2\}$, shown in Table 2.2 as slip system type 4.

The absolute values of the CRSS are strongly dependent on alloy content and test temperature. The small differences in CRSS at room temperature between the three types of slip systems with a basal ($\vec{a}$ type) Burgers vector, $\{10\bar{1}0\} < \{10\bar{1}1\} < (0002)$, become even smaller with increasing temperature [Lutjering, 2003].

By alloying Ti with other elements, either crystal structure can be selectively stabilized at room temperature, thus making it possible to manufacture stable α , α - β , and β alloys. Common alloying elements used to stabilize the α phase include aluminium, tin, nitrogen and oxygen. Molybdenum, iron, vanadium, chromium and manganese are the β stabilizers. Many alloys constituting a carefully chosen combination of the two types of elements, are classified into α - β alloys.

2.2.2 Tribology of Titanium

Major limitation of titanium is its chemical reactivity with other materials at elevated temperature [Callister, 1985]. Despite the excellent mechanical properties titanium alloys are characterised by poor tribological properties because of its high and unstable friction coefficients, severe adhesive wear, susceptibility to fretting wear, and a strong tendency to seize [Lund, 1990; Dong, 2000]. As a result, the use of Ti alloys has generally been restricted to non-tribological applications. Dong et al '(2000)' explained that mechanism behind the poor tribological characteristics is related to

electron configuration, crystal structure and lubrication characteristics as explained below.

Electron configuration: The chemical activity and the friction coefficient can be correlated with the d-bond character and lesser its percentage, more active is the metal and the greater is the friction. Since titanium possesses the lowest value of d-bond character (27%) [Dong, 2000], it is extremely active and ready to alloy with other materials.

Crystal structure: Hexagonal α -Ti with an axial c/a ratio of 1.588 (less than the ideal ratio 1.633) tends to make the basal plane less favourable for slip and allows prismatic $\{10\bar{1}0\}$ and the first-order pyramidal $\{10\bar{1}1\}$ slip to occur, thus increasing the number of possible slip systems (as discussed in section 2.2.1). The increased number of possible slip systems promotes continuous junction growth, which occurs by slip on different slip planes.

Lubrication characteristics: Conventional lubricants (mineral oils and greases), which are successfully and widely used for most metals, have been shown to be ineffective when applied to titanium alloys. Also, the low heat conductivity of titanium adds to the problem of the ineffectiveness of lubricants and it is believed to partially account for the high tendency of titanium alloys to scuff.

Although it is difficult to identify the dominant factor and its relative importance, the combined effect of all these factors determines the tribological characteristics of titanium and its alloys (Fig.2.2). The poor tribological characteristics

Fig. 2.2: Materials factors effecting the tribological performance of Ti [Dong, 2000]

of titanium and its alloys are related to their inherent materials nature and this problem may be overcome only by changing the nature of the surface, i.e., through surface engineering.

2.2.3 Titanium Oxides

The excellent corrosion resistance of titanium is due to a stable, protective, strongly adherent oxide film. This film, which is formed instantly at room temperature when a fresh surface is exposed to air or moisture, is 12-16 Angstroms thick. After 70 days it is about 50 Angstroms. It continues to grow slowly reaching a thickness of 80-90 Angstroms in 545 days and 250 Angstroms in four years [Brunette, 2001]. The film growth is accelerated under strongly oxidizing conditions such as heating in air, anodic polarization in an electrolyte or exposure to oxidizing agents such as HNO_3 , C(R)O_3 , etc. The composition of the natural oxide film (Fig. 2.3) formed at room temperature varies from TiO_2 at the surface to Ti_2O_3 , to TiO at the metal interface i.e. O/Ti ratio decreases from surface to interface [Brunette, 2001]. The oxidizing conditions promote the formation of TiO_2 so that in such environments the film is primarily TiO_2 . This film is transparent in its normal thin configuration and not detectable by visual means. The slow growth of this natural oxide film over time in a neutral or oxidizing medium generally results in increasing corrosion resistances and wear resistance of the metal. Therefore, any surface treatment that will thicken and toughen the oxide film will improve the metal's corrosion and wear resistance [Bloyce, 1998].

Fig. 2.3: Schematic view of the surface oxide film on pure titanium [Brunette, 2001]

Low atomic number elements i.e O, N, C and H, which are always present in titanium and form interstitial solid solutions, are located in the interstices between the titanium atoms. According to the Ti-O phase diagram, α -Ti can dissolve up to 33 at.% oxygen (Fig. 2.4), which is interstitially incorporated in to the lattice, either randomly or ordered at alternating (0002) planes of the hexagonal titanium lattice [Leyens, 2003]. Due to oxygen incorporation, the titanium ions in the hexagonal structure are shifted towards the c-axis.

Fig. 2.4: Phase diagram of Ti –TiO₂ system [Lyman, 1973]

Fig. 2.5: System of Ti-O showing the sub oxides of Ti₃O and Ti₆O [Lyman, 1973]

Nitrogen can dissolve in Ti up to 22 at.% and also changes the lattice parameter [Leyens, 2003]. A variety of stoichiometries of titanium oxide are known that cover a wide range of oxygen to Ti ratios: from Ti₃O to Ti₂O, Ti₃O₂, TiO, Ti₂O₃, Ti₃O₅ and TiO₂. However, suboxides Ti₃O and Ti₆O may also exist, as shown in Fig 2.5. This is

a consequence of the fact that titanium exists in different more or less stable oxidation states, and the fact that oxygen has a relatively high solubility in Ti. The most stable titanium oxide is TiO_2 , with Ti in the preferred oxidation state + IV. Titanium oxides, in particular, TiO_2 , are thermodynamically very stable and the Gibbs free energy for the formation of the oxide is highly negative for a variety of oxidation media such as oxygen, water or oxygen containing organic molecules [Brunette, 2001].

2.2.4 Titanium Dioxide (TiO_2)

For the past several decades, TiO_2 (Titania) has been one of the most extensively studied transition-metal oxides for its interesting electric, magnetic, catalytic and electrochemical properties [Diebold, 2003; Martin, 1997]. Based on these properties, it has been widely used as catalysts, sensors, dielectrics, ceramic membranes and pigments [Mo, 1995; Ding, 1998; Gouma, 2001].

TiO_2 exists in three crystallographic forms: rutile and anatase, with tetragonal and brookite, with orthorhombic structure (Fig. 2.6). Crystal structure data for the three phases are summarized in Table 2.2. Rutile and anatase contain 6 and 12 atoms per unit cell, respectively. In both structures, each Ti atom is coordinated to six O atoms while each O atom is coordinated to 3 Ti atoms. In each case, the TiO_6 octahedron is slightly distorted, with two Ti-O bonds slightly greater than the other four, and with some of the O-Ti-O bond angles deviating from 90° . This distortion is more in anatase than in rutile.

Fig. 2.6: Crystal structure of TiO_2 . (a) Rutile (b) anatase and (c) Brookite

Table. 2.3: Crystal structure data of TiO_2

	Rutile	Anatase	Brookite
Crystal structure	Tetragonal	Tetragonal	Orthorhombic
Lattice constants ($\text{\AA}$)	$a = 4.5936$ $c = 2.9587$	$a = 3.7840$ $c = 9.5150$	$a = 9.1840$ $b = 5.4470$ $c = 5.1450$
Space group	$P4_2/mnm$	$I4_1/amd$	$Pbca$
Molecule/cell	2	4	8
Volume/molecule ($\text{\AA}^3$)	31.216	34.061	32.172
Density (g/cm^3)	4.13	3.79	3.99
Ti-O bond length ($\text{\AA}$)	1.949 (4 bonds) 1.980 (2 bonds)	1.937 (4 bonds) 1.965 (2 bonds)	1.87 ~ 2.04
O – Ti – O bond angle	81.2° 90.0°	77.7° 92.6°	$77.0^\circ \sim 105^\circ$

The structure of rutile and anatase crystals has been described frequently in terms of chains of TiO_6 octahedra having common edges. 2 and 4 edges are shared in rutile and anatase, respectively. Brookite has a more complicated structure with eight formula units in the orthorhombic cell. The interatomic distances and the O-Ti-O bond angles are similar to those of rutile and anatase. The essential difference is that there are six different Ti-O bonds ranging from 1.87 to 2.04 $\text{\AA}$, and accordingly there are 12 different O-Ti-O bond angles ranging from 77° to 105° . In contrast, there are only 2 kinds of Ti-O bonds and O-Ti-O bond angles in rutile and anatase [Mo, 1995].

Fig. 2.7: Pressure temperature reaction boundary along which anatase (A) or brookite (B) is converted to TiO_2 or rutile [Lyman, 1973]

Rutile is the most stable phase and the common form of TiO_2 whereas anatase and brookite are both metastable at all temperatures [Juergen, 1997; Ding, 1998; Diebold 2003; Diebold 2003a]. Fig.2.7 shows the reaction boundaries between the anatase and brookite with rutile. Anatase, in particular, converts to rutile at temperatures between 400°C and 1200°C [Gouma, 1999, 2001]. Amorphous phase of Ti oxide also forms in the form of thin films.

2.2.5 Applications of TiO_2

The initial work on the photolysis of water on TiO_2 electrodes without an external bias, and the thought that surface defect states may play a role in the decomposition of water into H_2 and O_2 , has stimulated much of the early work on TiO_2 [Diebold, 2003]. The photoelectric and photochemical properties of TiO_2 are another focus of active research. The use of colloidal suspensions with the addition of dye molecules has been shown to improve efficiency of solar cells, and has moved TiO_2 -based photoelectrochemical converters into the realm of economic competitiveness.

A better understanding and improvement of catalytic reactions is the main driving force for surface investigations on TiO_2 . Because most of the heterogeneous catalysts consist of small metal clusters on an oxide support, many growth studies of metals on TiO_2 were performed. These metal/ TiO_2 systems often serve as a model for other metal/oxide surfaces. Traditionally, TiO_2 is a primary constituent in mixed vanadia/ titania catalysts used for selective oxidation reactions. Small additions of it can modify metal-based catalysts in a profound way. The so-called strong-metal support interaction (SMSI) is due to the encapsulation of metal particles by a reduced TiO_x overlayer. [Pesty, 1995; Zhang, 1999].

TiO_2 is a semiconductor and the electron-hole pair that is created upon irradiation with sunlight may separate and the resulting charge carriers might migrate to the surface where they react with adsorbed water and oxygen to produce radical species. These attack any adsorbed organic molecule and can lead to complete decomposition into CO_2 and H_2O . The applications of this process range from purification of wastewaters; disinfection based on the bactericidal properties of TiO_2 ; use of self-cleaning coatings on car windshields, to protective coatings of marble. [Diebold, 2003]. TiO_2 is not used as extensively as SnO_2 and ZnO , but it has received some attention as an oxygen gas sensor, e.g. to control the air/fuel mixture in car engines [Dutta, 1999].

TiO₂ pigment is used in virtually every kind of paint because of its high refractive index. The surface properties play a role even in these wide-spread applications, e.g. the photocatalytic degradation of binder in paints is a major problem for the paint industry. TiO₂ is non-toxic and safe, and can be dispersed easily. In pure form it is also used as a food additive, in pharmaceuticals, and in cosmetic products [Diebold, 2003].

Titanium dioxide is used extensively in thin-film optical-interference coatings. Such coatings are based on the interference effects between light reflected from both the upper and lower interface of a thin film. The relative ratios between transmission and reflection of light are governed by the index of refraction of the thin film and the surrounding media. By depositing a stack of layers with the appropriate optical index, the refraction/transmission properties of a stack of thin layers on a glass substrate can be designed to meet a great number of applications. Examples for such devices include antireflective coatings, dielectric mirrors for lasers, metal mirrors with enhanced reflection, and filters. Its excellent optical transmittance, high refractive index and high chemical stability are the attractive features for optical coatings [Williams, 1983; Lobl, 1994; Sasase, 1996; Miao, 2003].

Ultrathin metal oxide films might be well-suited as the gate material of the future, and TiO₂, with its high dielectric constant, would be an attractive candidate for this application. A new kind of gate oxide must meet very stringent requirements-no surface states, virtually pin-hole free, stoichiometric ultrathin films, good interface formation with the Si substrate, etc. [Wang, 2001]. TiO₂ could be a viable approach to dielectrics whose oxide equivalent thickness is less than 2.0 nm. CVD-grown TiO₂ films on Si show excellent electric characteristics, but a low resistivity layer, probably SiO₂, forms at the interface. Interestingly, modified TiO₂ films are also promising materials for spintronics applications, although TiO₂ itself is not a magnetic material. When anatase TiO₂ films are doped with a few percent of Co, they become ferromagnetic. Such films are optically transparent, semiconducting, and ferromagnetic at room temperature, and might be ideal candidates for spin-based electronic devices [Diebold, 2003].

Titanium is a relatively simple biomaterial, which is normally and successfully used especially for dental applications, owing to its demonstrated ability to allow a close bone-implant apposition and extensive long-term clinical documentation in oral implantology. Osteointegrated titanium screw implants have been used to provide

highly reliable restoration of the oral activity in totally or partially edentulous patients over many years of follow-up. The good biocompatibility and osteointegrability of titanium are due to a thin but adherent layer of native oxides, which is spontaneously formed on its surface. This so-called passive condition of titanium, when placed in a physiological environment, allows a good corrosion resistance [Hiromoto, 2004]. Yet titanium does interact with environment by releasing metal ions and compounds into the tissues and allowing oxygen diffusion into its structure. On the other side, the presence of the oxide layer on the surface can play an important role for the favourable tissue response to titanium implants. It is possible to increase the range of biomaterial applications by depositing a thicker layer of TiO_2 on titanium surface or by covering it with another biocompatible material, e.g. hydroxyapatite $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ [Casaletto, 2001]. It is also anticipated that the formation of a TiO_2 coating on other biomaterials, such as stainless steels, would render improved biocompatibility and corrosion resistance, but no efforts have been made in this connection.

2.2.6 Rutile- TiO_2

Rutile, the technologically preferred form, has a higher index of refraction and higher dielectric constant than anatase and is desired for these properties [Wiggins, 1996]. It has many unusual properties, which make it suitable for a variety of thin film applications. The dissolution of Ti metal ions from rutile with the body fluids (in bio-applications) is one order of magnitude lower than that from anatase, so that rutile is preferred phase with respect to biomedical applications [Leng, 2002]. TiO_2 films with rutile structure have been extensively used [Diebold, 2003]. In addition, wear resistance of rutile is greater than that of anatase. In order to exploit the superior biocompatibility and wear resistance of the rutile phase it has been the main interest in this project. Table 2.3 shows the properties of the rutile TiO_2 comparing to CP-Ti [Shackelford, 2001].

Table 2.4: Properties of rutile - TiO_2 and CP-Ti

Property	TiO_2	CP-Ti
Density	4.13 g/cc	4.51 g/cc
Hardness	1121 Hv	145 Hv
Poisson's Ratio	0.28	0.37
Thermal conductivity	6.69 W/m-K (at 100°C)	16.4 W/m-K
Fracture Toughness	3.2 $\text{MPa}\cdot\text{m}^{-1/2}$	66 $\text{MPa}\cdot\text{m}^{1/2}$
Coefficient of thermal expansion (CTE)	9 $\mu\text{m}/\text{m}\cdot^\circ\text{C}$	8.6 $\mu\text{m}/\text{m}\cdot^\circ\text{C}$

Modulus of elasticity	230 GPa	105 GPa
Shear modulus	90 GPa	45 GPa
Resistivity (25°C)	10^{12} ohm.cm	5.2e-005 ohm-cm

2.3 SURFACE ENGINEERING WITH TiO₂

2.3.1 Fabrication of TiO₂ Films

Great interests have been focused on titanium oxide films because of its wide range of applications as mentioned in earlier section. Titanium oxide films can be prepared by many techniques both wet and dry. An overall view of the classification of thin film fabrication techniques is shown in Fig. 2.8.

Fig. 2.8: Flow chart showing the classification of fabrication methods of thin films

In wet process the starting material is in liquid form, which is applied to the substrate and then made to solidify by solvent evaporation or cooling [Bunshah, 1994]. Sol-gel and anodic oxidation (anodisation) are popular wet methods that are primarily restricted to oxides. Sol-gel [Zhang, 2002] and anodic oxidation [Palombari 2002] processes have been successfully used for TiO₂ film formation also. The film produced by sol-gel method is rigid, porous and very thin (<100nm) [Mills, 2003].

Although thick Titania films were produced by a repeated “coat and bake” process of sol-gel method, the number of cycles (>10) of the process make the film fragile and often cracked [Mills, 2003]. TiO_2 film formed anodically in aqueous electrolytes, consists mainly of anatase [Brunette, 2001] and/or hydrated oxides of low crystallinity [Bloyce, 1998] and are characterized by significant porosity [Casaletto, 2001]. Besides these drawbacks wet process typically induces adsorption of chemicals and/or by-products of chemical reaction on the surface that pose difficulties in subsequent process steps and during reliability tests.

Dry coating treatment methods are recognised as having less environmental effects than many of the traditional wet processes [Rickerby, 1991]. The dry processes include chemical vapour deposition (CVD) and physical vapour deposition (PVD).

2.3.1.1 Chemical Vapour Deposition (CVD) of TiO_2

Chemical Vapour Deposition (CVD) involves the dissociation and/or chemical reactions of gaseous reactants in an activated (heat, light, plasma) environment, followed by the formation of a stable solid product. The deposition involves homogeneous gas phase reactions, which occur in the gas phase, and/or heterogeneous chemical reactions, which occur on/near the vicinity of a heated surface leading to the formation of powders or films, respectively [Choy, 2003].

The advantages of CVD include the capability of producing highly dense and pure materials, uniform films with good reproducibility and adhesion at reasonably high deposition rates and non-line-of-sight process with good throwing power [Choy, 2003]. The major disadvantage with CVD is that it is versatile only at temperature of $600\text{ }^\circ\text{C}$ and above, where many substrates are not thermally stable [Kang, 2003]. To overcome this limitation, many modified processes have been developed. Plasma Enhanced Chemical Vapour Deposition (PECVD) uses electron energy (plasma) as the activation method to enable deposition to occur at a low temperature and at a reasonable rate. Metalorganic Chemical Vapour Deposition (MOCVD) is a variant of CVD, which has been classified according to the use of metalorganics as precursors, since they are volatile at moderately low temperatures [Ohring, 1991]. TiO_2 films have been produced by CVD, PECVD [Nilson, 2000], MOCVD [Wang, 2001; Casaletto, 2001; Kang 2003]. In most of the cases the TiO_2 film produced is of anatase structure [Kang, 2003], which is not desired in many cases for the purpose discussed in the section 2.2.5. In addition to that the complexity in controlling stoichiometry and the

use of toxics, corrosive, flammable and/or explosive precursor gases limits CVD as a deposition process. In addition, the use of more sophisticated reactor and/or vacuum system by CVD variants tends to increase the cost of fabrication [Choy, 2003].

2.3.1.2 Physical Vapor Deposition (PVD) of TiO_2

Physical vapor deposition leads to film growth by reaction between a substrate surface and an adjacent vapor, which supplies the coating material in the form of atoms, molecules or ions to the substrate surface, on which condensation and/or reaction with atoms of the surface lattice take place [Brunette, 2001].

PVD processes are characterized by high coating density and strong adhesion, multi component layers, low substrate temperatures, and a wide range of possible coating and substrate materials. PVD processes are suitable for the manufacturing of single as well as multilayers without process interruption [Brunette, 2001].

The basic PVD processes are evaporation, sputtering and ion plating. In evaporation, atoms are removed from the source by thermal means, whereas in sputtering they are dislodged from solid target (source) surfaces through impact of gaseous ions [Ohring, 1991]. In the ion plating process, the material is vaporized similarly to the evaporation process, but passes through a gaseous glow discharge on its way to the substrate, thus ionising some of the vaporized atoms [Brunette, 2001].

Evaporation deposition initially attained rapid industrial adoption only after the advancement of vacuum technology. The deposition technique, which is primarily categorized by the evaporative source, involves transfer of the material of interest on to the substrate by means of thermal vaporization and minimal collision with residual gas molecules in the chamber [Rickerby, 1991]. Even though the target used was rutile TiO_2 , the coatings contained a mixture of anatase TiO_2 and amorphous TiO_{2-x} , due to the decomposition of the target into Ti, O, O_2 and TiO species by e-beam heating [Yang, 2004]. Besides the commonly encountered spitting problem in the deposition technique, evaporation of alloy and compound targets poses practical problems like fractionation due to the differences in boiling points of the constituent elements and solubilities in various phases [Ohring, 1991].

Ion plating is a generalized deposition and/or surface treatment technique involving ionisation of the target material/gas and bombardment/coating on the substrate. This technique, despite yielding dense coatings, can cause poor adhesion of the coating to the substrate due to the compressive stresses [Brunette, 2001].

2.3.1.3 Sputter Deposition of TiO_2 Film

In contrast to the drawbacks and limitations of the other PVD techniques sputter deposition process provides a number of unique advantages. Relatively denser and harder films, low temperature epitaxy, uniformity in thickness, decreased fractionation, easier control on deposition rate, greater energy of adatoms, greater versatility in terms of deposition of various materials, such as refractory materials, alloys of range of compositions, polymers, oxides, ceramics, glass etc., films of desired composition and quality, absence of spitting [Rickerby, 1991] are some of the advantages of the sputter deposition technique.

Sputtering is a process wherein materials are ejected from the surface of a solid or liquid because of the momentum exchange associated with bombardment by energetic particles. The bombarding species are generally ions of heavy inert gas. The source of ions may be an ion beam or a plasma discharge into which the material to be bombarded is immersed [Thornton, 1975].

The development of high performance magnetron sputtering sources that provide relatively high deposition rates with large deposition areas and low substrate heating has rendered the sputtering process more effective [Xuanyong, 2004]. Magnetron sputtering sources can be classified as diode devices in which the magnetic fields are used in concert with the cathode surface to form electron traps. The charged particles are confined by a closed magnetic field and high-density plasma is produced in the vicinity of the cathode. This results in a drastic increase in the deposition rate to $\sim 15 \text{ nm s}^{-1}$ at a typical substrate-target distance of $d = 50 \text{ mm}$. Enhanced plasma ionization can be achieved via either additional gas ionization or plasma confinement. The unbalanced magnetron, which ensures the enhancement of gas ionization near substrates even at a large distance of $\sim 100 \text{ mm}$, is based on magnetic plasma confinement. This sputtering system can deliver large ion currents to the substrates and can be operated under a wide range of pressures. The coatings can be produced on large substrates, even for complex shapes.

Compound target sputtering, especially of insulating type has been made possible by the advent of radio frequency (RF) sputtering. RF sputtering has the combined advantage of yielding gaseous entrapment-free insulating films. Plasma is stabilized at low pressures with the help of radio frequency alternating current. The discharge between the electrodes is superimposed with a DC bias to the target (cathode) by means of a series connection to a blocking capacitor. Electrical power

supply for the sputtering of the cathode by the positive ions is achieved with the help of a matching network. Fig.2.9 shows the difference in electrical lay out for the RF sputtering and DC sputtering. TiO₂ films produced by compound target sputter deposition results in non-stoichiometric compound formation [Miao, 2003; Hiratani, 2003].

Fig. 2.9: Difference in electrical layout between radio frequency (RF) and direct current (DC) sputtering

The sputtering efficiency is defined as the number of sputtered atoms to the number of energized particles. The efficiency depends on the mass of the sputtering ions and target and increases with the increasing angle of incidence referenced to the target normal with a maximum between 70° and 80°. At small angles, the process is limited by the energy transport into the surface and at larger angles, limited by increasing reflection of the bombarding ions. There is a material-dependent minimum ion energy. For argon and Ti as target materials, it is 20 eV and for Zr or Nb, it is 22 or 25 eV. Other factors affecting the sputtering process are the crystalline structure, surface roughness as well as thickness of any spontaneous adsorbed layers on the target [Xuanyong, 2004]. The temperature of the target material is of minor importance so long as it does not exceed 80% of the melting temperature.

2.3.2 Oxidation of Titanium

For reactive sputter deposition concentration of the constituent elements across the thickness is uniform due to the consistent adatom mobility on the growing film. This uniformity, in contrast to the solid-state diffusion-controlled concentration profile, renders reactive sputtering ineffective for the formation of hybrid-structured

coating with good adhesion with the substrate. Thermal oxidation, being a solid-state diffusion-controlled surface modification process, yields the hybrid-structured coating along with the desired oxide phase. As mentioned in section 2.2.1, the thickening of oxide layer on the Ti surface is also very important which can also be achieved by the thermal oxidation [Dong, 1999; Dong, 2000; Fukuzuka, 1980].

2.3.2.1 Thermal Oxidation of Bulk Titanium

The oxide film growth on Ti is accelerated under strongly oxidising condition, such as heating in air. Thermal oxidation (TO) of titanium has been studied extensively since it is the simplest method to produce TiO_2 film [Fukuzuka, 1980] and a cost effective and environmentally friendly surface engineering technique [Dong, 1999]. Enormous decrease in the friction and wear rate of Ti has been reported after the thermal oxidation [Bloyce, 1998; Dong, 1995, 2000]. The low friction is explained by the reduction in plasticity index, which is proportional to the ratio of E^r/H . The plastic deformation between the contacting surfaces makes important contribution to ‘high wear and friction, and a significant reduction in friction and wear is anticipated if the contact between surfaces is predominately elastic [Bloyce, 1998].’ The TO treatment not only reduced the E/H ratio but also increased the elastic recovery [Dong, 1995]. This caused the wear mechanism to shift from severe adhesive wear of untreated material to interfacial fatigue, as evidenced by the small craters and the beach marks [Dong, 1999].

Microstructure of oxide layer:

The oxide layer formed by TO in α -Ti showed the presence of several varieties of oxides i.e. TiO_2 , Ti_3O_5 , Ti_2O_3 and TiO at various depths. Although the formation of various oxides including TiO , TiO_2 , Ti_2O_3 and Ti_3O_5 is possible from thermodynamic standpoint, only the rutile modification of TiO_2 has generally been observed for oxidation in oxygen atmosphere below 1000°C [Imbrie, 2001]. From the external limit of the oxide layer to the metal oxide interface, TiO_2 , and then sub-oxides are present successively [David, 1980]. Thermal oxidation of commercial pure titanium at the β -region at temperatures 950 to 1100°C for up to 16 hours has also been carried out [Tanaka, 1995] which showed that the presence of oxygen could convert the phase of β to α , because O is a α -stabiliser in Ti.

Mechanism of Oxidation:

The early stages of oxidation of titanium (below 200°C) forms only one phase (TiO_2) through a three-step process characterized by (i) low oxidation rate plus the incorporation of un-reacted oxygen, (ii) faster oxidation with consumption of the diluted oxygen and (iii) titanium oxidation after the oxidation saturation at the surface is reached. Whereas oxidation between 200 and 350°C showed the formation of two phases of titanium oxides (TiO_2 and Ti_2O_3) through a three-step process (i) the appearance of only one oxide phase: Ti_2O_3 , followed by (ii) the appearance of TiO_2 and lowering in both Ti_2O_3 and Ti contents, and finally (iii) continuous reaction of Ti, as in the room temperature experiment, after reaching oxygen saturation at the surface [Vaquila, 1996]. A number of researchers reported that the TiO_2 oxide scale has a morphology that consists of two observable phases. The first phase is a comparatively compact zone that extends inward from the gas–oxide interface to a second phase of oxide that has a porous-laminar structure and extends to the metal–oxide interface. The various strata in the second phase vary in thickness, as well as number, depending upon the time and temperature of the exposed surface. Later, the presence of third oxide zone has been reported and that was referred to as a nonstratified coarse-grain crystallized structure appearing between the second phase and the metal–oxide interface. In addition, it is also reported that the individual layers were separated by cracks that extended over short distances, which became visible only after the cooling of the specimen [Imbrie, 2001].

Kinetics of Oxidation:

Several authors made a primary observation that oxidation kinetics is complex in nature. The growth rate of the oxide film formed by TO is markedly high in an early stage and slows down gradually with time [Fukuzuka, 1980]. Similar behaviour was observed in the oxidation of Ti-6Al-4V [Mungole, 2002]. The TO of Ti cannot grow titanium oxides indefinitely for temperatures below 700°C. If the oxidation temperature is above 800°C, Ti is severely oxidized with consequent rapid formation of porous oxide film, and hence it does not seem protective [Fukuzuka, 1980]. Different reaction rates and corresponding rate equations are needed to describe the oxidation behavior of titanium since its mechanisms change both with time and temperature. A parabolic rate law describes oxidation of titanium between 600 and

1000°C. This parabolic time dependence represents two distinct processes as oxygen dissolution and oxide-scale formation [Duc, 1980]. The rate law is valid throughout the entire temperature range, although titanium undergoes an allotropic transformation from *hcp* (α -Ti) to *bcc* (β -Ti) at 882°C. The phase change has little effect on the oxidation mechanisms, except for during the initial stages of the oxidation reaction [Imbrie, 2001].

The parabolic rate law describes the initial oxidation kinetics of titanium between 600 and 1000°C, the period for which it is valid is governed by the formation and growth of an initial coherent scale layer that grows to a critical thickness. Once the critical thickness reaches, stresses in the scale and the metal at the metal–oxide interface become large enough to cause failure, resulting in the growth of fresh oxide. The critical thickness is associated with a steady state, oxygen-concentration profile in the outer surface of the metal at the metal–oxide interface. At this point, there is a change from parabolic to linear oxidation and this transition is correlated to the oxygen concentration in the metal lattice at the interface. Andersson et al (1957), showed that oxygen concentrations, reaching a value that corresponds to a composition of $\text{TiO}_{0.35}$, lead to structural changes in the solid solution and generation of compressive stresses, which in turn cause the detachment of the $\text{TiO}_{0.35}$ layer followed by rapid oxidation of that layer. Thus, heavy oxide formation begins to take place and the oxidation follows a linear rate. While some studies showed a linear oxidation rate following an initial parabolic rate, some reported that the linear behavior is really a series of successive parabolic steps. And during each parabolic step, a new sublayer is formed by similar mechanisms as described above [Imbrie, 2001].

Studies on mechanisms for long-term parabolic oxidation have showed that the process is dominated by the diffusion of oxygen both in the scale and the metal core and that the scale growth is dependent upon the oxygen concentration gradient in the metal. During the initial stage of oxidation, oxygen is absorbed on the surface of the metal by physisorption. The oxygen molecules dissociate and create oxygen anions through a chemisorption process until a monolayer of oxide is formed. Depending upon the oxygen concentration gradient in the metal, oxygen ions either pass through the thin film and are dissolved into the hexagonal-titanium lattice at octahedral interstitial locations or produce fresh oxide. Continued growth of the oxide film is restricted by the need for the chemical potential of oxygen in the oxide film and the reacting titanium to be in equilibrium. If a non-equilibrium condition exists, the rate of

oxygen dissolution becomes the prevailing mechanism. However, once the titanium at the metal–oxide interface becomes saturated with oxygen, the rate-determining reaction is diffusion of oxygen ions through the oxide scale. Thus, there is an inward passage of oxygen produced by anion-vacancy diffusion through the rutile lattice. Since the activation energy for titanium-ion diffusion is much greater than that of oxygen-ion diffusion in TiO_2 , it is generally believed that diffusion of Ti ions outward through the oxide layer is negligible below 1000°C [Johnson, 1992]. The reason for poor solid-state diffusion of titanium is that monocrystalline rutile is stratified and contains micropores, grain boundaries, all of which act as solid-state diffusion barriers.

Dissolution of Oxygen in Ti:

Oxygen is highly soluble in hexagonal α -Ti by occupying the octahedral interstices. Its maximum solubility is about 33 at.%. In the rigid spheres model, the radius of the octahedral interstice is $0.61 \text{ \AA}$ and the atomic radii of oxygen ranges from 0.66 to $0.68 \text{ \AA}$ [David, 1980]. The effect of oxygen dissolution on lattice expansion and microhardness of Ti have been studied [David, 1980; Wiedemann, 1987]. Oxygen in interstitial position in α -Ti caused asymmetric deformation of the lattice by stretching stronger the Ti atoms in the ‘c’ direction, but only slightly in the ‘a’ axis [David, 1980; Bertin 1980]. When ‘a’ parameter considered as constant, the ‘c’ increases linearly until the oxygen content reaches 7%. From 7 to 15%, the rate of increase is lower and beyond 15% it is rapid as shown Fig. 2.10. The apparent contraction at 15% oxygen is related to the appearance of the disordered structure Ti_6O . The correlation between the ordering of oxygen atoms and the concentration is illustrated in Fig. 2.11. Beyond 15% this order is necessarily degraded and the ‘c’ increases again rapidly [Bertin, 1980].

Fig. 2.10: Variation of lattice parameter with oxygen content [Bertin, 1980]

Fig. 2.11: Schematic representation of the distance between basal plane of Ti : (a) pure, (b) disordered Ti_6O solid solution (c) ordered Ti_6O [Bertin, 1980]

2.3.2.2. Thermal Oxidation of Titanium Films

In addition to the advantages mentioned in earlier sections, TO is a low-cost, easy to manipulate process, which is applicable to large area samples. TiO_2 films with rutile structure have been the interest of many studies because of the wide range of its applications as mentioned in section 2.2.4. Obtaining rutile structure and also preferred orientation in some cases makes TO one of the popular techniques. TO of Ti films on several substrates including silicon [Burns, 1989; Dai, 1999], Ti6Al4V [Leng, 2004] and copper [Passeggi, 2002] have been studied.

In thermal oxidation of Ti thin films, passivation regime and the different equilibrium oxide stoichiometries depend on both substrate temperature and the substrate [Passeggi, 2002]. Ti film on silicon substrate with a thickness of about a nanometer converted to rutile even at temperatures as low as 500°C and for short time periods (few minutes) [Burns, 1989]. The studies on the effect of temperature across $400\text{--}1000^\circ\text{C}$, in steps of 100°C on TO of 170nm thick Ti film on Si substrate for 1 hour showed the formation of Rutile only for temperatures greater than 700°C [Ting, 2000]. The studies on the effect of duration of TO in the same work showed that at 550°C Rutile phase formed only after 5 hours [Ting, 2000]. At low temperature oxidation, a longer period is required for the transformation of Ti to TiO_2 as a result of slower oxidation kinetics. Though the layered structures of several Ti-O intermediate oxides are generated from the surface to the interior of the film, the other oxides Ti_3O_5 , Ti_2O_3 and TiO were undetected. Anatase TiO_2 was never detected at high temperatures (>700), which may be explained by the formation of the significant quantity of

oxygen vacancies in the oxidised films, known as Magneli phase, which is known to markedly accelerate the anatase to rutile transformation [Ting, 2000].

Rutile TiO₂ films with random or preferred orientation can be easily grown by thermal oxidation of sputtered films, having different degrees of crystallinity and preferred orientation. The preferential growth results from a competition between surface free energy effect and strain energy effect. Higher temperature oxidation promotes the formation of rutile (110) since it has lowest surface free energy [Ting, 2002]. Several authors have reported the thermal oxidation of Ti films on different substrates deposited by various methods at various temperature ranges between 300-1100 [Burns, 1989; Dai, 1999; Ting, 2000; Ting, 2002]. Though all the above studies were carried out for different oxidation durations, the most common temperature range was 600-800°C. TO process was also used to modify the as-deposited TiO₂ films to convert this amorphous to crystalline or from anatase to rutile [Leng, 2004; Martin 1997].

2.4 TRIBOLOGY

Tribology is defined as “the science and technology of interacting surfaces in relative motion” and embraces the study of friction, wear and lubrication [Hutchings, 1992; Rabinowicz, 1995].

2.4.1 Friction

Friction is the tangential resistance to motion, which is experienced when one body moves relative to another. Friction coefficient is the frictional force F divided by the normal load w on the contact.

$$\mu = F/w \quad (2.4.1)$$

Traditionally, it is believed that the friction mechanism in sliding contacts is due to the adhesion effect between surface asperities. When two asperities are forced into contact, they weld together due to the adhesion between the two materials. When one of the solids is moved in a tangential direction relative to the other, the interfacial bonds break but their shear strength causes a resistance to motion. During sliding, new bonds are formed and broken continuously [Holmberg, 1994].

Based on new a concept of friction, the effect of friction can be divided into three basic mechanisms: asperity deformation, adhesion, and ploughing (Fig 2.12). Plastic deformation occurs when the asperities of two sliding surface come into

contact. This is accompanied by a loss of energy, which accounts for the major part of metals friction [Bushan, 1991].

Fig. 2.12: The three components of sliding friction: (a) adhesion (b) ploughing (c) asperity deformation [Holmberg, 1994]

Adhesional friction depends on the interfacial shear strength and surface energy characteristics of the contacting pair of materials. The adhesion component of friction is given by

$$\mu_a = \tau_s / H \quad (2.4.2)$$

Where τ_s is the shear strength at the interface and H is the hardness of the softer material [Bushan, 1991]. High value of adhesional friction indicates a system of identical metals sliding against each other without any surface contamination or oxide layers, while low value corresponds to a well-lubricated surface [Holmberg, 1994].

If one of the sliding surfaces is harder than the other, the asperities of the harder surface may penetrate and plough into the softer surface. Ploughing into the softer surface also may occur as a result of impacted wear particles. Material and geometric properties of the asperities or penetrated wear particles may significantly influence the ploughing friction [Bushan, 1991].

Rolling friction, in general, is much smaller than sliding friction. It is affected by many factors: adhesion, microslip/ microsliding, elastic hysteresis, and plastic deformation. In rolling contact (e.g. a sphere on a flat surface), a combination of rolling and a small degree of sliding prevails [Bushan, 1991]. The mechanisms in rolling are mainly similar to the mechanisms in sliding contacts [Holmberg, 1994].

2.4.2 Wear

Wear is a process of removal of material from one or both of two solid surfaces in solid-state contact and it occurs when solid surfaces are in sliding or rolling motion relative to each other [Bushan, 1991]. Both friction and wear are simultaneously the results of the same tribological contact process that occur between two moving surfaces. It is common that low friction corresponds to low wear, but is not a general rule [Holmberg, 1994]. The types of wear mechanisms are adhesive, abrasive and fatigue wear (Fig. 2.13).

Adhesive wear is initiated by the interfacial adhesive junctions, which form if solid materials are in contact on an atomic scale. Relative tangential motion of the surfaces causes separation in the bulk of the softer asperities and material is removed. In the absence of surface films, the surfaces would adhere together, but very small amounts of contaminant minimise or even prevent adhesion under purely normal loading. The chain of events that leads to the generation of wear particles includes the adhesion and fracture of the mating surfaces.

The wear resulting from adhesive wear process is described by the Archard equation:

$$W_{ad} = V / L = (k F_N) / H \quad (2.4.3)$$

where W_{ad} is the wear rate, k wear coefficient, V wear volume, L sliding distance, F_N normal load, and H hardness of the softer material [Bushan, 1991].

Fig. 2.13: Basic mechanisms of wear: (a)adhesive (b)abrasive (c)fatigue [Holmberg, 1994]

Abrasive wear is described as damage to a surface by a harder material. In this process, asperities of the harder surface press into the softer surface, with plastic flow of the softer surface occurring around the asperities from the harder surface. When a tangential motion is imposed, the harder surface removes the softer material by combined effect of microploughing, microcutting, and microcracking. In the case of pure metals and non-metallic hard materials, a direct proportionality exists between the relative wear resistance and hardness. When the asperities of the harder surface are assumed to be conical, the abrasive wear rate is given by

$$W_{ab} = V / L = (k F_N \tan \theta) / (\pi H) \quad (2.4.4)$$

where $\tan \theta$ is the asperity slope of the penetrating abrasive particle [Bushan, 1991].

In rolling, where the stress field moves repeatedly over the surface, fatigue of the near surface material occurs. Crack formation, propagation, and coalescence liberate surface material to form wear debris, as shown in Fig. 2.13.

2.5 ADHESION TEST

Adhesion is defined as ‘the state in which two surfaces are held together by interfacial forces which may consist of valence forces or interlocking forces or both’ (ASTM D907-70). 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 or practical adhesion (EA) that depends on other factors, for instance the type of test, the residual stress levels in the film, or the interfacial flaw distribution. As a result, in reality BA is much greater than EA [Bull, 1991].

Adhesion test methods can conventionally be categorised into three main groups such as nucleation methods, mechanical methods and miscellaneous methods, which includes X-ray diffraction, thermal cycling and capacity measurements [Rickerby, 1998]. Mechanical methods are of most practical interest among those. The most common mechanical methods are pull-off methods, shockwave methods, indentation methods and the scratch adhesion test. Scratch test is the most widely used method of all these available tests [Bull, 1991].

2.5.1 Scratch Test

The scratch test has achieved the most widespread use to investigate and analyse the adhesive strength of coating/substrate systems as well as the assessment of the coating quality for tribological applications. A stylus (Vickers or Rockwell C) is drawn over the sample surface under a stepwise or continuously increasing normal force until the coating detaches. The film is seldom removed entirely from the channel so it is convenient to define a critical load (L_c), which is related to coating adhesion. The L_c is usually taken as the load at which the coating is removed in a regular way along the whole channel length. L_c transition is somewhat subjective since distribution of flaws at the coating substrate interface cause isolated areas of coating removal at lower loads. Fig. 2.14 illustrates schematic of the scratch test.

Fig. 2.14: Schematic showing scratch test

The L_c can be determined from microscopic observation (optical or SEM), acoustic emission analysis, or tridimensional force recording [Sekler, 1988]. SEM enables failure to be successfully identified in the largest possible number of coating-substrate combinations. Acoustic emission is also a useful method since each failure mode has a characteristic acoustic emission signal. For thin coatings on soft substrates there is a fairly good correlation between the generation of large pulses of acoustic emission and failure at the coating-substrate interface, but the same is no longer true as the hardness of the substrate or the coating thickness is increased. Frictional force measurement can be used to detect the adhesion failure of the films, where the adhesions between the stylus and coating and between the stylus and substrate are different. There will be a change in friction once the substrate is uncovered. Frictional

force measurement is particularly useful method for determining the adhesion of thin ceramic coatings on metallic substrates [Bull, 1991].

2.5.2 Adhesion Scratch Test Failure Modes

The scratch test failure modes determined by microscopic observations 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 Fig. 2.15

Fig. 2.15: Map of the main scratch test failure modes in terms of substrate and coating hardness [Bull, 1997]

Later failure modes have been classified into two general groups depending on whether the substrate behaves in a “brittle” or “ductile” manner during the test [Dyrda, 1999]. Generally, brittle failure is related to the hard ceramic substrates while ductile failure takes place in a sample coated on the ductile substrates. 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 confined within the track.

2.5.2.1 Brittle Failure Mode

The main brittle failure modes are schematically shown in Fig. 2.16 and explained below.

Large area spallation (Fig. 2.16a), 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 [Bull, 1997]. 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 (Fig. 2.16b). This failure mode leads to chipping at the trackside 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. Fig. 2.16c shows the recovery spallation that 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.

Fig. 2.16: 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 [Bull, 1997]

Fig. 2.16d demonstrates a failure mode typical of very brittle substrates. The tensile radials 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 [Bull, 1997]).

As the indenter moves, several of these rings are formed which intersect and create a network along the edge of the crack. Fig. 2.16e 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 [Yang, 1994].

2.5.2.2 Ductile Failure Mode

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 Fig 2.17. The spallation and buckling failure modes, Fig. 2.17 (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. Both of these failure modes take place ahead of the moving indenter. In general, spallation occurs where the adhesion is poor. In addition, Elastic recovery spallation initiated behind the indenter is not usually observed for ductile failure [Bull, 1997].

Fig. 2.17: Ductile failure modes in scratch test: (a) spallation, (b) buckling, (c) conformal cracking, and (d) tensile cracking [Bull, 1997]

Two other common modes of ductile failure are conformal cracking (Fig 2.17c) and tensile cracking (Fig 2.17d). 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 and the side of indenter causes bending of the coating, placing its surface into tension, and secondly the friction between the indenter tip and coating surface causes the maximum radial tensile stress taking place at the side of indenter. This is supplemented by the tensile stress at the back of the contact area where the indenter moves past the deformed material. The tangential friction contributes compressive stresses ahead of the indenter, which lead to spallation and bucking failures. Tensile stress 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 it then passes over and pushes into the track. The coating can become cracked further on the indenter tip when it is bent into the scratch track. This leads to through-thickness cracking or conformal cracking, Fig 2.17c. Cracking takes place as well at the back of the contact owing to the tensile stress generated on sliding as observed for the brittle materials, Fig. 2.17d.

CHAPTER 3 MATERIALS AND METHODS

The key experimental work carried out for thermal oxidation of bulk Ti (Fig.3.1a), thermal oxidation of Ti film (Fig.3.1b) and sputter deposition of Ti/ TiO₂ films (Fig.3.1c) was presented in the form of flow charts. Detailed experimental set up and conditions are described in the following sections.

Fig. 3.1a: Flowchart showing the key experimental steps of Ti bulk oxidation

Fig. 3.1b: Flowchart showing the key experimental steps of thermal oxidation of Ti film

Fig. 3.1c: Flowchart showing the key experimental steps of Ti/ TiO₂ film

3.1 SUBSTRATE MATERIALS AND PREPARATIONS

3.1.1 Substrate Materials for Ti bulk Oxidation

Commercial pure titanium (CP-Ti, grade 2) was used as substrate material for thermal oxidation and its chemical composition (wt %) is shown in Table 3.1. Samples of 10x10x4 mm were prepared by cutting the as-received Ti plate. Surface finishing was carried out by manual grinding using standard metallurgical SiC grinding papers (180, 320, 600, 800 and 1000 grid size) and then polishing by 6 & 1 μm diamond paste. The polished surface was then cleaned with ethanol before oxidation.

Table 3.1: Chemical composition of CP-Ti Samples

Element	O	N	C	H	Fe	Residuals	Ti
Wt %	0.25	0.03	0.08	0.015	0.3	0.4	Rest

Maximum values unless range is shown

3.1.2 Substrate Materials for Ti/TiO₂ Films

The substrate material used for Ti film deposition is surgical grade AISI 316L austenitic stainless steel and its chemical composition is shown in Table 3.2. Specimens 20 mm in diameter and 4 mm in thickness were prepared by cutting the as-received steel bar and the surface preparation was carried out as mentioned in previous section. Before Ti film deposition, the specimens were ultrasonically cleaned for 10 minutes in a bath of acetone and ethanol to remove grease, oil and stains.

Table 3.2: Chemical composition of stainless steel (316L) Samples

Element	Cr	Ni	C	Mo	Mn	P	S	Si	Fe
Wt %	16-18	10-14	0.08	2-3	2.00	0.045	0.03	1.00	Rest

Maximum values unless range is shown

3.2 Ti/ TiO₂ FILM DEPOSITION

An MSS3 type planar magnetron sputtering system, manufactured by Coaxial Power System Ltd (UK), was used to deposit Ti/TiO₂ based films in this work. A photograph of the system is shown in Figure 3.2. The system employs a simple chamber with two water-cooled 3 inch planar magnetron target holders. Sputtering can be carried out in both the DC and RF modes. The sputtering system has the ability to reach a base pressure of 10^{-5} Pa with the mechanical rotary pump and the turbo molecular pump. The system is also equipped with a substrate holder of 170 mm diameter made of molybdenum, which can rotate at 0 to 40 rpm speed. Below the substrate holder is a graphite heating element capable of heating the substrate to up to 800 °C. A thermocouple placed near to the substrate holder without directly contacting the samples, monitors the working temperature. Fig. 3.3 shows the schematic of the sputter deposition process inside the chamber.

Fig. 3.2: Photograph showing the MSS3 diode planar magnetron sputtering machine

Fig. 3.3: Schematic of typical DC magnetron sputtering system

Cleaned substrates were placed on the substrate holder before closing the chamber for evacuation. The foreline, which connects the vent-side of the turbo pump and vent-side of rotary pump, was evacuated to a pressure of 2×10^{-2} Pa. The gate valve, which connects the chamber to the turbo pump, was opened after the chamber pressure went below 2×10^{-2} Pa. After the base pressure of the chamber reached the desired level (less than 9×10^{-4} Pa), purified Argon gas was introduced. The pressure inside the chamber was set at about 20 mPa for the initiation of the plasma. After the stabilization of plasma, working pressure was set to the desired value of 5 mPa. Targets were sputter cleaned (pre-sputtering), after closing the shutters in front of the target, for a definite time by Ar gas alone, with a certain power, working pressure, and gas flow rate. After pre-sputtering, purified nitrogen gas was introduced into the chamber, and sufficient time was given for both the gases to mix. Individual flow rates of the gases were chosen as per the specific interest of the experiment.

In the present study, Titanium films were deposited on the stainless steel specimens by sputtering a titanium target (99.99% purity) using DC Power and TiO_2 films were deposited from rutile- TiO_2 target using RF power.

3.3 THERMAL OXIDATION (TO)

3.3.1 TO of Bulk Titanium

Thermal oxidation of the Ti samples was carried out in an air furnace at various temperatures ranging from 400 to 850°C for a period of 0.25-5 hours. After the

oxidation treatment some of the specimens were allowed to cool in the furnace itself and the rest outside the furnace in ambient air. The rate of furnace cooling was as low as 2-3°C/min and that of air-cooling was 20-30°C /min. Table 3.3 shows oxidation conditions of bulk Titanium.

Table 3.3: Experimental conditions for thermal oxidation of Ti bulk

Temperature (°C)	Time in hours	
	Air cooling	Furnace cooling
850	0.25, 1, 3, 5	0.25, 1, 3, 4, 5
800	5	5
750	5	-
700	5	5
600	5	5
500	5	-
400	5	-

3.3.2 TO of Titanium Films

Oxidation of Ti films was also carried out using the same procedure as Ti bulk but with different combinations of oxidation time and temperatures i.e between 500 and 800°C and for 10-30minutes. Details of TO conditions of Ti films are shown in Table 3.4.

Table 3.4: Experimental conditions for thermal oxidation of Ti film

Temperature (°C)	Time	
	Air cooling	Furnace cooling
800	10 (mins)	10 (mins)
750	10 (mins)	10 (mins)
700	10, 15, 20, 25 & 30 (mins)	10 (mins)
650	10, 15, 20, 25 (mins)	10 (mins)
600	1,2 & 3 hrs	-
550	2.5,5,7.5 & 10 hrs	-
500	5,10 & 15 hrs	-

3.4 CHARACTERISATION

3.4.1 X-Ray Diffraction (XRD)

X-rays are a form of electromagnetic radiation with high energies and short wavelengths (in the order of the atomic spacing for solids). Historically, much of our understanding regarding the atomic and molecular arrangements in solids had resulted from x-ray diffraction investigations; furthermore, x-rays are still very important in developing new materials.

According to the Bragg, diffraction from a crystalline sample can be explained and visualized by using a simple notion of mirror reflection of the incident x-ray beam from a series of crystallographic planes. Braggs' law for X-Ray diffraction (Fig.3.4) is defined as

$$n\lambda = 2d_{hkl} \sin\theta \quad (3.1)$$

Where ' λ ' is the wavelength of the X-ray beam which incident with an angle ' θ ' with the hkl planes. ' d ' is interplanar spacing between two hkl planes. The integer ' n ' is known as the order of reflection. Its value is taken as 1 in all calculations, since orders higher than one ($n > 1$) can always be represented by first order reflections ($n=1$) from a set of different crystallographic planes.

For hexagonal crystals Miller-Bravais notation (hkil) is used instead of the three-axis Miller notation (hkl). For geometrical reasons, it is essential to ensure that the plane indices comply with the condition $(h+k) = -i$. The Miller-Bravais system also accommodates directions, producing indices of the form $[uvw]$. The first three translations in the basal plane must be carefully adjusted so that the geometrical condition $u + v = -t$ applies. Miller notation (hkl) is used in the present XRD study.

Both θ - 2θ mode (Bragg-Brentano) and the grazing angle incidence 2θ mode (GIXD) X-ray diffraction have been used for phase identification of the resultant thin films. In this section the application of the two methods on thin film is briefly

described. Figure 3.4 shows the diffraction geometry of the two methods. Table 3.5 lists the primary differences between GIXD and Bragg-Brentano modes of XRD analyses.

Fig. 3.4b: Diffraction geometries of (a) Bragg Brentano and (b) GIXD methods

Table 3.5: Salient differences between GIXD and Bragg-Brentano mode of XRD

θ (GIXD)	$\theta - 2\theta$ (Bragg-Brentano)
X-rays are incident at constant glancing angle and detector alone moves across the 2θ angle.	Source and detector of X-rays make equal angles with the normal to the sample's surface through the rotation of sample holder at the half the speed of that of the detector
Background signal from the substrate is reduced, thereby increasing the sensitivity of phase identification.	Sensitivity is poorer compared to GIXD, as background signal from the substance is not reduced comparatively.
Collimated incident beam and soller-slits are used which do not contribute to the instrumental peak broadening	Incident beam, having finite divergence, is focused on to the substrate because of which instrumental peak broadening is comparatively more.
Grains, corresponding to each of the diffraction peak, are different and are oriented differently with respect to the surface	All the grains corresponding to different diffraction peaks are different and parallel to the surface
Phase profile across the depth is possible to determine, while the relative intensities do not give texture information directly	Texture information can be determined directly while phase profile across the depth can not be derived directly.
Rietveld analysis for structure refinement and quantitative phase analysis is not much established	Rietveld analysis is a common technique for structure refinement and quantitative phase analysis

In the case of conventional θ - 2θ scanning method, the specimen is rotated so that the incident angle of the specimen of the x-ray is θ . The crystal plane that causes diffraction is parallel to the surface of the specimen. Consequently, for a specimen that has a certain lattice plane that is strongly oriented with respect to the surface of the specimen, the peak from the crystal plane is very strong. On the contrary, a very weak peak indicates that the crystal plane is not oriented to the surface of the specimen. Since sputtered films usually have preferred orientation, this method is extremely valuable for studying the film orientation. In the grazing incidence (GIXD) method, the glancing angle, α , is fixed and only the detector scans, hence the crystal plane that satisfies diffraction conditions is inclined at an angle of exactly $(\theta + \alpha)$ with respect to the surface of the specimen. Consequently this method is not suitable for studying the crystal planes parallel to the surface.

But there are few advantages of this method in this study: 1) by increasing the incident angle in GIXD method, the X-ray penetration depth can be increased; 2) with a fixed glancing angle, the penetration depth will not change with change in 2θ . Thus the depth profile of the near surface microstructure can be obtained by this way; 3) the grazing incidence can also increase the volume of material detected by the X-ray penetration depth in the film, which induces higher diffraction intensity. This method is extremely useful in studying multi-layer structures.

Phase constituents of the titanium bulk samples were analysed by X-ray diffractometer (Rigaku, Dmax 2200, Fig. 3.5), using Cu-K α radiation with 1.54046 Å wavelength. Bragg-Brentano ($\theta/2\theta$) diffraction was carried out at a voltage of 50 kV and current of 30mA. The diffraction patterns were recorded between the 2θ values of 20 - 60° with a step width of 0.16° and at a speed of 1°/min.

Ti and TiO₂ films were also analysed by X-ray diffraction as mentioned above. In addition to the Bragg-Brentano, glancing incidence angle diffraction (GIXD) was also carried out for the oxidised films to identify the variation of phase composition along the thickness of the film.

Fig. 3.5: Rigaku Dmax 2200 XRD used for the XRD analysis

Lattice parameters of the cubic phases were determined with the help of method of least squares [Cullity, 1978]. According to this method a line is fit to the plot so that sum of the squares of deviation of all the points with respect to the line is least. This eliminates the random errors in the calculation. With the choice of an appropriate function for the lattice parameter systematic errors can also be eliminated. Error in the Bragg angles, caused due to the shift of the specimen in the direction perpendicular to the plane of the diffraction, is the largest single source of error. This error can be eliminated by plotting the lattice parameter against $\cos\theta \cdot \cot\theta$.

3.4.2 Secondary Electron Imaging (SEI)

Scanning electron microscope (SEM) and high-resolution field emission scanning electron microscope (FESEM) were used to examine the morphology of the surfaces and fractured cross-sections of the films. The principles of SEM image formation are briefly discussed below.

Secondary electrons are low energy electrons ejected from the sample as a result of inelastic collisions by a beam of electrons or ions. In Scanning electron microscope, primary electrons enter a surface with energy of 0.5 - 30 keV, and generate many low energy secondary electrons on the surface of the sample. The intensity of these secondary electrons is largely governed by the surface topography of the sample. They are produced near the surface of the sample, from a small area around the beam tip. An image of the sample surface can thus be constructed by

measuring secondary electron intensity as a function of the position of the scanning primary electron beam [Richard, 1992].

The benefits of SEM over conventional optical microscopy include very high resolution and depth of focus in comparison to the conventional optical microscopes. High lateral resolution is possible because the primary electron beam can be focused to a very small spot (<10 nm). Primary electrons, after impinging on the sample, are scattered with a profile schematically shown in Fig. 3.6. From the figure it is clear that the volume of the sample over which secondary electrons are generated is a function of diameter of the incident beam of primary electrons.

Variants of SEM are present depending on the source of primary electrons, thermionic (W, LaB₆) or field emission (sharp tips subjected to electric field). In the case of thermionic sources, in order to narrow the beam size, accelerating voltage of the primary electrons is increased. This increase in primary-electron beam energy causes destruction to the sample as well as increases the surface charging of poorly conducting samples. In the case of field emission SEM, 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. FESEM provides greater spatial resolution in comparison to the thermionic SEM due to the decrease in scattering volume on account of lower demanding accelerating voltages. Also greater depths of field can be achieved with FESEM due to the decrease in numerical aperture of the electron probe. Further, chromatic aberration is minimal in the case of FESEM due to decreased energy spread of the electrons and better quality of the images can be obtained due to increased signal to noise ratio due to increased electron intensity. Fig. 3.7 shows the JSM-6340F FESEM used for the present work. The accelerative voltage used for the imaging in the present is 5 kV.

Fig. 3.6: Schematic profile of primary electron inside the sample [Ohring, 1991]

Fig. 3.7: FESEM used for the characterization

3.4.3 Transmission Electron Microscopy

The results obtained for phase identification, by grazing angle incidence X-ray diffraction (GIXD) technique, and for film morphology and structure done by Field Emission Scanning Electron Microscope (FESEM), can be further confirmed by the transmission electron microscope (TEM). An electron beam accelerated by voltages of 200 kV was made to pass through samples thinned down to less than 100 nm and the transmitted electrons were analyzed in order to study the diffraction characteristics and morphology of various samples. Diffraction patterns were obtained with camera length of 30cm by focusing the image on the back focal plane (Fig. 3.8(a)) of the objective lens on to the image plane of the intermediate lens and is further magnified and projected on to a screen by projector lens. Defocused beam of coherent electrons was diffracted by the periodically arranged atoms in crystallites of various phases. These diffraction patterns were then indexed based on the knowledge on d-spacings of each of the identified phases. On the other hand, bright field images were obtained by

focusing the image on the image plane (Fig. 3.8(b)) of the objective lens on to the image plane of the intermediate lens and further magnified by projector lens. Image

Fig. 3.8: Electron ray diagram showing the focusing of (a) diffraction pattern in the diffraction mode and (b) bright field image in the image mode [Williams, 1996]

carries the net contrast in the intensity caused in the transmitted electron beam. The intensity-contrast is due to the variation in spatial distribution of scattered electrons. The differences in distribution of scattered electrons are due to the change in lattice spacing with the phase or defects in the crystalline atomic arrangement.

TEM- Jeol JEM 2010 (Fig. 3.9) was used for the characterization of TiO_2 films in the present work. The TEM samples were prepared for both top view and cross sectional studies. For the plan view studies dimpling was done at the centre of the silicon substrate, of size 3 mm in diameter, to bring down the thickness to about 20 micron from the previously lapped thickness of 80 micron. Dimpling (by Gatan 656) of the sample is followed by ion milling (Gatan 691) at ion energy of 5 KeV in order to thin down the film to a thickness of 100 nm and below. In the case of cross section TEM sample, special epoxy (Gatan-G-1/G-2) was used to join the faces of the films on two different samples, backed by 2 dummy silicon samples on either side. After curing the epoxy between these sandwiched films, it is cylindrically cut with the help of ultrasonic disc cutter (Gatan 601) so that the film comes at the centre of the 2.3 mm

diameter cylinder. This cylindrical sample is inserted into a copper tube by curing the epoxy applied between them and then cut into small slices of thickness (not more 700 micron) by precision diamond cutter. These slices are then thinned down to less than 100 nm through the means similar to the plan view samples.

Fig. 3.9: Transmission Electron Microscope (Jeol JEM 2010) used for characterization of stainless steel-nitrogen films

3.4.4 Atomic Force Microscopy

AFM technique is a powerful tool to study the surface topography of materials, and is known for its high spatial and depth resolution. In an AFM instrument, a sharp tip is attached to a flexible cantilever. As the tip is scanned over the surface, the cantilever will deflect up and down across the surface features. By monitoring the cantilever movement, the surface structure is mapped. The deflection of the cantilever can be monitored by optical, interferometry and tunneling method. A DimensionTM 3100 series scanning probe microscope was employed in this study and operated in tapping mode. The results obtained not only include the topographic images of the surface, but also include the quantitative surface roughness parameter, such as R_a value. In the present studies tapping mode scanning was used where the tip is in the repulsive regime of the tip-sample spacing. The image contrast was obtained by measuring the change in force required to keep the tip at a constant height above the surface, with a feed back loop in order to safeguard the tip from damaging due to the surface roughness.

Mean line: The mean line is commonly used in surface texture measurement and it is based on least square method. It is a line which bisects the profile such that the areas above it and below it are equal and minimum.

Roughness average (R_a): R_a is the arithmetic mean of the departures of the profile from the mean line.

3.4.5 Glow Discharge Optical Spectrometry

Glow Discharge Optical Spectrometry (GDOS) is an important and versatile technique for rapid depth profiling analysis of the chemical compositions of surface layers with thickness ranging from a few nanometers(nm) to several tens of micrometers(μm) [Bell, 1995]. This technique employs a Grimm type glow discharge source (lamp), where cathode sputtering is created by applying a controlled voltage to the sample with a controlled argon pressure across the sample surface (Fig. 3.10). Surface atoms removed by this sputtering process diffuse in to the argon plasma where excitation and emission occurs. Separation of atom removal and excitation provides spectra with a linear relationship between concentration and spectral intensity. When combined with deconvolution algorithms using modern powerful computational techniques, quantitative profiling analysis of surface layers can be achieved. This work was conducted at the University of Birmingham (UK) through research collaboration.

Fig. 3.10: Schematic diagram of Grimm type glow discharge source [Bell, 1995]

3.5 MECHANICAL PROPERTIES

3.5.1 Nanoindentation Test

Nanoindentation or indentation testing at the nanometer scale is one of the simplest ways to measure the mechanical properties of very thin films, for instance hardness, elastic modulus, scratch resistance, creep etc, [Hay, 2000]. The popularity of nanoindentation method is due to the fact that mechanical properties can be measured without removing the film from its substrate and the ability to probe a surface at numerous points and spatially map its mechanical properties [Pharr, 1992].

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 [Thurn, 2002]. Imaging projected area of contact of such impressions is difficult for thin films with the conventional hardness testing techniques, but becomes possible with the nanoindentation/ depth sensing indentation (DSI) 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 [Fischer, 2000]. The analysis method, however, requires careful calibration to determine the column compliance and indenter tip shape.

Nanoindentation of the oxidised films and SS substrate was carried out by NanoTestTM system (Micro Materials Ltd., Wrexham, United Kingdom). The schematic diagram of the NanoTestTM system is shown in Fig.3.11. 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. In the present work all

experiments were performed at a constant loading and unloading rate of 0.5 mN/s and to a maximum depth of 1000nm. Depth controlled load-unload indentation at different depths from 100 to 1000nm at intervals of 100nm was carried out. The unloading curves were used to derive the hardness and modulus values by the analytical techniques developed by Oliver and Pharr [Oliver, 1992].

Fig. 3.11: Schematic diagram of nanoindentation test

3.5.2 Microscratch Test

The adhesion strength of the coating to the substrate was evaluated by microscratch testing conducted with the scratch mode of the NanoTest 6 instrument manufactured by Micro Materials Ltd (UK). The test involved drawing of a diamond stylus with a tip radius 25 μm across the coating surface with increasing load under controlled loading rate of 5 mN/s and specimen travelling speed of 5 $\mu\text{m/s}$. The frictional force was recorded continuously during the test. The critical load at which the coating started to fail was evaluated from the sudden change in the frictional behaviour in the friction force vs. load curve as well as by microscopic examination of the scratch tracks after the test.

3.5.3 Tribology Test

Dry sliding friction and wear tests were carried out using the CSEM type ball-on-disc tribometer at room temperature and ambient conditions. Fig. 3.12 shows schematic of the ball on disk tribo test. An alumina ball of 6 mm in diameter was used as the counterface. During the test, the specimen was rotating against the stationary ball under an applied normal load of 1 N. The sliding speed of the specimen relative to the ball was 5 cm/s and the total sliding distance was 200 m. The friction coefficient of the sliding couple was recorded continuously during the test by a computer data-acquisition system. The wear volume from the specimen was evaluated after the test by measuring the surface profile across the wear track using a surface profilometer.

Fig. 3.12: Schematic of ball on disk tribology test

3.5.4 Corrosion Test

The corrosion behaviour of the specimens was tested in an electrolyte of 3wt% NaCl solution. Electrochemical corrosion test was carried out in an EG&G Parc three electrode electrochemical flat cell, with the specimen-exposed area of 1cm^2 . Fig. 3.13 shows the schematic arrangement of the electrochemical cell. Anodic polarization curves were measured potentiodynamically at a scan rate of 0.5 mV/s starting from -250 mV (vs. E_{corr}) to 2000 mV (vs. SCE) with potentiostat (ACM, UK) at room temperature. Before anodic polarization scanning, the specimen was kept at the open-circuit potential for 20 min to allow dynamic stabilization between the working electrode and the electrolyte.

Fig. 3.13: Schematic diagram showing three electrode electrochemical flat cell

3.5.5 Biocompatibility

Cytotoxicity test was conducted to evaluate the biocompatibility of the resultant films. Cell culture was carried out with L929 osteoblast cells in Minimum Essential Medium (MEM) (Invitrogen) supplemented with 10% Fetal Bovine Serum at 37.4 °C and for 24 hours. Poly vinyl chloride (PVC) was used as positive control and high-density polyethylene (HDPE) was the negative control.

CHAPTER 4

THERMAL OXIDATION OF TITANIUM

This chapter contains results and discussion of thermal oxidation (TO) of bulk titanium. The effect of oxidation temperature and time on the structure and properties of the oxidized layer are discussed. Thermal oxidation conditions were optimized to obtain oxidised surface with improved wear resistance and good adhesion strength.

TO of titanium was carried out for a number of well polished samples at temperatures ranging from 400 to 1000°C for 5 hours, samples of each temperature followed by both air-cooling and furnace cooling. Table 4.1 shows the details of thermal oxidation conditions and cooling methods applied for commercially pure titanium (CP-Ti). Preliminary studies were carried out up to 1000°C, however, further studies were restricted to scope of our study i.e. temperatures well below the α -Ti to β -Ti transformation temperature (883°C).

Table 4.1: Temperatures, duration, and cooling methods set for oxidation of CP-Ti

Air-cooling			Furnace-cooling	
Duration (hours)	Temperature (°C)		Duration (hours)	Temperature (°C)
5	400	750	5	550
	500	800		600
	550	850		700
	600	900		800
	700	1000		850
0.25 (15 minutes)	850		0.25 (15 minutes)	850
1			1	
3			3	
5			5	

4.1 X-RAY DIFFRACTION (XRD) ANALYSIS

Bragg-Brentano XRD profiles of CP-Ti, TO specimens at 400, 500, 600, 700, 800 and 850 °C and for 5 hours oxidation are shown in Fig.4.1. All the peaks present in the CP-Ti profile correspond to α -titanium with a HCP structure (JCPDS 5-0682). The profile corresponding to both 400 °C and 500 °C samples looks similar, except for unsymmetric broadening of the peaks corresponding to (002) and (101) planes towards higher 'd' values. For higher oxidation temperatures, new peaks related to oxygen diffused Ti peaks (ODT) are separated from the above-mentioned peaks. For 800°C

Fig. 4.1: XRD profiles of 5 hours oxidized and air-cooled CP-Ti samples at various temperatures

only a small proportion of rutile phase appeared, since the film was peeled off after oxidation. The rutile, which is the only phase present at 850°C, started appearing from 600 °C onwards. The proportion of rutile phase increased with increasing temperature. Preferred orientation of the plane (101) parallel to the surface was induced by oxidation at 850 °C even after 3 hours of oxidation (Fig. 4.2). Reason for the preferred orientation is that plane with least surface energy, (101) in the case of rutile phase, tends to be parallel to the surface [Ting, 2002].

For the samples oxidized at identical temperatures and times but cooled inside the furnace, XRD analysis showed similar phase evolution (Fig. 4.3). But the samples oxidized even at the highest temperatures, 800 and 850 °C did not peel off, in contrast to the air-cooled samples. The failure of the air-cooled samples is due to the thermal stresses, enhanced especially at higher rates of cooling. Thermal stresses can contribute from anisotropy of the thermal expansion and CTE mismatch. Anisotropy of the thermal expansion in this low symmetry system is evidenced by the presence of texture in the air-cooled sample compared to furnace-cooled. Even though thermal expansion coefficient mismatch between Ti (CTE of $9\mu\text{m/m-}^\circ\text{C}$) and rutile-TiO₂ ($8.6\mu\text{m/m-}^\circ\text{C}$) has low magnitude, but it may have slight impact on thermal stresses. The absence of texture in the furnace-cooled samples is apparent with the first three identical peaks being similar to that of the standard bulk sample.

Fig. 4.2: XRD profiles of 850 °C oxidized and air-cooled CP-Ti samples showing orientation change with time

Fig. 4.3: XRD profiles of 5 hours oxidized and furnace-cooled CP-Ti samples at various temperatures

The profile of phases formed across the depth of thermally oxidized bulk Ti shows the formation of oxygen rich phase on the surface and the formation of Ti rich phases gradually towards the interface. This is in accordance with the directional oxygen diffusion from the surface to the bulk of the Ti. Though an oxygen diffused zone also forms at temperatures above 800°C, the rutile layer formed is so thick that the X-rays could not penetrate to generate any peak corresponding to this phase. The rutile layer formed at all investigated temperatures did not show any obvious preferred growth orientation. In addition anatase phase was not found in any of the oxidised samples.

4.2 MORPHOLOGY

Surface morphology of oxide layers in the AC and FC samples shown in Fig. 4.4. Both surfaces show square based columnar grains with angular tips. Even though the size of the grains is bigger in the AC sample (approx. 2 μm) compared to the FC sample, the range of size distribution is narrow in the former (Fig. 4.4c). It is also clear that the rutile layer formed in the AC sample with the grains oriented perpendicular to the surface is more porous than that formed in the FC sample. This suggests that the

Fig. 4.4: FESEM images showing the surface morphology of oxidised AC samples at (a) 700 °C-5 hours, (b) 850 °C -1 hour, (c) 850 °C -5 hours and FC samples, and (d) 850 °C-5 hours

further development of the rutile layer during slow cooling helped to densify the layer and to reduce the grain size (Fig. 4.4d). The changes in surface morphologies occur even though the phase composition of oxide layers is same. It can also be inferred that the transition in morphology of the oxide layer takes place with respect to both temperature and time in a similar manner.

Fig. 4.5 shows the cross-sections of the oxide layers formed on both AC and FC samples. The poor adhesion of the oxide layer with substrate for the AC specimen (Fig. 4.5a,b) is due to the fast cooling which results in a large thermal stress arising from the high ratio of the coefficient of thermal expansion of Ti and rutile. Whereas, the FC sample showed very good adhesion between the oxide layer and the substrate (Fig. 4.5c,d). Slow furnace cooling obviously reduces the thermal stress induced during the cooling process and this helped to maintain the integrity of the thick layer

with the substrate, which is the key factor in the production of a thick and adherent rutile layer.

Fig. 4.5: SEM images showing cross-sectional view of the oxide layers of AC samples at (a) 800 °C - 5 hours, (b) 850 °C - 5 hours, FC samples, (c) 850 °C - 3 hours, and (d) 850 °C - 5 hours

4.3 THICKNESS OF THE OXIDE LAYER

Thickness of the oxide layers was measured from the SEM images of cross-sectioned samples. The increase in thickness of the oxide layer as a function of ramping oxidation temperature of samples oxidised for 5 hours treatment is shown in Fig. 4.6. For temperatures above 800°C, both the air cooled (AC) and furnace cooled (FC) samples showed a significant increase in growth rate of the oxide layer. In particular, the sharp increase in rutile layer thickness of the FC samples at 850°C

Fig. 4.6: Variation of thickness of oxide layer as a function of temperature for 5 hours treatment, followed by air-cooling (AC) and furnace-cooling (FC)

Fig. 4.7: Variation of thickness of oxide layer as a function of time for 850 $^{\circ}\text{C}$ treatment, followed by air-cooling (AC) and furnace-cooling (FC)

showed the possibility of producing a thick oxide layer (above 100 μm) at lower temperatures than the AC samples. The reason for this thick layer by furnace cooling is due to more effective oxidation time. Fig. 4.7 shows the increase in thickness as a function of oxidation time at 850 $^{\circ}\text{C}$. It can be seen that for both modes of cooling (AC and FC), the growth rate is significant only after 4 hours. From both Figures, it is supported that the growth of the oxide layer is a function of oxidation time and temperature. It is also observed that the thickness curve of the FC samples lies above

that AC samples since the effective oxidation time is more in the former. The rate of layer growth increased linearly with temperature until 800°C and showed parabolic increase thereafter. Such a linear increase in the growth and the change in the growth rate from parabolic to linear is discussed in section 2.3.2.1(Chapter 2). Similarly the transition at 800°C accompanied with the formation of porous morphology in the layers is in accordance to previous reports. A similar increase in thickness of the oxide layer with respect to oxidation time can be seen at 850°C in Fig.4.7.

4.4 DETERMINATION OF PRECISE LATTICE CONSTANTS

A change in solute concentration leads to a minute change in lattice parameters. Thus, it is necessary to measure the precise parameters in order to determine the quantity of solute with any accuracy. Lattice parameters of α -Ti and α -Ti (O) phases can be precisely calculated by the equations below:

$$\left. \begin{aligned} \sum \alpha \sin^2 \theta &= C \sum \alpha^2 + B \sum \alpha \gamma + A \sum \alpha \delta \\ \sum \gamma \sin^2 \theta &= C \sum \alpha \gamma + B \sum \gamma^2 + A \sum \gamma \delta \\ \sum \delta \sin^2 \theta &= C \sum \alpha \delta + B \sum \gamma \delta + A \sum \delta^2 \end{aligned} \right\} \quad (4.1) \quad [\text{Klug, 1974}].$$

$$\begin{aligned} \text{where } C &= (\lambda^2/3a^2) & \alpha_i &= (h^2 + hk + k^2)_i \\ B &= (\lambda^2/4c^2) & \gamma_i &= l_i^2 \\ A &= D/10 & \delta_i &= 10 \sin^2 2\theta_i \{ (1/\sin \theta_i) + (1/\theta_i) \} \end{aligned}$$

And those of rutile can be calculated by these equations:

$$\left. \begin{aligned} \sum \alpha \sin^2 \theta &= C \sum \alpha^2 + B \sum \alpha \gamma + A \sum \alpha \delta \\ \sum \gamma \sin^2 \theta &= C \sum \alpha \gamma + B \sum \gamma^2 + A \sum \gamma \delta \\ \sum \delta \sin^2 \theta &= C \sum \alpha \delta + B \sum \gamma \delta + A \sum \delta^2 \end{aligned} \right\} \quad (4.2) \quad [\text{Klug, 1974}].$$

$$\begin{aligned} \text{where } C &= (\lambda^2/4a^2) & \alpha_i &= (h^2 + k^2)_i \\ B &= (\lambda^2/4c^2) & \gamma_i &= l_i^2 \\ A &= D/10 & \delta_i &= 10 \sin^2 2\theta_i \{ (1/\sin \theta_i) + (1/\theta_i) \} \end{aligned}$$

where subscript i indicates that there is an equation for each line of the diffraction profile and each with its own values of α , γ , and δ . θ is the Bragg angle, D “drift” constant, λ the wavelength of the x-ray, (hkl) the corresponding plane index, a and c the lattice parameters of the crystal [Cullity, 1978; Klug, 1974].

Table 4.2 tabulates all calculated lattice constants of α -Ti, α -Ti(O), and rutile as a function of oxidation temperature and time. The change in lattice constants of α -Ti(O) phase with oxidation temperature is shown in Figure 4.8. It can be seen that increasing oxidation temperature causes noticeable increase in lattice constant c and only a slight increase in lattice constant a . It is well established that oxygen dissolution in octahedral interstitial position in α -Ti causes asymmetric deformation of the lattice, with considerable expansion in the c -axis, but only a slight in a -axis, as already mentioned in Section 2.3.2.1 (chapter 2).

Table 4.2: Calculated lattice constants of α -Ti, α -Ti(O), and rutile as a function of oxidation temperature and time, in comparison to JCPDS standard

Air-cooled samples						
α -Ti				Rutile		
Samples	a (Å)	c (Å)	c/a	Samples	a (Å)	c (Å)
JCPDS standard	2.95	4.686	1.5885	JCPDS standard	4.5933	2.9592
cpTi	2.9607	4.6932	1.5852	600-5ha	4.6025	2.9678
600-5ha	2.9464	4.6881	1.5911	700-5ha	4.5913	2.9608
α -Ti(O) (ODT)				750-5ha	4.5953	2.9606
600-5ha	2.9698	4.7516	1.6000	800-5ha	4.5971	2.9634
700-5ha	2.9687	4.7699	1.6067	850-5ha	4.5922	2.9610
750-5ha	2.9663	4.7684	1.6075	850-3ha	4.5838	2.9518
800-5ha	2.9706	4.7812	1.6095	850-1ha	4.5948	2.9626
				850-15ma	4.5932	2.9604
Furnace-cooled samples						
α -Ti				Rutile		
Samples	a (Å)	c (Å)	c/a	Samples	a (Å)	c (Å)
600-5hf	2.9464	4.6818	1.5890	600-5hf	4.5938	2.9619
α -Ti(O)				700-5hf	4.5956	2.9628
600-5hf	2.9652	4.7667	1.6075	800-5hf	4.5937	2.9614
700-5hf	2.9684	4.7727	1.6078	850-5hf	4.5931	2.9606
				850-15mf	4.5971	2.9654
				850-1hf	4.5835	2.9516
				850-3hf	4.5893	2.9609

Note: 600-5ha indicates the Ti being oxidised at 600°C for 5 hours and air-cooled.

Fig. 4.8: Effect of oxidation temperature on variation of lattice constants 'a', 'c' (a) and its ratio (b) of α -Ti(O) phase

4.5 OXYGEN CONTENT AND DIFFUSION LAYER THICKNESS

The amount of oxygen content in titanium can be calculated as a function of oxidation temperature from the lattice expansion, obtained in earlier section 4.4. Subsequently, the thickness of the diffusion layer can be calculated by adopting Fick's second law (semi-infinite nonsteady-state diffusion). It is given by:

$$\frac{C_x - C_o}{C_s - C_o} = 1 - \operatorname{erf} \left[\frac{x}{2 (Dt)^{1/2}} \right] \quad (4.3)$$

where C_s is the constant surface concentration, C_o bulk solute concentration, C_x solute concentration at any distance x from the surface, D diffusion coefficient of the solute in the solvent, and t is diffusion time [Callister, 1985]. In the case of oxygen diffusion in α -Ti, C_s is 34 at% [David, 1980] and C_o is 0.74 at% (converted from 0.25 wt% of oxygen in cp-Ti grade 2).

Diffusion coefficient is temperature dependent and the relation is given by:

$$D = D_o \exp (-Q / RT) \quad (4.4)$$

Diffusion of oxygen in α -Ti has D_0 value of $4.08 \times 10^{-5} \text{ m}^2/\text{s}$ and Q of 197 KJ/mol [Tanaka, 1995]. The calculations are presented in table 4.3 together with the approximated oxygen concentration as a function of oxidation temperature. However, the thickness calculation is restricted to air-cooled samples, since exact diffusion time in furnace-cooled samples cannot be calculated.

Table 4.3: Diffusion coefficient of oxygen in α -Ti, oxygen content and thickness of diffusion layer as a function of oxidation temperature.

Air-cooled samples				
Samples	$D \text{ (m}^2/\text{s)}$	c/a ratio	O content (%)	Thickness (μm)
600-5ha	6.65×10^{-17}	1.6000	8.83	1.81
700-5ha	1.08×10^{-15}	1.6067	16.82	4.38
750-5ha	3.56×10^{-15}	1.6075	17.23	7.72
800-5ha	1.05×10^{-14}	1.6095	18.11	12.43
Furnace-cooled samples				
600-5hf	6.65×10^{-17}	1.6075	17.23	
700-5hf	1.08×10^{-15}	1.6078	17.43	

Note: 600-5ha indicates the Ti sample being oxidised at 600 °C for 5 hours and air-cooled.

Figure 4.9 (a) shows the parabolic increase of oxygen concentration with increasing oxidation temperature. This is reasonable because of the diffusion-controlled kinetics [Johnson, 1992]. Also, the reduction in relative amount of oxygen in the diffusion layer can be addressed as a consequence of reduced oxygen gradient caused by the onset of accelerated rutile growth rate at higher temperatures [Frangini, 1994]. This reason is in agreement with the rapid growth of rutile observed in Figure 4.7. In addition to oxygen content, the diffusion layer thickness increases exponentially with increasing temperature. This is rational, since there is exponential dependence of diffusion coefficient of oxygen in α -Ti on temperature.

Fig. 4.9: (a) Oxygen content and (b) thickness of the diffusion layer as a function of oxidation temperature in AC samples

4.6 HARDNESS

Hardness of oxide layers was measured by Vickers microindenter on cross-sectioned samples. Hardness depth profiles were not taken as reported in other studies [Yan, 2002], because of the difficulties in measuring the accurate distance from the surface, as the oxide layer in AC samples is either peeled off or loosely adhered to the substrate (Fig. 4.5). More than 3-fold increase in microhardness has been observed after the oxidation in both AC and FC samples (Fig. 4.10). Compared to the oxide layer of the AC sample, the oxide layer of the FC sample has higher hardness and shows less deviation from average value, when 10 readings were taken. The reason for this high hardness and less scatter is due to more densely packed grains in FC samples than AC samples (Fig.4.4d).

Fig. 4.10: Comparison of the micro hardness values(HV0.1) of the CP-Ti and the rutile layers in both AC and FC samples oxidised at 850 °C for 5 hours

4.7 TRIBOLOGY TEST

Tribological testing under dry sliding conditions has demonstrated that thermal oxidation can significantly improve the friction characteristics and wear resistance of titanium. Fig. 4.11 shows the friction coefficient curves recorded for the CP-Ti and the FC sample oxidised at 850°C for 5 hours. Although the same test has been carried out for the AC sample, the result is not shown here since the oxide layer peeled off during the test owing to the poor adhesion with the substrate. The CP-Ti sample exhibits very poor friction behaviour, characterised by high and unstable friction coefficients, which fluctuated greatly during the sliding cycles. This is typical of poor tribological materials, which experience “stick-slip” during dry sliding. On the other hand, thermal oxidation of the Ti followed by furnace cooling has significantly improved the friction characteristics in two aspects. First, the overall friction coefficient was reduced during the test. Second, the friction curve became much smoother and the tribosystem experienced much less frictional noise and fluctuation.

Fig. 4.11: Friction coefficient curves recorded for the CP-Ti and Oxidised specimens

The improvement in tribological behaviour by thermal oxidation is further demonstrated by the mild wear mechanism involved in the thermally oxidised Ti (Fig. 4.12) and the much reduced wear rate (Fig. 4.13). Examination of the wear tracks revealed that the unoxidised CP-Ti was worn severely by the adhesive wear mechanism, such that the wear tracks were wide and deep with a very rough surface

appearance (Fig. 4.12a). On the contrary the thick oxide layer experienced only mild wear caused by the abrasion of the hard alumina counterface. The resultant wear track is narrow and shallow with a smooth and polished appearance. No debonding and flaking of the oxide layer has been observed in the track. The superior wear resistance of the rutile layer in the FC specimen is derived from its good adhesion with the substrate, large thickness, high hardness and much improved frictional behaviour.

Fig. 4.12: SEM images showing wear tracks of the (a) CP-Ti and (b) 5 hours oxidised FC sample at 850 °C

The tribological property of the oxide layer at various depth levels from the surface was tested by removing layer by layer to study the wear and friction behaviour of the oxide layer throughout the thickness. The wear rate at different depths from the surface is shown in Fig. 4.13 and the corresponding XRD patterns at these depths are shown in Fig. 4.14. It can be seen that the wear rate of the oxide layer suddenly increased from a depth of 80 μm. The reason for this sudden increase in wear rate is due to the presence of ODT phase after removing about 80 μm from the surface. Even in the rutile layer (below 80 μm) variation in the wear rate was observed with thickness i.e. very little wear up to 10 μm and then gradual increase until 80 μm. This difference in the wear rate is well correlated with the texture of the rutile film where it shows (110) up to 10 μm and then changes to (101), which lower number of slip systems. The results of this test demonstrate that the thick rutile layer is effective in achieving reduced wear rate. The service life expected for such a rutile layer is therefore believed to be suitable for many engineering tribological applications.

Fig. 4.13: Comparison of the wear rates of CP-Ti and at various depths (in μm) across the oxide layer of 5 hours oxidised FC sample at 850°C

Fig. 4.14: XRD patterns of CP-Ti and at different depths (in μm) across the oxide layer of 5 hours oxidised FC sample at 850°C

4.8 DISCUSSION

4.8.1 Poor Adhesion of Oxide Layer on Titanium Substrate

The reason for poor adhesion of the oxide layer of AC samples is the presence of thermal stresses, which occur due to the anisotropic thermal expansion and also due to difference in coefficient of thermal expansion (CTE) between the film and substrate. Thermal stresses induced in the oxide layer can be calculated by the following equation:

$$\sigma_{th} = (\alpha_f - \alpha_s) \times \Delta T \times E_f / (1 - \nu_f) \quad (4.5)$$

where α_f and α_s are the coefficients of thermal expansion of the film and substrate, respectively, ΔT is the change in temperature, E_f is modulus of elasticity of the film and ν_f is Poisson's ratio of the film. The magnitude of thermal stresses combined with the intrinsic stress (related to any defects in the structure) may come close or even exceed the stress level required for plastic deformation of the film, leading to either peeling off or cracking of the film [Bottiger, 2001].

Slow cooling results in the substrate remaining at elevated temperatures long enough to promote residual stress relaxation by flow and creep² mechanisms, while subsequent cooling through lower temperatures does not contribute to significant residual stresses.

In addition, higher oxidation temperatures tend to accelerate the formation of rutile. As a result, the effect of mismatch between rutile and titanium substrate will be more pronounced. Dong et. al, 1995 reported that debonding of the oxide formed at high temperature, leads to a large mismatch, can also be attributed to a high Pilling-Bedworth ratio¹ (P-B Ratio) and the high CTE ratio of Ti to rutile.

One way to circumvent the thermal stresses occurred due to high temperatures is to eliminate the rapid change in temperature, which can be achieved by employing slow cooling method (i.e. furnace-cooling). This method prevents abrupt change in film dimensions upon cooling brought about by its thermal expansion coefficient, which in turn minimises the induced thermal strain. Also, furnace cooling may

¹ Ratio of the volume of the metal oxide, which is produced by the reaction of metal and oxygen, to the consumed metal volume.

² Progressive deformation at constant stress occurs above 0.4Tm

enhance the formation of diffusion layer that serves as intermediate layer which allows a continuous transition from one lattice to the other, thus reducing the interfacial energy and resulting in better adhesion [Wolf, 2000].

4.8.2 Preferred Orientation of Rutile Phase at High Temperatures

Preferential growth of rutile can be explained by the fact that crystallinity and orientation of the substrate may influence the nucleation of the films [Berry, 1968]. Ting et al. showed that crystalline Ti film with (002) orientation has a greater tendency towards the growth of (200) oriented rutile during oxidation [Ting, 2002].

Previous experimental studies suggest that preferential crystal growth is determined by the competition between the two driving forces, i.e., surface free energy and strain energy [Ting, 2002]. The surface energy of a solid is different for different crystallographic planes. The work required to create the surface, γ (surface tension), depends on the number of bonds broken per atom when the surface is created, and the number of atoms per area of surface. The relation between Gibbs (G) free energy and γ is given by:

$$dG = -S dT + V dP + \gamma dA \quad (4.6)$$

At constant pressure (P) and temperature (T), $dG = \gamma dA$, where A is the surface area [Regone, 1995]. Hence, for a system to be stable (i.e. having minimum G), it has to have minimum surface energy and area.

In rutile TiO_2 , crystal plane with the highest atomic density exhibits lowest surface free energy [Ting, 2002]. It is apparent that (110) has the highest planar atomic density and more number of nearest neighbouring atoms by looking at the crystal structure of rutile as shown in Fig. 4.14. Thus, without any other factors, the system will be driven to the orientation of (110) (i.e. no preferred orientation) to minimise the overall free energy.

Surface energy is related to the number of bonds broken per atom when surface is created. But the surface free energy also depends on the nearest neighbouring atoms of the particular plane [Wang, 2000]. In rutile TiO_2 crystal, plane (110) has highest atomic density but the individual bond length of the each atom sharing with the neighbouring atom is relatively low compared to the (100) plane. Since the surface

energy is the product of number of bonds broken and times the bond length, (110) shows lowest free energy.

Fig. 4.15: Crystal structure of Rutile -TiO_2 , (100) and (110) planes comparison [Lyman, 1973]

However, in the case of oxidation of titanium that produces rutile, it was postulated that the $\alpha\text{-Ti(O)}$ phase formed during the process acted as a crystallographic intermediate template and produced strain energy due to lattice mismatch between the substrate and oxide crystal [Ting, 2002]. In the work of Ting et al., the $\alpha\text{-Ti(O)}$ phase approached sub-oxide of Ti_2O and it was suspected that a localised coherent relationship between Ti_2O and TiO_2 might exist, which further promoted the growth of TiO_2 with (200) orientation. The strain energy could be minimised when (200)-oriented TiO_2 (relative to (110)-oriented TiO_2) developed on the (002)-oriented Ti crystallites whereupon the interfacial mismatch was optimised.

4.8.3 Absence of Anatase Phase

No anatase phase was detected in the present study even though titanium was oxidised at temperature range, where the anatase-to-rutile transformation would occur, supporting the earlier observations [Ting, 2002]. The formation of significant quantity of oxygen vacancies in the oxidised film, known as the oxygen deficient Magneli phase, which is known to markedly accelerate the anatase-to-rutile transformation [Ting 2000] would be the valid reason for the absence of anatase.

4.8.4 Wear Resistance of the Un-Oxidised and Oxidised Titanium

The un-oxidised CP-Ti exhibited a much higher wear rate than the oxidised and furnace-cooled specimen, obviously due to the poor wear resistance of titanium. Thermal oxidation significantly improved the wear resistance of titanium. The wear rate of the oxide layer is an order of magnitude lower than that of the base material.

Strong adhesion can occur at the areas of real contact during sliding of alumina ball against untreated titanium, owing to the electron structure, crystal structure, and high plasticity index (modulus of elasticity E / hardness H) of titanium [Dong, 1995].

In electron configuration, the lesser the percentage of d-bond character, the more active is the metal. Titanium has the lowest value of d-bond character, thus making it extremely active and readily forming alloys with other materials. The axial ratio (c/a) of the HCP crystal structure of α -Ti is less than the ideal for closest packing. As a result, the basal plane is less favourable for slip and prismatic $\{10 \bar{1}0\}$ and the first-order pyramidal $\{10 \bar{1}1\}$ slip occur, thus increasing the number of possible slip systems [Dong, 1995]. High plasticity index causes considerable amount of plastic deformation between surfaces that contributes to wear and friction [Dong, 1995].

It is reasonable to expect low metallurgical compatibility between rutile and alumina, which leads to low adhesive wear. Furthermore, wear rate is believed to be inversely proportional to hardness or increasing solute concentration [Bushan, 1991]. This is consistent with the fact that rutile is much harder than titanium, due to the presence of oxygen atoms. Higher hardness helps in lowering plasticity index, which in turn limits the degree of plastic deformation and keeps the surface contact predominately elastic [Dong, 1995].

Increasing applied normal force caused an increase in the wear rate. This is obvious based on equation 2.3, that the wear rate is proportional to the normal force. The higher the force, the greater is the applied stress imposed on the film, thus making it easier to fracture the material and more debris to be liberated from the surface.

4.9 SUMMARY

Thermal oxidation of titanium was carried out for various temperatures up to 850 °C, followed by both air-cooling and furnace-cooling to produce a thick oxide layer. Oxidation followed by air cooling results in relatively thin and non-adherent

oxide layers. Debonding of the oxide film formed at higher temperatures (above 800°C) was due to the presence of thermal stresses, which are attributed to the high Pilling-Bedworth and high CTE ratio of Ti to rutile. Furnace cooling helped to form a thick and adherent layer which consists of rutile-TiO₂ at the top and α -Ti (O) structure near the interface. Especially, the sample oxidised at 850°C for 5 hours, followed by furnace cooling produced a very thick layer (>100 μ m) and it exhibits good adhesion strength with the substrate. The oxide layer possesses superior tribological properties in terms of the much improved friction characteristics, the low wear rate and the mild wear mechanism involved during the sliding process.

Texture present in the rutile-TiO₂ layer results in variation in the wear resistance. Rutile (110) has superior wear resistance compared to the (101) in the same TiO₂ layer due to a greater number of slip system in the latter. Increased oxidation temperature caused noticeable increase in the lattice constant 'c' and only a slight and insignificant increase in the lattice constant 'a'. Parabolic increase of oxygen concentration was observed with increased oxidation temperature.

CHAPTER 5

THERMAL OXIDATION OF TITANIUM FILMS

This chapter contains results and discussion of thermal oxidation (TO) of Ti films on stainless steel substrates for improved tribological properties, corrosion resistance and biocompatibility. The effects of oxidation temperature and time on the structure and properties of the oxidized films are discussed. Thermal oxidation conditions were optimized to obtain films with improved wear resistance and good adhesion strength.

5.1 AS-DEPOSITED TITANIUM FILMS

Titanium films on stainless steel substrates were deposited by DC magnetron sputtering. Film thickness of about 1 μm is achieved for 2 hours deposition under the conditions listed in Table 5.1. Prior to the deposition, specimens were sputter-cleaned by applying 100 W RF power discharge for 20 minutes.

Table 5.1: Deposition conditions of Ti film on stainless steel substrates

Power density	Argon gas Flow rate	Working pressure	Substrate Temperature	Target – Substrate distance
6.79 W/Sq.cm (300 watts DC)	20 sccm	5 mTorr	300 °C	11 cm

Fig. 5.1 shows the GIXD profiles of the stainless steel substrate and as-deposited Ti film at 2° angle of incidence. The as-deposited Ti film shows (002) texture as can be seen from the strongest peak corresponding to (002), as opposed to the (101) of the standard Titanium phase profile (α -Ti, JCPDS 5-0682).

The chemical composition profile of the as-deposited Ti film is shown in Fig. 5.2. The inner part of the film shows pure titanium, whereas the outer part contains a considerable amount of oxygen. The presence of oxygen is possibly due to oxygen contamination from the ambient atmosphere before the GDOS spectroscopy analysis. The Ti/stainless steel interface on the Ti film side is narrower due to the limited diffusion of substrate elements into the Ti film in comparison to the diffusion of Ti into the substrate. This directional inter-diffusion would be due to the easier diffusion of Ti into the substrate surface favoured by the impingement of energetic Ti sputtered species.

Fig. 5.1: GIXD phase profiles of (a) stainless steel (SS) substrate and (b) as-deposited Ti-film

Fig. 5.2: GDOS elemental concentration profiles of Ti-film on stainless steel substrate

Surface morphology of the as-deposited Ti film is shown in Fig. 5.3a, whereas, Fig. 5.3b shows the cross-sectional view of the Ti film on the Si substrate deposited in the same batch. The as-deposited surface exhibits pebble-like growth of grains with the size range of about 300-500 nm. Small voids are also seen in the film, indicating low density of the as-deposited film as expected at the grain boundary triple points for the coarser and granular morphologies under the sputtering conditions of low energy ion bombardment. The cross-sectional view shows that the Ti film deposited is initially very dense and the porosity and grain size increases with thickness. Cross-

section also shows pebble like grain growth with very low quantity of voids between them. It is also observed that good adhesion exists between the Ti film and substrate.

Fig. 5.3: FESEM Image showing (a) Surface morphology and (b) Cross-sectioned view of as-deposited Ti film

5.2 THERMAL OXIDATION OF TI FILMS

The experimental observations from CP- Ti (chapter 4) suggest that 650-800°C can be the suitable range for thermal oxidation of Ti films on stainless steel substrates. Since oxidation process also encompasses the oxidation time, an initial study on TO was carried out for different times, between 10-30 minutes in the above said temperature range. All those details are given in appendix A, from which it is concluded that 700 °C for 25 minutes are the optimum oxidation conditions to achieve good tribological properties combined with high adhesion strength in this temperature range. The present study emphasized the search for the optimum oxidation conditions at lowest possible temperature to avoid the problem of inter granular corrosion (IGC) [Pickering, 1984] of substrate material 316L SS. Therefore, further study was carried out at lower temperatures to understand the effect of temperature on the structure and properties of the films.

Preliminary experiments were conducted to establish the optimal oxidation temperature and time in terms of film-substrate integrity and tribological properties. It was found that oxidation at temperatures lower than 500°C resulted in insufficient incorporation of oxygen into the titanium film to facilitate the conversion to titanium oxide. On the other hand oxidation at temperatures higher than 700°C even for a few minutes resulted in complete transformation of the titanium film to titanium oxide and debonding of the film from the substrate. This can be understood from the lattice

mismatch and thermal expansion mismatch between rutile-TiO₂ and stainless steel substrate, which caused excessively high residual stresses and debonding of the rutile film. Only when the titanium film was partially converted to rutile, then the film-substrate integrity was maintained with good adhesion strength after thermal oxidation. Further experiments were thus conducted between 500°C and 700°C as listed in Table 5.2.

Table 5.2: Details of TO parameters and corresponding sample codes

Sample	Temp (°C)	Time (hrs)		Sample	Temp (°C)	Time(hrs)
500-5	500	5		550-7.5	550	7.5
500-10	500	10		550-10	550	10
500-15	500	15		600-2	600	2
550-2.5	550	2.5		700-0.42	700	0.42(25min)
550-5	550	5		-	-	-

5.2.1 Phase Identifications by XRD

Phase identification of all the above mentioned oxidised samples was studied by X-Ray diffraction. GIXD phase profiles of oxidized samples for temperatures 500, 550, 600 and 700 °C are shown in Figs. 5.4 to 5.6. After thermal oxidation, rutile-TiO₂, which has a random orientation, turns out to be the major phase detected by XRD. In addition, an Oxygen Diffusion Titanium (ODT) phase, which is a solid solution of Oxygen in Titanium, also exists in the oxidised films similar to the CP-Ti oxidation (Section 4.1). None of the oxidized samples exhibited anatase or any other TiO₂ phases (except rutile) showing the consistency with the earlier studies [Ting, 2000]. Also, there is no indication of any inter-metallic or any other phases, since the line profiles show only peaks from substrates and Titanium oxides. It is evident that the incidence angle (2°) chosen is sufficient to cover the whole thickness of the film as substrate peaks can be observed in all the profiles.

Fig. 5.4: GIXD Profiles of Ti-film oxidised at 500 °C and for a period of (a) 5 (b) 10 and (c) 15 hours

Fig. 5.5: GIXD Profiles of Ti-film oxidized at 550 °C and for a period of (a) 2.5 (b) 5 (c) 7.5 and (d) 10 hours

Although, the phase profiles of all oxidized samples look similar and show rutile as the major phase, careful observation shows that both crystallinity and phase proportions of rutile increases from 500°C (Fig. 5.4) to 550°C (Fig. 5.5) and even further for higher temperatures, i.e., 600 and 700 °C (Fig. 5.6). These changes also occur with oxidation

time at a particular temperature. 500°C profile shows additional peaks compared to other oxidised samples as indicated with arrow in Fig. 5.4. These peaks are related to TiO phase (JCPDS 09-0240) which is supported from the fact that suboxide (transient phase) appears only at lower temperatures because of relatively slower kinetics. Even though there is no clear indication of existence of other sub oxides, small proportions may be present and those are not detectable by XRD as these peaks are overlapped with other Ti-O phases.

Fig. 5.6: GIXD Profiles of oxidized Ti-films (a) 600-2hrs and (b) 700 -0.42hrs

In order to understand the existence of phases along the thickness of the film, XRD has been carried out by varying angles of incidence (VAI). Fig. 5.7 shows XRD profiles of 550 °C/5hrs (550-5) sample at various incidence angles between 1 and 6°. It is observed that no extra peaks are visible at any incidence angle, except for changes in the intensities of existing peaks. Relative intensities of Rutile gradually decreases with increasing incidence angle (i.e. depth of penetration), whereas substrate peaks increases, which indicates the presence of Rutile at the surface of the film. The peaks indicated with arrows on XRD profiles correspond to ODT, and their intensities increase with increasing incidence angle (penetration depth). From the above XRD results it can be inferred that the existence of phases along the thickness of the oxidized film is as shown in Fig. 5.8, which illustrates the arrangement of layers after partial oxidation of the film. The relative thickness of the individual layers changes with time at a particular temperature and the overall film thickness increases with

oxidation. It has to be noted that the interface between any of the two layers may not be as sharp as shown in the figure and there is a possibility of co-existence of more than one layer in certain areas.

Fig. 5.7: GIXD profiles of 550-5 oxidized sample at varying angles of incidence (VAI) (a) 1 (b) 2 (c) 3 (d) 4 and (e) 5 degrees

Fig. 5.8: Schematic showing the phase profile of oxidised films after partial oxidation of the film

5.2.2 Structural Characterization

Elemental concentration profile of the Ti film, as discussed in section 5.1 demonstrates the presence of very minute amount oxygen at the surface of pure Ti. However, the compositional profiles are completely changed after thermal oxidation (Fig. 5.9). In addition to the incorporation of oxygen in the film, nitrogen was also detected in the inner part of the film. The presence of nitrogen is obviously due to the fact that oxidation was carried out in an air furnace, where a significant amount of

nitrogen gas was present. Since titanium nitride was not detected by XRD, it is believed that nitrogen in this region is dissolved in the α -Ti lattice in accordance with the Ti-N system, where α -Ti can dissolve up to 22 at.% nitrogen [Leyens, 2003]. The compositional profile of the oxidized specimen can be divided into 3 zones as indicated in Fig. 5.9. Zone I consists of a large amount of oxygen, correlating to the formation of a rutile-TiO₂ layer, as indicated by the approximate atomic ratio of O to Ti in this zone. It can be seen that nitrogen dissolution in this rutile layer is negligible.

Fig. 5.9: GDOS elemental concentration profiles across an oxidized film, showing the development of three zones in the oxidized specimen

Zone II can be characterized by rapid decrease in the amount of oxygen and dissolution of a fairly large amount of nitrogen. It also contains mixture of Ti sub-oxides. The expansion of Ti lattice due to oxygen and nitrogen dissolution can be observed from the XRD profile as discussed in earlier section (Fig. 5.7). In zone III, diffusion of Ti into the stainless substrate was observed. Solid solution of Ti in

stainless steel is evident from the diffusion-type distribution of Ti in this zone. Diffusion of stainless steel components (Fe, Cr, and Ni) to a short distance into the Ti film can also be noted from the place in the case of as-deposited film, is due to the elevated temperatures of oxidation. GDOS results agree well with XRD results (section 5.2.1) and suggest that during thermal oxidation, Ti film transforms into gradient oxide layer of decreasing O/Ti ratio; rutile-TiO₂ at the surface and oxygen diffused Ti towards the substrate.

Ball-crater test is one of the methods to measure the thickness of films on various substrates and the thickness of different layers in the film [Kusano, 2004; Costa, 2003]. The three structural zones, indicated in the GDOS profile (Fig. 5.9), can also be viewed quantitatively from the ball-crater, made on the oxidized surface (Figs. 5.10 & 11). The three structural zones of the oxidized films as measured by ball-crater test are reported in Fig. 5.12. After oxidation, the total thickness of the film is larger than that of the as-deposited titanium film (~1 µm). This is due to the volume expansion associated with the rutile formation in zone I and lattice expansion in α-Ti due to oxygen and nitrogen dissolution in zone II and the diffusion of Ti into the substrate at the interface (zone III). Oxidation at 600°C and 700°C, even for much shorter times, produced the thick rutile layer (zone I), whilst oxidation at lower temperatures for long duration leads to the formation of a thicker transient region (Zone II), which may account for the observed better tribological properties of the resultant films as discussed in the section 5.2.4. Based on GDOS and ball crater results the following observations are made.

- Overall film thickness increases with oxidation temperature and time (predominantly temperature) and this will continue till the complete oxidation of the film
- As oxidation continues, all three zones shift towards substrate but with different growth rates
- Even though all the zones grow with oxidation, Zone I grows at the expense of zone II and zone II grows with the expense of zone III

Fig.5.12b shows % thickness of the all individual zones against total thickness of oxidation samples at different temperatures. Though all the samples show similar

ratios of all three zones, the sample 600-2h shows least percentage of zone II and whereas 550-5h sample shows highest percentage.

(a)

(b)

Fig. 5.10: Optical micrographs showing a ball-crater made on the oxidized film, showing the layered structure (a)full and (b)part at high magnification

(a)

(b)

Fig. 5.11: SEM micrographs showing EDAX line scan profiles on the oxidized film ball-crater area, showing the layered structure (a)full and (b)part at high magnification

(a)

(b)

Fig. 5.12: Thickness of individual zones across oxidized films (a)Thickness (b) % of total thickness

Fig. 5.13: FESEM micrograph showing the surface morphology of the 700C oxidized films at (a)10 (b)15 (c) 20 and (d)25 minutes showing transition from Ti to rutile

Surface morphologies of the oxidized films are shown in Figs. 5.13&14. After thermal oxidation, although the oxide film contains a fraction of tiny pores in between the grains, the film becomes denser and the overall grain size is reduced significantly and reaches the average diameter of around 100nm. The formation of the rutile phase also leads to volume expansion due to the high volume ratio of rutile-to-Ti (1.73) [Burns, 1989], which may also contribute to the densification of the film. Fig. 5.13 shows morphological transformations at different stages of oxidation from as deposited film. This morphological change is obviously related to the evolution of the rutile-TiO₂ phase, which seems to have followed the nucleation and growth stages resulting in the formation of many smaller new grains (Fig. 5.13a) within each individual α -Ti grain and its further growth (Figs. 5.13b,c&d). It is also observed that the amount of pores is increasing with the phase proportion / crystallinity of rutile, as it shows higher number of pores (Fig. 5.14d). It is also observed that lowest temperature surface (Fig. 5.14a) show relatively large grains (close to the original Ti grain) with lower amount of pores, which is beneficial for corrosion resistance. Whereas higher temperature samples show considerable amount of tiny pores on the surface due to the growth of oxide grains (Fig. 5.14d).

Fig. 5.14: FESEM micrograph showing the surface morphology of the selected oxidized films (a)500 -5 (b) 500 -10 (c) 550 -5 and (d) 600 -2

5.2.3 Nano-Mechanical Properties and Scratch Resistance

Fig. 5.15 shows the hardness values determined by nanoindentation of films as a function of penetration depth. The as-deposited Ti film showed hardness of about 1.5 – 3.0 GPa when the penetration depth was below 600 nm, beyond which the apparent hardness of the film increased gradually, approaching to that of the stainless steel substrate. After thermal oxidation, the hardness of the film is significantly increased and showed a maximum hardness value between 9-15 GPa, which is close to the theoretical hardness of rutile [Leyens, 2003]. However, the hardness values determined at the lowest depth (~100nm (5%variation), first measurement) for most of the specimens are less than that at immediately higher depth (~200nm (5%variation), second measurement). This is probably due to the surface contamination and the existence of many small and shallow pores on the oxidized surface, as seen from Fig. 5.10b and 5.14. The monotonic decrease in the apparent hardness value with further increase in indentation depth is due to the stainless steel substrate effect. Substrate effect can be deduced by various finite elemental and computational methods [Anthony, 2002] but they involve tedious calculations, which is out of the scope of present study. From Fig. 5.15 it is observed that hardness increases with oxidation temperature and time as rutile phase thickness increases.

Fig. 5.15: Nanoindentation test results showing hardness as a function of indentation penetration depth of the oxidized films

In Fig. 5.16, the ratio of measured reduced modulus to hardness (E_r/H) for Ti film before and after oxidation is plotted against penetration depth. The E_r/H ratio is a measure of the plastic index of materials, and a small ratio favours elastic deformation during contact motion and thus is beneficial for enhancing tribological performance of the material [Dong, 1999; Leyland, 2000]. From Fig. 5.16, it is clear that thermal oxidation of the titanium film significantly reduces the E_r/H ratio of stainless steel ($E_r/H \sim 100$) and is expected to offer much enhanced tribological performance. Among all the oxidised samples, 550-5h sample shows lowest E_r/H ratio, which demonstrates best tribological properties (explained later in Section 5.2.4).

Fig. 5.16: Nanoindentation test results showing ratio of reduced modulus to hardness (a) as a function of indentation penetration depth of as-deposited and oxide films (b) E_r/H ratio comparison for all oxide samples

Fig. 5.17 compares the friction force versus load curves measured during the microscratch test of the as-deposited and the thermally-oxidised specimens. It can be seen that the friction force measured from the oxidised film is much lower than that of the as-deposited film across the load range. This demonstrates improved frictional properties of the oxidised film as confirmed by tribological testing discussed in the next section. The frictional behaviour of the as-deposited film changed suddenly at a load of around 470 mN, due to adhesive failure of the film as confirmed by microscopic examination (Figs. 5.18a,c). The reduced friction coefficient of rutile may have also contributed to the observed improved L_c since the tangential friction force is proportion to the friction coefficient of the surface. After thermal oxidation, the adhesion strength of the film with the substrate was increased remarkably as the film did not show adhesive failure. Hence, the scratch test was further employed up to a

maximum available load (5000 mN) and even then no adhesive failure was observed. Failure of hybrid films was found to occur by chipping at the edges of and Hertz-type cracking inside the scratch track for high loads (Figs. 5.18b,d). This is different from the adhesive failures by flaking and gross spallation of the as-deposited film at loads above the critical value (Figs. 5.18a,c). The critical load (L_c) in the scratch adhesion test is a measure of adhesive strength in the absence of complete delamination of the film with the substrate [Bull, 1997]. Fig. 5.17b shows the critical loads (L_c) of all the samples obtained by the microscratch test. From the results it is clear that 500°C oxidation shows lowest critical limit and 550°C treatments shows better performance. Poor performance of adhesion (low critical load) is well correlate with high friction due to the relatively rough surface with thin rutile layer.

Fig. 5.17: Microscratch test results showing (a) friction curves recorded for the Ti film before and after oxidation (b) Critical load (L_c) comparison for oxidised samples

Fig. 5.18: SEM micrographs showing the scratch tracks produced on the surface of as-deposited (a and c) and oxidised Ti film (b and d)

5.2.4 Tribological Properties

Fig. 5.19 shows unlubricated-sliding friction and wear behaviour of the as-deposited film, the substrate and the oxidised specimens against an alumina counterface under 1 N load for 200m sliding distance. The results showed that the oxidised surface possesses significantly improved tribological properties. The friction coefficient versus distance plots of the stainless steel substrate and the as-deposited film showed similar friction coefficient values between 0.6 and 0.8. This is consistent with the typical values for ceramic and metallic materials in contact [Dong, 2000]. The plots of the oxidized films showed a much reduced friction coefficient. In addition, both the uncoated stainless steel substrate and as-deposited titanium film exhibit high

friction with large fluctuation, typical of poor tribological materials with adhesive wear and stick-slip tendency^{*}. On the other hand, the friction curve for the oxidised

(a)

(b)

^{*} When two solids are in sliding contact, they alternatively stick together and slip past each other [Peter, 1990].

(c)

Fig. 5.19: Friction coefficient curves recorded for various specimens under a test load of (a) 1N and (b) 3N and (c) mean friction coefficient of the oxidised samples tested

film is smooth with much reduced friction coefficient values and less scattering. The average friction coefficient is lower than 0.2 under unlubricated test shows the effectiveness of rutile- TiO_2 film on the stainless steel. Oxidation temperature of 550°C and time of 5 h represent the best combination of conditions for the production of a low-friction oxidised film. Indeed, the steady state friction coefficient measured for this film is 0.19.

Further tribo tests were conducted by increasing the applied normal load to 3 N. Fig. 5.19 showing friction-coefficient curves of the selected oxidized films under the load of 3N which follow the similar trend as 1N for 550 °C. Whereas for higher temperatures(600 and 700 °C), there is an abrupt rise and fall in the friction curve, indicating the counterface reaching the zone II & III as shown in Fig. 5.12. Further, for the case of 500 °C, the fluctuations at the end of the curve suggest that the counterface reached the substrate since the film is peeled-off as shown in micrograph (Fig.5.21d). Fig. 5.19c shows the summary of the mean values of coefficient of friction (COF) of all the samples tested at 1N. Insufficient oxide thickness/ smaller rutile film (500 °C) shows highest friction as there is significant contribution from the transient and interface zones. Even though higher temperatures produce thicker oxide film, it shows relatively higher COF than 550°C due to the possible increase of stress level and crystal size.

Microscopic examination of the wear tracks shows that the substrate material and the as-deposited Ti film suffered from large amount of wear, where severe

adhesive wear, together with surface and subsurface plastic deformation occurred, such that a wide, deep and rough wear track was produced (Fig. 5.20). In contrast, the

Fig. 5.20: SEM micrographs showing the wear track produced on the surface of stainless steel substrates (a), as-deposited Ti film (c) and oxidised film (e) under a load of 1N. Right side images (b, d and f) are of high magnification in the wear track

wear track produced on the oxidized film has a very smooth and polished appearance and the amount of material loss from the oxidised specimens was so small such that, it could not be detected with certainty by surface profilometer, when the test load was small. Further, images at higher magnification observed inside the wear track showed the adherence of the counterface to the surface, for both stainless steel (Fig. 5.20b) and as-deposited film (Fig. 5.20d), whereas there is no sign of material transfer in the case

of oxidized film (Fig. 5.20f). The 550-5h oxidised films completely survived the test at 3 N for 200 m sliding distance, but with measurable material loss (Fig. 5.21a). The 700-0.42 oxidized film survived the majority of the test duration, but failed near the end of the test resulting in a relatively large amount of material loss (Fig. 5.21b). The worst performance was found for the 600-2 oxidised film which failed catastrophically at the middle of the test, leading to the formation of relatively wide and deep wear track, in turn, resulting in large amount of material loss. Lowest temperature (500-10) sample also shows relatively less material loss and narrow wear track (Fig. 5.21c) compared with 550°C, but oxide film in the wear track is peeled-off at the end of the test (Fig. 5.21d).

Fig. 5.21: SEM micrographs of wear tracks produced under a load of 3N oxidised samples. (a)550 -5 (b)700 -0.42 (c) 500 -10 and (d) 500 -10 at high magnification showing film peeling

Fig. 5.22 shows the images of wear tracks acquired from the 3-d profilometer, from which the wear rate was calculated. SS substrate show narrow and deep wear track (Fig. 5.22a) matching with SEM image (Fig. 5.20a) and also protrusions observed at the edges of the wear track shows typical metallic wear behaviour. As-

Fig. 5.22 Profilometer Images showing 3D-wear tracks on (a) stainless steel substrates, (b) as-deposited Ti film and (c) oxidised film

deposited films show wide wear track (Fig. 5.22b) with gross material loss due to the poor adhesion of the film with substrate. Fig. 5.23 compares the wear rate measured for various oxidised specimens, along with the uncoated substrate and as-deposited titanium film. It can be seen that oxidation under proper temperature/time combinations can increase the wear resistance of the stainless steel by three orders of magnitude. Low temperature oxidation (500°C and 550°C) provided the best load bearing capacity in the present study. The combination of 550°C and 5 h for oxidation resulted in the best wear resistance of the oxidised film, although the rutile zone is not the thickest in this film (Fig. 5.12).

Fig. 5.23: Comparison of wear rate (a) resulting from various specimens under test load of 3N and (b) magnified portion of 500 and 550°C

5.2.5 Corrosion Resistance

The potentiodynamic polarization curves obtained from the cyclic electrochemical test of the substrate, as-deposited film and selected oxidised films are shown

in Fig.5.24. The results demonstrate the benefits of thermal oxidation in enhancing the corrosion resistance of the titanium film on stainless steel. By comparing the curves, two salient differences between the electrochemical behaviour of the uncoated substrate, as-deposited film and oxidised film are observed. First, the current density at any given potential for the oxidised film is always lower than that of the uncoated substrate. Second, pitting occurs in the AISI 316L uncoated substrates, at potentials above 500mV, while no pits were formed on the oxidised film even at potentials as high as 1000mV. The as-deposited titanium coating is obviously effective in improving the pitting corrosion resistance of the stainless steel by decreasing the intensity of pits, in turn pitting hysteresis loop and also delaying the formation of pits from 500 to 800 mV. After thermal oxidation, pitting corrosion was completely

Fig. 5.24: Potentiodynamic polarization curves of the uncoated substrate and the oxidised film in 3% NaCl electrolyte

eliminated as no visible pits were observed in all the oxidised specimens. Further the polarization curve in the reverse sweep of the cyclic test follows the same trend of the forward sweep curve for both the oxidized samples and especially the 500-10 sample shows close match indicating its high corrosion resistance to chloride solution. The main contribution for best corrosion resistance, besides the presence of rutile layer, is the porous free surface (5.14b). The above results show that the formation of a rutile- TiO_2 based film on 316L steel not only improved the general corrosion resistance of the steel in the stated electrolyte, but also effectively alleviated the pitting corrosion problem of the stainless steel in chlorine containing environment. The observed significant enhancement in corrosion resistance by thermal oxidation of the titanium coating on the stainless steel is obviously associated with the formation of the rutile- TiO_2 layer at the surface.

5.2.6 Biocompatibility

Cytotoxicity test was conducted to evaluate the biocompatibility of the best wear resistant oxidized film (550C-5h) due to the limitation with availability of cells. Cell culture was carried out with L929 osteoblast cells in Minimum Essential Medium (MEM) (Invitrogen) supplemented with 10% Fetal Bovine Serum at 37.4 °C and for 24 hours. After the incubation, cell adherence was observed with SEM on oxidised film along with positive control Poly vinyl chloride (PVC) and negative control high-density polyethylene (HDPE) (Fig. 5.25). Both the positive control and oxidised film shows good adherence of the cells on the surface. No cells were found on the surface of HDPE negative control. The thermally oxidized rutile surface is suitable for cell growth and shows good biocompatibility behaviour.

Fig. 5.25: FESEM images after cell culture test showing adhesion of L626 cells after an incubation period of 24 hours on positive control (b) 550-5h oxidised sample at low magnification (c) and at high magnification (d) and no cells observed on the negative control (a)

5.3 DISCUSSION

5.3.1 Phase Transformations During Thermal Oxidation

The development of the rutile phase is enhanced at higher oxidation temperatures even for shorter times. This indicates the dominance of temperature in governing the growth of the oxide phase. In all the specimens, no intermetallic compound phases were detected by XRD, indicating that no chemical reactions between the titanium film and the stainless steel substrate at the interface took place during the oxidation process. This is in agreement with the observations of Kale et. al. [Jose, 2000] that in a titanium-stainless steel diffusion couple at temperatures between 700°C and 850°C, only a diffusional interface with titanium and stainless steel components interdiffusion was formed without compound formation at the interface, although intermetallic compounds were found by other investigators in the titanium-stainless steel couple at higher diffusion temperature of 950 °C [Ghosh, 2003]. The shift of the α -Ti(O) peaks to lower angles is the result of the incorporation of oxygen and nitrogen in titanium, which leads to the expansion of the α -Ti lattice. Oxygen (33at. %) and Nitrogen (22 at.%) can diffuse into Ti lattice without disturbing its crystal structure and forms solid solution (ODT) [Leyens, 2003]. Though the oxidized film has three layers which are clearly separable (Fig. 5.8) but it is difficult to distinguish the exact amount of the individual phases. Especially, when high amounts of oxygen and nitrogen diffuses into α -Ti, transient phase TiO and ODT in the XRD profile are difficult to distinguish as peaks from both the phases are close to each other. Rogers et. al. [Rogers, 1988] reported the presence of four layer model which consists of TiO₂ phase, two mixed oxide regions and ODT layer. This was also not overruled in the present study as it is difficult to reveal it by XRD technique due to the problem of overlapping of Ti oxides peaks, especially when the phases are in relatively low amount.

5.3.2 Crystallite Size

Crystallite size of the rutile was calculated by using the following formula as it is one of the fundamental properties which affect some of the properties of the material.

$$d_{(hkl)} = \lambda / \beta_{2\theta} \cos \theta \quad (5.1) \text{ [Cullity, 2005]}$$

Where

d = crystallite size (nm)

λ = wave length of the x-rays (nm)

θ = Diffraction angle of the peak under consideration at FWHM(°)

β = Observed FWHM (radians)

Fig 5.26 shows the crystallite size of the rutile phase for the selected samples calculated by using TOPAS software, which takes care of all instrumental errors and corrections. Both (110) and (200) planes follow similar trend for all the samples but with different sizes. Crystallite size increases with severity (time-temp combination) of oxidation and the trend is consistent with the zone I thickness of the oxidized films (Fig. 5.12). Similarly the porosity present in the top layer (zone I) of the oxidized film also follows the same trend (Fig. 5.14). By combining above observations it is clear that with increasing the severity of oxidation, the thickness of the zone I (rutile) is increasing with overall thickness of the film and both crystallite size and porosity also increases.

Fig 5.26: Crystallite size of the rutile phase calculated by the Scherrer formula for selected oxidized samples

5.3.3 Hardness

After thermal oxidation, the surface hardness increased enormously and reached the hardness of bulk rutile phase [Leyens, 2003], when the penetration depth

is below 300 nm. From the Fig. 5.15 it can be seen that the hardness of the oxidised surface decreases with increasing penetration depth. This is due to the substrate effect contribution. Nevertheless, the oxidised surface always shows higher hardness than that of as-deposited surface, suggesting higher load carrying capacity of the oxidised film. The surface hardness is well correlated with the thickness of the rutile layer though all the samples have rutile at the surface. Further, it is established that the hardness of the surface is influenced by the zone beneath the indent especially for films harder than the substrate. The depth of indentation should be below one tenth of the layer thickness for negligible contribution from the substrate [Sun, 1995]. In the present case of lower hardness gradient, the influence of the softer layer beneath the indent should thus be present. Due to the above two reasons zone III was understood to contribute to the mechanical performance of the oxidized layer.

5.3.4 Adhesion

The remarkable improvement in the adhesion strength by thermal oxidation treatment could be explained by the hybrid structure produced. According to the Ti-O phase diagram, both TiO_2 and $\alpha\text{-Ti}$ exist in equilibrium with solid solution of $\alpha\text{-Ti(O)}$. Such oxygen dissolved Ti zone being co-existent with Ti-rich $\alpha\text{-Ti}$ and oxygen-rich rutile phase favours easy formation of hybrid structure for improved adhesion. In addition, the adhesion enhancement can be attributed to the interdiffused zone between the titanium film and the stainless steel substrate as the interfacial region is expected to play an important role in the enhancement of adhesion strength.

5.3.5 Friction and Wear

As discussed in section 5.2.3, a fair amount of nitrogen is incorporated in zone II of the oxidised film, forming the solid solution. This obviously would cause solid solution hardening in this zone, and contribute to the measured increase in hardness of the film and the improved wear resistance. Since zone I, i.e the rutile- TiO_2 zone at the surface is free from nitrogen (Fig. 3b), it can be reasonably considered that nitrogen does not have a significant effect on the friction and corrosion properties which are more surface-characteristic.

The best wear resistance properties are exhibited for the sample oxidized at $550^\circ\text{C}/5$ hr combination. This is due to the low E/H ratio, which is the index for wear

resistance properties [Dong 1999]. Lower the E/H ratio, better the wear resistance properties. This could be explained by the low friction, which helps to reduce the shear stress at the film-substrate interface, and the thicker interfacial zone (zone III) (Fig. 5.12), which helps to enhance the film-substrate integrity and thus load bearing capacity.

5.3.6 Corrosion Resistance

It is observed that oxidation enhances the resistance to corrosion for Ti films on stainless steel substrate for all the combinations of samples considered. However, the corrosion resistance is less for the samples at higher temperatures (600 and 700°C) when compared to the samples at lower temperatures (500 and 550°C). Further, the sample at 500°C demonstrated higher corrosion resistance than that of the sample at 550°C, because of the presence of pore-free rutile layer on the surface (Fig. 5.14). A pore-free rutile- TiO_2 film on aluminium [Sun, 2004], titanium and its alloys [Gurrappa, 2003] is known to be effective in protection against corrosion under many environmental conditions. The presence of pores and its magnitude is well correlated with the corrosion resistance, though all the oxide films have rutile on the surface. The reason for this is that the pores allow the flow of liquid beneath the rutile surface layer, leading to reaction of chloride solution with less corrosion resistant layers in the film. Indeed, thermal oxidation of titanium alloys at temperatures below 700 °C have been exploited and used to produce a relatively thick (a few micron) and dense TiO_2 layer for corrosion resistance enhancement [Dong, 2000a; Sun, 2004]. In the present case, the formation of a layered structure with a rutile layer at the stainless steel surface is extremely effective in enhancing the corrosion resistance of the stainless steel by several orders of magnitude and moved the corrosion potential to a more noble value.

5.4 SUMMARY

The work reported in this chapter has demonstrated that proper control of the oxidation temperature and time condition converts the pure titanium film on stainless steel to a rutile- TiO_2 based film with a layered structure, which comprises of a rutile- TiO_2 layer at the top, an oxygen and nitrogen dissolved α -Ti layer in the middle and a diffused-type interfacial region. Such a hybrid structured coating system proved to possess high hardness, good adhesion strength with the stainless steel substrate,

improved corrosion resistance, low and stable friction coefficient as well as much enhanced wear resistance. Low temperature (500°C-550°C) oxidation for a relatively long time (5-10hrs) offers the lowest friction coefficient, best wear resistance and high corrosion resistance to the resultant oxidised film, whilst high temperature oxidation deteriorates the quality of the oxidised film in tribological and corrosion applications.

With increasing oxidation severity, crystallite size of the rutile-TiO₂ increases and generates stresses in the films, subsequently causing deterioration of the properties. Oxidation at high temperatures increases island size and in turn increases porosity, which leads to a decrease in the corrosion resistance.

CHAPTER 6

MAGNETRON SPUTTER DEPOSITED TiO₂ FILMS

This chapter describes the fabrication of TiO₂ films onto 316L stainless steel by non-reactive magnetron sputtering with and without a titanium underlayer. Phase formation in TiO₂ films deposited through sputtering of oxide target on various surfaces was studied. Influence of substrate/underlayer surface characteristics and oxide layer process parameters were investigated. Mechanical, tribological and corrosion properties of the selected oxide films were also reported.

6.1 PRELIMINARY STUDIES ON THE MICROSTRUCTURE OF THE FILMS

316L stainless steel was used as a substrate material and pre-deposition treatment was carried out as described in chapter 3. The deposition conditions for both Ti underlayer and TiO₂ overlayer are shown in Table 6.1. It should be noted that unless specified otherwise, all the depositions were carried out on 300 °C heated substrates for a period of 60 minutes for Ti films and 120 minutes for TiO₂ films. Batch specifications, sample codes and details of all the samples are described in Table 6.2. Titanium (T), Rutile (R), and Anatase (A) diffraction peaks from JCPDS files (05-0682, 21-1276 and 21-1272 respectively) were indicated by means of vertical lines on XRD line profiles for reference/ comparison. Whereas stainless steel substrate peaks are indicated with 'S' on the line profile.

Table 6.1: Magnetron sputter deposition conditions of Ti and TiO₂ films.

Film	Power density	Argon gas Flow rate	Working pressure	Substrate Temperature	Target – Substrate distance
Titanium (underlayer)	6.79 W/cm ² (300W, DC)	20 sccm	5 mTorr	RT, 300 °C	11 cm
TiO ₂ (overlayer)	4.53 W/cm ² (200W, RF)	20 sccm	5 mTorr	RT, 300 °C	13 cm

Table 6.2: Details of the samples deposition conditions and its phase constituents.

Sample details		Underlayer conditions		Oxide layer conditions		Phase formation	
Condition studied / Batch	Specifics of the condition	Temp (°C)	Time (min)	Temp (°C)	Time (min)	UL Surface (Planes)	OL phase constituent(s)
Substrates (Batch 1)	Si	-	-	300	120	Native Oxide	Anatase
	Ti	-	-	300	120	Native Oxide	Anatase
	Ti6Al4V	-	-	300	120	Native Oxide	Anatase
	Stainless steel	-	-	300	120	Native Oxide	Anatase
	Rutile (TO)	-	-	300	120	Rutile	Anatase
Underlayers thickness when both the layers deposited at 300 °C (Batch 2)	30 min	300	30	300	120	T (100)	Rutile
	60 min	300	60	300	120	T (100)	Rutile
	90 min	300	90	300	120	T (002), (100), (101), (102)	Amorphous + Rutile*
	120 min	300	120	300	120	T (002), (100), (101), (102)	Amorphous
Underlayers temperatures when oxide layers deposited at 300 °C (Batch 3)	RT	RT	60	300	120	T (002), (100), (101), (102)	Rutile + Anatase
	300 °C	300	60	300	120	T (100)	Rutile
Underlayers temperatures when oxide layers deposited at RT (Batch 4)	RT	RT	60	<i>RT</i>	120	T (002), (100), (101), (102)	Amorphous
	300 °C	300	60	<i>RT</i>	120	T (100)	Amorphous

T- titanium, UL – Underlayer, OL- oxide layer/Overlayer, RT – room temp (on un-heated substrates). * Incipient crystallinity

6.1.1 Substrate Surface

Initially, oxide films were sputter deposited at 300 °C on various substrates Si, Ti, Ti6Al4V, 316L stainless steel and rutile (obtained by thermal oxidation of Ti) (Batch1). XRD profiles (Fig. 6.1) of oxide film on all the substrates show formation of Anatase-TiO₂ phase (JCPDS 21-1272). This indicates that the native oxides (which form immediately on fresh surface) on the metallic substrates as well as the rutile surface favoured the nucleation of anatase. Another set of TiO₂ films with same deposition conditions were prepared through depositions on sputter deposited Ti underlayers (ULs) at 300 °C for different lengths of time, 30, 60, 90 and 120 minutes (Batch2). Interestingly, striking differences were found in that Rutile phase surfaced in the films deposited on 30 and 60 min underlayers (Fig. 6.2a,b). Rutile phase was formed with only incipient crystallinity on 90 min underlayer (Fig. 6.2c) and hardly formed on 120 min underlayer (Fig. 6.2d). From the XRD profile it is evident that the oxide film formed on the 120 min UL is considered as amorphous phase as no other peaks are visible except for the substrate (SS) and underlayer (Ti). Based on the above results it was realized that the presence of Ti UL and its thickness would have direct influence on phase evolutions in TiO₂ films which is an interesting phenomenon. In order to confirm this underlayer effect on phase formation of oxide film, depositions were also carried out on Si substrates along with stainless steel samples. Fig. 6.3 shows XRD profile of the TiO₂ film on Si sample showing consistency with the SS sample (Fig. 6.2b). In addition to the differences in the oxide layer phase, XRD profiles also exhibit some differences in underlayer peaks i.e., absence of some reflections in shorter-time films which is discussed later in section 6.1.3.

The morphology of the TiO₂ films deposited on the stainless steel substrate with and without Ti underlayers are shown in Fig. 6.4. There is a striking difference between the morphologies of the TiO₂ films deposited on Ti underlayers (Fig.6.4 b-d) and that deposited directly on the stainless steel substrate (Fig.6.4 a). In the case of TiO₂ films deposited directly on stainless steel substrate, where anatase phase formed, morphology showed square-based pyramidal grains with narrow size distribution. Whereas oxide layer on Ti under layer shows islands with relatively large average size. There is a clear distinction between the films with amorphous (Fig.6.4 d) and rutile phase (Fig.6.4b&c). Films with amorphous phase shows globular islands with increased roughness and average size compared to rutile films.

Fig. 6.1: GIXD profiles of TiO_2 films deposited on (a) Si (100) wafer (b) CP-Ti (c) Ti6Al4V (d) 316L SS and (e) rutile (thermally oxidized) substrates.

Fig. 6.2: GIXD profiles of TiO_2 films deposited on Ti Underlayers with varying thickness obtained by deposition period of (a) 30 (b) 60 (c) 90 and (d) 120 minutes.

Fig. 6.3: GIXD profiles of TiO_2 and Ti Underlayer on Si substrate (same batch of Fig. 6.2 b)

Fig.6.4: FESEM micrograph showing the surface morphology of the TiO_2 film on stainless steel substrate (a) without underlayer and with (b) 30 min. (c) 60min. and (d) 120min. Ti underlayers

6.1.2 Substrate Temperature

In order to understand the effect of temperature on the phase formations, films were also deposited on unheated substrates (referred to as RT substrate hereafter). Therefore sets of films were thus prepared by changing UL deposition temperature and oxide layer (OL) deposition temperature, each at a time, while keeping rest of the process parameters the same (Batch3). It can be seen from Fig. 6.5 that Rutile was the only oxide phase forming in 300°C oxide layer on UL deposited at 300°C (sample300-300). In contrast a prominent Anatase diffraction peak suggests the co-existence of Anatase phase in the film on UL deposited on unheated substrate (sampleRT-300). In the case of deposition of RT oxide layer deposited on RT and 300°C underlayers (samples RT-RT & 300-RT), no oxide phase is observed (Fig. 6.6). From the above observations, it is suggested that thermal assisted depositions are required for the crystalline oxide phase formations, which is also consistent with the earlier studies [Lobl, 1994]. From all the above results it was understood that substrate surface plays a major role in oxide phase formation of TiO_2 films deposited under the same conditions.

Fig. 6.5: GIXD profiles of TiO_2 films deposited at 300°C on 60 minutes Ti underlayer deposited at (a) RT and (b) 300°C.

Fig. 6.6: GIXD profiles of TiO_2 films deposited at RT on 60 minutes Ti underlayer deposited at (a) RT and (b) 300°C .

6.1.3 Underlayer Characteristics

Further characterization was carried out on Ti underlayers for understanding the reasons for the above differences. Fig. 6.7 showing XRD profiles of Ti films deposited on SS substrates with different thicknesses (similar deposition conditions of underlayers as in Fig. 6.2). Interestingly, 30 and 60 minutes underlayers, which promoted rutile formation in oxide layer showed only a single (110)Ti peak in the XRD profile. In contrast, all four Ti peaks were observed in the thick underlayers (90 & 120 mins) that allowed only incipient/ no rutile formation (Fig. 6.2c,d). The above observation of absence of such peaks is related to the texture formation. In order to verify the texture, diffraction was carried out by Bragg-Brentano geometry (θ - 2θ) and the results were shown in Fig. 6.8. Comparing to GIXD, the θ - 2θ diffraction profiles show the appearance of (002) peak in 30 & 60min ULs and variation in its relative intensities in the case of thick under layers.

Fig. 6.7: GIXD profiles of Ti films deposited on SS substrate for a period of (a) 30 (b) 60 (c) 90 and (d) 120 minutes.

It was also observed that the presence of a small hump to the left of (002) peak in GIXD profiles of thick underlayers (90 & 120 min), whereas it is not visible in 30 min UL. In 60 min UL, though it is not clearly visible, the dissimilar broadening of right side of the (100) peak in the profile indicates the presence of an extra peak with relatively small intensity. The reason for this hump formation is due to the shifting of the (002) peak towards lower 2θ side. This (002) peak corresponds to the basal plane of the HCP-Ti, where oxygen occupies octahedral voids of the Titanium HCP lattice, between the basal planes. This oxygen dissolved Ti layer is referred to, hereafter, as Oxygen-Diffused-Titanium (ODT) phase.

From the above XRD results, it is evident that the change in texture is present in Ti underlayers with the deposition time. It was not clear whether or not the texture changes in the 30, 60 and 90 mins underlayer are similar to that of the 120 mins underlayer which incorporates the other three in itself. In order to confirm those changes, diffraction was carried out at varying angles of incidence (VAI) on the thickest underlayer (120min, Fig. 6.9). Based on the VAI XRD patterns, phase profile of the 120 mins underlayer has been constructed as shown in schematic (Fig. 6.10).

Fig. 6.8: θ - 2θ XRD profiles of Ti films deposited on SS substrate for a period of (a) 30 (b) 60 and (c) 120 minutes.

Fig. 6.9: GIXD profiles of 120 min Ti films deposited on SS substrate at varying incidence angles as indicated.

Fig. 6.10: Schematic showing the arrangement phase profile in Ti underlayer

From the above schematic (Fig 6.10), the phase profile was differentiated as separate layers based on the changes in texture. Further to support the same, morphological studies were carried out using SEM. The cross-sectional view of Ti films was shown in Fig 6.11. The results show that the Ti film deposited on substrate is initially very dense and the porosity and grain size increase with time (thickness).

Fig. 6.11: SEM images showing cross-sectioned view of (a) 30 (b) 60 (c) 90 and (d) 120 minutes Ti underlayers.

The increase in grain size was also confirmed with AFM measurement (Fig 6.12). The results showed angular grains of typical metallic nature for thickest underlayer which shows highest roughness. Roughness increases with the thickness (Fig 6.11e) due to the atomic shadowing effect [Chan, 2005]. The sudden increase in the average roughness values for thickest sample could be due to change in texture, where $\langle 002 \rangle$ component is dominated with the change in island arrangement.

Fig. 6.12: AFM images of Ti films on SS substrate deposited for (a) 30 (b) 60 (c) 90 (d) 120 minutes and its average roughness values (e)

TEM study was carried out for the detailed chemical analysis. Fig. 6.13(a & b) shows TEM cross-sectional view of TiO_2 film deposited on 60 min underlayer on Si substrate and EDAX concentration profile of the same sample respectively. From the elemental analysis, it is clear that the presence of oxygen and its variation across the underlayer supports the presence of ODT phase in XRD results. It is also evident from both XRD and TEM results that the ODT phase is prominent in early stages of deposition. The changes in the texture of underlayer are due to the presence of oxygen in the deposition chamber.

Fig. 6.13: TEM image showing cross-sectional view of TiO_2 film on 60 min UL (a) and EDAX concentration profile obtained on the same sample

It is to be noted that Ti films deposited on heated and unheated substrates show difference in texture behaviour. This is confirmed by the GIXD line profiles of 60 min underlayer deposited at various temperatures (Fig. 6.14). Ti underlayer deposited on heated substrate (300°C) shows $\langle 100 \rangle$ texture and $\langle 002 \rangle$ component for unheated substrate (RT). The reason for this texture formation is related to the presence of oxygen which helps in surface energy minimization of $\langle 100 \rangle$ [Knorr, 1998]. It should be noted that affinity of Ti towards oxygen increases with temperature and it is confirmed by the elemental concentration profiles (Fig. 6.15), where a hump in the oxygen concentration is seen in the underlayer region. This results in differences in chemical nature of the surface of the Ti UL. Besides the structural changes, morphological changes have also been observed in underlayers with variation in deposition temperature (Fig. 6.16). The $\langle 002 \rangle$ orientation shows porous and faceted

clusters perpendicular the surface, where as $\langle 100 \rangle$ texture shows flat clusters parallel to the surface.

Fig. 6.14: GIXD profiles of 60 min Ti film deposited on 300°C heated and unheated SS substrate

Fig. 6.15: GDOS elemental concentration profiles across the oxide layer and Ti film (a) RT-300 and (b) 300-300

Fig. 6.16: FESEM images showing surface morphology of Ti underlayer deposited on (a) unheated substrate and (b) heated substrate (300°C)

6.1.4 Verification on Oxide layer phase formation

Sample RT-300, which shows the formation of both Rutile and Anatase has been used for further study to explore the reason for combined phase formation. Fig. 6.17a shows the GIXD line profile at various incident angles. It was performed with Varying Incident Angles (VAI) as delineated in the schematic; Fig. 6.17b, a systematic phase composition variation (Fig. 6.17c) can be deduced across the depth of the films. It can conspicuously be seen from 6.17a that the relative peak intensities of Rutile and Anatase reversed with linearly varying depth of penetration. This result suggests that existence of anatase rich region towards the surface. This observation is confirmed by the surface morphology (Fig. 6.18b) where the appearance of additional angular grains within the islands compared to rutile surface (Fig. 6.18a) could be related to anatase phase referring to Fig. 6.4a.

In order to verify the understanding and to check the repeatability experiments were carried on Ti/ TiO_2 multilayers. Table 6.3 shows the details of the multilayer film stack. First set and the subsequent Ti interlayers, oxide layers were deposited with same conditions of RT-300 (Fig 6.19) except for the deposition time, which is shorter. This is to avoid the impact of surface roughness, which was caused by continuous deposition that could lead to the amorphous phase formation in oxide layer. XRD phase profiles clearly show that rutile phase formation on $\langle 110 \rangle$ textured underlayers confirms the underlayer surface role on the oxide layer phase formations.

Fig. 6.17: (a) GIXD profile of the sample (Fig. 6.4 RT) at varying incidence angles showing variation of intensities of rutile and anatase major peaks with depth. (b) Schematic showing the depth of penetration of x-rays with increasing angle of incidence. (c) Schematic of the phase profile in the composite film.

Fig. 6.18: FESEM images showing surface morphologies of oxide layer deposited on (a) 300°C and (b) RT underlayer.

Table 6.3: Layer stack of multilayer samples

Sample	Layers
1	UL (RT, 30min)+ OL
2	UL (RT, 30min)+ OL + IL + OL
3	UL (RT, 30min)+ OL + IL + OL + IL + OL

UL- Undrlayer, OL – Oxide layer, IL-Interlayer

Fig. 6.19: GIXD profiles of the multilayer samples (1 to 3) as described in Table 6.3.

6.2 PROPERTY EVALUATION

The samples with rutile phase (with 30& 60 mins underlayers), amorphous phase (120 mins) and anatase phase (without underlayer) were chosen for further study to evaluate mechanical, tribological and corrosion properties. Table 6.4 shows the selected tables and its corresponding underlayer thicknesses and these values are used as sample codes for subsequent sections.

Table 6.4: Deposition conditions of Ti film on stainless steel substrates

Sample code	Underlayer deposition time	Underlayer thickness (μm)
RT	0	0
30	30min	0.16
60	60 min	0.44
120	120min	0.92

6.2.1 Hardness Measurement by Nanoindentation

Fig. 6.20 shows the hardness values determined by nanoindentation of the films to a depth of 30 nm. It is clearly observed that the films with underlayer show higher hardness as rutile is harder than anatase. Within the rutile films (where all the TiO_2 films are of the same thickness), it can be seen that hardness increases with the increase in underlayer thickness. However, the hardness did not increase continuously with further increasing underlayer thickness due to the contribution from larger voids and pores in the TiO_2 film on the thickest (0.96 μm , 120min) Ti underlayer.

Fig.6.20: Nanoindentation test results showing hardness (H) of all the tested samples at a depth of 30 nm.

6.2.2 Adhesion Strength by Scratch

Fig. 6.21 compares the scratch tracks on TiO_2 films caused by microscratch test. None of the samples show adhesive failure even for loads up to 5000 mN employed in the test. But close observation of the scratch tracks indicates that there is difference in the width of the tracks. The tracks of the samples 0 and 30min. are wider than the other two and especially the sample 60min shows the narrowest track amongst all. High magnification images on the right side show surface condition of the films after scratch test. The beach marks observed for the sample 0 indicates that indenter has

Fig. 6.21: SEM micrographs showing the scratch tracks produced on the surface of TiO_2 films on (a) 0 (c)30 (e) 60 (g)120 underlayers and (b) (d) (f) and (h) are corresponding high magnification images from centre of the scratch track

reached the metallic substrate. The thickest film among the tested samples with amorphous phase (120 min.) shows the coating failure initiation by spallation. The critical load (L_c) in the scratch adhesion test is a measure of adhesive strength in the absence of complete delamination of the film with substrate [Bull, 1997]. Fig. 6.22 shows the critical loads (L_c) of all the samples obtained by the microscratch test. It can be seen that the critical load to adhesive failure increases when the underlayer is present in comparison to the film without Ti underlayer. It can be understood that a ductile and compliant metallic (Ti) underlayer can relax the residual stresses caused due to the sputter deposition of the TiO_2 films. However, a sudden decrease in critical load for the TiO_2 film on the thickest Ti underlayer can be seen from the figure. This is also attributed to the presence of larger voids and pores present in the amorphous TiO_2 film (Fig.6.4d). The defects in the film act as stress raisers and deteriorate the adhesion strength, as the load is linearly increased during the scratch.

Fig. 6.22: Critical load (L_c) values of all the samples resulting from the microscratch adhesion test.

6.2.3 Friction and Wear Properties

Unlubricated- sliding friction and wear tests have been carried out under a load of 1N and 3N. Fig. 6.23 shows the friction coefficient versus distance plots recorded during the tribology test at a load of 1N. Both samples 0 and 30 exhibit high friction and large fluctuation, a phenomenon typical of poor tribological materials which show adhesive wear and stick-slip tendency. On the other hand, the friction curve for the samples with thick Ti underlayer, samples 60 and 120, is smooth with much reduced

friction coefficient values and less fluctuation. Mean friction coefficients of the contacts between the ball and the TiO_2 surfaces are 0.512, 0.479, 0.377 and 0.382 for samples 0, 30, 60 and 120, respectively. It shows that the coefficient of friction decreases with the underlayer thickness. The sample with no underlayer and the least thick underlayer shows relatively high friction coefficients as the sliding media reaches metallic substrate.

Fig.6.23: Friction curves recorded during the tribology test for the samples tested.

Microscopic examination of the wear tracks shows that the TiO_2 film without Ti underlayer suffered from large amount of wear, where severe adhesive wear, together with surface and subsurface plastic deformation occurred, such that a wide, deep and rough wear track was produced (Fig.6.24a). In contrast, the wear track produced on the samples with underlayer has a very smooth and polished appearance, especially sample 60 shows very narrow wear track (Fig.6.24b). Even the thicker film (120) survived at 1N load, but it was a failed at the end of the test under 3N loading conditions and resulted in wide wear track comparing to 60 sample. Fig. 6.25 shows the wear rates calculated by measuring the volume loss from the surfaces of the tested samples. However, for the films that failed under 1N load during pin on disc test, testing was not further done under 3N. It was found that in the case of films on Ti underlayer, the wear rate decreased with respect to the TiO_2 film without the underlayer, due to superior tribological properties of rutile over

Fig.6.24: Optical micrographs showing the wear tracks produced on the surface of TiO_2 film under a load of 1N (a) 0 and (b) 60 and under 3N load (c) 60 and (d) 120

Fig.6.25: Comparison of wear rates resulting from the various specimens tested under a load of 1N and 3N.

anatase. Further, wear rate decreased with the increase in the underlayer thickness. However, similar to the case of hardness and adhesion strengths, increased wear rate was observed for the TiO₂ film on the thickest Ti underlayer. This can also be attributed to the amorphous phase TiO₂ relatively lower hardness with large voids and pores.

6.2.4 Corrosion Resistance

The potentiodynamic polarization curves of the selected TiO₂ films substrate samples are shown in Fig. 6.26. By comparing the curves, two salient differences between the electrochemical behaviour of the uncoated substrate and TiO₂ film can be seen. First, the current density at any given potential for the TiO₂ film is always lower than that of the uncoated substrate. Second, the polarization curve in the reverse sweep of the cyclic test follows the same trend for the TiO₂ films. The results show that the formation of a rutile-TiO₂ based film on 316L steel improves the general corrosion resistance of the steel in the chloride solution. Further, the presence of Ti underlayer below the TiO₂ film helped to further improve the corrosion resistance by showing close match between forward and reverse cycles.

Fig.6.26: Potentiodynamic polarization curves of the uncoated substrate and the TiO_2 films on 60 min. Ti underlayer in 3% NaCl electrolyte

6.3 DISCUSSION

6.3.1 Underlayer Texture

Texture difference was observed in the Ti underlayers with variation in sputter deposition process conditions such as substrate temperature and deposition time. (100) texture component was observed for shorter deposition times (up to 60mins) when deposition was carried out on heated substrates (300°C). No texture component was observed in the films deposited on un-heated (RT) substrates. The reason for this texture formation is due to the presence of oxygen impurity, which helps in minimizing the surface energy of (100) component against the closely packed (002) in Ti. Similar observation of impurity impact on surface energy minimization and texture formation is reported elsewhere [Knorr, 1998]. The Ti film deposited on unheated substrate did not show texture formation due to the slower rate of oxygen diffusion at lower temperatures, as it is well known that the diffusivity has a strong dependence on the temperature.

Texture formation mechanism: Polycrystalline films deposited on polycrystalline substrates leads to the Island (Volmer–Weber) growth [Venables, 1994,]. Fig. 6.27 shows the three important interfacial energies: the film/substrate interfacial energy, $\gamma_{\text{film/substrate}}$, the film surface energy, $\gamma_{\text{s}}^{\text{film}}$, and the substrate surface energy, $\gamma_{\text{s}}^{\text{substrate}}$. All exert an influence on the wetting characteristics of an isolated island early in the deposition process, $\gamma_{\text{film/substrate}}$ and $\gamma_{\text{s}}^{\text{film}}$ is a primary driver for texture development. The $\gamma_{\text{film/substrate}}$ is most important during the initial film formation stage, when the film is discontinuous. The $\gamma_{\text{s}}^{\text{film}}$ also contributes during film formation and becomes dominant during film thickening. The minimization of $\gamma_{\text{s}}^{\text{film}}$ is most often associated with specific crystallographic orientations and can be visualized as a “cusp” in the Wulff plot of surface energy as a function of orientation [Knorr, 1998]. Close-packed planes usually have the lowest $\gamma_{\text{s}}^{\text{film}}$, which implies <0002> in Ti, depending on the deposition temperature [Petrov, 2003].

Fig. 6.27: Schematic representation of wetting of an island [Knorr, 1998]

6.3.2 Underlayer Roughness

Texture differences in the underlayer lead to the roughness variation in the Titanium underlayer. Ti films with (002) orientation show rougher surface than the (001) textured films for the same length of deposition as observed in the Fig. 6.16. Roughness also increases with the deposition time with in the (002) oriented films. The surface roughness develops in a fractal geometry [Chan, 2005] which, due to wide angular distribution of the deposition flux, atomic shadowing, and limited surface diffusion, leads to extensive porosity [Petrov, 2003]. The faceted column tops result, as noted above, in surface roughness which increases with thickness giving rise to open column boundaries due to atomic shadowing. The degree of (002) orientation increases with film thickness and is accompanied by greater surface roughness. Geometrical shadowing was reported to be the cause of the “grain threshold phenomenon” observed using IBA techniques [Pascallan, 1999].

6.3.3 Overlayer phase formation

Oxide layer deposited on unheated substrates show amorphous phase and thermal assisted depositions are needed for crystalline TiO_2 phase formations. Adequate adatom-mobility has to be achieved for nucleation and growth of crystalline phases. This can be achieved by increasing the kinetic energy of the sputter species or by increasing the substrate temperature. While both of these parameters contribute to the increase in mean-free path of the rearranging adatoms, depending on the diffusivity of the adatom species in the nucleated phase, temperature helps in crystalline packing in the subsurface region of the growing film which is not possible otherwise through increase of kinetic energy of sputtered species.

The crystalline phase formed on the heated substrates shows variation in its formation depends on surface conditions. Rutile phase was observed on the underlayer surface with $\langle 100 \rangle$ texture. The $\langle 002 \rangle$ orientation results in anatase and rutile phase on underlayer with smoother surface, whereas rough surface leads to the amorphous oxide layer. The reason for this amorphous phase could be due to the compromise between the anatase and rutile phases.

6.4 SUMMARY

Titanium dioxide films deposited by magnetron sputtering from rutile-TiO₂ target showed different phase formations, depending on the substrate surface condition. Anatase- TiO₂ formed when oxide films deposited on native oxide surfaces. The possibility of rutile phase formation at relatively lower temperatures (300°C) has been reported with the help of Ti underlayers. The effect of titanium underlayer surface, which vary with the deposition time and temperature, has been investigated. Texture differences observed in the underlayer with variation of deposition conditions lead to different phase formations in the oxide layers. High temperature deposition leads to (100) texture in Ti film due to the oxygen diffusion (depending on the oxygen availability), which in turn helps in surface energy minimization.

Thermal assisted deposition conditions are needed for crystalline phase formations in the oxide layer. Rutile phase formed when oxide layers deposited on Ti underlayer with <100> texture. In contrast <002> orientation leads to the mixed phase of anatase and rutile or amorphous phase depend on the roughness.

The thickness of Ti underlayer also has significant influence on the phase composition and properties of the resultant films. Such a varied film system can significantly enhance the surface hardness, tribological properties and corrosion resistance of the stainless steel in terms of much reduced friction coefficient and increased wear resistance. The TiO₂ film with 60 minutes underlayer showed high hardness, good adhesion strength and superior wear and corrosion resistance.

CHAPTER 7

CONCLUSIONS AND RECOMMENDATIONS

The primary objective of the thesis work was to obtain rutile based hybrid films with optimal wear, friction and adhesion properties. Three approaches were chosen to fabricate the TiO₂ films on 316L stainless steels i.e.,

- 1) Thermal oxidation of bulk titanium
- 2) Thermal oxidation of titanium thin films
- 2) Direct deposition of TiO₂ films using TiO₂ as the target

7.1 CONCLUSIONS

The following findings are summarized from the experiments carried out during the course of the study.

1) Thermal Oxidation of Bulk Titanium: In order to establish the thermal oxidation (TO) experimental conditions for titanium films and to understand the phase evaluation and kinetics of oxidation, studies were carried out through thermal oxidation of bulk titanium.

- ❖ Thermal oxidation of bulk titanium produces oxide layer with gradient composition with decreasing O/Ti ratio from the surface. The resultant oxide layer consists of rutile-TiO₂ at the surface and oxygen diffused titanium (ODT) structure near the interface.
- ❖ Thermal oxidation followed by furnace cooling (slower cooling rate) yields thick and adherent oxide layer, whereas air-cooling (faster cooling rate) produces thin and non-adherent layer, which can easily be delaminated from the substrate surface.
- ❖ The oxide layer produced by thermal oxidation possesses superior tribological properties because of the much improved friction characteristics, low wear rate and mild wear mechanism involved during the sliding process.
- ❖ Thermal oxidation at 850°C and for a period of 5 hours, followed by furnace cooling produces a very thick (>100 µm) and adherent oxide layer on the bulk titanium.

2) Thermal Oxidation of Titanium Films: Ti films were deposited on stainless steel substrates by magnetron sputtering method and then oxidation was carried out to obtain partially oxidised films. The effect of oxidation temperature and time on the structure and properties of the oxidized films were studied. Thermal oxidation conditions to obtain films with improved wear resistance and good adhesion strength were optimised.

- ❖ Thermal oxidation can convert sputter deposited titanium films to hybrid rutile-TiO₂ based films on stainless steel substrates. The resultant oxidised film consists of layered structure, which comprises a rutile-TiO₂ at the surface, oxygen and nitrogen dissolved α -Ti layer in the middle and with a diffuse-type interfacial region.
- ❖ Thermal oxidation of titanium films at relatively higher temperatures (>600 °C) deteriorates its adhesion strength with substrate due to the induced thermal stresses caused by residual stresses and CTE mismatch. Whereas, relatively low temperature oxidation (<500°C) takes prolonged time for conversion and produces films with moderate properties.
- ❖ Oxidation of titanium film on 316L substrate, for the thickness chosen, presents optimal tribological properties at 550°C temperature and 5 hours deposition time, due to lower plasticity index. Whereas, superior corrosion resistance can be achieved for 500°C and 10 hours oxidation.

3) Sputter Deposition of Titanium Dioxide Films: TiO₂ films on 316L stainless steel were fabricated by non-reactive magnetron sputtering with and without a titanium underlayer. Phase formation in TiO₂ films deposited through sputtering of oxide target on various surfaces was studied. Influence of substrate/underlayer surface characteristics and oxide layer process parameters were investigated.

- ❖ Rutile phase can be formed in TiO₂ films deposited by non-reactive magnetron sputter deposition using rutile-TiO₂ target at relatively low temperatures (300°C) without any post treatment.
- ❖ Substrate surface plays a major role in the phase formation of titanium dioxide overlayer films deposited by magnetron sputtering from rutile-TiO₂ target. Rutile-TiO₂ phase forms on the Ti underlayer with <100> texture, whereas, Ti

film with $\langle 002 \rangle$ component either leads to mixed phase of anatase and rutile or amorphous phase depending upon the substrate surface roughness.

- ❖ Texture differences occur in the Ti underlayer with process conditions like substrate temperature and deposition time. High temperature deposition leads to $\langle 110 \rangle$ texture in Ti film due to the oxygen diffusion (depending on the oxygen availability), which in turn helps in surface energy minimization, and leads to texture formation.

7.2 PROCESS COMPARISION

Wear performance of the rutile surface obtained by three methods shows that rutile layer produced by TO on the bulk -Ti ~~shows~~ **has the** highest wear resistance among them followed **by** TO of film and then sputter deposited TiO₂ film. Individual process methods' merits, demerits and application suitability **are** is discussed below.

1) Thermal Oxidation of Bulk Titanium (Method 1): Thick oxide layer on bulk titanium with high adhesion strength capability makes this process suitable for high wear/corrosion resistant applications. Though thermal oxidation of bulk Ti is a well known method, novelty of slow cooling approach after oxidation has been surfaced out making this process a primary choice where thick oxide layer is needed. Potential areas include chemical, off-shore, biomedical, automotive, performance sports, power generation and general engineering in which tribological and corrosion behavior are often a major concern for titanium component designers.

2) Thermal Oxidation of Titanium Films (Method 2): High wear and corrosion resistant adhesive rutile based hybrid film on stainless steel substrate makes this method suitable for tribological and corrosion applications of stainless steel components. Novelty of this process lies in stainless steel substrate surface modification with Tt₂O₂. Potential areas of this process include industrial wear resistant, marine and biomedical applications where stainless steel can be used as **a** substrate material.

3) Sputter Deposition of Titanium Dioxide Films (Method 3): Wear and corrosion resistant adhesive rutile based film on stainless steel substrate by sputter deposition alone makes this method also suitable to produce stainless steel components for tribological and corrosion applications. Not limited to stainless steel substrates only, this method, but also be applied to other substrates such as Si substrate. The major advantage

of this process is selective TiO₂ phase formation, which is required, for applications like photo catalysis.

Although, both methods 2 and 3 are to produce stainless steel substrate with rutile surface, however, relatively high wear/ corrosion resistance of the thermal oxidation of Ti film (Method2) makes suitable for wide range of applications where post oxidation process is allowed. In contrast, direct sputter deposited films (Method3) are suitable for relatively moderate wear / corrosion applications, where post oxidation process is not feasible.

7.3 RECOMMENDATIONS

- ❖ In the current work, thermal oxidation of titanium film was studied for only constant thickness. The scope of the thermal oxidation of films can be extended for a range of thickness for manufacturability. The possible way is to create a model with both oxidation temperature and time as variables. Efforts are due to emphasize on the correlation of oxidation mechanism with the defects in the underlayer and diffusion of reactant species.
- ❖ The possibility of obtaining mixed phase (anatase and rutile) in the sputter deposited TiO₂ films can be further explored due to its significance in the photo catalytic applications. It would be beneficial to quantify the mixed phase and correlate with the titanium underlayer characteristics. Understanding on the mechanism has to be correlated with the Ti underlayer microstructure for enhanced control on the phase evolution in the oxide films.

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APPENDIX

A.1 TO OF TITANIUM FILMS AT HIGHER TEMPERATURES

The experimental observations made in chapter 4, thermal oxidation of Ti bulk suggests that 650-800°C can be the suitable range for oxidation of Ti films on stainless steel substrates. Since oxidation process also encompasses the oxidation time, TO was carried out for different times between 10-30 minutes across the temperature range. Table A.1 shows the thermal oxidation conditions in the above mentioned temperature range.

Table A.1 : Experimental conditions for thermal oxidation of Ti film.

Temperature (°C)	Time in minutes	
	Air cooling	Furnace cooling
800	10	10
750	10	10
700	10, 15, 20, 25, 30	10
650	10, 15, 20, 25	10

A.2 STRUCTURAL CHARACTERISATION

A.2.1 X-Ray Diffraction Analysis (XRD)

Initially TO was carried out at temperatures of 650, 700, 750 and 800°C for 10 minutes followed by both furnace cooling (FC) and air-cooling (AC). The XRD patterns of the air-cooled samples comparing to the as-deposited film are shown in Fig. A.1. From the figure it can be seen that all the oxidised and air-cooled Ti films show the presence of peaks from substrate since the patterns were recorded in Bragg-Brentano mode XRD. Rutile -TiO₂ (JCPDS 21-1276) is the primary phase in all the oxidised samples (within the sensitivity of the XRD analysis) and no anatase (another form of TiO₂) was found at all in any of the samples. This observation is contrary to the report that Rutile phase forms from Anatase between the temperatures 700-900°C [Lobl, 1994] The proportion of the rutile phase increased with oxidation temperature as rutile phase is more stable at high temperatures.

Fig. A.2 shows the XRD patterns of the furnace-cooled (FC) samples at the same temperatures as in the air-cooling. TO at 650, 700 and 750°C, furnace cooled samples yielded almost similar XRD patterns as those of the air-cooled ones of 700, 750 and 800°C, respectively. Since the effective time of oxidation is more in the case of furnace cooling, a temperature difference of about 50°C manifested in TO for 10 minutes with respect to air-

cooling. The sample at 800°C shows only the peaks from substrate along with some peaks of rutile since the film peeled off the substrate after cooling.

Fig. A.1: XRD profiles of 10 minutes oxidised and air-cooled (AC) samples at various temperatures as indicated in the figure.

Fig. A.2: XRD profiles of 10 minutes oxidised and furnace-cooled (FC) samples at various temperatures as indicated in the figure.

The studies were thus confined to lower temperatures owing to the fact that spallation occurred for furnace cooled high temperature TO samples. Accordingly, the study

was extended for times of 15, 20, 25 minutes at lower temperatures, 650 and 700 °C. The GIXD patterns of air-cooled samples at 650 °C for different times are shown in Fig. A.3. The rutile is the major phase in all the samples and its proportion increases with oxidation time. The formation of rutile phase increases the volume of the film by about 1.73 times (Pilling-Bedworth ratio of Ti to TiO₂) [Burns, 1989] due to the similar expansion of the volume of the rutile phase with respect to the Ti lattice. This is supported by the decrease in the relative intensity of substrate peaks and ODT, which is expected to present towards the interface between the film and the substrate, with respect to the strongest peak of the rutile phase.

Fig. A.3: XRD profiles oxidised and furnace-cooled (FC) samples at 650°C for (a) 10 (b) 15 (c) 20 and (d) 25 minutes.

The GIXD patterns of the TO samples at 700°C followed by air-cooling for the same oxidation times as 650 °C are shown in Fig. A.4. These samples also show rutile as the only major phase, especially for longer oxidation times i.e. 25 minutes. ODT is present in samples of lower oxidation times. Neither anatase nor any other TiO₂ is present except rutile in all the oxidised samples at 700°C.

Fig. A.4: XRD profiles oxidised and furnace-cooled (FC) samples at 650°C for (a) 10 (b) 15 (c) 20 and (d) 25 minutes.

A.2.2 Surface Morphology

Surface morphology of all oxidised samples was observed with the help of FESEM. Surface morphology of films oxidised at 800°C for 10 minutes is shown in Fig.A.5. After oxidation, Ti film was peeled off in the furnace-cooled sample whereas air-cooled sample showed well-adhered but porous film.

Film flaking was also observed in the air-cooled sample oxidised at 700°C for 30 minutes (Fig.A.6a). Even oxidation at 750°C for 25 minutes followed by air cooling rate caused the failure of film (Fig.A.6b). The XRD analysis, morphological study and film thickness measurement also suggest that the temperatures higher than 700 °C and the oxidation times longer than 25 minutes are not suitable for this current study, because of porosity, spallation and complete transformation of film as mentioned above.

So the thermal oxidation was confined to only 650 and 700 °C temperatures and 10, 15, 20 and 25 minutes followed by air cooling for further study so that for none of the oxidized samples the ratio of oxidized film to the as-deposited film is greater than PB ratio (Fig.A.7). Details of the TO conditions and corresponding codes are given in table A.2.

Fig. A.5: FESEM images showing surface morphology of TO samples of 800°C and 10 minutes followed by (a) Furnace cooling (b) Air cooling.

Fig. A.6: FESEM images showing film failure of film at (a) 700°C, 30minutes followed by air-cooling (b) 700°C, 25minutes followed by furnace-cooling.

Fig. A.7: Plot showing the variation of thickness ratio of oxidised to as deposited film as a function of oxidation time at 650 and 700°C air-cooled samples.

A.3 PROPERTY EVALUATION

A.3.1 Nanoindentation Test

Hardness and reduced modulus values as a function of depth for substrate material and TO samples were obtained by nanoindentation. Fig.A.8 shows the variation of the modulus to hardness (E_r/H) with increase in depth from surface. The E_r/H ratio reduced to a great extent after oxidation. Among the oxidised samples, 700-25a shows the lowest E_r/H ratio at all the depths and the ratio is almost constant to a depth of 400 nm. A decrease in the ratio of E_r/H effectively limits the degree of plastic deformation of the material during tribological process. As a consequence, a high degree of elastic contact can be anticipated, which favours low adhesion between contacting surfaces and hence low friction [Dong, 1997].

Fig. A.8: Plot showing the variation of bulk modulus to hardness ratio of the samples tested.

A.3.2 Tribology Test

Tribological testing under dry sliding conditions at a load of 1N and for a sliding distance of about 0.2 Km was studied for all the samples. Fig.A.9 shows the variation of friction coefficient with sliding distance for all the TO specimens. The 700-25a specimen, which has the lowest friction coefficient among all oxidised samples, supports the scratch test results. It is demonstrated that thermal oxidation of the Ti coating can significantly improve the friction characteristics and wear resistance of the AISI 316L steel. Fig. A.10 shows the friction coefficient curves recorded for the stainless steel substrate material, the as-deposited Ti coating and the thermal oxidised coating (700-25a). The fact established is that both the substrate material and the as-deposited Ti coating exhibit very poor friction behaviour, characterised by high and unstable friction coefficients, which fluctuate greatly during the sliding cycles. The reason is strong adhesion occurring at the areas of real contact by virtue of electronic structure, crystal structure, and high E/H ratio of the Ti film [Dong, 1997]. This is typical of poor tribological materials that experience stick-slip, which is caused by the fact that the friction force does not remain constant as function of distance, time, or velocity. On the other hand, thermal oxidation of the Ti coating has significantly improved the friction characteristics in two aspects. First, the overall friction coefficient was

reduced during the test. Second, the friction curve became much smoother and the tribosystem

Fig. A.9: Friction coefficient curves recorded for the oxidised samples (a) 650 and (b) 700°C air-cooled samples.

experienced much less frictional noise and fluctuation. The main reason for this low friction is primarily due to the presence of rutile at the surface as confirmed by earlier characterisation techniques. As mentioned in section 4.3.2.1 the low friction is explained by low plasticity index of Rutile, being proportional to the ratio of E'/H . The plastic deformation between the contacting surfaces makes important contribution to high wear and friction and a significant reduction in friction and wear is anticipated, if the contact between surfaces is predominately elastic [Fontana, 1998]. As confirmed by the nanoindentation results the thermal oxidation treatment not only surface hardness and reduced the E/H ratio but also increased the elastic recovery.

The improvement in tribological behaviour by thermal oxidation is further demonstrated by the much reduced wear rate (Fig. A.11) and the mild wear mechanism involved in the thermally oxidised coating (Fig. A.12). Without thermal oxidation, the as-deposited specimen exhibited a much higher wear rate than the stainless steel substrate material, obviously due to the poor wear resistance of titanium. Thermal oxidation significantly improved the wear resistance of the coating and the stainless steel substrate. The wear rate from the hybrid rutile-TiO₂/ODT coating is nearly an order of magnitude less than that from the substrate material.

Examination of the wear tracks revealed that both the substrate and the as-deposited coating were worn severely by the adhesive wear mechanism, such that the wear tracks are wide and deep with a very rough surface appearance, particularly in the as-deposited specimen. While the rutile-TiO₂/ODT coating only experienced mild wear by the micropolishing of the hard alumina counterface. The resultant wear track is narrow and shallow with a smooth and polished appearance. No debonding and flaking of the hybrid coating has been observed in the track. The superior wear resistance of the oxidised specimen is derived from the formation of the hybrid rutile-TiO₂/ODT structure, which resulted in increased hardness, improved frictional behaviour and much enhanced adhesion between the coating and the substrate.

A.4 SUMMARY

Thermal oxidation of sputter deposited titanium films on the stainless steel substrate in the temperature range of 650-800°C produces hybrid structure with rutile-TiO₂ / ODT structure. For the chosen thickness of titanium film, oxidation at 700 °C and 25 minutes are optimum conditions for superior friction, adhesion and wear properties.