AN INVESTIGATION OF MATERIAL PROPERTIES AND TRIBOLOGICAL PERFORMANCE OF MAGNETRON SPUTTERED THIN FILM COATINGS

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AN INVESTIGATION OF MATERIAL PROPERTIES AND TRIBOLOGICAL PERFORMANCE OF MAGNETRON SPUTTERED THIN FILM COATINGS

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ABSTRACT

This dissertation is divided into two categories based upon lubrication functionality and its application. The categories are: Dry/Solid film lubrication with thin film coatings and Fluid film lubrication with thin film coatings. The thin film coatings examined in this work were deposited using closed field unbalanced magnetron sputtering and RF-DC Coupled magnetron sputtering systems.

In Dry/Solid film lubrication, the mechanical, structural and tribological properties of two Molybdenum disulphide (MoS₂) based coatings are examined and evaluated. Among the two coatings, one coating is doped with Ti (Ti-MoS₂) and the other is a combination of metal, lubricant and oxide (Sb₂O₃/Au - MoS₂). These coatings are known to provide low friction in vacuum environments. The goal of this work was to evaluate friction and wear performance of MoS₂ doped coatings in unidirectional and reciprocating sliding contact under different environmental conditions. Sliding contact results showed friction and wear dependence on temperature and humidity. The formation and removal of transfer films and the recrystallization and reorientation of basal layers on the steel counterface was observed as the mechanism for low friction. Structural analysis revealed a relationship between the microstructural properties and tribological performance. It was also observed that the addition of dopants (Ti, Au, Sb₂O₃) improved the mechanical properties as compared to pure MoS₂ coatings.
Further, the rolling contact performance of the coatings was measured on a five ball on rod tribometer and a Thrust bearing tribometer under vacuum and air environments. The rolling contact experiments indicated that life of the rolling components depend on the amount of material present between the contacts.

Fluid film lubrication with thin film coatings investigates the possibilities to improve the performance and durability of tribological components when oils and thin films are synergistically coupled. In this work, the ability of a Diamond Like Carbon coating to increase the durability of contacting surfaces under boundary lubrication were studied. The performance of highly hydrogenated Diamond Like Carbon (DLC) was evaluated in a mixed sliding and rolling contact. Experimental results show significant improvement in fatigue life of steel specimens after coating with a highly hydrogenated Diamond Like Carbon coating. The improved fatigue life is attributed to the coating microstructure and the mechanical properties.
DEDICATION

I would like to dedicate this dissertation to my daughter Haneet kaur.
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CHAPTER I
INTRODUCTION

1.1 Solid Film Lubrication

Rotating parts in mechanical systems, ranging from spacecraft to microelectromechanical systems (MEMS), can experience extreme operating conditions with large variations of pressure and temperature. These extreme operating conditions preclude the use of conventional lubricants (i.e., oils and greases), and consequently, tribological damage to the contacting surfaces of mechanical components is the performance limiting condition.

Mechanical systems in satellites and launch vehicles operate in environments where they are exposed to radiation, high temperature (-80° C to 250° C) and pressure (vacuum to several atmospheres) swings, and variable environments (humid air to vacuum) [1]. Conventional oil and grease lubricants that can function over the required temperature, pressure, and environmental ranges do not exist. Liquid lubricants can volatilize or evaporate at extreme pressure conditions and can contaminate the systems. At high temperatures or in radiation environments, liquid lubricants can decompose or oxidize whereas at cryogenic temperatures liquids can solidify or become highly viscous [2]. On the other hand, solid lubricants can provide an effective solution to minimize or diminish the tribological effects of friction and wear and enable components to achieve greater
operational lifetimes. Molybdenum disulfide (MoS$_2$) based films are widely used as solid lubricants in space applications such as release mechanisms, precision bearing applications, and gimbal bearings [3]. MoS$_2$ exhibits very good tribological performance as a solid lubricant in vacuum and inert atmospheres [4]. Because of the easy shearing between basal layers, MoS$_2$ can form what is known as a “velocity accommodation layer” between mating contacts. That is, the relative motion between contacts is entirely accommodated within the MoS$_2$. Unfortunately, the ability of MoS$_2$ to form an effective velocity accommodation layer diminishes when the material is exposed to moist conditions, since adsorbed water between the layers impedes the shearing ability of the basal planes [5]. However, metal-doped MoS$_2$ (M-MoS$_2$) has shown to be tribologically more effective than MoS$_2$ when operating in both dry and humid environments [6]. Whereas the friction coefficient of M-MoS$_2$ is the same as MoS$_2$, its wear resistance is much greater [7]. While the published literature on M-MoS$_2$ reports tests of these films under only sliding contact, none of the literature report the performance of M-MoS$_2$ under rolling contact even though these films are being utilized in rolling element bearings. Consequently, M-MoS$_2$ films in the literature were not optimized for rolling contact and may not have been evaluated on actual bearings. Therefore, it is not known how these materials will perform in the wide range of application conditions when applied to rolling element bearings. The focus of this research is to develop a more complete understanding of the relationships between the mechanical, structural, and compositional properties of a metal-doped MoS$_2$ and its tribological performance in rolling contact under challenging operating conditions.
1.2 Fluid Film Lubrication

Tribological practices are employed to ensure that mechanical components such as bearings and gears can operate with high efficiencies and attain desirable life cycles. The majority of tribological components and machine elements are lubricated with conventional oils and greases. These lubricants are designed to provide films to separate asperities from mating surfaces, to carry away heat from the contact, protect against rust, and other functions required of typical operating environments. However, the performance envelope of the mechanical systems that operate with conventional oils and greases is constantly expanding, therefore these are insufficient to provide effective lubrication under challenging conditions. For instance, wind power which is an emerging field of interest due to its prospects as a source of renewable energy, but wind turbines have high failure rates and reliability issues that are often linked to the gearbox components such as bearings and gears [8]. Gears and bearings in wind turbines operate in challenging conditions where they undergo transient torsional reversals, frequent stresses from wind turbulence, variable environments (humid, dry) and extreme temperature conditions [9]. The typical failures modes associated with gears and bearings are surface initiated fatigue, white etched cracking, smearing, false brinneling (i.e., fretting and fretting corrosion), and abrasive wear from contamination [8,10,11].

Surface initiated fatigue commonly known as micro-pitting is a common mode of failure encountered in gears and bearings.[12] Specifically, main shaft bearings in wind turbines are identified as life limiting due to large number of failures which are associated with surface contact fatigue.[8] In elastohydrodynamic theory, the lambda value (Λ) [defined as the ratio of the lubricant film thickness to the composite surface roughness in
the contact) is used to identify the different regimes of a lubricated, tribological contact. When micropitting and smearing occur, $\Lambda$ is less than 1. Therefore, the properties of the contacting component surfaces are the most critical attributes with regard to micropitting and smearing failures.

A number of solutions have been provided to address contact fatigue failures apart from oils packed with additives. Super finishing processes are used to produce surfaces with isotropic low roughness, topographies thereby reducing asperity interactions in the boundary lubrication regime.[13] Apart from controlling the surface roughness/texture and design parameters, surface engineering techniques are employed to reduce asperity contact and provide a barrier to wear.[14] Physical vapor deposition (PVD) coatings composed of nitrides, sulphides and carbides have been employed to prevent micro-pitting.[15,16] Engineered surfaces have been shown to provide a barrier to prevent micro-pitting by reducing/eliminating wear.[17] Among other coatings, Diamond like carbon coatings (DLC) are also used due to their exceptional tribological properties.[18] Surface treatments such as black oxide and phosphate coatings are also applied chemically on steel parts to counter micro-pitting.[19–21] Most of the studies performed on fatigue prevention is carried using hard DLC coatings deposited by physical vapor deposition methods, few if any studies are being done on soft DLC coatings (Hardness < 10 GPa).

Thin film coatings along with compatible lubricants should be an effective surface engineering technique to address these technologically important issues. Carbon-based thin film coatings have found widespread applications during the past decade because of their exceptional tribological properties, and have been optimized to provide ultra-low friction and wear in different environments. The focus of this part of the research is to evaluate the
ability of carbon-based thin film coatings to improve the durability of mechanical components and to mitigate surface fatigue occurring in rolling/sliding contacts.

1.3 Tribology Overview

Tribology is a branch of engineering which deals with the mechanisms of friction, wear and lubrication of interacting surfaces in relative motion. The word tribology originated from the Greek word Tribos means “rubbing”, so in other words it is the science of rubbing surfaces. The concept of tribology is not new, during the Paleolithic period, drills were made for drilling holes and were fitted with bearings from bones. A ball thrust bearing dated about 40 A.D. was found in lake Nimi near Rome [22]. The term tribology became widely acceptable after a Peter Jost report issued by a committee of the British Ministry of State Education and Science in 1966 [23]. The report concluded that huge savings would be possible by utilizing improved design and lubrication to reduce friction and wear. The American Society of Mechanical Engineers (ASME), then adopted the term for its tribology division in 1983 and the American Society of Lubrication Engineers (ASLE) revised its name to Society of Tribologists and Lubrication Engineers (STLE) in 1985 [24].

- Friction

Friction is a component of tribology. In 1508, Leonardo da Vinci first postulated the concept of a coefficient of friction as the ratio of friction force to the normal load i.e. \( \mu = \frac{F}{P} \). In Paris in December 1699, Guillaume Amontons presented details of the experimental results and defined the first and second laws of friction:

1. Friction force is directly proportional to the load.

2. Frictional force is independent of the apparent area of contact.
Later various other inventors namely Euler, Leibnitz, Coulomb defined friction based formulas based on their experiments [25].

Friction is a resistance offered to surfaces in relative motion. Friction can be productive or unproductive. Productive friction is one which is useful for day to day operations (E.g. brakes in cars, climb stairs, use a mouse to surf the web) and unproductive friction which is not useful (e.g. - equipment’s with bearing and gears). Let us consider a simple case of two bodies in contact as shown in Figure 1.1. A gradually increasing force \( F_1 \) is applied to the black body and the body tends to slide over the surface. However, the black body will not start sliding until it reaches a certain limiting value; this is because tangential forces are generated between the contacting surfaces. These tangential forces hinder motion to a certain limit. The relation between normal load and friction force is represented by coefficient of friction (\( \mu \)).

![Figure 1.1 Schematic representing Friction](image)

\[
\mu = \frac{F_f}{F_N} \tag{1}
\]

The coefficient of friction is the dimensionless ratio of the friction force and the normal force. The proportionality between normal force and friction force is given in dry
and boundary friction but not in fluid film lubrication. The value of $\mu$ depends on various factors such as

- Surface topography
- Environmental conditions
- Sliding velocity between surfaces
- Presence of third body between two sliding surfaces

**Wear**

Friction is the dissipation of energy between sliding surfaces, which is always accompanied by wear when the surfaces are in contact. Wear is a progressive loss of material from one or both the surfaces that are in contact with a relative motion between them. The occurrence of wear is undesirable since it can lead to system failure or a deterioration of functional capability [22,26].

In 1953 Archard postulated a model to measure wear which states that the total wear volume is proportional to the sliding distance times the real area of contact. The assumptions for the equation are that the contact between the surfaces occurs at asperities and the true contact area is the sum of the individual asperity contacts. This area is proportional to the normal load and the local deformation is assumed to be plastic.

$$K = \frac{VH}{wd}$$  \hspace{1cm} (2)

Where “$K$” is wear coefficient, $V$ wear volume, $W$ normal load, $H$ Indentation hardness of the wearing material [24]. The value $K$ is always less than unity and has value of 0.001 or less.
Wear is caused by various mechanisms occurring in the engineering applications. The major types of wear mechanisms are summarized as following:

- **Adhesive wear**

  It is a process in which sliding surfaces under high pressure form bonds between similar or dissimilar materials and subsequently material will be detached from one surface and adhere to the opposite surface. Highest adhesion rates occur between similar metals whereas dissimilar materials exhibit lower amounts of adhesion. Adhesion leads to an increase in friction, wear, an increase of debris particles, and in extreme cases cause seizure and scuffing. Adhesive can sometimes be controlled by thicker lubricant films, by the formation of contaminate layers on the surface due to oxidation or impurities, and by lubricant additives.

- **Abrasive wear**

  Abrasive process occurs when there is sliding between surfaces of equal or greater hardness. The rough peaks of hard material penetrate into the soft surface to remove material by plastic deformation. There are two basic modes of abrasive wear; two body and three body abrasive wear. In two body wear the hard particles or asperities rigidly attached to the hard surface and abrades the soft surface. Three body abrasion is carried by movement of debris particles between the contacting surfaces. Particle hardness, shape and size affect the abrading process. Material abrasion occurs by various mechanisms such as like micro-plowing, micro cutting, micro fracture, and grain pullout.

- **Surface Fatigue**

  Cyclic loading and unloading on surfaces can cause material fatigue. The asperities on one surface come in contact with those on the opposing surfaces under very
high contact stresses which are repeated in the course of sliding/rolling. Cyclic elastoplastic deformations leads to the formation of cracks and ultimately material removal. Surface fatigue can be caused by material imperfections, asperity contact, and plastic deformation, chemical effects of lubricants and self-propagating nature of fatigue cracks.

- Corrosive/oxidative wear

  Tribo-corrosion is often used to describe wear of material accelerated by the corrosive or oxidative surface reactions. Chemical reactions can mechanically weaken the surface and increase the proclivity of the surface to wear when another surface is moving against it. Although chemically modified surface layers may be useful for inhibiting adhesion wear, the weakened surface is usually responsible for a higher rate of material removal.

- Fretting wear

  Fretting fatigue occur when the surfaces are sliding or reciprocating at very small amplitudes due to vibrations caused by machine itself or from surroundings. The sliding is microscopic in nature and movement within the contact takes place without gross sliding. The center of contact may remain stationary and the edges reciprocate at very small amplitude.

- Erosive wear

  Erosive wear is caused by the high impact of solid or liquid particles on opposing surfaces. This phenomenon is most commonly observed in turbine blades and various machines. The wear mechanism involves is controlled by the particle size, particle velocity, particle material and angle of impingement.
1.4 Lubrication

Lubrication is a methodology used to increase the separation between asperities of mating surfaces and provide cooling to the contact area. Low shear strength liquids and solids are interposed to separate the surfaces and to minimize the damage. Friction and wear is unwanted and undesirable for most engineering applications such as bearings, gears, cutting tools and many more. Lubrication is the primary way to reduce, diminish or eliminate friction and wear.

Lubrication can be divided into two categories:

1. Fluid Film Lubrication
2. Solid Film Lubrication

1.4.1. Fluid film lubrication

In fluid film lubrication, the load is supported by the viscous forces of the lubricant. Fluid film lubrication is divided into five types.

- Hydrodynamic lubrication

  In this lubrication, contacting surfaces are separated by a thick lubricant film and asperity contact does not occur during steady state operation. The lubricant pressure is self-generated by the moving surfaces at high enough velocity to completely separate the surfaces and support the applied load. For a normal load to be supported, a positive pressure profile must exist over the load bearing area. Hydrodynamic lubrication is generally characterized by conformal contacts.

- Hydrostatic lubrication

  A form of lubrication in which the oil is pumped under pressure by an external source between the contacting surfaces. Hydrostatic films have considerable thickness and
ensure a complete absence of sticking friction. These films can carry large masses and requires minimal force to move from their stationary position.

- Elasto-hydrodynamic lubrication (EHL)

  The form of lubrication where the local pressures are high enough to elastically deform the moving surfaces is termed elasto-hydrodynamic lubrication. The increase in viscosity of oil under extreme pressures and elastic deformation of the contacting surfaces are fundamental to understanding the mechanism. This regime is often studied for non-conformal contacts but can occur in conformal contact under extreme pressure in pad and journal bearing.

- Mixed Lubrication

  The lubrication regime which lies between the elasto-hydrodynamic and boundary lubrication is termed as mixed lubrication. In this regime the separation between the sliding contact or bearing decreases and the surface asperities come into contact. This occurs at low speeds, high loads and at high temperatures which leads to the reduction in viscosity. The total load applied during mixed lubrication is assumed to partially carried by the asperities and the partially by the oil film. This region requires a detailed understanding of surface topography, fluid behavior, and surface contact in addition to the hydrodynamic and boundary lubrication.

- Boundary lubrication

  In this regime the surfaces are separated by very thin fluid films and there is considerable asperity contact. The lubrication mechanisms is governed by the thin surface films and not by the properties of bulk lubricant. The boundary lubrication mechanism is
controlled by the additives present in the base oil. The friction and wear is much higher in boundary than in the hydrodynamic and elasto-hydrodynamic regime.

1.4.2 Lubrication Regimes

The degree of separation between lubricated surfaces depends on the speed, load and viscosity. The different lubrication regimes are illustrated by plot between friction and dimensionless parameter called Hersey number ($\eta\omega/P$), where $\eta$ is the lubricant dynamic viscosity, $\omega$ is the rotational speed and $P$ is the applied load. This plot is useful for understanding the lubrication mechanism in a particular regime and is refereed as the Stribeck curve. At a low Hersey number, there is significant asperity contact, resulting in high friction. With an increase in the Hersey number, after a certain threshold, there is significant decrease in the friction coefficient due to the increase in lubricant film thickness. The friction reaches its lowest value with a further increase which is the onset of hydrodynamic regime. The elasto-hydrodynamic lubrication is commonly observed in rolling element bearings, cams and gears, when lubricant is exposed to high contact pressure and causes elastic deformation of the surfaces. The region which lies between boundary lubrication and elasto-hydrodynamic regime is called mixed lubrication regime. The coefficient of friction in the mixed lubrication regime can vary over a wide span depending on load carried by asperity interactions and hydrodynamic action respectively. Figure 1.2 gives the rough indication over which various lubrication modes occur.
The lubrication regime is derived by the calculating the film parameter Lambda ($\lambda$) which is the ratio of film thickness to surface roughness.

$$\lambda = \frac{h_{\text{min}}}{\sqrt{(R_a^2 + R_b^2)}}$$  \hspace{1cm} (3)

Where, $h_{\text{min}}$ is the minimum film thickness, $R_a$ and $R_b$ are the rms values of the surface finish. When lambda is greater than 5, the point of contact is in full lubrication regime. If Lambda is less than 1 then the contact is in boundary lubrication. If the lambda ratio lies in between then the contact is in mixed lubrication regime.[27]

The minimum film thickness between the contacting surfaces is calculated by equation 4 (See Appendix 1 for complete details). The film thickness is affected by the dimensionless load, speed and materials parameters.
\[ \frac{h_c}{R'} = 2.69 \times \left( \frac{U \eta_0}{E' R'} \right)^{0.67} \times (\alpha E')^{0.53} \times W \left( \frac{W}{E' R'^2} \right)^{-0.067} \left( 1 - 0.61 e^{-0.73K} \right) \] (4)

Where \( h_c \) is central film thickness (m).

\( U \) is the entraining surface velocity.

\( \eta \) the viscosity at atmospheric pressure of the lubricant.

\( E' \) is the reduced young’s modulus.

\( R' \) is the reduced radius of curvature.

\( \alpha \) is the pressure-viscosity coefficient (m\(^2\)/N).

\( W \) is the contact load, N.

\( K \) is the ellipticity parameter.

1.4.3 Solid Film Lubrication

Solid lubricants are materials which provide friction resistance between surfaces during relative motion without the use of a liquid media. These materials shear easily to provide low friction and prevent wear damage when applied between contacting surfaces. Solid lubricants are primarily used in severe application conditions (high vacuum, aerospace, high speeds, cryogenic and high temperatures) to control friction and wear. Solid lubricants have low vapor pressure, which prevents their degradation by sublimation and therefore, allows them to operate in vacuum and at high temperatures. Molybdenum disulfide (MoS\(_2\)) and graphite are the two most commonly used solid lubricants in vacuum.
and terrestrial applications. Both MoS$_2$ and graphite are lamellar solids and exhibit excellent tribological properties.

- Classification of Solid Lubricants

Solid lubricants can be divided into many categories based on their application (vacuum or humid), crystal structure, chemistry and lubricity. In general, soft metals, polymers and layered lattice compounds are the three main categories of solid lubricants.

- Soft Metals

Soft metals such as Gold, Silver, Copper, Lead, Indium and Zinc, possess low shear strengths and limited or no sensitivity to temperature and environment$^{[28]}$. These metals provide lubrication by reducing friction from room temperature to elevated temperatures as well as in vacuum and air atmospheres$^{[3,29]}$. The FCC structures of soft metals provides low shear strength, easy slip of atomic planes and provides a fluid like lubricating behavior. The multiple slip planes in the crystal structure do not allow work hardening to occur in these metals. Soft metals serve as effective lubricants when deposited with optimum thickness as thin film on hard substrates. These metal coatings have been applied onto sliding and rolling mechanical components which involves critical circumstances such as high vacuum, radioactive and gaseous atmosphere and high temperature in nuclear, aerospace and biomedical industries$^{[30]}$.

- Polymers

Polymers (polymide, nylon, PTFE, PEEK) are used in corrosive environments or where cleanliness is of utmost importance. Polymers are inert compounds, relatively inexpensive, light weight and easy to fabricate. These are soft materials with low load bearing capability and a tendency to flow under load. Other materials are added to polymers
to increase the load bearing capacity, wear resistance and lower the friction coefficient. Polytetrafluoroethylene (PTFE) is the most widely used polymer in pure form or as a composite in both vacuum and in the presence of water vapors [31]. The macromolecules of PTFE slip easily, similar to lamellar structures. The low thermal conductivity of PTFE inhibits heat dissipation, which can cause premature failure due to melting and limits use to low-speed sliding applications[2].

- Layer Lattice Materials

Layer lattice is used to describe materials which consist of basal planes that are parallel to each other and have hexagonal crystal structure. Solid lubricants such as transition metal dichalcogenides MX$_2$ (where M can be Mo, W, and X is sulfur or selenium), hexagonal boron nitride, boric acid, graphite can provide excellent lubrication due to lamellar or layered crystal structure [4,32–35]. The crystal structure is such that the atoms on the same layer are close packed and bonded strongly to each other, whereas the layers themselves are far apart and held by weak forces. The layered materials when applied between contacting surfaces, align their layers parallel to the sliding surface and shear with relative ease to provide low friction coefficient. This mechanism of aligning layers is an important factor but not the sole criterion responsible for low friction. The environmental conditions such as humid, vacuum also play an important role in the lubrication mechanism of layered compounds. These materials are also classified in two categories based on their shearing mechanism: Intrinsic and Extrinsic lubricants. In extrinsic lubricants, the presence of chemical adsorbate is required for easy shear of the solids. For example, graphite where the presence of water vapor is necessary to terminate the dangling bonds at edge sites[36]. In intrinsic lubricants, shearing occur solely due to
the atomic structure near the top surface and no additives are required e.g. MoS$_2$, where low friction and easy cleavage of molybdenum is result of its crystal structure. Graphite and MoS$_2$ both are inorganic solid lubricant and has hexagonal crystal structure. In the graphite layered structure, there are large Columbic attractions between the layers resulting from inter-planar electron pair distribution whereas in the MoS$_2$ crystal structure, there are strong covalent bonds between atoms within a layer and relatively weak bonds between atoms of different layers which allow the lamina to slide on one another and thus provide low friction coefficient [37,38]. However, graphite is an excellent lubricant for humid atmospheres whereas MoS$_2$ in vacuum environment.

The three categories mentioned above are the general categories. With the help of modern practices and advanced techniques more exotic coatings architectures have been developed. The doping of metals, oxides and surface texture are some of the methods employed to develop these exotic structures. Diamond like carbon is a coating which is highly studied and has many variants based on composition, structure, doping and application.
CHAPTER II
LITERATURE REVIEW

2.1 Historical perspective on MoS$_2$ as a solid lubricant

Molybdenum disulfide (MoS$_2$) is an inorganic material commonly used as solid lubricant in vacuum, dry and inert atmospheres [3]. Molybdenum disulfide belongs to the transition metal dichalcogenide family which includes the disulfides, diselenides and ditellurides of Ti, Zr, Hf, V, Nb, Ta, Cr, Mo and W. These compounds exist in various forms but only Mo and W exist in hexagonal crystal structure with good lubricating properties. MoS$_2$ exist in two crystalline forms, hexagonal and rhombohedral. The hexagonal form is used as a lubricant which has six fold symmetry, a layered type structure and two molecules per unit cell. The crystal structure of MoS$_2$ consists of three molybdenum atoms equidistant from each sulfur atom and each molybdenum is surrounded by six equidistant sulfur atoms at the corners of a triangular prism [37]. The distance between the Mo and S atom is 1.54 Å which is smaller than 3.08 Å distance within the S layers. Figure 2.1 shows the schematic representing crystal structure. The excellent tribological properties of MoS$_2$ are attributed to the easy cleavage of MoS$_2$ layers which are held by weak van der Waals forces within layers whereas atoms in the same layer are held by strong covalent bonds [39]. During sliding these planes reorients preferentially (parallel to the surface) to allow the easy shear of the basal planes.
MoS$_2$ is an intrinsic solid lubricant, unlike graphite which does not require adsorbed water vapor to provide low friction coefficient. MoS$_2$ demonstrates excellent tribological properties in the absence of these chemical species and is therefore used in vacuum or dry environments for lubrication. MoS$_2$ when used on sliding surfaces in high humidity or adsorbed water vapor exhibits high friction coefficients and wear rates [40]. The edge sites of MoS$_2$ which are parallel to the c-axis exhibit preferential affinity for polar compounds and at the edge sites Mo can exist in number of different oxidation states [41]. These edge sites react when they come in contact with air, disrupts the easy shear of basal layers and results in high friction. MoS$_2$ is stable up to 1100º C in vacuum, but in the presence of oxygen Mo edge sites oxidize at 350ºC, to form molybdenum trioxide (MoO$_3$) and sulfur dioxide (SO$_2$) [5,42].

\[
MoS_2 + \frac{7}{2} O_2 \rightarrow MoO_3 + 2SO_2
\]

Figure 1.1 Schematic representing the crystal structure
MoS$_2$ coatings have been applied to tribological surfaces by number of different methods, such as burnishing, resin bonding, and sputtering. Burnished and resin bonded coatings have poor adhesion and high wear rates which limits their use. In particular, burnished films have higher friction coefficients and wear rates than sputtered films [4]. Physical vapor deposition (PVD) techniques such as magnetron sputtering, pulsed layer deposition and ion beam assisted deposition overcome the limitation of burnished films. PVD coatings offer good adhesion, controllability, oxidative stability and low wear [43,44]. Among several PVD techniques, closed field unbalanced magnetron sputtering, which is one of many variants of sputtering, has become very popular for deposition of MoS$_2$ films due to the high ion current density produced by the system [45].

Spalvins first deposited MoS$_2$ coatings by Radio Frequency (R.F.) sputtering in 1969. RF sputtered MoS$_2$ coatings are typically porous, have low densities and composed of freestanding columnar grains. These coatings have a three tired structure, wherein at the
substrate there is ridge formation zone, equiaxed transition zone in the middle and on top columnar grains [39]. The columnar grains have [002] planes oriented perpendicular to the substrate. During sliding, the columnar grains break at the initiation point (base), partly transfer to the counter-face and align parallel [002] to the sliding direction [46]. The [002] aligned surfaces slide like a deck of cards to provide low friction.

The tribological performance of MoS$_2$ films is greatly influenced by the sputter deposition process. For example, negative bias voltage and high working pressure during sputter deposition improve adhesion and uniformity, and suppress columnar morphology typical in physical vapor deposition films [47–50]. DC sputtered MoS$_2$ coatings were found to be dense and coherent unlike the loose columnar coating typical in RF sputtering [50]. It is reported that the sputter deposited MoS$_2$ coatings are sub stoichiometric in sulfur with a general composition of MoS$_x$ where $x < 2$ [51]. Christy et al reported that MoS$_2$ coatings with stoichiometric (S/Mo=2) composition have better tribological properties than sub stoichiometric coatings [52]. The lowest friction coefficients are reported for pure and stoichiometric coatings [53,54]. The negative bias voltage applied to the substrate influences the stoichiometry of MoS$_2$ by intensifying the Ion bombardment. Ion bombardment leads to preferential sputtering of the Sulfur atoms deposited on the substrate which results in sub-stoichiometric coatings [47,51,55].

The deposition temperature also influences the structure and chemical composition as mentioned by various authors. It is reported that the MoS$_2$ coatings deposited at room temperature are amorphous and sub stoichiometric [4,55]; however some researchers reported nano-crystalline coatings [56,57]. MoS$_2$ coatings deposited at elevated temperatures are reported to be crystalline [39,48,51,56]. The tribological performance of
MoS$_2$ coatings is also affected by various processing contaminants such as carbon, oxygen and hydrogen during deposition. It was found that residual water vapor in the coating chamber negatively impact the coating properties.

The demands for higher performance and longer wear lives have led researchers to improve the tribological performance of MoS$_2$ in vacuum as well as in a humid environment. The main purpose was to reduce water and oxygen adsorption onto the MoS$_2$ surface and create a material that can provide the same low friction on earth and in space for thousands or millions of cycles. Researchers developed a novel method to dope MoS$_2$ with certain metals (Au, Ni, Ti, Pb, C) and compounds (TiN, PbO, Sb$_2$O$_3$, ) with a focus to improve the tribological and mechanical properties [58–65]. Haltner and Oliver first reported the enhancement of MoS$_2$ properties with the non-lubricant additives [66]. These additives improved the high temperature performance of MoS$_2$ coatings. Several oxides and sulfides (PbO, Sb$_2$O$_3$, PbS, PtS ) were added to MoS$_2$ crystal structure, however Sb$_2$O$_3$, in particular was identified as superior additive in many applications [67]. Centers in 1987 correlated the mechanical and thermal properties of MoS$_2$ oxide films with tribological performance [68,69]. A direct relationship between shear strength and wear was proposed by Centers. It was shown that oxides with higher hardness exhibit high wear volume during tribological testing at higher temperature. Oxides such as Sb$_2$O$_3$ showed less wear due to their low shear strength and it was believed that a softening of the oxide induces plastic deformation at higher temperature. Several researchers studied the oxide addition in MoS$_2$ and attributed the performance increase due to reduction in oxidation and densification of the coating [61,68,70].
Stupp first reported that the co-deposited metals with MoS$_2$ resulted in an increased performance of MoS$_2$ coatings under air atmosphere in 1981 [6,63]. The addition of (Cr, Co, Ni, Au and Ta) lead to enhanced tribological performance which was attributed to coating densification and hardness. MoS$_2$ doped films showed higher performance, longer wear lives, and improved friction characteristics. Specifically, Nickel was chosen as an additive to MoS$_2$ and determined that the 5-7% Ni is optimum for enhanced tribological performance. Jamison et al reported that dopants not only increase hardness and density but also increase the lubricity by increasing the inter-lamellar spacing and weakening the lamellar interaction to promote easy shearing [71]. Following Stupp’s work, Spalvins in 1984 co-deposited Au and MoS$_2$ and showed that only 5% of Au can significantly enhance the performance of MoS$_2$ in vacuum [65]. Lince et al studied a range of Au composition (20% < to 95%) in MoS$_2$ at different contact stress for various applications. It was shown that the optimum composition of Au content depended upon the Hertzian contact stress. The performance was related to the shear strength at different stress and change in particle size and fracture toughness of the films with increasing Au content [60,72]. Simmonds et al found that the Au with 10% to 15% atomic percent is optimum for increase in life time in air atmosphere [73]. The addition of Au affected the grain size, lattice spacing and degree of edge orientation in the coatings. The size and mass of Au act as diffusion barrier and higher Au content provides protection form sub-surface oxidation [73].

The addition of Titanium (Ti) has shown excellent tribological behavior [33,74–77]. Specifically, MoS$_2$ films with a Ti content of 5–20 at.% were found to have excellent tribological performance [78]. At 5-20 at% Ti, the structure is amorphous with a very small grain size and contains no inclusions. Ti is believed to be either in solid solution within
MoS$_2$ or between the neighboring planes. Although, no clear understanding is obtained yet about the Ti position in MoS$_2$ crystal structure. Above 20\%, the solubility level of Ti is exceeded and multilayers were formed resulted in decrease in the tribological performance [49]. The Ti – MoS$_2$ were found to be harder and hardness increased with up to 20 at \% Ti content which is probably due to distortion caused by the Ti atoms [33]. Ti-MoS$_2$ films were first reported by Teer et al [77,79,80], who attributed the Ti content with the increase over un-doped MoS$_2$ in load bearing capacity, higher wear resistance and lower friction in humid air. In a subsequent publication, Renevier et al. stated that the dense, coherent characteristic of MoS$_2$/metal composite coatings are probably due to the high ion current density produced by the deposition system [75]. The addition of Ti does not affect the excellent tribological properties of MoS$_2$ in vacuum but imparts additional benefits by reduction of oxygen and hydrogen contaminants during deposition. The presence of Ti within the MoS$_2$ structure may be responsible for reducing the sensitivity of the coating to the water vapor.

Stoyanov et al studied the micro and macro tribological behavior of MoS$_2$ with ~9at. \% Ti and revealed that at the macro scale the dominant velocity accommodation mode was interfacial sliding and film shearing whereas at the micro-scale interfacial sliding, transfer film shearing and micro-plowing were the dominant modes which depend on the contact pressure, contact area and contact tip [81,82].

To further improve the properties of MoS$_2$ in humid atmospheres, researchers combined graphite with MoS$_2$ due to its excellent properties in air atmosphere [83]. The aim was to increase the range of operating environment, however these films found limited application due to rapid oxidation of graphite in low earth orbit and leading to debris
formation [84]. The next effort was towards tertiary MoS$_2$ based films. Zabinski et al first studied the MoS$_2$-Sb$_2$O$_3$-Au coatings and measured excellent tribological properties. 2.5 % Au and ~35% Sb$_2$O$_3$ was added to the MoS$_2$ matrix and observed uniform, dense, harder films with increased tribological performance [85]. Later Zabinski et al studied MoS$_2$/Sb$_2$O$_3$/C composite films which showed good friction and wear characteristics in vacuum, dry air and humid air as surface chemistry changes with environment. In this coating, active lubricant layer of MoS$_2$ or graphite was generated over the surface of Sb$_2$O$_3$ particles with change in environment. Carbon addition to MoS$_2$ improved MoS$_2$ performance in humid air [86]. Various other coatings were designed to improve the tribological properties in moist air which includes MoS$_2$-PTFE-graphite, MoS$_2$ -PbO-graphite.

In a recent study by Scharf et al, MoS$_2$/Sb$_2$O$_3$/Au coating with 82% MoS$_2$, 11% Sb$_2$O$_3$ and 7% Au composition was deposited and tested. It was concluded that the presence of Au nanoparticles in the sub surface region imparted wear resistance, reduced porosity and increased hardness. These dopants lead to increase in coating density (Sb$_2$O$_3$), hardness (Au) and wear life [59]. Hamilton et al studied friction as function of contact temperature from -80 to 180$^0$ C for a series of MoS$_2$ doped coatings (MoS$_2$/Sb$_2$O$_3$/Au, MoS$_2$/Sb$_2$O$_3$/C, MoS$_2$/Sb$_2$O$_3$, MoS$_2$/Ti, and MoS2/Ni) and compared their steady state wear rates. In this study, Sb$_2$O$_3$ doped MoS$_2$ coatings showed lowest steady state coefficient of friction and wear [87]. Thus, it was concluded that the MoS$_2$ doping with Sb$_2$O$_3$ and Au imparts environmental robustness and increases the tribological behavior of MoS$_2$.

Friction coefficients and wear rates of doped MoS$_2$ films have been studied under unidirectional and reciprocating sliding contacts only. However, the tribological
performance of these films in rolling contact has not been reported previously. Sliding tests may be appropriate for exploring the friction and wear mechanisms of coatings, but their results do not always correlate with the tribological performance of the materials in actual mechanical systems. This is especially true for rolling contact bearings. In contrast to pure sliding, rolling elements in bearings typically undergo both sliding and rolling on raceways. Solid lubricant coatings are commonly employed in mechanical systems operating in environments where oil or grease lubrication is not feasible. In particular, solid lubricant coatings are currently being used in rolling element bearings operating in vacuum environments and/or at high temperatures. Since the functional lifetimes of solid lubricant coatings in rolling element bearings are derived from sliding contact experiments, it is beneficial and important to understand if the actual performance of the coatings in rolling contact bears a relationship to their sliding contact performance. Further, it is important to understand how microstructural changes in the coating effects the performance in sliding and rolling contacts.

Solid lubricants have potential for future tribological systems. As demands are increasing from advanced technological and industrials systems, the use of solid lubricants is expected to increase in the near future as no such lubricant is available which can provide effective lubrication in a broad set of test conditions. With the development of modern vacuum deposition techniques such as PVD and CVD allows the production of complex or multicomponent coatings. Great strides have been made in controlling the chemistry, microstructure, morphology and thickness of solid lubricants, because of these techniques. These nanostructured designs offer adaptive coatings which can resist friction, wear and change surface chemistry. Solid lubricants are fulfilling the needs of various complex
systems from years and will continue to improve and meet the demands for critical tribological needs.

2.2 Diamond like Carbon coatings

Carbon is a remarkable element which is used in different forms in various applications. Carbon's ability to exist in three hybridization sp\textsuperscript{3}, sp\textsuperscript{2}, and sp\textsuperscript{1} results in a variety of crystalline and disordered structures. Carbon-based materials have emerged as potential lubricants due to their excellent lubricating properties as thin films or as an additive in oils [88]. Carbon nano-onions, nanotubes, graphene, fullerene, nano-diamond have been studied extensively. Among carbon-based materials, Diamond like Carbon (DLC) is perhaps the largest researched material during the last three decades in the field of tribology. Diamond like carbon is a metastable form of carbon and compositionally it contains sp\textsuperscript{3}, sp\textsuperscript{2}, and sp\textsuperscript{1} hybridization states and atomic H. The structure of DLC films depends on the deposition method and the carbon gases used and in turn, results in large variation in their properties. Some DLC films function excellently in humid atmospheres while others performed in vacuum or inert atmospheres [89]. DLC films can have chemical inertness, high mechanical hardness, high elastic modulus and optical transparency, low wear and friction coefficient. Due to their exceptional properties, DLC is used in various applications such as automotive components, magnetic storage disks, optical windows, microelectromechanical devices and several others.

DLC films can be deposited by several PVD and CVD techniques. These advanced techniques led to the development of a large number of DLC films such as hydrogenated, non-hydrogenated and doped. These films are deposited at room to high temperatures (400 °C), different bias voltage, gas flows, and deposition pressure. Based on the deposition
parameters, the sp\textsuperscript{2} and sp\textsuperscript{3} content varies from one DLC film to another [90]. The films also contain sp\textsuperscript{1} bonds in trace amount, but the bulk of bonds are predominantly sp\textsuperscript{2} and sp\textsuperscript{3}. Based on hydrogen content and sp\textsuperscript{3} bonding these films, they can be divided into categories of hydrogenated and non-hydrogenated. The non-hydrogenated tetrahedral amorphous carbon (ta-C) contain high fraction of sp\textsuperscript{3} hybridized carbon, the range of which varies from 5-90\% and hydrogen content less than 5\%. The hydrogenated amorphous carbon contain 20-60\% hydrogen content and sp\textsuperscript{3} content varies between 20-65\% [18].

In addition to the hybridized carbon, various dopants such as W, Ti, Si, Cr, Ni B are used to modify the structure [91–95]. DLC films (a-C) exhibit low adhesion resulting from high internal stresses. To provide better adhesion and hindering of crack propagating metals such as Ti, Si and Cr are used. Addition of Ti, Si and Cr as an interlayer between the substrate and top layer improved the adhesion. These metals were further alloyed with DLC and are referred to as Me-a-C or Me-a-C:H where Me is a metal. The addition of metal increased the mechanical toughness of the films and found to reduce stress and the friction coefficient [96,97]. To further increase the toughness, nano-composite films are utilized with carbide crystals of 15 nm precipitated into amorphous carbon or hydrocarbon matrices [95]. This helped to reduce stresses further by the help of grain boundary movement to release the accumulated strain [98].

The tribological behavior of DLC films may vary depending on the structural and chemical nature of the films. The test conditions and environment also play a significant role on the friction and wear behavior. Depending on the type of film whether highly hydrogenated, non-hydrogenated or metal doped, the friction and wear performance is a function of environment (dry, humid, vacuum or inert) [18,88]. DLC films provide low
friction coefficients by the formation of transfer films on the counter-face while films which do not form transfer films the friction coefficients are generally high. These transfer films are of amorphous nature, which do not possess crystallographic planes for easy shear like other solid lubricants (MoS\(_2\), graphite). The friction coefficients of hydrogenated film varies between 0.007-0.05 in vacuum, whereas certain highly hydrogenated films (hydrogen more than 40%) reported to have a friction of 0.001 in dry nitrogen or inert atmospheres. The hydrogen free DLC exhibit high friction values in the range of 0.03-0.8 in vacuum atmospheres while in humid environments the friction coefficient varies between 0.05-0.23. The metal doped DLC films generally have stable friction coefficient (0.3-0.4) in both vacuum and humid atmospheres [88,99].
CHAPTER III
MATERIALS AND METHODS

3.1 Coating Deposition

The coatings used for tribological testing and evaluation were deposited using magnetron sputtering techniques which are explained in details in the following sections.

3.1.1 Sputtering

Sputtering is a vacuum deposition technique used for the deposition of thin films, etching and analysis. In this method, the source material to be deposited is called a target and the surface on which it is deposited is called substrate. The target is connected to a negative voltage supply, either DC or RF and substrate is also connected to negative voltage. Material is deposited atom by atom, which is ejected from the target when bombarded by charged ions of high kinetic energy (more than the binding energy of the surface atoms). These ions (also called primary particles) can be supplied either with inert gas such as Argon and Krypton or by small molecular ions such as $\text{N}_2^+$ and $\text{O}_2^+$. The bombarded particles remove the target material (atoms) which subsequently condense on the substrate and form a thin film. Some sputtered particles ballistically fly away from the target in straight lines and can cause re-sputtering via collisions with the substrate or the vacuum chamber. Secondary electrons are also emitted during target bombardment which
is essential for maintaining the plasma. For efficient momentum transfer, the atomic weight of the sputtering gas should be close to the atomic weight of the target. Figure 3.1 presents the schematic of target sputtering mechanism [100].

The sputter yield depends on the:

The Kinetic Energy of the incident ions.

The mass of the individual ions with comparison to the target atoms.

The surface binding energy of atoms of the substrate.

The incident angle of ions which are bombarding the target.

![Figure 3.1 Schematic showing sputtering mechanism](image)

Efficiency of the sputtering can be measured by :-

\[
S = \frac{\text{Number of ejected atoms or molecules}}{\text{Number of incident ions}}
\]

In a conventional diode sputtering process, the main drawback is low deposition rate. An increase in deposition rate by increasing voltage is not possible, since the
ionization cross-section decreases for energies higher than 100 eV. Increase in operating pressure increases the collisions between the sputtered ions/atoms which reduces the deposition rate. Therefore, it is not possible to increase the sputtering rate in conventional sputtering. Magnetron sputtering is an alternate used to achieve high deposition rate.

3.1.2 Magnetron Sputtering

Magnetron sputtering uses a magnetic field to trap the gas plasma in front of target with the help of magnets deployed in the target holder. The magnets are arranged in such a way that one pole is positioned at the central axis of the target and the second pole is formed by a ring of magnets around the outer edge of the target. Figure 3.2 illustrates the conventional magnetron sputtering showing film growth and mechanism. The magnetic field traps the electrons and carves an extensive, circuitous path for electrons, which increases the probability of ionizing a neutral gas molecule by several orders of magnitude.

The increased ionization efficiency of the magnetron arrangement produces a dense plasma in the target region which usually extends up to 60 mm from the target surface. But substrates kept beyond this region are exposed to very low plasma densities, leading to low deposition.
There are several benefits of using the magnetrons for sputtering. Magnetrons increase the sputtering rate on the substrate due to confinement of electrons close to the target. Electron confinement also helps in reducing the deposition rate on the walls of the chamber. Another advantage is that the plasma can be generated at comparatively lower pressures (typically $10^3$ mbar as compared to $10^2$ mbar).

The main drawback of magnetrons is that an erosion track is formed on the target which leads to poor efficiency of ‘sputtering yield versus target volume’ as compared to non-magnetron sputtering. Figure 3-3 shows the erosion wear track on the target surface. Substrates have to be kept in close proximity due to the limited region of plasma.

3.1.3 Reactive Magnetron Sputtering

Thin film coatings are deposited by sputtering target material using inert gases such as Argon. However for certain applications, compounds films are produced by reacting sputtered target material with reactive gases such as oxygen and nitrogen. Oxides, nitrides and carbides are most commonly deposited by reactive sputtering. Due to the non-
conductive nature of the oxide targets these films are difficult to sputter and typically requires the use of R.F. power. If directly sputtered using DC power, the poor stability of the compound targets may result in cracking or shattering or may have difficulty in bonding to the cathode. Reactive sputtering has received great attention because of the high deposition rate, controlled deposition and ability to use DC rather than RF power. The reactive gas is introduced in the chamber in addition to the inert gas. The reactive gas reacts with the ejected target material on the surface of the substrate and can also react with the target when the deposited films may not be able to absorb extra unused gas. The unused gas can form an oxide layer on the target surface, and causes an irreversible change. The formation of unwanted layer ion target is called poisoning. Figure 3.3 shows the schematic of target poisoning during reactive sputtering. If chemical reactions are faster than the sputter rate, then the target material can be poisoned. Poisoning is a formation of compound film on the target in addition to the substrate. Poisoning reduces the sputter yield and thereby reduces the deposition rate. The reactive gas partial pressure at increasing/decreasing gas flow due to poisoning requires additional means of stabilization[101]. Another issue with reactive sputter deposition is the formation of oxide or non-conducting films on the on the surface of the anode. In most cases, chamber walls function as the anode, films gets deposited on the chamber walls, the anode become oxidized and the current is reduced which leads to the arcing and results in poor film quality. Several approaches have been used to fix this problem by monitoring pressure and voltage to control the reactive gas flow, by increasing pumping speed and by using dual cathodes in which the power is alternated to each cathode. In a dual cathode system, during each cycle one cathode functions as the cathode and the other functions as an anode and
then the powers are reversed. Alternately cathodes are sputter etched to provide a fresh unoxidized surface to function as anode [102].

![Figure 3.3 Schematic showing target poisoning during reactive sputtering](image)

The composition of the thin film can be altered by adjusting the relative pressures of these gases in the chamber. Good stoichiometry can be obtained by adjusting reactive gas flow and magnetron power.

Most often used reactive gasses are:

1. Oxygen (O₂) is used for deposition of oxide films [103].

2. Nitrogen (N₂) is used for deposition of nitride films [104].

3. Acetylene (C₂H₂) is used for deposition of metal-DLC, hydrogenated carbides, and carbon-nitride films [89,92,105].

4. Methane (CH₄) is used for similar applications as Acetylene [89].

Gases that are inert in ambient conditions (e.g. molecular N₂) become reactive when present in a plasma discharge due to collisions with energetic particles and subsequent
dissociation into atomic neutral and charged components. Several reactive gasses can be mixed (e.g. O\textsubscript{2} + N\textsubscript{2}) in order to deposit multi-component functional thin films, such as oxy-nitrides (e.g. Cr-O-N) or oxy-carbides (e.g. Si-O-C). Additional reactive gas is sometimes used to enhance a certain deposition process [106].

3.1.4 Closed Field Unbalanced Magnetron Sputtering (CFUMS)

The differences in design between a conventional magnetron and an unbalanced magnetron are only slight, but the differences in performance of coatings deposited by the two types of magnetrons are very significant. Unbalanced magnetron sputtering means that the strength of the permanent magnets behind the target are different. In an unbalanced magnetron, the outer magnetic poles may be stronger than the inner poles therefore the field lines stretch further into the vacuum chamber. The plasma expands away from the surface of the target towards the substrate. Figure 3.4 shows the closed field unbalanced magnetron sputtering systems arrangement used for deposition of Ti-MoS\textsubscript{2} films.

Further closed filed unbalanced magnetron sputtering system uses magnetic fields in such a way that the plasma is confined by the magnetic field lines. The magnets within the magnetrons are arranged such that alternating poles are next to each other resulting in the linkage of field lines. This traps the electrons and ions more efficiently and prevents them from escaping to the chamber walls resulting in much higher ion current densities.[107]
Figure 3.4 Closed field unbalanced magnetron sputtering systems arrangement used for deposition of Ti-MoS$_2$ films

Early magnetrons made use of ferrite magnets which gave maximum field strength at the target surface of the order of 300-500G but with improved magnetron design as well as rare earth metals, field strengths in excess of 1kG are now obtainable at the target surface.[108,109] The increased field strength enhances the ionization efficiency in the plasma considerably. Such systems are able to transport high ion currents to the substrates, which leads to hard and well adhered coatings.

This type of system is used where dense films are required but without excessive intrinsic stresses (as in the case of normal magnetron sputtering). The sputtered coating is denser and of significantly better quality, but due to involvement of more energy, substrates
can reach higher values as compared with normal magnetron sputtering. Higher substrate temperatures are beneficial for many applications.

3.2 Deposition system used in this dissertation work

Two type of deposition systems were used in this work. Ti-MoS$_2$ films were deposited by using Closed Field Unbalanced Magnetron Sputtering System (CFUMS) and MoS$_2$-Sb$_2$O$_3$-Au films were deposited using R.F. and D.C coupled conventional magnetron sputtering system.

3.2.1 TESL Closed Field Unbalanced Magnetron Sputtering System (CFUMS) used for deposition of Titanium doped MoS$_2$ films

The TESL deposition system is a pulsed direct current (DC) physical vapor deposition system with dimensions of 3x3x3 ft in size. This system uses a DC power supply in the range of 500 to 5000W, and has four cathode positions where a target of 381 x 127 x 10 mm (height - width - thickness) dimensions are mounted. Figure 3.5 shows the target configuration and geometry. A copper plate is placed behind the target to support the target and to remove heat from the target generated during sputtering. Two rotating tables of different dimensions were used. A 12 station table (12 rotating spindles) of diameter 914mm and 355mm spindle height was used for ball coatings. Whereas for flat specimens, a 6 station table of the same dimension was used. These tables have two and three fold rotation arrangements to deposit more uniform coatings on the substrates. Thermocouple are placed on the rotating table to accurately measure the temperature during deposition.

Other features of the deposition system include the use of magnets to control the degree of unbalancing to control the plasma density around the substrates. In addition, field coils are used to control degree of unbalancing the magnetic field of the sputter cathodes.
Each target is protected by shutter to protect the targets from cross contamination when not in use, to prevent contamination during etching process and to control the coating composition during deposition. The vacuum is obtained in the chamber using a two stage mechanical backing pump and water cooled diffusion pump. Mechanical backing pump serves two purposes: it work as rough vacuum pump to increase vacuum to $1 \times 10^{-3}$ torr and also backs the diffusion pump that is used to obtain high vacuum levels of $10^{-6}$ torr. The flow of gases is controlled by the mass flow controllers.

3.2.2 TESL Radio-Frequency (RF) and Direct Current (DC) coupled magnetron sputtering system used for deposition of Sb$_2$O$_3$/Au-doped MoS$_2$ films

Figure 3.6 shows the RF- DC coupled magnetron sputtering system used for deposition of Sb$_2$O$_3$/Au-doped MoS$_2$ films. This vacuum deposition system is equipped with both radio frequency (RF) and direct current (DC) magnetrons. Two targets of 50
mmm diameter size can be mounted on the target holder. The RF magnetron is used for sputtering nonconductive or oxide target while conductive targets are mounted on the DC magnetron. The cathode discharge on non-conducting target is generated by a 13.56 MHz R.F. source coupled capacitively via a matching box and DC power supply applied to the conducting target. Substrate can be kept neutral or negatively biased depending on the film requirements. The pumping system is composed of a mechanical pump and a diffusion pump. Mechanical pump is used for backing the diffusion pump and roughening the chamber to a pressure $10^{-3}$ torr. High vacuum in the range of $10^{-5}$-$10^{-6}$ is obtained with the use of diffusion pump.

![Diagram](image)

Figure 3.6 Radio-Frequency (RF) and Direct Coupled (DC) magnetron sputtering system used for deposition of composite of Sb$_2$O$_3$/Au doped MoS$_2$ Films

The RF magnetron was used to sputter a target composed of 82% MoS$_2$, 11% Sb$_2$O$_3$ and 7% Au, and the DC magnetron was used to sputter a 99.99% pure titanium (Ti) target. The Ti target was sputtered to create a Ti bond layer between the steel specimen and the
MoS\textsubscript{2} composite top layer. Before deposition, steel specimens were degreased in a solvent, ultrasonically cleaned in an alkaline detergent, rinsed in DI water and, finally, dried in hot air. The cleaned samples were mounted onto a specimen holder in the deposition chamber and evacuated to a pressure of 7.5 x 10\textsuperscript{-3} Pa (5.6 x 10\textsuperscript{-5} Torr). Specimens were sputter etched with a pulsed DC bias voltage of -400 V in an Ar partial pressure of 0.63 Pa (4.7 x 10\textsuperscript{-3} Torr). After etching, a Ti adhesion layer of ~100 nm was deposited, followed by a ~800 nm layer from the composite target. The bias voltage during the deposition of the MoS\textsubscript{2} composite layer was kept constant at -60V. Coatings were deposited with an Ar gas flow (purity 99.9\%) maintained at 0.83 N-m\textsuperscript{-3}-s\textsuperscript{-1} (50 sccm) and 100\degree C substrate temperature. The coated specimens were allowed to cool before venting the chamber.

3.3 Characterization Techniques

Several characterization techniques were used for the characterization and analysis of films before and after testing. These techniques are listed in the following sections.

3.3.1 Calotest (Thickness Measurement)

Coating thickness was measured using a ball crater technique- calotest using CSEM tester. In this technique, a ball of 20 mm diameter in size is used to grind a crater on the coated surface. Diamond slurry is used to accelerate the grinding process. The coating thickness is calculated by measuring the outer and inner diameter of the coating using optical microscope. Formula used to calculate thickness is:

\[ t = \frac{D^2 - d^2}{8R} \]
where, \( t = \) coating thickness, \( D = \) outer diameter, \( d = \) inner diameter, \( R = \) radius of the ball

Figure 3.7 Thickness calculation by measurement of inner and outer diameter of the scar using ball crater technique

3.3.2 Nano-indentation Test

Hardness and Elastic modulus of the coatings were measured using a Nanovea nano-mechanical tester. In this method, an indenter tip with a known geometry is driven into the coating with an increasing load. Load is applied using a piezo actuator at controlled rate which is measured by a load cell. The hardness is determined from maximum load \((P_{\text{max}})\) by the projected contact area. See Figure 3.8.

\[
H = \frac{P_{\text{max}}}{A}
\]
The reduced modulus, $Er$ is measured by:

$$Er = \frac{\sqrt{\pi} \; S}{2 \; \sqrt{A_c}}$$

$S$ and $A_c$ can be calculated from the indentation curve using an area function, $A_c$ is the projected area of the indenter.

![Figure 3.8 Load displacement curve used for determining and calculation of hardness and modulus values](image)

Young’s modulus $E$, can be obtained from:

$$\frac{1}{Er} = \frac{1 - v^2}{E} + \frac{1 - v_i^2}{E_i}$$

Where $E_i$ and $v_i$ are the Young’s modulus of the indenter and $v$ the Poisson coefficient of the tested sample.

3.3.3 Adhesion Characterization

Adhesion was characterized using Rockwell indentation and Scratch tester methods. These methods are explained in more details below.
• **Diamler Benz Method**

Adhesion was measured using Diamler Benz method originally developed by Gerhard Meyer. It uses a Rockwell hardness tester fitted with a Rockwell C type diamond cone indenter with an applied load of 150 kg. Adhesion is classified HF1 to HF6 based on the cracking and delamination in the coating optical appearance.

![Figure 3.9 Topographical characteristics of the coating cracking and delamination to determine adhesion to the substrate [110]](image)

- **Scratch Tester**

Adhesion of the deposited coatings to the steel substrates was qualitatively determined using a Nanovea micro-scratch tester with a 0.2 mm Rockwell C diamond tip. The applied load in the micro-scratch tests was increased from 0 to 100 N at a table speed of 4mm/min\(^1\). Scratch testers are used for characterizing the mechanical properties of thin films and coatings e.g adhesion, fracture and deformation. The scratch tester technique involves generating a controlled scratch with a sharp tip on a selected area. The sharp tip is moved across a selected surface under a constant load, incremental, or progressive load.
The scratched area is then optically characterized to measure the coating properties and the critical load to failure.

3.3.4 Surface Topology

Three-dimensional optical interferometry (Zygo New View 7300) was used to study the surface topography of the counter-faces and film prior and subsequent to tribological testing. This device was also used to obtain wear depths and cross-sectional areas that are used to calculate wear volumes and transfer film formation on the counter-faces. A Zygo New View 7300 is a 3-D profilometer for characterizing and qualifying surface roughness, heights variation, critical dimensions, and other topographical features with excellent precision and accuracy using wavelength of light. Optical profiling uses the wave properties of light to compare the optical path difference between a test and reference surface. Profilometers are capable of measuring in nanometer in size with good accuracy.

![3-D optical images showing surface topography of bearing raceway after testing generated using Zygo New View 7300](image)

Figure 3.10 3-D optical images showing surface topography of bearing raceway after testing generated using Zygo New View 7300
3.3.5 Scanning Electron Microscopy (SEM)

Film composition was characterized by a JEOL 6400 scanning electron microscope (SEM) equipped with X-Ray energy dispersive spectroscopy. SEM uses a beam of electrons for imaging sample characteristics. The beam of electrons is produced by a thermal emission source, such as a tungsten gun. The generated electrons are focused by a series of electromagnetic lenses in the SEM column. Scanning coils near the end of column positions the focused beam onto the sample surface. The beam can be focused at a single point or scanned along a line for X-ray analysis.

The incident electron cause electrons to be emitted from the sample due to elastic and inelastic scattering events within the sample surface. An SEM image is created when an incident electron beam is scanned in a raster pattern across the sample surface. The emitted electrons from each position are detected by an electron detector. The intensity of the emitted electron signal is displayed as a brightness on image.

3.3.6 Energy Dispersive X-Ray Spectrometer (EDS)

EDS is a chemical analysis technique used in conjunction with scanning electron microscope. The EDS technique detects X-rays emitted from the sample during electron bombardment of the sample to characterize elemental composition. When electrons bombard the sample, some electrons are ejected from the atoms of the sample. The vacancy created by an ejected electron is filled by an electron from the atom’s outer shell. X-rays are emitted by the higher state electron to balance the energy of the ejected electron. The emitted x-ray radiation is characteristic of the element from where it was ejected. The EDS x-ray detector measure the relative abundance of emitted x-rays vs their energy.
Figure 3.11 EDS spectra showing elemental composition

3.3.7 Transmission Electron Microscopy (HRTEM)

Transmission electron microscope uses a beam of high energy electrons to create an image of the specimen. The electron beam is partially transmitted through a very thin specimen which carries information about the structure of the specimen. The spatial variation in this information is then magnified by a series of magnetic lenses until it is recorded by hitting a fluorescent screen or a light sensitive sensor such as charge coupled device camera (CCD). The image detected by CCD can be displayed in real time on a computer screen.

The illumination system can be operated in two principal modes: parallel beam and convergent beam. Parallel beam is used primarily for TEM imaging and selected area diffraction (SAD) while convergent beam is used mainly for scanning (STEM) imaging, x-ray analysis and convergent beam electron diffraction pattern. High resolution transmission electron microscopy (HRTEM) is an imaging mode of that allows direct
imaging of the atomic structure of the sample. The strength of HRTEM lies in its ability to resolve detailed structures of complex planar faults, disordered structures, and interfaces.

Coating micro-structures were evaluated using an FEI Tecnai G2 F20 S-Twin 200 keV field-emission scanning transmission electron microscope. Transmission electron microscopy (TEM) specimens were prepared by using a FEI Nova 200 Nanolab dual-beam focused ion beam (FIB/SEM). A Pt film was deposited on the Ti-MoS$_2$ before ion beam-milling the TEM samples. Focused ion beam (FIB) cuts were made inside and outside the wear scar created in the reciprocating sliding contact experiment, and high angle annular dark field-scanning transmission electron microscopy (HAADF-STEM) scans were performed on some of the specimens. Wear surfaces on the films and the counter-faces of the steel balls were also studied using SEM.

3.3.8 Raman Spectrometry

A Raman spectrometer was used to analyze structural changes in the coatings prior and subsequent to testing. The Raman technique is based on inelastic scattering of monochromatic light (from a laser source). Photons of the laser light are absorbed by the sample and then remitted. The frequency of the remitted photons is lower or higher than the incident photon which is called Raman Effect. The shift in the frequency of incident photons provides information about the vibration, rotational and other frequency vibrations of the molecule or solid.

The collisions between the photons and interacting species can be elastic and inelastic. In elastic collision, photons are deflected back with same energy as the incident energy which is called Rayleigh scattering. When inelastic collision occurs, energy is transferred between the photons and the particles of the matter. These energy exchanges
bring about transfer in the quantized energy levels of molecules or interatomic bonding. In such cases, the photons gets deflected back with a higher or a lower state of energy. When molecules or bonded atoms undergo excitation, they emit light with lower frequency then the excitation wavelength while when they undergo relaxation, the scattered photons are of higher frequency. These photons give rise to the Stokes and antistokes lines. Anti-stokes lines are less intense than stoke lines, as a result stoke lines are generally used. The positions of Raman lines are expressed in terms of Raman shift which is defined by

$$\Delta \nu = (\nu_s - \nu_o) \text{ cm}^{-1}$$

Where \(\nu_s\) and \(\nu_o\) are the wavenumbers of the incident radiation and observed line, respectively.

3.3.9 Atom Probe Microscopy

Atom probe microscopy is a technique capable of generating 3D elemental maps imaging the distribution of atomic clusters. It is an effective characterization technique which can provide unique microstructural information by 3D compositional measurements of small features, crystallographic information and tomographic reconstruction.

The physical processes behind atom probe microscopy are field ionization and field evaporation. Field ionization is applied, typically in the range 10-40 V nm\(^{-1}\), which depends on the material to break surface bonds and ionize the sample. There are two stages of field ionization: thermally-activated ion escape over an activation energy barrier and then post field ionization into a higher energy state. After escape, positive ion charge may have a 1, 2 or 3 state, depending on the ions chemical nature. The ions generated are projected from the surface of the specimen and fly towards a negatively biased detector. The detector
collects the ions and records their impact location. The time of flight of each ion is detected and related to mass-to-charge ratio to determine the element.

Basic information is obtained from the sequence of atom coordinates and the mass-to-charge ratio, m/n of each ion collected. Data are collected and reconstructed into a image of the volume analyzed. The reconstructed volume is a truncated cone in which the radius increases during the experiment due to the tapered angle of the needle shaped specimen. Every dataset contains millions to billions of atoms collected from the sample.

Figure 3.12 shows the detector hit map of Ti-MoS\textsubscript{2} specimen ions. These images are produced by the detector based on the roughness of the surface associated with poles and zone lines that induce subtle homogeneities in the electric field distribution close to the specimen. Trajectory aberrations around pole and zone lines translate into regions of low and high density on the detector as shown in the detector hit map. Variations in ion trajectories distinguish between elements or phases of different evaporation fields.
3.4 Tribological Instruments

The tribological performance of deposited thin film coatings was evaluated in a variety of sliding and rolling contact tribometers. Each tribometer is explained in brief in the following.

3.4.1 Pin on Disk Tribometer

A pin on disk tribometer is the most common method of measuring friction between contacting surfaces where a ball or a pin is used as a counter-face against a rotating disk. The CSEM Pin on Disk tribometer used in this work is capable of measuring friction at different speeds, over a broad range of temperatures, and with different loads. An uncoated steel ball (6mm diameter) was used as the stationary against a rotating 50mm diameter coated disks. Friction is calculated by measuring the tangential force recorded by a strain sensor divided by the load.

\[
\mu = \frac{F_t}{F_N}
\]

where \( \mu \) is coefficient of friction, and \( F_t \) and \( F_N \) are the tangential force and normal force.

Wear was calculated using Archard law which related wear volume with the applied load and sliding distance.

\[
K_B = \frac{Q}{S} W
\]

Where \( Q \) is wear volume in \( \text{mm}^3 \), \( W \) is applied load in N and \( S \) is sliding distance in m.

The schematic of ball on flat tribometer and an image of the CSEM tribometer used in this research are shown in figure 3.13.
3.4.2 High Frequency Reciprocating Rig (HFRR)

A PCS high frequency reciprocating ring (HFRR) was used to measure friction and wear under reciprocating sliding motion. A circular flat of 3mm diameter and 3mm thick was used as the static specimen and 6mm diameter ball as the reciprocating upper specimen (counter-face). Both specimens were made of AISI 52100 steel. This instrument is capable of measuring friction over a broad range of speeds (frequency- 10-200Hz), different stroke lengths (20 µm to 2.0 mm), and temperatures (25° C to 400° C). Figure 3.14 (a) shows a schematic of specimen and direction of motion (b) HFRR rig used for the tests.
3.4.3 Thrust Bearing Tribometer

The thrust bearing tribometer is usually used for evaluation of lubrication performance in bearings. A schematic of the thrust bearing tribometer is shown in figure 3.15. Thrust bearings are pressed in a fixture before mounting on the testing stage, where a load is applied from the bottom and the mounting is rotated from the top by an AC motor. Torque and temperature sensors are fixed to the test assembly for continuous measurements. The test termination criteria is based on torque or temperature thresholds for performance evaluation.
3.4.4 Vacuum Rolling Contact Fatigue Tribometer

A new vacuum rolling contact fatigue tester was designed and built to evaluate the performance of coated rolling elements under pure rolling conditions in vacuum. The basic principle of the vacuum fatigue tester is that a cylindrical specimen is stressed alternatively by five balls radially loaded against the test specimen by spring loaded bearing cups. Thrust loads are applied to the cups by the upper cup housing attached to the spring retainer plate. An accelerometer is attached to the fixture to stop rotation when the system exceeds a preset threshold vibration limit. The increase in vibration indicates the occurrence of a fatigue spall, pitting or an adhesive wear after the lubricant coating is worn. The test assembly is enclosed in a stainless steel chamber to create controlled atmosphere. A motor is mounted on the chamber to rotate the test rod by the use of a magnetic feed through. Vacuum is generated inside the test chamber by a diffusion pump attached at the bottom.
of test rig, see figure 3.16 and 3.17. The cylindrical test specimen is a rod of diameter 9.525 mm and length 76.2 mm is held by a precision collet and rotates at 3540 rpm around 12.7 mm diameter balls equally spaced by a retainer.

Figure 3.16 CAD model of the vacuum rolling contact fatigue tester
Figure 3.17 Schematic of the ball-on-rod tribometer showing the arrangement of rods, cups and a full complement of balls and image on the right shows the assembled image of vacuum rolling contact fatigue tester

3.4.5 Micropitting Rig (MPR)

A PCS Instruments Micropitting Rig (MPR) was used for testing. The MPR is a computer controlled three rings on roller tribometer. A 12mm diameter roller is mounted in the center and in contact with three rings of 54mm diameter at an angle of 120°. Figure 3.18 (a) shows the MPR test chamber and the arrangement of rings and roller inside the test chamber is shown in Figure 3.19 (b). A thermocouple was installed to measure the contact temperature and an external cooler was connected to control the temperature of the oil inside the test chamber. A load was applied to the top ring (0° position) by means of motorized ball screw, and vibration was measured with a piezoelectric accelerometer. The rig has a capability to control entrainment speed (0 - 4 m/s), slide to roll ratio (0 to 200%), temperature (25 - 135 C), and load (0 to 1250 N).
Figure 3.18. (a) Micropitting rig test chamber and (b) arrangement of roller and discs inside the test chamber
CHAPTER IV
MATERIAL PROPERTIES AND TRIBOLOGICAL INVESTIGATION ON Ti DOPED MoS₂ IN ROLLING AND SLIDING CONTACT

4.1 Introduction

MoS₂-based coatings are used as solid lubricants in various applications on earth and space such as cutting tools, gears, bearings, actuators and slip rings, among many others [3,111,112]. The tendency of MoS₂ to re-orient, from an initially random orientation, the \{002\} basal planes parallel to the surface is believed to be a major reason for its success as a solid lubricant [43,113]. MoS₂ has a hexagonal crystal structure (D₄h \(^6\) – P6₃/mmc) with a low friction coefficient due to the ease of its basal plane shearing. Basal planes have strong covalent bonds between S-Mo-S and weak van der Waals bonds between the planes. However, MoS₂ is susceptible to humid environments due to reactive edge sites that inhibit basal plane shearing and thereby increase its friction coefficient in the presence of oxygen and moisture [4,37,39,114]. Various elements (such as Ti, Cr, Zr, Au, Pb, Ni) and oxides (SbOₓ, PbO) have been incorporated into MoS₂ coatings to improve their tribological performance [49,60,61,63,85,115]. The addition of metals or oxides greatly affects the tribological, mechanical and structural properties of MoS₂ composite films [33,59].
The tribological performance of MoS$_2$ films is greatly influenced by deposition process. For example, low bias voltage and high working pressure during sputter improve adhesion and uniformity, and suppress columnar morphology typical in physical vapor deposition films [33,49,59,116]. The tribological performance of MoS$_2$ films may also be affected by various processing contaminants such as carbon, oxygen and hydrogen during deposition.

Numerous researchers have studied and reported the mechanical, structural and tribological properties of alloyed and multilayered MoS$_2$ films [33,59–61,64,116,117]. Ti-MoS$_2$ and MoS$_2$-Sb$_2$O$_3$-Au are two promising solid lubricant coatings [45,59,76,111]. Ti-MoS$_2$ films were first reported by Teer Coatings Ltd. [77,79] who attributed the Ti content with the increase over undoped MoS$_2$ in load bearing capacity, higher wear resistance and lower friction in humid air. In a subsequent publication, Renevier et al. stated that the excellent properties of MoS$_2$/metal composite coatings are probably due to the high ion current density produced by the deposition system [45]. Specifically, MoS$_2$ films with a Ti content of 5–20 at.\% were found to have excellent tribological performance [78].

Friction coefficients and wear rates of Ti-MoS$_2$ films have been extensively studied under unidirectional and reciprocating sliding contacts. However, the tribological performance of these films in rolling contact has not been reported previously. In this study, Ti-containing MoS$_2$ films were sputter-deposited and their tribological performance studied in both sliding and rolling contact in humid air and vacuum environments. One objective for this study was to quantify the useful life of Ti-MoS$_2$ films in their function as solid lubricants in both sliding and rolling contact.
4.2 Coating Deposition and Characterization

Ti-MoS$_2$ films were deposited onto AISI 52100 and M50 steel specimens in a closed-field unbalanced magnetron sputtering system (CFUMS). Before deposition, specimens were degreased in a solvent, cleaned ultrasonically in an alkaline detergent, rinsed in DI water and, finally, dried in hot air. The cleaned samples were then mounted on fixtures in the CFUMS system, shown schematically in Figure 1. The deposition chamber was evacuated to a pressure of 1x10$^{-5}$ Torr, and the substrates were plasma etched at bias voltage of -500 V in an argon partial pressure of 1.6x10$^{-3}$ Torr. Two MoS$_2$ and two Ti targets were sputtered with currents of 1.3 A and 0.6 A, respectively. The films were deposited with an Ar (purity 99.9%) gas flow maintained at 50 sccm and substrate temperature of less than 80°C. The total thickness of the Ti-MoS$_2$ film is about 1µm, including a Ti adhesion layer with thickness ~200 nm. Balls were mounted on small magnets during the deposition process. The coating thickness was measured nondestructively by x-ray fluorescence, and was highly uniform on the balls – with the exception of the uncoated spots that were in contact with the magnets during the deposition. The schematic of the system is shown on page 38 (Figure 3.4).

Adhesion of the deposited Ti-MoS$_2$ films to the steel substrates was qualitatively determined using Rockwell C indentation and a Nanovea micro-scratch tester with a 0.2 mm Rockwell C diamond tip. The applied load in the micro-scratch tests was increased from 0 to 100 N at a table speed of 4mm/min$^{-1}$.

Film composition was characterized by a JEOL 6400 scanning electron microscope (SEM) equipped with energy dispersive spectroscopy. The micro-structure was evaluated using an FEI Tecnai G2 F20 S-Twin 200 keV field-emission scanning transmission
electron microscope. Transmission electron microscopy (TEM) specimens were prepared by using a FEI Nova 200 Nanolab dual-beam focused ion beam (FIB/SEM). A Pt film was deposited on the Ti-MoS$_2$ before ion beam-milling the TEM samples. Focused ion beam (FIB) cuts were made inside and outside the wear scar created in the reciprocating sliding contact experiment, and high angle annular dark field-scanning transmission electron microscopy (HAADF-STEM) scans were performed on some of the specimens. Wear surfaces on the films and the counter-faces of the steel balls were also studied using SEM. A Horiba LabRam Micro-Raman spectrometer with an excitation wavelength of 532 nm was used for pre- and post-test analysis of Ti-MoS$_2$ specimens.

Hardness values and elastic moduli were obtained from measurements of films on polished steel specimens using a Nanovea nano-mechanical tester equipped with a Berkovich indenter. Five indentation measurements were made under a controlled load of 5 mN for each measurement. The maximum indentation depth was $< 15\%$ of the film thickness.

Three-dimensional optical interferometry (Zygo New View 7300) was used to study the surface topography of the counter-faces and film prior and subsequent to tribological testing. This device was also used to obtain wear depths and cross-sectional areas that are used to calculate wear volumes and transfer film formation on the counter-faces.
4.3 Tribological Testing

Friction and wear measurements were carried out on Ti-MoS$_2$ films under unidirectional (ball on disk) and High Frequency Reciprocating Contact Rig (HFRR) sliding contacts at a contact stress of 0.83 GPa. AISI 52100 steel balls 6 mm in diameter with a surface roughness of Ra = 0.05 µm were used as the counter-faces. Pin on disk (POD) tests were performed as a function of both temperature (25 and 100°C) and humidity (15%–20% and 45%–50% RH). A sliding speed of 20 cm/s and a 2 N load were used for all the tests, which were stopped after completing 10,000 cycles. HFRR tests were conducted at a humidity of 45%–50% RH and at two different temperatures (25 and 100°C). A 1000 µm stroke length, 2 N load and 100 Hz frequency were used for all the reciprocating tests. Dry air was used as a purge gas to control the humidity at the desired level.

Rolling contact experiments were performed on a five ball-on-rod tribometer and a thrust bearing tribometer at a contact stress of 2.5 GPa. Ball-on-rod and bearing tests were conducted in full complement configurations (i.e., no ball retainer). Ball-on-rod tests were conducted in both vacuum and humid (40%–45% RH) air at rotational speeds of 3450 rpm in vacuum and 3600 rpm in humid air. Vacuum tribometer tests began after the chamber pressure reached 1x10$^{-5}$ Torr, and were terminated when vibration corresponding to a 4G value measured with an accelerometer sensor was encountered. Since balls do not precess in ball-on-rod tribometers, the balls were oriented in the assembly such that their uncoated spots did not come into contact with the rods or cups. Thrust bearing (Part number 51306) tests were carried out at room temperature, 15%–20% RH and at a speed of 800 rpm. Tests were terminated when the bearings achieved a rotational torque of 1.75 N-m. Balls in thrust
bearings precess during operation, so intermittent contact between the uncoated spots on the balls and raceways is unavoidable.

4.4 Coating Characterization on as deposited film

Figure 4.1 Images of a micro-scratch test performed on a Ti-MoS$_2$ film taken in the vicinities of three different loads. The images indicate the film has excellent adhesion to the substrate and excellent fracture strength since no delamination or cracking is present.

Figure 4.2 Image showing the Rockwell indentation on the Ti-MoS$_2$ coated steel substrate. Image confirms that the film has excellent adhesion as no cracks or coating delamination occurred.
Figure 4.1 shows images of scratch test measurements performed on a Ti-MoS2 film. The film is completely intact and no chipping or cracking is observed for a load of up to 100 N, which indicates that the Ti-MoS2 film has excellent fracture strength and adhesion to the steel substrate. Rockwell indentation (Figure 4.2) produced no cracking or delamination in the vicinity of the indent, which correlates to an adhesion judgment rating of “excellent.” EDS analysis of the Ti-MoS2 films confirmed that the films are sub-stoichiometric in sulfur with a S/Mo ratio of 1.8 and contained ~16 at.% Ti. The 1.8 stoichiometric ratio cited here should be viewed as approximate since there is large uncertainty in S/Mo ratios measured using EDS because of the overlap between the S and Mo peaks. Nano-indentation measurements indicate that the average hardness and modulus values of the films are 7.9 ± 0.2 GPa and 172 ± 11 GPa, respectively.

Figure 4.3 HRTEM image showing a cross-section of a Ti-MoS2 film deposited on an AISI 52100 substrate.
Figure 4.4 STEM-EDX line profile of the Ti-MoS$_2$ film showing thickness and composition (a 0.5 micron layer of Pt on top to protect the film during the FIB process).

A cross-sectional HRTEM image of a Ti-MoS$_2$ film on an AISI 52100 HFRR specimen is shown in Figure 4.3. The film system is composed of an adhesion-promoting Ti layer, a Ti-MoS$_2$ top layer, and in between, a layer compositionally graded from Ti to Ti-MoS$_2$. The Ti interlayer has a dense microstructure, typical of films deposited under high energetic ion bombardment. The HRTEM cross-sectional image shows that the Ti-MoS$_2$ top layer is dense, non-porous and featureless. It has been suggested that the addition of Ti to MoS$_2$ films inhibits crystallinity, drives the grain size to nm dimensions, and leads to a dense and incoherent microstructure [7,49,118]. Figure 4.4 shows a STEM-EDS elemental line profile of a Ti-MoS$_2$ film with a $\sim$1$\mu$m Ti-containing MoS$_2$ layer on top of a $\sim$200 nm Ti layer. The gradient layer residing between the Ti-MoS$_2$ and the Ti layer is also about $\sim$200 nm thick.
Figure 4.5 Raman spectrum of an as-deposited Ti-MoS$_2$ film on an AISI 52100 substrate. Broad features at 150 and 250 cm$^{-1}$ have been attributed to amorphous MoS$_2$ [81,82].

Figure 4.5 shows the Raman spectrum of an as-deposited film. Although no distinct peaks corresponding to crystalline MoS$_2$ are evident in the spectrum, broad features around 150 and 250 cm$^{-1}$ have been observed in amorphous MoS$_2$ films.
Figure 4.6 HRTEM cross-sectional images showing nanometer-size Ti crystals of random orientation. The FFT pattern (inset) can be indexed to crystalline Ti (P63/mmc).
Figure 4.7 HRTEM images showing the amorphous structure of the Ti-MoS2 top layer. The FFT pattern (inset) indicates that the Ti-MoS2 is amorphous.

Figure 4.6 shows HRTEM cross-sectional images of the Ti layer. These images elucidate the structure of the layer at the nanometer scale. Boxes displayed in the lower-magnification images indicate the location of the higher-magnification images. The FFT pattern shown in the inset indicates that the 200 nm-thick Ti adhesion layer contains randomly oriented, nm-sized Ti crystals (P63/mmc). Figure 4.7 shows the HRTEM cross-sectional images of the Ti-MoS2 layer, and no crystalline order is apparent at the nanometer scale. The grain size is extremely small and a halo around the bright spot in the center from the transmitted electrons of the FFT pattern arises from diffuse diffraction rings typical of
amorphous materials. The TEM results are consistent with Raman analysis on as-deposited samples.

4.5 Friction and Wear Analysis under Unidirectional and Reciprocating Sliding

Figure 4.8 POD friction coefficients versus number of cycles of Ti-MoS2 tested under different conditions (15%–20% and 45%–50% RH at 25°C and 100°C).

POD friction measurements of a Ti-MoS2 film plotted versus cycles under different conditions (15%–20% and 45%–50% RH at 25°C and 100°C) are shown in Figure 4.8. It is evident from the plots that the film survived 10,000 cycles under all test conditions without gross delamination or high wear. The frictional behavior of the test performed in 45%–50% RH at 25°C differs from that of the other tests in that there is an increase in friction during the first 500–600 cycles before the friction decreases and stabilizes at about 0.14. For all other tests, the friction decreases from its initial value and a low friction interface forms after about 1000 cycles, the point at which the friction stabilizes. Evidently the higher humidity at both temperatures affects the formation and/or functionality of the interface. The exact mechanism responsible for this is not explored in this study.

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Figure 4.9 Reciprocating sliding tests (HFRR) on a Ti-MoS2 film performed at 45%–50% RH at 25°C: (a) coefficient of friction versus number of cycles; (b) wear volume versus dissipated energy. Data corresponding to T-1, T-2, T-3, T-4 and T-5 are obtained at about 330, 60, 90, 120 and 150 thousand cycles, respectively.

The lowest stable friction (~0.06) is seen in the test performed at 15%–20% RH at 100°C, while tests performed at 15%–20% RH at 25°C and 45%–50% RH at 100°C exhibit the same stable friction (~0.08). The POD wear rates of Ti-MoS2 films are homologous to the friction coefficients. Whereas no measurable wear volume is observed for the 15%–20% at 100°C test, a wear rate of 1.14x10^6 mm³/Nm is measured following the 45%–50% RH at 25°C test.
Figure 4.10 Reciprocating sliding tests (HFRR) on Ti-MoS2 films performed at 45%–50% RH and 100°C. The friction coefficients versus number of cycles are shown in (a), while (b) shows the measured wear volume versus dissipated energy.

Reciprocating sliding experiments at 25°C and 100°C were performed as a function of dissipated energy following the procedure outlined by Fouvry et al. [119] on the HFRR tribometer. HFRR tests on Ti-MoS2 films performed in 45%–50% RH at 25°C are shown
Five tests (T-1, T-2, T-3, T-4 and T-5) were performed at different sliding cycles ranging from 30,000 to 150,000 cycles. Error bars on the friction plots exhibit the deviation in the measurement of the friction coefficient during tests. Mean friction coefficient values vary from 0.06 (15%–20% RH at 100°C) to 0.14 (45%–50% RH at 25°C), but display no statistical difference as a function of test cycles. HFRR wear volume is plotted versus dissipated energy in Figure 9(b). A linear fit \( V = 7777 \mu m^3 J^{-1} x E_d - 4235 \mu m^3 \) to the data is shown.

The mean values of friction coefficients for HFRR tests carried out at 100°C are shown in Figure 4.10(a). The values are also independent of the number of cycles, but are lower than those obtained in the 25°C tests. HFRR wear volume is plotted versus dissipated energy in Figure 10(b), and is fit with the linear fit relationship, \( V = 1592 \mu m^3 J^{-1} x E_d + 1346 \mu m^3 \). On average, the film experiences about 50% of the wear at 100°C that it does at 25°C for the same dissipated energy. The lower friction and wear at 100°C is consistent with a reduction in the amount of moisture affecting the tribological performance of Ti-MoS\(_2\). A similar behavior has been seen in sputtered MoS\(_2\) films that was attributed to a tribologically driven reorientation of the MoS\(_2\) \{002\} basal planes parallel to the direction of sliding [120].

4.6 Wear Track Analysis on HFRR tested Specimens

Wear scars produced in the HFRR tests were studied using 3D optical interferometry (Zygo NewView 7300), Raman scattering and TEM techniques. Optical interferometry of the HFRR wear scars shows a variation in the shape of wear scars as the test progressed at both 25°C and 100°C. For example, test T-1, with a 30,000 cycle
duration, produces nearly round wear scars, while the wear scars for all other tests are rectangular in shape. The wear scar shapes on the Ti-MoS$_2$ films appear to correlate with the wear scar shapes of transfer films formed on the AISI 52100 steel ball counter-faces.

![Image](image.png)

Figure 4.11 X-HRTEM revealing the micro-structural changes inside the HFRR wear scar tested at 25°C. An iron oxide layer has formed on the surface of the wear track.

FIB cuts were made inside the wear tracks of the HFRR test specimens to investigate a possible correlation between tribological behavior and changes in the Ti-MoS$_2$ microstructure. Figure 4.11 shows an HRTEM cross-sectional image of a wear track tested at 25°C. While the image displays no long-range order of basal planes in the wear track, randomly oriented short-range order MoS$_2$ has been generated in localized areas. This evidence points to the fact that a mixture of Ti-MoS$_2$ and MoS$_2$ exists in the wear track film. An iron oxide layer has also formed on top of the Ti-MoS$_2$, which is probably transferred from the steel ball counter-face.
Figure 4.12 Raman spectrum of (a) a transfer film formed on the steel ball counter-face. Spectra shown in (b) are obtained from various places in the HFRR wear scar tested at 25°C.

Raman analysis was performed on both the transfer film on the AISI 52100 steel ball counter-face and on the wear track of the Ti-MoS$_2$. Raman spectra collected from the wear scar in the film and transfer film on a ball are shown in Figures 4.12a and b, respectively. Unlike the Raman spectra of the as-deposited film (Figure 4.5), the spectra of
the wear scar and transfer film exhibit distinct peaks. The transfer film formed on the steel ball counter-face contains broad peaks around 150 cm⁻¹, 250 cm⁻¹ and 500 cm⁻¹ that are characteristic of amorphous Ti-MoS₂, plus sharper features around 383 cm⁻¹ and 408 cm⁻¹ that are consistent with the in-plane E₂g and out-of-plane E₁g modes of MoS₂, respectively [82,121]. Features at higher frequencies are also present, but their origins have not yet been identified.

Raman spectra obtained inside the wear track show similar features, indicating that the transfer film formed on the steel counter-face is compositionally and micro-structurally similar to the wear track of the film. The presence of features corresponding to frequencies of Raman-active vibrations of MoS₂ in the transfer film and wear track is consistent with the findings of the TEM investigation; that is, a small amount of crystalline MoS₂ has formed in the wear track of the amorphous Ti-MoS₂ films that is randomly oriented with respect to the direction of sliding.

Figure 4.13 STEM-HAADF image and STEM-EDX line profile of the film stack acquired in the region marked by the square.
Figure 4.13 shows a cross-sectional STEM-HAADF image and an elemental depth profile taken from the location of the box in the wear track of the film tested at 45%–50% RH at 25°C. The gradient layer is located in the region of the depth profile identified by the dashed line.

![Figure 4.14](image)

Figure 4.14: STEM-HAADF image and STEM-EDX elemental maps of the film stack acquired in the region marked by the rectangle.

Elemental mappings were performed in different areas to investigate the uniformity of the iron oxide layer in the wear track. EDX maps shown in Figure 4.14 were acquired from the region identified by the rectangular box labeled “1.” These maps do not show a significant presence of Fe and O in this region, indicating that the iron oxide film is not uniformly present throughout the wear track. Furthermore, the STEM-EDX line profile in Figure 4.13 confirms that the x-ray counts from oxygen and iron are within the noise range and not qualitatively noticeable.

4.7 Thrust bearing testing on coated and uncoated rolling elements and raceways

The schematic of the full-complement thrust ball bearing loading assembly is shown in Figure 3.15. Thrust ball bearing test and loading assembly: (a) Thrust Bearing and
(b) Schematic (Page 56). A full complement of 12 balls was used in these experiments to eliminate tribological contributions arising from the retainers. Bearing test measurements were performed without fluid lubrication on four different material pairs: (a) uncoated balls and uncoated raceways; (b) Ti-MoS$_2$ balls and uncoated raceways; (c) uncoated balls and Ti-MoS$_2$ raceways; and (d) Ti-MoS$_2$ balls and Ti-MoS$_2$ raceways. Torque and temperature data were recorded every 30 seconds during the tests, and testing was terminated when the bearing torque exceeded 1.75 N-m. The average number of cycles attained for the four combinations of material pairs is shown in Figure 4.15. For the uncoated balls and uncoated raceway combination, the torque exceeds 1.75 N-m immediately when the axial load of 4448 N is applied and severe wear of the bearing elements occurs. Tests involving either Ti-MoS$_2$ balls/uncoated raceways or Ti-MoS$_2$ raceways/uncoated balls attain about 20,000 cycles with a mean torque of ~0.2 N-m. It is believed that the formation of transfer films on the uncoated counter-faces enables the bearings to operate for extended durations with relatively low torque and temperature. But when the supply of transfer film material is exhausted, torque and temperature rapidly increase and severe wear of the components ensues. The longest lasting combination of materials is Ti-MoS$_2$ balls/Ti-MoS$_2$ raceways, attaining about 160,000 cycles with a mean torque of ~0.1 N-m. This mean torque value is about 50% less than that measured for the Ti-MoS$_2$ balls/uncoated raceway or Ti-MoS$_2$ raceway/uncoated balls combinations. Figure 4.16 compares the torque measurements for the Ti-MoS$_2$ raceway/uncoated balls and Ti-MoS$_2$ raceway/Ti-MoS$_2$ balls combinations. An initial increase in torque during the first 2,000 cycles shown in the Ti-MoS$_2$ raceway/uncoated balls trace is probably due to a break-in effect, which is much less pronounced in the Ti-MoS$_2$ raceway/Ti-MoS$_2$ balls experiment. Increases in torque that
denote the end of useful solid lubricant capability differ in the two cases: The torque rise is very sharp in the Ti-MoS$_2$ raceway/Ti-MoS$_2$ balls experiment, but it is more gradual in the Ti-MoS$_2$ raceway/uncoated balls trace.

Figure 4.15 A comparison of rolling contact behavior of thrust ball bearings with four material combinations: uncoated raceways/uncoated balls, uncoated raceways/Ti-MoS$_2$ balls, Ti-MoS$_2$ raceways/uncoated balls, and Ti-MoS$_2$ raceways/Ti-MoS$_2$ balls.
Figure 4.16 Torque characteristics of thrust bearings tested with Ti-MoS2 only on raceways and on both raceways and balls.

4.8 Ball-on-rod tribometer testing on coated rods, cups and balls

Ball-on-rod tribometers were used to quantify the useful life of Ti-MoS2 films in rolling contact in both vacuum and humid air (40%–50% RH). The schematic of a tribometer and the arrangement of cups, rod and balls is shown in Figure 3.17 (Page 58). The end of Ti-MoS2 useful life as a solid lubricant is defined to occur when vibration of the test heads exceeds 4 G. Figures 4.17a and 4.17b display results of different material pairs tested in humid air and vacuum environments, respectively. These tests examine four material pairs: (a) uncoated rods and cups/uncoated balls; (b) Ti-MoS2 rods and cups/uncoated balls; (c) uncoated rods and cups/Ti-MoS2 balls; and (d) Ti-MoS2 rods and cups/Ti-MoS2 balls. As shown in Figure 4.17a, the uncoated/uncoated combination survives only a few thousand cycles on average before the vibration threshold of 4 G is reached. Ti-MoS2 rods and cups/uncoated balls reach an average of about 1 million cycles, while uncoated rods and cups/Ti-MoS2 balls survive an average of about 3.6 million cycles. Similar to the thrust bearing test results, the Ti-MoS2 rods and cups/Ti-MoS2 balls combination is the longest lasting in 40%–45% RH air.
It is well known that sputtered MoS$_2$ films exhibit much better unidirectional and reciprocating sliding tribological performance in vacuum than in humid air, and similar results are observed in Figure 4.17b with Ti-MoS$_2$ films tested in rolling contact. Specifically, the durability of each material combination is at least two times greater in vacuum than in a humid environment. The uncoated/uncoated combination attained an average of less than 1 million cycles, followed by Ti-MoS$_2$ rods and cups/uncoated balls.
at ~4.5 million cycles. In contrast, the Ti-MoS$_2$ rods and cups/Ti-MoS$_2$ balls and uncoated rods and cups/Ti-MoS$_2$ balls tests reached the greatest number of stress cycles; i.e., 13 and 15 million cycles, respectively. Since the spread in the experimental results of these two tests overlaps, no statistical difference in the useful solid lubricant life between the two materials combinations is achieved.

Figure 4.18 Optical images at 100x magnification of wear scars created on M50 rods in tests performed against Ti-MoS$_2$ balls in ambient (a) and vacuum (c) environments. Line profiles of the wear scars in (a) and (c) are shown in (b) and (d), respectively.

Post-test analyses of the components shown in Figure 4.18 reveal that whereas the vibration cutoff level of all tests involving Ti-MoS$_2$ performed in humid air correlates with the depletion of Ti-MoS$_2$ and the onset of adhesive wear, the vibration limit in the Ti-MoS$_2$ rods and cups/Ti-MoS$_2$ balls and uncoated rods and cups/Ti-MoS$_2$ balls tests performed in vacuum indicates the onset of micrometer-sized pits on the rods. Vacuum rolling contact test results of Ti-MoS$_2$ differ from those reported on silver by Danyluk and Dhingra, where vibrations were found to arise from depletion and spalls of the silver films, not from spalls being generated on the M50 rods [122].
Figure 4.19 Comparison of vibration traces of Ti-MoS$_2$ on rods and cups versus uncoated and Ti-MoS$_2$ balls measured in the vacuum ball-on-rod tribometer.

Figure 4.19 compares the vibration signature of Ti-MoS$_2$ rods and cups/Ti-MoS$_2$ balls and Ti-MoS$_2$ rods and cups/uncoated balls tests conducted in vacuum. The vibration signature of the Ti-MoS$_2$ rods and cups/Ti-MoS$_2$ balls test is very stable until it reaches the end-of-life event at about 22 million cycles. However, the trace of the Ti-MoS$_2$ rods and cups/uncoated balls test is much noisier throughout the entirety of the test. The vibrational noise in the Ti-MoS$_2$ rods and cups/uncoated balls test is probably associated with non-uniformity in the formation of transfer films on the uncoated balls.

4.9 Discussion

The experimental results demonstrate excellent performance of Ti-MoS$_2$ films and the friction results are in good agreement with the literature. The excellent tribological performance of Ti-MoS$_2$ films is believed to arise from their dense structure, featureless morphology and amount of Ti doping in the MoS$_2$ structure [114]. Friction and wear results
for unidirectional and reciprocating sliding contact obtained in this study are in good agreement with the literature and indicate that both temperature and humidity have a strong influence. In the POD results, room temperature (25°C) tests showed increase in friction coefficient at 45-50% RH but were significantly lower at higher temperature (100°C) at same humidity levels. The high friction at lower temperature is driven by water in the atmosphere while at high temperature the water removal from the sliding contact is responsible for low friction. Water is detrimental to MoS$_2$ performance at lower temperature, while at high temperature (above 100°C) oxygen is believed to be a cause of increased friction [5]. Greater amounts of debris are observed in the wear tracks of the films as the humidity increases, and appear to be associated with a larger degree of instability in the transfer film formation on the uncoated steel counter-faces. In dryer conditions, the transfer films are more stable and remain intact for longer periods on the counter-face, which is consistent with previous findings [81]. HFRR measurements performed at 25°C have higher friction coefficients and wear rates than those performed at 100°C, which is also consistent with reported results citing a reduction in the detrimental effect of moisture on the tribological performance of Ti-MoS$_2$ at higher temperatures [120]. The temperature effect on the tribological performance of Ti-MoS$_2$ may also be consistent with thermally activated friction behavior, which was postulated by Hamilton [87], and/or by a reduced adsorption of water on the surface. In reciprocating sliding contact, the wear volume exhibits a linear relationship with dissipated energy for experiments performed at 25°C and 100°C. Although these relationships are useful in predicting the wear life of Ti-MoS$_2$ in reciprocating sliding contact, changes in environmental conditions such as humidity during operation can greatly alter the wear behavior [123]. Raman and TEM
experiments reveal regions of randomly oriented nano-crystalline MoS$_2$ in the transfer film as well as in the wear track. Since nano-crystalline MoS$_2$ is completely absent in the as-deposited films, it appears that its formation in the wear track is thermodynamically driven by localized frictional heating and contact pressure. Furthermore, since Ti doping is believed to be responsible for inhibiting the formation of crystalline MoS$_2$ in the as-deposited films, it is postulated that Ti diffusion allows regions of MoS$_2$ to crystallize. A Hertzian stress-driven decrease in friction in sputtered MoS$_2$ resulting from a reorientation of basal layers parallel to the sliding surface has been reported previously [124].

Dry thrust ball bearing experiments reveal the capability of Ti-MoS$_2$ to function as a solid lubricant in humid air environments. Bearings with Ti-MoS$_2$ rings and balls achieve the greatest number of cycles with the least mean torque of all the tested combinations. In contrast, bearings with Ti-MoS$_2$ on only one element (either raceways or balls) are able to achieve only about 30% of the number of cycles, with a torque about two times higher. Since bearings with Ti-MoS$_2$ on all elements are able to achieve many more cycles with lower torque than bearings with Ti-MoS$_2$ on only one element, it appears that the amount of Ti-MoS$_2$ present in the bearing correlates with its ability to function as a solid lubricant in humid air environments.
A comparison of five ball-on-rod experiments performed both in vacuum and in humid (40%–45% RH) air is shown in Figure 4.20. Tests performed with Ti-MoS$_2$ on all components (rods, cups and balls) perform better than all other combinations in humid air; tests with Ti-MoS$_2$ on all elements and Ti-MoS$_2$ only on the balls performed the best in vacuum. The durability of the Ti-MoS$_2$ coatings is ~2 times greater in vacuum than in humid (40%–45% RH) air. While the vibration threshold of tests conducted in the humid air environment indicates the onset of adhesive wear, the vibration threshold of the tests of Ti-MoS$_2$ balls against uncoated rods in the vacuum tests correlates with the onset of pitting fatigue of the M50 rods. Although adhesive wear appears to initiate in the humid air experiments after the supply of Ti-MoS$_2$ to the interface is exhausted, Ti-MoS$_2$ is still partially present on the balls after the pitting initiates on the M50 rods in the vacuum tests.
In this work, the torque and endurance of Ti-MoS₂ films are measured and the effect of sputter-deposited Ti-MoS₂ as a solid lubricant is studied in rolling contact for the first time. The Ti-MoS₂ films in this study are amorphous, contain about 16% Ti and are slightly sub-stoichiometric in sulfur.

4.10 Chapter Summary

The tribological behavior of the Ti-MoS₂ films examined in this study is in excellent agreement with previously published reports on unidirectional and reciprocating sliding contact, exhibiting low friction and wear rates at both 25°C and 100°C in POD and HFRR tests. Microstructural changes observed to occur in the Ti-MoS₂ wear tracks and transfer films on steel counter-faces are attributed to tribological mechanisms.

Thrust bearing and five ball-on-rod testing in humid environments demonstrates that the effectiveness of Ti-MoS₂ as a solid lubricant is dependent upon the amount of material that can participate in the contact. While Ti-MoS₂ is present in the contact, it appears to be a barrier to adhesive wear in the humid air experiments. On the other hand, Ti-MoS₂ films on balls do not become completely exhausted in the vacuum experiments and are still partially present at the onset of pitting fatigue of the M50 rods. As a solid lubricant on bearings in humid air environments, Ti-MoS₂ films should be applied to raceways and rolling elements to postpone the onset of adhesive wear. However, Ti-MoS₂ films on rolling elements should be sufficient only for bearings operating in vacuum environments.
CHAPTER V

INVESTIGATION OF MICROSTRUCTURE EVALUATION AND TRIBOLOGICAL PERFORMANCE OF Sb$_2$O$_3$/Au DOPED MoS$_2$

5.1 Introduction

The demand for environmentally robust and adaptable coatings to mitigate friction and wear in different environments is continuously increasing [59,125–127], and numerous studies have been performed to evaluate the tribological and mechanical properties of solid lubricants [6,35,37,39,58,59,112,113,125,127–129]. Among solid lubricant coatings, transition metal dichalcogenides (TMDs) such as MoS$_2$ and WS$_2$ have been studied extensively due to their excellent lubricity in vacuum, dry or inert environments [4,6,37,39,58,59,112,113,128]. TMDs include MX$_2$ materials where M is a metal (W, Mo) and X is a chalcogenide (S, Se). M and X atoms in TMDs are held by strong covalent forces in a prismatic arrangement, and layers are held by weak van der Waals forces [37].

Anisotropy in the MoS$_2$ structure results in easy shearing of stacked basal planes and provides a low-friction interface. The tribological performance of MoS$_2$ depends upon conditions that include film morphology, temperature, presence of contaminants, environment and contact pressure [49,59,71,82,85,120,124,128,130,131].
It is well known that the humidity alters the tribological performance of MoS$_2$ and it is believed that the adsorption of moisture inhibits the ease of basal plane shearing and elevates friction [37].

Doping with metals and oxides is reported to improve the friction performance of MoS$_2$ in humid environments [6,61,65,80,85,131]. Dopants not only improve the friction coefficient, but also increase the hardness, density and oxidation resistance of the films [59,70,131]. Ti, Au and Sb$_2$O$_3$ are dopants that have been reported to improve the tribological performance of MoS$_2$ [6,59,85,114,131,132].

Sb$_2$O$_3$/Au-doped MoS$_2$ and Ti-doped MoS$_2$ are two specific MoS$_2$-based films that have come to be employed in various applications [7,59,85,117]. The presence of Au and Sb$_2$O$_3$ dopants in the MoS$_2$ matrix is credited for imparting oxidation resistance, wear resistance, reduced porosity, and an increase in coating density and hardness [59,70,85,131]. The lubrication mechanisms of doped and undoped MoS$_2$ are similar, since both incorporate the formation of transfer layers on the counterface and the reorientation of MoS$_2$ basal layers parallel to the sliding surface. These two mechanisms are credited with the ability to provide a low-friction interface for both doped and undoped MoS$_2$ [39,59].

The tribological performance of MoS$_2$-based films has been studied often under pure sliding conditions. Sliding tests may be appropriate for exploring the friction and wear mechanisms of coatings, but their results do not always correlate with the tribological performance of the materials in actual mechanical systems. This is especially true for rolling contact bearings. In contrast to pure sliding, rolling elements in bearings typically undergo both sliding and rolling on raceways. Although MoS$_2$ and other solid lubricant
coatings are incorporated in rolling element bearings that operate in vacuum environments, no studies have been reported on the performance of doped MoS$_2$ coatings in predominantly rolling contact.

Therefore, the goal of this work is to deposit Sb$_2$O$_3$/Au-doped MoS$_2$ coatings and evaluate the unlubricated tribological performance under both predominantly rolling and pure sliding contact. Sliding contact tests were performed in ball-on-flat tribometers in both unidirectional and reciprocating motion. Rolling contact performance was examined in unlubricated thrust ball bearings at different loads. Additionally, microstructural examinations were conducted inside and outside the wear tracks on the coated specimens and in the transfer films generated on the uncoated counterfaces.

5.2 Deposition Procedure

Sb$_2$O$_3$/Au-doped MoS$_2$ films were deposited onto AISI 52100 steel specimens in a vacuum deposition system equipped with both radio frequency (RF) and direct current (DC) magnetrons. The RF magnetron was used to sputter a target composed of 82% MoS$_2$, 11% Sb$_2$O$_3$ and 7% Au, and the DC magnetron was used to sputter a 99.99% pure titanium (Ti) target. The Ti target was sputtered to create a Ti bond layer between the steel specimen and the MoS$_2$ composite top layer. Before deposition, steel specimens were degreased in a solvent, ultrasonically cleaned in an alkaline detergent, rinsed in DI water and, finally, dried in hot air. The cleaned samples were mounted onto a specimen holder in the deposition chamber and evacuated to a pressure of 7.5 x 10$^{-3}$ Pa (5.6 x 10$^{-5}$ Torr). Specimens were sputter etched with a pulsed DC bias voltage of -400 V in an Ar partial pressure of 0.63 Pa (4.7 x 10$^{-3}$ Torr). After etching, a Ti adhesion layer of ~100 nm was deposited, followed by a ~800 nm layer from the composite target. The bias voltage during
the deposition of the MoS$_2$ composite layer was kept constant at 60V. Coatings were deposited with an Ar gas flow (purity 99.9%) maintained at 0.83 N-m$^{-3}$-s$^{-1}$ (50 sccm) and 100°C substrate temperature. The coated specimens were allowed to cool before venting the chamber.

5.3 Characterization

Adhesion of the Sb$_2$O$_3$/Au-doped MoS$_2$ coatings to their steel substrates was measured qualitatively by Rockwell indentation and by a Nanovea scratch tester. The scratch test load was increased from 0 to 100 N at a table speed of 4 mm/min. The hardness and elastic moduli of the films were measured using a Hysitron Ti 950 triboindentator at a load control up to 10 µN. Surface topographies of tested and untested specimens were studied using three-dimensional optical interferometry (Zygo New View 7300). A JEOL-JSM5310 scanning electron microscope equipped with XEDS was used for analyzing the tested and untested specimens. A Bruker Senterra Raman spectrometer was used for pre- and post-test analysis of Sb$_2$O$_3$/Au-doped MoS$_2$ coated bearing raceways with an excitation wavelength of 532 nm. Transmission electron microscopy (TEM) was conducted with an FEI Technai F30 operated at 300 KV, and an FEI Helios 650 dual beam SEM/FIB was used to prepare lift-outs (X-TEM) for imaging under transmission electron microscopy. Lift-outs were prepared by first depositing a Pt film by electron beam (e-Pt) then by ion beam sputtering (i-Pt) to protect the X-TEM surface from beam damage. Low-voltage Ga ion beams were used to mill and polish the X-TEM samples.

5.4 Tribological Measurements

CSEM ball-on-disc and PCS Instruments high-frequency reciprocating (HFRR) tribometers were used to perform unidirectional and reciprocating sliding friction and wear
measurements, respectively. Unidirectional sliding measurements were performed at 1.0 GPa Hertzian contact stress in vacuum, dry nitrogen and humid laboratory environments using the ball-on-disc tribometers. These tests were performed for a total of 10,000 cycles at a constant sliding speed of 20 cm-s\(^{-1}\). Reciprocating sliding tests were conducted at 0.8 and 1.0 GPa Hertzian contact stress in air, at 15\%–20\% RH and 45\%–50\% RH and room temperature, and with 100 Hz and 1000 µm stroke length. AISI 52100 steel balls (6 mm diameter and 0.05 µm roughness) were used as counterfaces for both unidirectional and reciprocating sliding tests.

Rolling contact experiments were performed in a thrust bearing tribometer at loads of 800 N, 1600 N and 2400 N. The thrust bearing test assembly is shown schematically in Figure 3.15 (Page no. 55). This tribometer is equipped with the capability to measure torque and temperature in situ. Commercially available 51306 ball bearings in a full complement configuration (i.e., no cage) were used as the test articles in the thrust bearing tribometer. The raceways of the thrust bearings were coated with the Sb\(_2\)O\(_3\)/Au-doped MoS\(_2\) and tested against uncoated 52100 steel balls. These tests were carried out at room temperature, 15\%–20\% RH, and at a speed of 800 rpm. Tests were terminated automatically when the bearings achieved a rotational torque greater than 0.07 N-m.
5.5 Results and Discussions

Figure 5.1 Image showing the Rockwell indentation on the Sb$_2$O$_3$/Au doped MoS$_2$ coated steel substrate. Image confirms that the film has excellent adhesion as no cracks or coating delamination occurred.

Figure 5.2 Images of a micro-scratch test performed on a Sb$_2$O$_3$/Au doped MoS$_2$ film. The images indicate the film has excellent adhesion to the substrate and excellent fracture strength since no delamination or cracking is present.
The total thickness of the Sb$_2$O$_3$/Au-doped MoS$_2$ coating is ~1 µm as measured by the Calotest ball-crater method. The as-deposited coating architecture consists of a ~100 nm Ti bond layer on the steel substrate, a gradient layer of ~100 nm containing a mixture of Ti and Sb$_2$O$_3$/Au-doped MoS$_2$, and a top layer ~800 nm of the Sb$_2$O$_3$/Au-doped MoS$_2$. Rockwell indentation testing indicates that the coating has excellent adhesion to the steel substrate as no flaking and cracking were observed which gives Daimler Benz scale rating of 1 (See Figure 5.1). Scratch test results shown in Figure 5.2 indicate acceptable film toughness as no cracks or detachment were observed between the steel substrate and the coating, even at an applied load of 100 N. A plan view SEM image of the Sb$_2$O$_3$/Au-doped MoS$_2$ is shown in Figure 5.3, exhibiting the surface topography and coating porosity. Although the coating shows some porosity, the porosity is much less than that typically observed in pure MoS$_2$ [59].
Figure 5.4 Plot of hardness as a function of indentation depth of Au/Sb$_2$O$_3$-doped MoS$_2$ on AISI 52100 steel substrate

Figure 5.4 shows a plot of indentation hardness as a function of indentation depth. Six indentations were made for each load from 1 µN to 10 µN and the results shown are an average of these indentations. Hardness is observed to decrease with increasing indentation depth at extremely small depths ($h/t < 0.03$), which could be related to strain gradient plasticity or due to indentation size effects. Hardness is constant at a depth between $0.03 < h/t < 0.05$. The accuracy of these measurements is compromised somewhat due to material pileup along the sides of the indenter.
Figure 5.5 (a) HRTEM and Figure 4(b) HAADF-STEM image of as deposited Au/Sb$_2$O$_3$-doped MoS$_2$ coating

Figure 5.5(a) displays an X-HRTEM image of the Sb$_2$O$_3$/Au-doped MoS$_2$. The nanocomposite coating shows Au nanoparticles of ~2 to 3 nm in an amorphous MoS$_2$-Sb$_2$O$_3$ matrix. It appears that the Sb$_2$O$_3$ is in solution with MoS$_2$ since the structure is completely amorphous with Au nanoparticles homogeneously distributed throughout the coating. The inset in Figure 4(a) shows the selected area diffraction pattern of the coating arising from randomly oriented crystallites of Au. Figure 5.5(b) displays the HAADF-STEM image of the as-deposited coating, revealing a columnar porosity within the composite coating. The bright spots in the image are from the Au particles.
Figure 5.6 Friction plots of Au/Sb$_2$O$_3$-doped MoS$_2$ as a function of sliding cycles in vacuum, air and nitrogen atmospheres.

Figure 5.6 shows the friction curves of the Sb$_2$O$_3$/Au-doped MoS$_2$ tested in the unidirectional ball-on-disc tribometer. Friction measurements are obtained at 1.0 GPa under nitrogen, vacuum and laboratory air atmospheres. Every test completed 8,000 cycles without delamination under all test conditions. Friction coefficients of ~0.04 and ~0.013 are measured in vacuum and air (40% RH) environments, respectively. Friction decreased from its initial state during the first 1000 to 1,500 cycles before achieving a steady-state value. Friction measured in a nitrogen atmosphere (~0.062) falls between traces obtained in air and vacuum; however, intermittent spikes are observed that may indicate the cyclic removal and formation of a low shear surface. The effect of moisture in laboratory air on the friction behavior is consistent with the viewpoint that tribo-oxidation products such as MoO$_3$ are forming and inhibit the easy shearing of the basal layers. The results are consistent with previous studies on the effects of humidity on the MoS$_2$-based coatings [59,124,133,134].
Reciprocating sliding tests performed in air (45%–50% RH and 15%–20% RH) at 0.8 and 1.0 GPa are shown in Figure 5.7. The initial Hertzian contact stress is indicated by arrows on the friction curves. Tests conducted at 15%–20% RH completed 60,000 cycles without wearing through the coating at both 0.8 and 1.0 GPa, although the friction coefficient is 2 times higher in the test performed at 0.8 GPa than in the test performed at 1.0 GPa.
1.0 GPa. Lower friction at higher loads is typical for solid lubricants such as MoS$_2$, which do not follow Amontons’ first law (friction is independent of load).

The load-dependent friction behavior of MoS$_2$ films has been studied by several groups [124,131,135], and the decrease in friction with increasing load has been attributed to shear-driven reorientation of (0002) MoS$_2$ basal planes that align with the sliding direction. As shown in the TEM investigation, the as-deposited Sb$_2$O$_3$/Au-doped MoS$_2$ coatings are amorphous and exhibit no basal plane orientation. So, if shear forces are driving a basal plane orientation in these films, it appears that the same forces may first be driving some degree of MoS$_2$ crystallization. The mean friction coefficients measured at the higher-humidity condition in the 0.8 and 1.0 GPa tests are both ~0.14, a result consistent with expectations from Amontons’ Law. The higher-humidity environment may be opposing the shear-induced basal-plane orientation of the MoS$_2$ mechanism in this material. Since the HFRR test conducted at 1.0 GPa (45%–50% RH) was able to attain only 50,000 cycles before steel-on-steel contact initiated, humidity is also increasing the wear rate of the coating.
Figure 5.8 Wear track analysis of HFRR wear track of Au/Sb$_2$O$_3$-doped MoS$_2$ in 40%–50% RH and 15%–20% RH and at 0.8 GPa and 1.0 GPa.

Figure 5.8 shows cross-section profiles of the wear tracks tested at different humidity levels and contact stresses. These wear profiles indicate that the wear rates increase with both load and humidity. Whereas the coating survived 60,000 cycles at 1.0 GPa contact stress at lower humidity, the coating was completely worn through by 50,000 cycles at higher humidity. The wear track profiles indicate that the 0.8 GPa, test wore about ~650 nm of material while the 1.0 GPa test removed about ~800 nm of coating when tested at 15%–20% RH.

5.5.3 Microstructural Analysis

In order to elucidate the change in microstructure after tribological testing, X-TEM and XEDS analyses were performed at site-specific areas. TEM performed on the HFRR wear tracks formed in the 0.8 GPa, 15%–20% RH test is shown in Figure 5.9. Figure 5.9(a) reveals that the coating architecture has been tribologically altered during the testing.
Evident in the figure are the 52100 substrate, the Ti adhesion layer and the Sb₂O₃/Au-doped MoS₂ layer that all appear in the as-deposited material. Also present are two new layers, one layer containing mostly Au and a top layer containing a mixture of Au and MoS₂. About ~150 nm of the Sb₂O₃/Au-doped MoS₂ layer remains after completing 60,000 cycles.

Figure 5.9 (a) HRTEM image of HFRR wear track of Au/Sb₂O₃-doped MoS₂ tested at 0.8 GPa and 15%–20% RH; (b), (c), (d) higher-magnification images of the top surface showing the Au agglomeration and 2H-MoS₂ basal layers.

Figures 5.9(b–d) explore the mechanically mixed layer in greater detail. Au precipitates in the Sb₂O₃/Au-doped MoS₂ are clearly visible. The mechanically mixed top layer is composed of oriented 2H-MoS₂ basal layers, Au nanoparticles and amorphous MoS₂-Sb₂O₃. TEM examination reveals that shear-induced crystallization and an
orientation of the MoS$_2$ basal planes have taken place, as well as an agglomeration of Au particles near the top surface. Long-range order crystalline planes are seen, along with oriented MoS$_2$ basal layers. This observation is consistent with the shear-induced orientation mechanism proposed to explain decreasing friction with increasing load in MoS$_2$-based films. Local surface temperatures in the contact zone may help drive the diffusion and agglomeration of Au. These tests were conducted at high contact stress and high sliding speed (100 cycles per second), so local surface temperatures may be sufficient to initiate the diffusion of the gold particles through the MoS$_2$/Sb$_2$O$_3$ matrix. An increase in surface temperature may also increase the Au agglomeration due to an Ostwald ripening effect [131].

In addition to Ostwald ripening, another phenomenon has been proposed by Scharf et al. to explain the friction-induced coarsening of Au nanoparticles in Sb$_2$O$_3$/Au-doped MoS$_2$ [59]. According to this phenomenon, hard particles in a soft amorphous matrix tend to diffuse toward the surface because of a pronounced mechanical mixing and motion development during vorticity. Furthermore, highly strained areas at the point of contact are believed to give rise to large Au clusters.

The coarsening of Au particles may provide a load support for the reorientation of the MoS$_2$ basal layers. The mixed layer is composed of Au nanoparticles surrounded by MoS$_2$ basal layers. A higher-magnification image in Figure 5.9 shows the MoS$_2$ transformation from an amorphous to a crystalline structure above the Au layer.
The role of Sb$_2$O$_3$ in the MoS$_2$ matrix may bear similarities to that of Ti as a dopant in Ti-MoS$_2$ coatings [132]. Specifically, the incorporation of both Ti and Sb$_2$O$_3$ in MoS$_2$ films results in densification, increased hardness, decreased columnar morphology and reduction in crystallite size. All of these attributes contribute to a reduction in friction and wear over undoped MoS$_2$. An additional benefit of Sb$_2$O$_3$, like titanium, is that it may act as an oxygen getter to increase coating lifetime in humid environments [69,136]. Furthermore, Sb$_2$O$_3$ may act as a thermal and diffusion barrier and provide mechanical support to MoS$_2$-enriched surfaces [69,70]. Although the location of Sb$_2$O$_3$ in the matrix could not be ascertained from the current TEM measurements, hypotheses have been advanced that the Sb$_2$O$_3$ resides either between the MoS$_2$ planes (as an intercalant) or at the Au grain boundaries [68–70,85].

Figure 5.10 displays an XEDS spectrum and HADDF-STEM image from a wear scar formed during the 0.8 GPa, 15%–20% RH HFRR test. Four XEDS measurements...
were made at different locations inside the wear scar, and two spectra are shown here from locations indicated by the arrows. The spectrum from Region 1 (with no Au presence) exhibits mainly Mo and S peaks with a few Cu and Sb peaks. The Cu signal is associated with the TEM grid. Region 2, located near an Au nanoparticle, has Mo, S and Au as the dominant peaks. This result is consistent with the hypothesis that Sb$_2$O$_3$ resides at the Au grain boundaries. The presence of Sb in the mechanically mixed layer may indicate that Sb$_2$O$_3$ could also function as a lubricant. Sb$_2$O$_3$ has a high-temperature orthorhombic phase (valentinite, D$_{5h}$/Pccn) consisting of Sb-O–Sb-O chains linked by oxide bridges between Sb centers. Moreover, valentinite is a soft oxide with a low shear strength and the capability to deform at low temperatures. Therefore, it may also act as a lubricant when deformed as a sheet-like structure [68,69].

Figure 5.11 HRTEM images of transferred material on AISI 52100 steel counterface revealing the 2H-MoS$_2$ basal layer orientation in the transfer film.

Figure 5.11 shows an HRTEM image obtained from a transfer film formed on the steel counterface during the HFRR 0.8 GPa, 15% - 20% RH test. The transferred material
consists of 2H-MoS$_2$ basal layers aligned parallel to the surface. The sliding between basal plane-oriented material on the counterface and inside the wear track on the disc may account for the low friction and wear during the test. The formation of basal plane-oriented MoS$_2$ on the counterface has been previously reported to result from interfacial shear between contacting surfaces, thereby providing low friction and wear interfaces [39,59,86].

Based upon these experimental results, the lubrication mechanism of Sb$_2$O$_3$/Au-doped MoS$_2$ coating in sliding contact may be summarized as: (1) an increase in film endurance and load-bearing capacity with doping of Au and Sb$_2$O$_3$; (2) coarsening or agglomeration of Au particles near the top surface that may provide a support for the orientation of MoS$_2$ layers; (3) shear-induced orientation of 2H-MoS$_2$ basal planes in the wear track parallel to the sliding surface; and (4) transfer film formation on the counterface leading to basal plane sliding between the contacts.

5.6 Rolling Contact Measurements

Rolling contact tests were performed on Sb$_2$O$_3$/Au-doped MoS$_2$-coated raceways of thrust ball bearings. Figure 5.12(a) shows the torque and temperature profiles of the coated bearings. Three stages in the bearing torque signature based upon the current operating conditions are shown in Figure 5.13. These stages are: (a) an initial run-in period; (2) a steady-state period; and (3) the failure period. The initial run-in period lasts for ~4,000 to 5,000 cycles, during which time the initial torque is high but decreases and becomes stable after a few thousand cycles. In the steady-state period, the torque remains stable for long durations and the coating provides good lubrication performance. In the failure stage, the bearing torque starts to increase gradually, coinciding with the end of the coating’s lubrication functionality. The bearing temperature profiles correlate with the torque –
specifically, bearing temperature remains constant during the steady-state period but rises sharply during the failure period. All tests showed the three stages in the torque profile with the longest being the steady-state period.

Figure 5.12 (a) Characteristic torque regimes of coated thrust ball bearings and (b) longevity of bearings at different load conditions
Figures 12(a) and (b) show, respectively, the torque profile and average longevity of the coated thrust bearings as a function of load. Bearings operating with lower contact stress are able to operate longer than bearings operating at higher contact stress, and a linear relationship is observed to exist between load and longevity.

Figure 5.13 Torque measurements of a thrust bearing with coated bearings during (a) run-in, (b) steady state and (c) failure period

Table 5.1 shows the torque and longevity at various loads. Bearing torque is observed to be directly proportional to the load and life cycles where 0.035 N-m, 0.056 N-m, 0.077 N-m and 0.084 N-m were measured at 800, 1600, 2400 and 3400 N loads, respectively. The measured torque increases linearly with the applied load and exhibits a direct relationship to the longevity of the coated bearings.
Table 5.1 Test load and corresponding torque, number of cycles and temperature

<table>
<thead>
<tr>
<th>No.</th>
<th>Load (N)</th>
<th>Mean Torque (N-m)</th>
<th>Number of Cycles (K)</th>
<th>Final Temperature (°C )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>800</td>
<td>0.035</td>
<td>158</td>
<td>29.4</td>
</tr>
<tr>
<td>2</td>
<td>1600</td>
<td>0.056</td>
<td>145</td>
<td>30</td>
</tr>
<tr>
<td>3</td>
<td>2400</td>
<td>0.077</td>
<td>72</td>
<td>25</td>
</tr>
<tr>
<td>4</td>
<td>3200</td>
<td>0.084</td>
<td>40</td>
<td>35</td>
</tr>
</tbody>
</table>

Figure 5.14 3-D optical images of an uncoated raceway, a Au/Sb$_2$O$_3$-doped MoS$_2$ coated raceway and the wear track of tested bearing raceway

Figure 5.14 shows 3-D optical images of an uncoated raceway, a Sb$_2$O$_3$/Au-doped MoS$_2$-coated raceway and a tested raceway. The surface topographies of the raceway changed after coating and after testing. The PV and $R_a$ values of the uncoated raceways are 4.367 μm and 0.535 μm, but after coating these values changed to 2.686 μm and 0.337 μm, respectively. Surfaces in the wear track are very smooth with PV = 1.07 μm and $R_a$ = 0.14 μm.
Figure 5.15(a) SEM image showing the wear track on the bearing raceway; (b) high-magnification image from the center of the wear track showing shearing of MoS\textsubscript{2} layers.

Analysis of coating wear on the thrust bearing raceways indicates that the formation and removal of transfer films on the balls is the main lubricating mechanism. The transfer of material from one surface to another is attributed mainly to adhesive and ploughing wear mechanisms. Material tends to accumulate from the wear track onto the ball surface and sloughs off, and then the cycle starts again. At the end of testing, very little coating remains inside the wear track on the raceways or on the balls.

Microstructural changes occurring in the coating on the raceway wear track were investigated with Raman spectroscopy using a 532 nm excitation wavelength and an aperture size of 50 \(\mu\)m. Figures 16(a) and (b) show a spectrum of the as-deposited Sb\textsubscript{2}O\textsubscript{3}/Au-doped MoS\textsubscript{2} and a spectrum from the center of the tested bearing raceway. The as-deposited spectrum shows no characteristics of either crystalline MoS\textsubscript{2} or Sb\textsubscript{2}O\textsubscript{3}, which is consistent with the amorphous structure of the coating as ascertained by TEM. Features at 408 cm\(^{-1}\) and 202 cm\(^{-1}\) are visible in the spectrum of the as-deposited coating and have been attributed to vibrations from MoS\textsubscript{2} [40] and Sb\textsubscript{2}O\textsubscript{3} [27], respectively. Other features in the spectrum have not yet been identified.
The spectrum of the coating on the tested bearing raceway shows numerous features consisting of both first- and second-order bands. Features around 383 cm$^{-1}$ and 408 cm$^{-1}$ are consistent with the in-plane E$_{2g}$ and out-of-plane A$_{1g}$ vibrations of MoS$_2$, respectively [70,137]. Sb$_2$O$_3$ first-order bands are also visible at 191 and 256 cm$^{-1}$ [70]. Features at 526 cm$^{-1}$ (E$_{1g}$+LA(M)) and 650 cm$^{-1}$ (A$_{1g}$+LA(M)) correspond to second-order MoS$_2$ vibrations [137]. Raman analysis indicates that the amorphous as-deposited coatings become more ordered under applied load and stress cycles. The pronounced post-test features of MoS$_2$ and Sb$_2$O$_3$ in the spectrum of the coating also indicate that the mechanically mixed surface is composed of both MoS$_2$ and Sb$_2$O$_3$.

![Raman spectra](image)

Figure 5.16(a) Raman spectrum of as-deposited Au/Sb$_2$O$_3$-doped MoS$_2$ coating on bearing raceway; (b) Raman spectrum of a coating on the tested raceway taken at the center of wear track

5.7 Chapter Summary

The current work on Sb$_2$O$_3$/Au-doped MoS$_2$ is focused on studying the microstructural evolution, lubrication mechanisms and durability that the coating provides to thrust ball bearings. Evaluation of bearing test data reveals that the longevity of these coated bearings in unlubricated testing is directly proportional to the contact stress and the amount of coating material present. Based upon the results of the sliding contact
experiments, it appears that the material does not obey Amontons’ Law in low humidity due to thermally and mechanically driven microstructural changes occurring in the coating. As load is increased, the coating becomes more crystalline, and MoS$_2$ basal planes orient parallel to the raceway surface. In ball bearing testing, the coating also appears to undergo microstructural changes in the raceway and in the transfer films formed on the balls.

This observation is consistent with results reported by Scharf et al. where load-dependent orientation of WS$_2$ was observed on the counterfaces in rolling contact [136]. However, there is no extended opportunity for basal plane-on-basal plane shearing, since the balls precess on the raceways during operation. So, although the shear-induced crystallization and basal plane orientation of MoS$_2$ may be occurring in the predominantly rolling contact of the thrust ball bearing testing, this attribute does not appear to contribute to the functionality of Sb$_2$O$_3$/Au-doped MoS$_2$ as a solid lubricant in rolling element bearings. Bearing torque increases with load (consistent with Amontons’ Law), and the coating’s ability to function as a solid lubricant in bearings scales inversely with load and depends upon the amount of coating on the raceway.

Finally, based upon the results of this study, we can conclude that sliding contact experiments on this coating provide no direct correlation to how this material performs in rolling element bearings.
CHAPTER VI

AN ATOM PROBE TOMOGRAPHY INVESTIGATION OF Ti-MoS$_2$ AND MoS$_2$-Sb$_2$O$_3$-Au THIN FILMS

6.1 Introduction

Transition metal dichalcogenides such as molybdenum disulphide (MoS$_2$) and tungsten disulphide (WS$_2$) have interesting lubrication properties useful in wide range of tribological applications. MoS$_2$ is widely studied due to its low friction and high wear resistance in vacuum and inert environments. In humid environments, MoS$_2$ dangling bonds react with moisture and oxygen which inhibits easy shearing of the MoS$_2$ basal planes. MoS$_2$ doping with metal and oxides improves oxidation resistance while maintaining a low friction coefficient. MoS$_2$ doped thin films are attractive candidates for mitigating friction and wear in challenging operating conditions [59,132,138]. MoS$_2$ based solid lubricants adapt themselves to different environments to enable operation of contacting components in space applications. Mechanical systems in space applications such as satellites and launch vehicles operate in environments where they are exposed to radiation, large temperature (-80° C to 250° C ) and pressure (vacuum to several atmospheres) swings, and variable environments (humid air to vacuum) [1].
Metal or oxide doped MoS$_2$ is tribologically more effective than pure MoS$_2$ when operating in both dry and humid environments [6,7,59]. In particular, Ti or Sb$_2$O$_3$/Au dopants in MoS$_2$ have resulted in successful tribological films that have been incorporated in commercial use [7,132,138,139]. These dopants can lead to increases in coating hardness, and density. They suppress columnar grain morphology and improve oxidation resistance in humid conditions over pure MoS$_2$ films [59,132]. Research into the role of dopants in modifying film properties, suppressing crystalline order and the location of dopants in the MoS$_2$ lattice is ongoing. HRTEM studies has been performed but so far have been unable to resolve the position of dopants in the MoS$_2$ lattice. Hsu et al used XRD and Raman spectroscopy to identify the origin of a Ti signal but could not find concrete evidence of the Ti position [140]. Singh et. al. magnetron sputtered Ti-MoS$_2$ films and characterized them using HRTEM to reveal that the coatings were completely amorphous and had featureless morphologies [132]. Furthermore, no second phase was observed even though the films contain about 16 at.% Ti. Scharf et al and Singh et al studied Sb$_2$O$_3$/Au doped MoS$_2$ coating and observed that the coatings contain Au nano particles in amorphous matrices of Sb$_2$O$_3$ and MoS$_2$[59,139,141]. It was observed that MoS$_2$ forms a solid solution with Sb$_2$O$_3$ similar to the Ti dopant in MoS$_2$. The mechanism behind this solubility is unclear but it is believed that the dopants are lying either between the MoS$_2$ basal planes or within the MoS$_2$ crystal structure.

Three dimensional atom probe tomography (3D-APT) is one technique that is capable of resolving the atomic level composition and with near atomic-scale spatial resolution [142–144]. APT uses time of flight mass spectroscopy for elemental identification and generates 3-D chemical maps imaging the distribution of individual
atoms. This technique is used to study thin metal films in semiconductors to investigate composition variations in the structure, segregation in nano crystalline materials and to understand precipitate morphology and evolution in alloy development [145,146]. Thus, the aim of this study is to use atom probe tomography (APT) on Ti doped and Au/Sb$_2$O$_3$ doped MoS$_2$ coatings prepared by magnetron sputtering to determine the elemental distribution, dopant position in the MoS$_2$ lattice, and composition of the MoS$_2$ doped films.

6.2 Experimental Details

Ti-MoS$_2$ and Sb$_2$O$_3$/Au-doped MoS$_2$ films were deposited by magnetron sputtering onto AISI 52100 steel specimens. Steel specimens were degreased in a solvent, ultrasonically cleaned in an alkaline detergent, rinsed in DI water and, finally, dried in hot air before mounting on fixtures in the deposition chamber. Ti-MoS$_2$ films were deposited in a closed-field unbalanced magnetron sputtering system (CFUMS). Two MoS$_2$ and two Ti targets were sputtered with an Ar (purity 99.9%) gas flow maintained at 50 sccm. The total thickness of the Ti-MoS$_2$ film is about 1µm, including a Ti adhesion layer with a thickness ~200 nm.

Sb$_2$O$_3$/Au-doped MoS$_2$ films were deposited in a vacuum deposition system equipped with both radio frequency (RF) and direct current (DC) magnetrons. The RF magnetron was used to sputter a composite target composed of 82% MoS$_2$, 11% Sb$_2$O$_3$ and 7% Au, and the DC magnetron was used to sputter a 99.99% pure titanium (Ti) target. The Ti target was sputtered to create a Ti bond layer between the steel specimen and the MoS$_2$ composite top layer. A Ti adhesion layer of ~100 nm was deposited, followed by a ~800 nm layer from the composite target. For more details about the coatings deposition see references [141,147]
APT specimens were prepared using a FEI Helios Nanolab FIB with an Omniprobe 200 micromanipulator to prepare site specific specimens [148,149]. A thin protective layer of Ni was deposited by ion beam sputtering before preparing FIB specimens. Bar shaped specimens were milled and lifted out and sections were transferred onto standard atom probe silicon microposts. The microposts were then sharpened using annular milling patterns at 30 KV and at 5 KV to produce sharp needle samples with a 50-100 nm tip radius. A Cameca LEAP4000XSi was used to perform the APT analysis. The field evaporation was assisted by pulses with a focused ultra violet (355 nm) laser beam with pulse energies of 40-100pJ per pulse, and a 250-500 kHz pulse repetition rate, at a base specimen temperature of 30K. The atomic species are field evaporated from the surface of the tip with the aid of the pulsed laser. The evaporated atoms are collected and analyzed by means of a spatially resolved time of flight mass spectrometry. Several specimens for both Ti-MoS\textsubscript{2} and Au/Sb\textsubscript{2}O\textsubscript{3} doped MoS\textsubscript{2} were successfully analyzed.

6.3 Results and Discussion

Figure 1 shows X-HRTEM images of both Ti-MoS\textsubscript{2} and Sb\textsubscript{2}O\textsubscript{3}/Au-doped MoS\textsubscript{2} thin films. The total thickness of the Ti-MoS\textsubscript{2} and Sb\textsubscript{2}O\textsubscript{3}/Au-doped MoS\textsubscript{2} films is \(\sim1\ \mu\text{m}\). The architecture for both films consist of an adhesion promoting bond layer on the steel substrate, a compositionally graded layer of Ti and MoS\textsubscript{2}, and a top layer of Ti-MoS\textsubscript{2} or Sb\textsubscript{2}O\textsubscript{3}/Au-doped MoS\textsubscript{2}. The TEM cross-sectional image shows that the Ti-MoS\textsubscript{2} top layer is dense, non-porous and featureless whereas Sb\textsubscript{2}O\textsubscript{3}/Au-doped MoS\textsubscript{2} exhibits columnar morphology. The differences in film structure arise from the two deposition processes involved. Ti-MoS\textsubscript{2} films were deposited by a closed –field unbalanced magnetron sputtering system (CFUMS) which produces dense coating morphologies due to high
energy ion bombardment. A description of the closed field unbalance magnetron sputtering system can be found in the literature [150].

![HRTEM images showing coating architecture of (a) Ti doped MoS$_2$ (b) Sb$_2$O$_3$/Au doped MoS$_2$. Films are composed of adhesion promoting bond layer to the steel substrate, a compositionally graded layer of Ti and MoS$_2$, and a top layer of Ti-MoS$_2$ and Sb$_2$O$_3$/Au-doped MoS$_2$.](image)

Figure 6.1 HRTEM images showing coating architecture of (a) Ti doped MoS$_2$ (b) Sb$_2$O$_3$/Au doped MoS$_2$. (Films are composed of adhesion promoting bond layer to the steel substrate, a compositionally graded layer of Ti and MoS$_2$, and a top layer of Ti-MoS$_2$ and Sb$_2$O$_3$/Au-doped MoS$_2$.)
Figure 3(a) shows the 3D atom by atom reconstruction of the Ti-MoS\(_2\) top layer. The reconstruction is obtained parallel to the film growth direction. S, Mo and Ti atoms are shown as blue green and red, respectively. The shape of the tip changes overtime due to the fact that the tip gets blunt, which increases the voltage leading to an increase in analyzed area. The sample analysis reveals that the Ti, Mo and S atoms are well mixed with no sign of clusters or precipitates. No crystalline features related to a crystalline structure could be observed in the 3D maps, which is in good agreement with the TEM observations that the film is amorphous. The reconstruction map indicates that Ti atoms are uniformly distributed in the MoS\(_2\) matrix and there is no presence of Ti rich clusters or precipitates.

The site specific samples for APT analysis were prepared using FIB milling process described by Thompson et al. [148]. An approximately 100 nm Ni thick layer was first deposited to protect the surface of the sample from ion beam damage in the FIB. Once the protective layer deposited, the area of interest on the sample was milled and lifted out. The bar shaped lift outs were then attached to micro-post and sliced to remove a small area of the long bar. Pt deposition was used to attach the sliced region to the atom probe microtip array. A microtip array is a group of Si posts fabricated on a Si substrate. Once the region of interest was mounted on a microtip, the specific area was first cut to a truncated four sided pyramidal shape with an ion beam (30 Ke-V) and then an annular patterns were used to sharpen the samples. The final step involves a cleanup with low energy Ga ions at 2-5 Ke-V. Needle shaped specimens with tip diameters of ~50 to 100 nm were prepared for APT analysis. A smaller diameter is essential to achieve the required evaporation fields at lower voltage.
Figure 6.2 Images (a)-(f) shows the sequence of steps used for APT sample preparation using a FIB-SEM lift out, mounting and tip sharpening technique.

Figure 3(a) shows the 3D atom by atom reconstruction of the Ti-MoS$_2$ top layer. The reconstruction is obtained parallel to the film growth direction. S, Mo and Ti atoms are shown as blue green and red, respectively. The shape of the tip changes overtime due to the fact that the tip gets blunt, which increases the voltage leading to an increase in analyzed area. The sample analysis reveals that the Ti, Mo and S atoms are well mixed with no sign of clusters or precipitates. No crystalline features related to a crystalline structure could be observed in the 3D maps, which is in good agreement with the TEM observations that the film is amorphous. The reconstruction map indicates that Ti atoms are uniformly distributed in the MoS$_2$ matrix and there is no presence of Ti rich clusters or precipitates.
Figure 6.3 (a) Three dimensional tomographic reconstruction of the Ti-MoS$_2$ layer. (S, Mo and Ti are shown in blue, green and red color, respectively) (b) Corresponding concentration profile along the long axis of the reconstruction, which corresponds to the growth direction of the film. (c) Tomographic reconstruction of Ti distribution in the Ti-MoS$_2$ film.

The mass spectra obtained for Ti-MoS$_2$ film was somewhat complex as there was a high percentage of multiple events (more than one ion is detected from a single laser pulse) for this sample. The multiple events can lead to reduced compositional accuracy.
The analyses were conducted at lower temperature to cause a lower partial overlap of the peaks for the various molecular ions. The 1-D concentration profile as a function of distance integrated over the cross-section of the sample is shown in Figure 3(b). Both the concentration profile and distribution analysis by radial distribution functions and concentration frequency distribution analysis suggest that the elemental distribution of the constituents is completely random. The concentration of Mo, S and Ti is constant with depth in the film and there are no local significant variations of the concentrations of either of Ti, Mo and S along the investigated length of ~ 180 nm. A trace amount of nitrogen impurity is also present but not shown here. The film contains about 30 at.% Mo, and 50 at.% S which is indicative that the films are sub-stoichiometric in sulfur. This result corresponds well with earlier measurements conducted on the film [141]. The Ti concentration profile does not indicate a formation of layered structure even though during the deposition, substrates were sequentially passed in front of MoS$_2$ and Ti targets. Figure 3(c) shows the atomic distribution of Ti inside the MoS$_2$ matrix. The uniform distribution of Ti visualizes that there are no precipitates and the Ti is in solid solution with the MoS$_2$.

Figure 4 (a) presents a 3-D atom map showing about 100nm of the top Ti-MoS$_2$ layer, about 400nm of the gradient layer and about 100nm of the Ti adhesion layer. For excellent tribological behavior, strong adhesion between film and bond layer is required with appropriate morphology. Gradient layer provides a strong bonding between the top layer and the Ti layer, to prevent coating delamination at the interface under high shear stresses and load conditions. The image shows about 20 nm of the top layer where the Ti concentration is less than 20%. Below that layer, the Ti composition increases and reaches 90% at the adhesion layer. Composition of Ti, Mo and S is presented using red, green and
blue colors, respectively. 3-D maps show that with an increase in Ti concentration, columnar grains begin to appear towards the end. No grains are discernible until the concentration of Ti reaches a certain limit. Figure 4 (b) shows the 1-D concentration profile traversing from left to right the top layer, the gradient layer and the adhesion layer. The first ~100 nm of the film shows the concentration of top layer, followed by about 400 nm of gradient layer and ~ 150 nm of adhesion layer. The gradient layer is useful for tribological application under high stress and shear conditions to not delaminate or crack at the top layer.
Figure 6.4 APT 3D tomographic reconstruction and analysis of combined Ti-MoS$_2$ top layer and gradient layer (a) 3-D atom map showing about 100nm top Ti-MoS$_2$ layer, about 400nm gradient layer and about 100nm adhesion layer (b) 1-dimensional concentration profile along the growth direction (c) Distribution of Ti atoms throughout the investigated stack.
The cross-section from the bottom of the analyzed stack is shown in Figure 5. The cross-section illustrates the columnar morphology of the Ti adhesion layer. Furthermore, grain boundaries are clearly visible and concentration profiles of the specimen confirmed that the boundaries contain oxygen (~4 at. %) and carbon (~ 1 at. %) impurities. Since Ti has a tendency to form molecular ions, compound ions such as TiC, TiO, TiO2 were observed in the mass spectrum. Atomic O ions produce a peak at 16 amu in the mass spectrum. Since Ti can evaporate as a triply charged ion, Ti3+, a statistically significant distinction between 48Ti3+ and 16O+ can be made only if this peak is large enough to observe the other 4 isotopes of Ti (46Ti3+, 47Ti3+, 49Ti3+, 50Ti3+). Similarly, (48Ti16O)2+ overlaps with (16O2)+ at 32 amu peak position. Observation suggested that small O contents preferably evaporate as molecular ions. A lower limit of the oxygen concentration with good fidelity can be estimated by taking into account only the peaks in the mass spectrum that can be identified in this way without ambiguity. Titanium’s affinity to impurities is useful such as O and C is well known and purposefully used e.g. in removing unwanted impurities from the chamber before deposition of top layer in a gettering process.
Figure 6.5 A slice through the 3D APT tomographic reconstruction in cross-section from the bottom of the analyzed stack (Figure 5) in the Ti adhesion layer.

The APT specimens prepared from the Sb$_2$O$_3$/Au doped MoS$_2$ film tended to fracture during analysis due to lower film density as shown in TEM image (Fig 2), even though less forceful APT experimental conditions (Temperature 30K, evaporation rate; 0.2-0.5% ion/pulse, repetition rate; 500KHz, laser energy; 50pj) were chosen to minimize fracture. However, atom probe tips prepared in the vicinity of the gradient layer were successfully analyzed. Figure 6 (a) shows the 3-D map of the top 20nm Sb$_2$O$_3$/Au doped MoS$_2$ top layer, about 100 nm gradient layer and about 5nm Ti adhesion layer. S, Mo, Ti, Au, Sb are shown in blue, green, red, gold and cyan colors, respectively.

The atom map from the Figure 6(a) indicates that the atoms are well mixed on a larger scale. Figure 6(b) is a concentration profile for Ti, S, Au, and Sb along the depth
direction of film. Fig 6(c) shows the distribution of Ti atoms in the gradient layer. Au atoms are found to be clustered in small Au rich particles which were identified with a cluster finding algorithm in the data analysis software (IVAS). The distribution of these gold-rich particles inside the Sb$_2$O$_3$ and MoS$_2$ matrix is shown in Figure 6(d). Sb and O enrichments are detected, which are preferentially located at the surfaces of these small Au-rich clusters. The concentration profile Fig. 6(b) of the analyzed sample provides detailed and quantitative information of the overall elemental distribution in the top and gradient layers.

Owing to the tendency of the amorphous alloys to evaporate in an irregular pattern, the reconstruction is hampered by atomic density fluctuations. Due to the difference in the evaporation fields of different chemical environments, certain local magnification and trajectories overlap effects can occur, which may result in artifacts. However, the artifacts do not significantly influence the compositional information of the sample [151]. In addition, the preferential evaporation of certain elements can also result in reconstruction artifacts.
Figure 6.6 (a) 3D Atom by atom tomographic APT reconstruction of the Au/Sb2O3 doped MoS2 film showing the uniform distribution of atoms; (b) a concentration depth profile along the growth direction.
Figure 6.7 (c) Ti concentration distribution in the investigated stack; (d) 2-D projection showing the Au clusters in the film after filtering with a cluster-identification algorithm.
Cluster ions with multiple atoms can be formed in laser assisted APT analysis which makes the analysis of the mass spectra more complicated. Isheim et al. reported that the formation of Mo₂ dimers with 15 different combined isotope weights, considering the seven stable Mo isotopes with mass numbers 92, 94, 95, 96, 97, 98 and 100 and the permutations in diatomic clusters [152]. They also observed triply charged diatomic Mo₂ cluster ions in their experiments. It is important to consider here that the presence of complex ions requires careful analysis of the mass spectrum in addition to monoatomic and diatomic more complex ion species with different elements can possibly be observed.

6.4 Chapter Summary

Ti doped MoS₂ and Sb₂O₃/Au doped MoS₂ films were sputter deposited using magnetron sputtering. TEM revealed that the Ti doped MoS₂ is dense, incoherent and has an amorphous structure while Sb₂O₃/Au doped MoS₂ has a lower density and a columnar structure.

- APT analysis on the Ti-MoS₂ film showed that there is homogeneous distribution of Ti in the MoS₂ matrix and there are no regions of high Ti concentration or Ti clustering.
- Concentration profiles confirmed that composition is uniform throughout the analyzed top Ti-MoS₂ layer. Analysis on the gradient layer showed the formation of columnar grains as the Ti concentration approached above 80 at. %.
- Sb₂O₃/Au doped MoS₂ films also showed homogeneous elemental distribution throughout the MoS₂ matrix along with Au clusters.
In conclusion, results show that there is uniform distribution of Ti atoms but it is difficult to ascertain the exact configuration of the coordination polyhedral of dopant atoms in the amorphous film from APT data.
CHAPTER VII
TRIBOLOGICAL PERFORMANCE OF HIGHLY HYDROGENATED DIAMOND LIKE CARBON COATINGS IN MIXED SLIDING AND ROLLING CONTACT

7.1 Introduction

Wind energy is a promising and fastest growing power generation source [153]. An increase in the number of utility scale wind plants have increased the focus on the high operation and maintenance costs of wind turbines as these ultimately impact the cost of wind energy [154,155]. The drive train and actuators of wind turbines are major sources of failures arising from the variability of wind, torque reversals, fluctuation in energy demands, misalignment, and harsh environment conditions [156]. Bearings and gears in wind turbine drive trains suffer from failure modes like micropitting, scuffing, spalling, and smearing [10,157], although these elements were designed to meet twenty year service lives assuming that proper lubrication and maintenance practices, and especially no unusual loads were encountered. If a bearing has a low concentration of non-metallic inclusions in the steel, operates at the designed contact stress, and maintains an adequate lubricant film thickness in the contact, then end of service life will be due to sub-surface originated spalling [158].
Surface originated fatigue or pitting is caused by surface or near surface stress risers such as non-metallic inclusions, plastically deformed material, martensite transformation products, or several other factors. A particular type of surface initiated fatigue is known as micropitting which is a common failure mode encountered by gears and bearings [12]. Specifically, many main shaft spherical roller bearings in wind turbines are life limited due to spalls arising from micropitting wear [8]. Micropitting is associated with the initiation and propagation of micro-cracks in the direction of traction forces. The progression of micro-pits alters the surface profile of a bearing raceway or gear tooth which generates regions of large stress concentrations. The increase in localized stresses leads to fatigue failure through the formation of macro-pits or spalls. Micropitting is affected by several factors such as lubricant type, contaminants, temperature, contact stresses, hardness, sliding speed, and surface roughness [159].

Studies were carried out over the last few decades to understand the mechanism of micropitting. According to Morales-Espejel and Brizmer, micropitting depends on the lubrication conditions and roughness of the contacting surfaces, the presence of slip (between 0.5 and 2%), and the associated boundary friction shear stress are required for the generation of micropitting [160]. Oila and Bull suggested that contact stress has the greatest impact on micropitting initiation, while the progression of micropitting is affected mostly by speed and slide to roll ratio [159]. Lubrication conditions are best quantified by the parameter \( \lambda \), which is the ratio of the lubricant film thickness to the square root of composite surface roughness. Operating temperature, viscosity, and operating speed all affect the lubricant film thickness and hence \( \lambda \). Brechet et al reported that oils with antiwear and extreme pressure additives that are used to prevent scuffing and wear can
promote micropitting [161]. Micropitting has proven to be difficult to eliminate through lubricant chemistry alone.

A number of solutions have been suggested to mitigate micropitting. Super-finishing is a process used on gear teeth to increase load bearing area and reduce the severity of asperity interactions in boundary lubrication (i.e., $\lambda < 1$) [13]. Apart from super-finishing, other surface engineering techniques are also employed to reduce asperity contact and provide barriers to wear [14]. Physical vapor deposition (PVD) coatings composed of nitrides, sulfides and carbides were examined for their ability to prevent micropitting [15,16]. PVD coatings can be very effective at reducing or eliminating many wear modes [17]. Among these coatings, diamond like carbon (DLC) coatings are now being used in numerous applications for wear resistant purposes due to their desirable tribological performance [18]. DLC has been modified over the years to possess ultra-low friction and high wear resistance. DLC coatings can be doped or alloyed to increase their functionality. The properties (hardness, toughness, thermal stability) of DLC coatings are further increased by using novel coating architectures that consist of nanocrystalline precipitates and nanosized multilayers [89]. Hydrogen-free DLC coatings deposited from solid carbon targets can be extremely hard, while hydrogenated DLCs are usually much softer. In this research, coatings having indentation hardness values greater than 10 GPa are referred to as hard coatings, while coatings with indentation hardness values less than 10 GPa are referred to as soft coatings. Precursor hydrocarbon gases such as methane and acetylene are typically used in the deposition of DLC that contain large amounts of hydrogen. Hard DLC have been shown to be very successful at mitigating many wear issues encountered by bearings and gears operation in boundary lubrication, including
micropitting [19,162]. Surface treatments such as black oxide and phosphate conversions are also applied to bearings and gears to address micropitting [19–21]. These conversions are thick, sacrificial layers that work to rapidly break-in the surfaces of the components, reducing asperity contact, and delaying the onset of micropitting. Most of the studies reported on exploring the use of DLC to mitigate micropitting prevention were carried out with hard DLC coatings. Few if any studies were performed using soft DLC coatings.

In this research, a soft highly hydrogenated DLC coating was sputter-deposited on rings and roller specimens, and the tribological performance of the coated specimens was evaluated in a micropitting rig. Four different material pairs were tested in a polyalphaolefin (PAO) base stock oil. The as-deposited and tested specimens were then examined using optical microscopy and Raman spectroscopy in an attempt to understand underlying mechanisms.

7.2 Test Apparatus, Material and Test Parameters

A PCS Instruments Micropitting Rig (MPR) was used for testing. MPR test chamber and the arrangement of rings and roller inside the test chamber is shown in Figure 3.18 (Page 58).

The test material used in this study and their properties are given in Table 7.1. The roller had a 10° chamfer on each side of a 1 mm track width as shown in Figure 1c. Rollers and rings were made of AISI 52100 steel and heat-treated to hardness values of 57-60 HRC and 62-65 HRC, respectively. The average surface roughness measured on the ring was about $R_a = 0.3 \ \mu m$ and roughness of the rollers was about $R_a = 0.2 \ \mu m$. Figure 7.1 shows an optical image of the cylindrical roller and the track width prior to testing.
Figure 7.1(a) Steel roller specimen with dimensions, and (b) surface topography and track width of the roller prior to testing.

Table 7.1 Test Material and Properties

<table>
<thead>
<tr>
<th>Specimen Type</th>
<th>Material</th>
<th>Hardness (HRC)</th>
<th>Roughness, µm</th>
<th>Diameter, mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rings</td>
<td>AISI 52100 Steel</td>
<td>63-65</td>
<td>0.2</td>
<td>54.15</td>
</tr>
<tr>
<td>Roller</td>
<td>AISI 52100 Steel</td>
<td>57-60</td>
<td>0.3</td>
<td>12</td>
</tr>
</tbody>
</table>

Table 7.2 Test Parameters

<table>
<thead>
<tr>
<th>Oil</th>
<th>Force, N</th>
<th>Hertzian Stress, GPa</th>
<th>Lambda, λ</th>
<th>Speed, m/s</th>
<th>Slide to Roll Ratio (SRR)</th>
<th>Temperature, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAO4</td>
<td>430 N</td>
<td>1.8</td>
<td>0.36</td>
<td>3</td>
<td>40 %</td>
<td>55</td>
</tr>
</tbody>
</table>

Table 7.2 presents the test parameters used for evaluating the tribological performance of different material combinations. An unadditized polyalphaolefin base stock oil of viscosity grade 4 was used as the lubricant, which was used to eliminate the
contribution of additives on the performance of the coatings and also to ensure that a severe boundary regime was in place. Tests were performed at a 430 N load, 1.79 max. Hertzain contact pressure, 3 ms\(^{-1}\) speed, 40% slide-to-roll ratio (SRR) and at a constant operating temperature of 55º C. The \(\lambda\) values were estimated to be 0.36 which confirms direct metal-to-metal contact.

Rollers and rings were coated with the highly hydrogenated diamond-like carbon (H-DLC) coating. This coating is a variant of the Near Frictionless Carbon coating developed at Argonne National Laboratory [163]. Prior to coating, specimens were ultrasonically cleaned using a solvent and dried in hot air before mounting on fixtures inside the deposition chamber. A pulsed magnetron sputtering system was used for the deposition of the coatings using one carbon target. Prior to deposition of carbon film, a thin (~ 50 nm) Cr adhesion layer was deposited on the surface. The carbon target power was in the range of 1000-2000W and pulsed DC bias of -35 to -50 volts was supplied at 250 KHz. Methane (CH\(_4\)) and Argon (Ar) gas mixtures were maintained at 12 sccm and 70 sccm, respectively. The final carbon coating thickness was in the range of ~ 1 \(\mu m\).

7.3 Characterization and Performance

Rolling element bearings operating in wind turbine gearboxes employ coatings that are either applied only to rolling elements (hard DLC) or both rolling elements and raceways (i.e., black oxide) [21]. The material pairs tested in this study were designed to be consistent with the application of coatings on wind turbine bearing components. The performance of the H-DLC coatings was examined by testing four material pairs: uncoated roller on uncoated rings, H-DLC coated roller on uncoated rings, uncoated roller on H-DLC coated rings, and H-DLC coated roller on H-DLC coated rings. The uncoated on
uncoated pairing was used as the baseline in comparison with the other materials pairs. A value of 1200 Peak/Peak acceleration (vibration) was used as the cut-off limit in the tests to determine the cycles to failure. The 1200 P/P acceleration was a vibration reading from the accelerometer that was placed close to the contact zone and provided a view toward the progression of surface damage. Tests were suspended if the vibration exceeded the cut-off limit or exceeded 100 million contact cycles.

Raman spectra shown in Figure 7.2 were obtained from an uncoated steel roller, and untested H-DLC-coated roller, and the PAO-4 base oil. Both steel and the as-deposited H-DLC show a broad and featureless spectrum that is typical for the materials. The PAO-4 base oil shows a strong characteristic feature at 2800 cm\(^{-1}\) and few small peaks between 1000 cm\(^{-1}\) and 1500 cm\(^{-1}\).

Mechanical properties of the coating were measured by nanoindentation using a Hysitron Triboindenter TI – 950 equipped with a Berkovich diamond probe and loads in the range of 0.5 mN to 12mN. Figure 7.3 shows the nano-indentation measurements on the H-DLC coatings. Nanoindentation measurements revealed that the hardness and elastic modulus values of the coating are about 6 ± 1 GPa and 55 ± 10 GPa, respectively.
Figure 7.2 Raman spectra of (a) Steel roller (b) H-DLC coated roller and (c) PAO base oil

Figure 7.3 Elastic modulus and hardness as a function of indentation depth of the coating
Traction coefficients and P/P acceleration are plotted against contact cycles and are shown in Figure 5 for the four materials pairs. Also shown in the Figure 5 are images of the roller wear tracks from each test. Vertical lines in the plot indicate instances where tests were stopped, the roller surface was inspected, and then the test was restarted. Figure 7.4a shows the measurements obtained from the uncoated on uncoated pairing. Whereas the traction coefficient remained approximately constant at ~ 0.05 through the test, the P/P acceleration trace indicates that surface damage initiated at the beginning of the test and gradually increased until about 28 million cycles. Thereafter, the P/P acceleration rapidly increased and exceeded the cut off limit at about 31 million cycles. The image of the roller surface shows a large amount of damage. A close inspection of the image coupled with the P/P acceleration data suggests that micropits formed rapidly on the roller surface, grew in size, and coalesced to produce an almost continuously damaged surface within the wear track.

Figure 7.4b shows the traction coefficient and P/P acceleration as a function of number of contact cycles on the roller for the H-DLC-coated roller on uncoated rings pairing. This test achieved 100 million cycles without exceeding the P/P acceleration limit. The traction coefficient remained steady at ~ 0.05 for first 40 million cycles and then began to decrease gradually until about 65 million cycles, and then remained steady for the rest of period at ~ 0.035. The P/P acceleration was inversely correlated with the traction coefficient. The optical image of the roller wear track after test termination is shown on right, and the image shows that small regions of the coating delaminated. Since the coating delamination could account for an increase in the P/P acceleration, it is speculated that the
decrease in the traction coefficient may also be associated in some way with the coating delamination.

Figure 7.4 Traction coefficient and P/P acceleration (vibration) as a function of contact cycles on the roller for (a) uncoated roller and uncoated rings (b) H-DLC roller and uncoated rings (c) uncoated roller and H-DLC rings and
Figure 7.5 (a) uncoated roller and H-DLC rings and (b) H-DLC rings and H-DLC roller pairs. Images on the right show surface of roller after testing.

Figure 7.5a shows the traction coefficient and P/P acceleration as a function of number of contact cycles for the pairing of the uncoated roller and H-DLC-coated rings. No changes in the traction coefficient or P/P acceleration were observed in the test. The traction coefficient was measured to be about ~ 0.04 and the P/P acceleration value was ~ 200 after completing 100 million cycles. The image of the uncoated steel roller shown on the right indicates that no micro or macro pits formed during testing and that a tribofilm was generated over a large region of the wear track.
Figure 7.5b shows the traction coefficient and P/P acceleration as a function of number of contact cycles for the pairing of the H-DLC-coated roller and H-DLC-coated rings. The test was suspended after 100 million cycles. The traction coefficient was constant at ~0.04 throughout the test while the P/P acceleration increased slightly after about 45 million cycles from a value of 200 to 300 and remained at this value until the end of test. The image of the wear track on the roller contains a few pits, but no significant damage was observed.

All the tests where at least one surface was coated with the H-DLC lasted for 100 million cycles without experiencing a significant amount of surface damage. Figures 7.6a-d show high magnification topographical images of roller surfaces after testing for (a) uncoated roller on uncoated rings (b) H-DLC-coated roller on uncoated rings (c) uncoated roller on H-DLC-coated rings, and (d) H-DLC-coated roller on H-DLC-coated rings.
Figure 7.6 High magnification optical images of the roller surface after test for (a) uncoated roller and uncoated rings (b) H-DLC coated roller and uncoated rings (c) uncoated roller and H-DLC coated rings and (d) H-DLC coated roller and H-DLC coated rings pairs.
Roller wear was quantified according to a change in width of the roller wear track. An optical microscope was used to measure the track width at multiple locations. Values shown in Figure 7.7 are averages and standard deviations of four measurements of the change in roller track width. The data shown in the figure was normalized based on the number of contact cycles. The calculated track width was divided by the total number of contact cycles after failure or after termination. The total change in width of wear track was below 50 µm in all tests but the uncoated pairing showed the largest change in track width. A clear trend is seen between change in track width and the amount of coating available to participate in the tribological contact. For example, the least amount of coating passing through the contact was for the H-DLC-coated roller on uncoated ring pair, while the largest amount of coating passing through the contact was for the H-DLC-coated roller on
H-DLC-coated ring pair, considering the difference in coated sample surface area. This trend suggests that the wear occurring on the roller depended upon the amount of H-DLC present in the contacts.

![Raman spectra](image)

**Figure 7.8.** Raman spectra of rollers after test completion for (a) uncoated roller on uncoated ring (b) H-DLC coated roller on uncoated rings (c) uncoated roller on H-DLC coated rings (d) H-DLC coated roller on H-DLC coated rings material pairs

Raman spectra obtained on the tested specimens are shown in Figure 7.8. No significant differences are observed from spectrum of the untested roller in Figure 7.2 and the spectrum of the steel roller after testing. The Raman spectrum from the H-DLC-coated roller on uncoated rings pairing shows D and G peaks at around 1332 cm\(^{-1}\) and 1580 cm\(^{-1}\).
, respectively, which are typical of DLCs with high sp$^2$ bond characters [164]. A minor peak around 600 cm$^{-1}$ corresponds to α-Fe$_2$O$_3$ [165] that was probably generated from asperities on the rings. The Raman spectrum of the tribofilm formed on the roller during the uncoated roller on H-DLC-coated ring test shows similar D & G features, a strong peak at 670 cm$^{-1}$ from Fe$_3$O$_4$ or FeO, and minor peaks around 222 cm$^{-1}$ and 298 cm$^{-1}$ from α-Fe$_2$O$_3$ [165]. Since the tribofilm formed on the roller in the uncoated roller on H-DLC coated ring test has similar D & G features in its Raman spectrum as the Raman spectra of the wear tracks from the H-DLC-coated roller on H-DLC-coated ring and H-DLC-coated roller on uncoated ring testing, there is a strong indication that the H-DLC coating undergoes a transition from its initial amorphous hydrocarbon state to disordered graphite within the wear track and then transfers from the coated rings to the wear track on the uncoated roller.

7.4 Discussion

Experimental results showed that the uncoated, steel on steel, material pair failed after 32 million cycles due to excessive surface damage. Large pits were observed on the roller due to damage accumulation and caused the P/P acceleration to exceed the cut-off limit. Based upon the observations of Fajdiga et al., the surface damage on the roller appears to have initiated with micropits, evolved into macropits, that coalesced and formed the continuous surface damage in the wear track [166]. Remarkable reductions in surface damage of the roller were observed when one or both elements were coated with H-DLC. Traction coefficients were ~ 0.04 and remained relatively constant throughout the testing for the three cases where at least one of the contacting surfaces was coated. Furthermore, no failures were observed and the tests were suspended after ~ 100 million cycles. H-DLC
appears to be a promising surface treatment candidate to mitigate fatigue-initiated micropitting wear on surfaces of components operating in low λ ratio rolling and rolling/sliding contacts.

Friction reduction and wear protection are the primary motivations for using coatings on bearings and gears. Surface modifications that use coatings and thin films offer numerous technical advantages over untreated materials. Under boundary conditions in wind turbine drive trains, PVD coatings such as WC/a-C:H, and conversion coatings such as black oxide are widely used on the bearings and gears to improve tribological performance. Although conversion coatings are typically considered to be sacrificial and used primarily to prevent adhesive wear damage during run-in, new evidence has been generated that suggests that black oxide surface treatments on the raceways and rollers of wind turbine gearbox bearings may delay the onset of another failure mode termed white etch cracking [28]. Mahmoudi et al. [20] and Evans et al. [23] reported that black oxide is not an attractive candidate for preventing scuffing wear arising from roller/raceway skidding in highly stressed, low λ environments. Although a hard WC/a-C:H (14 GPa) coating applied to the rolling elements of bearings functioned very well in mitigating micropitting, scuffing, and fatigue life reduction from debris damage [29], fracture-type wear of the coating was observed to occur at high contact stress cycles and ±10% slide/roll ratios [20]. The WC/aC:H coating is believed to provide wear protection by polishing the uncoated mating surface and form a barrier to the adhesive interactions of asperities [29].

Both of these proposed mechanisms have a positive effect on fatigue wear by increasing the λ ratio and transitioning the EHL lubrication regime from boundary to mixed. Fewer investigations have been performed on the abilities of soft coatings to improve fatigue
performance. Moorthy et al compared the rolling contact fatigue performance of a soft Nb-S coating to a hard WC/a-C:H coating [15, 30]. Although the Nb-S coating exhibited no polishing effect during the tests, no significant micropitting was observed. Mutyala et al examined the performance of balls coated with a soft Ti-doped MoS$_2$ and found a significant increase in the rolling contact fatigue life of M50 steel specimens over uncoated specimens [31, 32]. In that study, it was reported that MoS$_2$ from the coating combined with hydrocarbons from the synthetic base oil to form a a-C:H/MoS$_2$ tribofilm on the uncoated M50 rods. It was speculated that this tribofilm was responsible for the significant increase in rolling contact fatigue life of the rod specimen. Clearly soft coatings like Nb-S, Ti-MoS$_2$, and H-DLC must function differently from hard coatings like WC/a-C:H to provide fatigue life improvements to steel components. Furthermore, since black oxide surface conversions do not mitigate micropitting (surface fatigue wear), the soft coatings must also function differently from a soft black oxide.

Based upon the observations gleaned from this study, and previously reported studies on rolling contact fatigue studies of soft coatings, it is speculated here that the H-DLC coating functions similarly to the Ti-MoS$_2$ coating in mitigating surface fatigue. That is, carbon from the H-DLC (and also possibly from the synthetic base oil) forms an amorphous carbon tribofilm containing iron oxide on uncoated steel surfaces during testing. This notion is supported by the Raman spectrum of the tribofilm formed on the uncoated roller (H-DLC ring/uncoated roller pairing) shown in Figure 7.7. The spectrum shows the D and G mode vibrational signature of amorphous carbon. The low friction of the amorphous carbon tribofilm may be sufficient to reduce the magnitude of shear stresses generated on the roller surface during testing. Morales-Espejel and Brizmer point out that
the presence of slip and the associated boundary friction shear stress are required for the generation of micropitting [11]. Lubricant additives or low friction coatings that can reduce boundary friction shear stress should delay or mitigate micropitting. A friction coefficient between 0.001 - 0.005 and wear rates between $10^{-11}$-$10^{-10}$ mm$^3$/Nm have been measured on H-DLC films in vacuum environments [167]. The H-DLC coating has a low friction coefficient that may delay the onset of micropitting and increase fatigue life through a reduction in shear stresses. The low hardness and modulus of the H-DLC resist fracture and delamination of the coating under high contact stress cycles and high slide/roll ratios.

7.5 Chapter Summary

This research evaluated the tribological performance of highly hydrogenated diamond like carbon films in mixed rolling and sliding contacts for bearings and gears in wind turbine drive train. H-DLC films were deposited on cylindrical specimens and compared against untreated samples using PAO4 synthetic base oil as a lubricant. H-DLC coated samples provided significant improvement in mitigating surface fatigue (micropitting) compared to uncoated steel samples. The results concluded from the experimental investigation are as follows:

- Nano-indentation results revealed that the coatings are highly elastic in nature and have hardness values (~ 6 GPa) comparable to that of steel substrate.
- Uncoated steel/steel pairs failed after 32 million cycles whereas no failure was observed with soft-highly hydrogenated diamond like carbon coated test samples up to 100 million cycles.
- Raman analysis showed microstructural transformations of the H-DLC inside the roller wear track.
• Results indicate that coating only one side of the material pair is sufficient to delay the onset of surface fatigue of test rollers by more than 100 million cycles. H-DLC appears to be an effective solution for components that suffer from surface initiated fatigue.

• Further work is needed to evaluate the performance of H-DLC on actual bearings and gears in fully formulated lubricants.
CHAPTER VIII
LUBRICANT ADDITIVE EFFECTS ON THE PERFORMANCE OF Ti AND W
DOPED DIAMOND LIKE CARBON (DLC) COATINGS IN SLIDING/ROLLING
CONTACT

8.1 Introduction

Stringent legislative guidelines to increase fuel economy and reduce air pollution have directed focus towards a significant reduction in vehicle weight. Since the drive train system (i.e. axles and transmission) carries a majority of the vehicle weight, one focus is to develop high power density driveline systems. However, weight and size reduction of drive train systems must not reduce the fatigue life of the components. One way to compensate the loss of material weight is by the development and use of surface engineering (coatings/materials) and improved lubricants[168,169]. Synergism between coatings and lubricants additives is essential for low friction, wear resistance and increasing in fatigue life.

Diamond Like Carbon (DLC) coatings are being used in numerous applications in various fields such as mechanical, biomedical, and electronics [167,170,171]. DLC coatings can be doped or alloyed to increase their functionality. Therefore, a wide variety
of DLCs doped with hydrogen, metals, nitrogen, and carbides have been developed. Due to their high mechanical hardness, and load bearing capacity the use of these coatings in automotive applications has grown dramatically in recent years [172]. In addition, DLC coatings show excellent wear resistance and running in performance[173,174]. Under boundary lubricated conditions, tetrahedrally bonded amorphous carbon coated engine components are reported to have 80% reduction in friction over the uncoated components when tested in lubricants with polar additives [175].

The performance of DLC coatings is affected by temperature and environment. Since DLC’s have poor thermal conductivity, lubricant oils acts as a coolant to conduct heat away from the contacting point and keep the temperature in allowable limit to improve its performnace. On the other hand, lubricant oils containing additives can have both positive and adverse effects on DLC coatings [176–178].

Research on DLC coatings in combination with lubricating oils containing additives is ongoing. Literature available on DLC interactions with lubricant additives is contradictory. Podgornik et al. found no interaction of a DLC coating when tested against fully formulated gearbox oils [173,174]. Kano and Yasuda performed sliding experiments on DLC coatings with engine oil containing EP additives and friction modifiers and found no tribochemical film on the DLC surface [179]. In contrast, DLC coatings were observed to have metal like behavior due to increased surface reactivity with MoDTC and ZDDP additives [180–182]. Gangopadhyay et al. investigated the tribological performance of five different DLC coatings in fully formulated engine oils and reported that the type and composition of the DLC has an influence on film formation [176]. It is interesting to note
here that the reported results are contradictory and there is further need to investigate the DLC/lubricant interactions.

DLC coatings, in particular Me-C:H are used in various automotive components, including drive and power train components [183]. Commercially available transmission gear oils are currently being used in combination with DLC coatings. Gear oils containing extreme pressure (EP), antiwear (AW), and friction modifier (FM) additives were originally designed to work with metallic (Fe based) surfaces which are a cause of concern when used with DLC coatings. The additives are effective only when there is a synergism between the lubricant and the coating. Moreover, drive train systems such as transmissions and axles encounter both sliding and rolling motions. However, the majority of the published studies have reported the performance of DLC coatings with lubricating oils in sliding contact only.

In this study, uncoated gear steel, Ti-DLC coated and W-DLC coated gear steel were tested the fatigue limit in a rolling/sliding contact. Two lubricants; PAO4 synthetic base stock oil and commercial available fully formulated gear oil (FF gear oil) containing S-P additives were used to investigate the tribological performance of the coatings. The purpose of this study was to evaluate the fatigue performance and explore the lubricant interaction mechanism with the metal doped coatings under sliding/rolling contact. Tested specimens were examined under optical microscopy to evaluate the surface topography after failure.
8.2 Materials and Methods

8.2.1 Test Apparatus  
A PCS Instruments Micropitting Rig (MPR) was used for testing. Figure 3.18a shows the MPR test chamber and the arrangement of rings and roller inside the test chamber is shown in Figure 3.18.(On Page 58).

![Figure 3.18](image)

Figure 8.1 (a) Steel roller specimen with dimensions, and (b) surface topography and track width of the roller prior to testing.

In the experiments, three materials pairs were studied; steel on steel, W-DLC on W-DLC and Ti-DLC on Ti-DLC all of which were tested in PAO4 and FF gear oil. The nominal composition and properties of the steel material are given in Table 8.1 and Table 8.2. Rollers and rings were made of 16MnCr gear steel and heat-treated to hardness values of 680 HV and 780HV, respectively. The average surface roughness measured on the uncoated roller and ring was about $R_a = 0.25$ and 0.3, respectively. Figure 8.1b shows an optical image of the cylindrical roller and the track width prior to testing. The roller had a 10° chamfer on each side of a 1 mm track width as shown in Figure 8.1a.
Table 8.1 AISI 5115 Steel Composition, %

<table>
<thead>
<tr>
<th>Steel</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Cr</th>
<th>S</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>16MnCr5</td>
<td>0.13-0.18</td>
<td>0.15-0.35</td>
<td>0.7-0.9</td>
<td>0.7-0.9</td>
<td>0.04</td>
<td>0.035</td>
</tr>
</tbody>
</table>

Table 8.2 Properties of uncoated steel Specimen

<table>
<thead>
<tr>
<th>Specimen Type</th>
<th>Material</th>
<th>Hardness (HV)</th>
<th>Roughness, µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rings</td>
<td>AISI 5115 Steel</td>
<td>780</td>
<td>0.3</td>
</tr>
<tr>
<td>Roller</td>
<td>AISI 5115 Steel</td>
<td>680</td>
<td>0.25</td>
</tr>
</tbody>
</table>

Table 8.3 Test Parameters

<table>
<thead>
<tr>
<th>Force, N</th>
<th>Initial Max. contact Pressure, GPa</th>
<th>Speed, m/s</th>
<th>Slide to Roll Ratio (SRR)</th>
<th>Temperature, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>430 N</td>
<td>1.8</td>
<td>3</td>
<td>40 %</td>
<td>60</td>
</tr>
</tbody>
</table>

Table 8.4 Viscosity of the Lubricants

<table>
<thead>
<tr>
<th>Oils</th>
<th>Viscosity, cSt</th>
<th>Temperature, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>40</td>
</tr>
<tr>
<td>PAO4</td>
<td>17</td>
<td>4</td>
</tr>
<tr>
<td>FF Gear Oil</td>
<td>130</td>
<td>15</td>
</tr>
</tbody>
</table>

The uncoated steel pair was used as the baseline to compare with the other test combinations. A value of 1200 Peak/Peak acceleration (vibration) was used as the cut-off limit in the tests to determine the cycles to failure. The 1200 P/P acceleration was a vibration reading from the accelerometer that was placed close to the contact zone and provided a view toward the progression of surface damage. Tests were suspended if the vibration exceeded the cut-off limit or exceeded 100 million contact cycles.
Table 8.3 presents the test parameters used for evaluating the tribological performance of different material combinations. An unadditized polyalphaolefin base stock oil of viscosity grade 4 was used to eliminate the contribution of additives on the performance and to ensure severe contact was in place (boundary lubrication regime). The drive towards the use of low viscosity grade synthetic oils was another reason for selecting the PAO4 synthetic base stock oil. A fully formulated gear oil (FF gear oil) currently used in automotive transmission system was selected to investigate the additive’s effect on the performance of metal doped coatings. Table 8.4 shows the viscosity of the lubricants used. Tests were performed at a 430 N load, 3 ms\(^{-1}\) speed, 40% slide-to-roll ratio (SRR) and at a constant operating temperature of 60\(^\circ\)C. A three stage ramping process was used to begin the test at the given test conditions. The first stage was a speed ramp from 1 to 3 ms\(^{-1}\) in a one min time interval. The second stage was load ramped from 50 N to 430 N and the third stage was a slide to roll ratio (SRR) ramping from 0 to 40% each in 4 min intervals. The ramping process accounts for about 0.1 million cycles. The traction coefficient and vibration values plotted here are from the tests progressed at actual test conditions. The \(\lambda\) values were estimated to be ~0.4 for PAO4 and ~0.95 for FF gear oil which ensure boundary lubrication regime.

Rollers and rings were coated with metal doped diamond like carbon coatings (Ti-DLC and W-DLC) on AISI 5115 steel (16MnCr5). A closed filed unbalanced magnetron sputtering system was used for the deposition of the coatings. Prior to coating, specimens were ultrasonically cleaned using an alkaline solvent at 65 °C, rinsed in deionized water and dried in hot air before mounting on fixtures inside the deposition chamber. A description of the closed field unbalance magnetron sputtering system can be found in the
After insertion into the deposition chamber, specimens were sputter etched at -500 V for 30 min to remove residual contaminants. Substrates were continually rotated in a 3 fold rotation for uniform coating deposition. The coating properties and microstructure are presented in Table 8.5.

Table 8.5 Coating properties and microstructure

<table>
<thead>
<tr>
<th>Coating</th>
<th>Mechanical Hardness, GPa</th>
<th>Elastic Modulus, GPa</th>
<th>Composition (at%)</th>
<th>Microstructure</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>W-DLC</td>
<td>14</td>
<td>130</td>
<td>W-11; C-89</td>
<td>Alternating W and C rich layers; Nanoparticles of tungsten carbide dispersed in an amorphous hydrocarbon matrix</td>
<td>[95,184]</td>
</tr>
<tr>
<td>Ti-DLC</td>
<td>12</td>
<td>125</td>
<td>Ti &lt; 20</td>
<td>Nanoparticles of titanium carbide dispersed in an amorphous carbon matrix</td>
<td>[185,186]</td>
</tr>
</tbody>
</table>

W-DLC was deposited using two W and two Cr targets while for Ti-DLC, two titanium and two carbon targets were used. Prior to deposition of the DLC, thin (~ 100 nm) layers of Cr and Ti were deposited to form strong bonding to the steel substrates for the W-DLC and Ti-DLC, respectively. Argon (purity 99.99%) gas flow was maintained at 8.33 x 10^-7 m^3 sec^-1 (50 sccm) and substrate bias was kept constant at -100 V during deposition of both coatings. The films were deposited by using acetylene reactive gas process in combination with argon. Scharf et al determined that the microstructure of W-DLC contain alternating W and C rich layers containing nanoparticles of tungsten carbide.
dispersed in an amorphous hydrocarbon matrix [95]. The microstructure of Ti-DLC contain nanoparticles of titanium carbide in an amorphous carbon matrix as determined by Feng et al [185]. Metal doped coatings were considered due to their high strength, which results from the formation of metal carbides in the carbon network [187].

8.3 Results

Traction coefficients for coated and uncoated material pairs with PAO4 oil are shown in Figure 8.2. The traction coefficient and P/P acceleration are plotted as a function of contact cycles. The steel on steel pair with the PAO4 lubricant lasted 15 million cycles as shown in Figure 8.2a. The P/P acceleration was low at 200 at the beginning of the test, rises to 400 in 2 million cycles where it remained constant for about 5 million cycles and then gradually increases to 1200 P/P acceleration. The gradual increase of P/P acceleration indicates the progression of surface damage with the increase in number of cycles. Optical image of the roller show a large amount of micropitting on the surface but no significant wear (See Figure 8.3). It was observed that the roller worn at the initial stage but there was no further loss of wear diameter as test progressed. The damage accumulation over time caused the P/P acceleration to reach cut off limit.
Figure 8.2 Plot shows Steel, W-DLC and Ti-DLC material pairs tested with PAO4 oil (a) steel on steel exceeded the cut off limit of 1200 P/P acceleration (b) W-DLC test was terminated after the completion of 100 million cycles (c) Ti-DLC exceeded the cut off limit after about 4 million cycles
The FF gear oil and steel combination was terminated around 50 million cycles due to significant amount of wear measured on the roller surface. Figure 8.4a shows the traction coefficient and P/P acceleration as a function of contact cycles. Vertical lines in the plot indicate instances where the tests were stopped and restarted. The P/P acceleration and traction coefficient show an inverse behavior. At the beginning of the test, P/P acceleration began to increase until about 10 million cycles and remained constant for the rest of the test. However, the traction coefficient continually decreased until it reached 10 million cycles and remained steady thereafter. The decrease in traction coefficient is related to the wear progression on the roller surface, which changes the Lambda (λ) value and contact pressure. The wear track appearance after test termination is shown in Figure 8.4b. Images show micropitting accompanied with a large amount of wear. The measured track width changed from ~1 µm at the beginning of the test to ~1.5 µm after test termination.

Figure 8.3 Surface topography of steel rollers (a) with PAO4 oil after test failure at 15 million cycles (b) with FF gear oil after test termination at 50 million cycles due to large amount of wear.
The W-DLC coating in combination with PAO4 lasted 100 million cycles without significant damage. Figure 8.4b shows the traction coefficient and P/P acceleration as a function of the number of contact cycles for the pairing of W-DLC roller/rings and PAO4 oil. Both the traction coefficient (~ 0.04) and P/P acceleration (~200) remained steady throughout the test. The optical image (Figure 8.5a) of the roller shows that there is no damage on the surface apart from small pits on the edges of the wear track resulting from edge stresses. Discrete patches of tribofilm formation can also be seen on the roller surface.

The FF gear oil and W-DLC pair was terminated after 50 million cycles (see Figure 8.5). In this pair, the traction coefficient was observed to be remained steady and P/P acceleration was steady for the first 10 million cycles. After 10 million cycles, the P/P acceleration began to rise gradually and reached a stage where it became constant around 800. The test was terminated due to the large amount of wear on the roller surface. Figure 8.6 shows the optical images of the tested roller for W-DLC and commercial oil after test termination. The roller surface shows a large amount of micropitting and wear.
Figure 8.4 Plot shows three types of failure criterion. (a) Steel on steel with PAO4 oil exceeded the cut off limit of 1200 P/P acceleration (b) Steel on steel with fully formulated gear oil was terminated due to large amount of wear (c) W-DLC in PAO4 was terminated after the completion of 100 million cycles
Figure 8.5 Surface topography of W-DLC rollers (a) with PAO4 after 100 million cycles (b) with FF gear oil after test termination at 50 million cycles

Figure 8.6 Surface appearance of the Ti-DLC rollers (a) with PAO4 oil after 10 million cycles (b) with FF gear oil terminated at 100 million cycles

The Ti-DLC and PAO4 pair lasted only about 4 million cycles while Ti-DLC with FF gear oil was suspended after reaching 100 million cycles (See Figure 8.2c and 8.4c). In both the cases, the traction coefficients remained steady throughout the tests. Figure 7 shows the optical images of both the Ti-DLC with PAO4 oil and FF gear oil material pairs. The image of the Ti-DLC roller surface tested with PAO4 shows a large amount of damage. A close inspection of the image coupled with the P/P acceleration data suggests that micropits formed rapidly on the roller surface and grew in size to trigger the P/P threshold limit. However, the image of the Ti-DLC roller tested with the FF gear oil shows a smooth
surface with a few micropits. It is also apparent from the optical images that a thick tribofilm has formed on the roller surface.

![Change in Track Width](image)

Figure 8.7 Change in track width after test completion for different material pair and oil combinations (dotted horizontal line indicates the initial track width prior to testing.

Among all the tests, only the W-DLC/PAO4 and Ti-DLC/FF gear oil pairings lasted 100 million cycles without experiencing excessive damage while all the other tests reached the vibration cutoff limit or were suspended due to excessive wear. These results show that W-DLC and Ti-DLC have different interactions mechanism with the oil chemistry. W-DLC lasted longest in base oil (PAO4) whereas Ti-DLC showed excellent performance in fully formulated commercial gear oil.

8.4 Discussion

Experimental results showed that the failure mechanisms for all the material pairs differ from one another. Steel on steel plus PAO4 combination failed due to excessive surface damage on the surface of roller which exceeded the vibration cut off limit. Figure 4a shows that the surface damage on the roller appears to have initiated with micropits,
evolved into macropits, that coalesced and formed the continuous surface damage in the wear track which is in good agreement with Fajdija et al. [166] The track width comparison of the steel roller with base oil and gear oil indicates that the steel pair with FF gear oil generated a large amount of tribochemical wear, as shown in figure 4b. Steel has a higher polar nature and strong affinity for additive interactions which resulted in the formation of a tribofilm within the contacting surfaces. It can be interpreted from the roller surface that the formation and breakdown of the sacrificial tribofilms under high shear stresses resulted in high wear. In addition, glassy phosphates passivate the surface which can enable thermo-oxidative reactions and result in corrosive wear [188]. The rate of tribofilm formation and removal increased the fatigue life by continuous wear and thus eliminated the formation of large micropits to reach the cut off limit.

Different failure mechanisms were observed when metal doped DLC coatings were used with PAO4 and FF gear oil. The results obtained show that W-DLC did not show significant surface damage with PAO4 base oil while severe pitting was observed on the Ti-DLC roller. This suggests that the coating properties have a direct influence on the fatigue performance under sliding and rolling contact conditions. Optical analysis on the counterface of W-DLC showed polishing effect whereas the Ti-DLC counterface showed coating delamination. The multilayer W-DLC coating containing alternating tungsten and carbon rich layers appears to be resistant to high shear stress cycles. Hard W-DLC coatings applied to rolling element bearings functioned very well in mitigating micropitting, scuffing, and fatigue life reduction from debris damage [189].

In contrast to the base oil performance, Ti-DLC out-performed W-DLC in FF gear oil and the test was terminated after 100 million cycles. Optical analysis revealed that the
additives in the oil act synergistically in forming a tribofilm on the Ti-DLC surface. W-DLC roller surface also showed the formation of tribofilm on the surface but the additive interaction was not as significant to reduce wear and increase the fatigue life. Singh et al. studied the scuffing performance of W-DLC and Ti-DLC with PAO4 and FF gear oil and found similar behavior as observed in these tests. Ti-DLC did not scuff up to a 2800 N load while W-DLC scuffed at a load of 1550N with FF commercial gear oil [190].

Hydrogen plays a critical role in the wetting behavior of DLC coatings. The hydrogen carbon combination produces a non-polar, inert surface having a low energy that causes poor wettability and results in no additive interaction on the coated surface [169]. Poor wettability is more of an issue when the carbon network is highly hydrogenated. Kalin and Polajnar measured surface energies of several DLCs (a-C:H, ta-C, hydrogenated Si-DLC, N-DLC and F-DLC) and reported small difference in the total surface energy between the steel and DLC coatings except for F doped DLC [191]. However, they observed major differences in the polar surface energy which points to the fact that surface polarity plays major role in the lubricant additive interaction.

Metal dopants in the coatings also have a significant contribution on the formation of tribofilms. It is reported in the literature that DLC coatings with metals can lead to high surface energies that promotes interactions between the coatings and the lubricant[192,193]. However, high surface energies are not the only significant factor for tribofilm formation. The reactivity of the metal dopant with the lubricant additives is also equally important. Podgorrnik et al and Kalin et al reported that the W has lower reactivity with the lubricant additives that takes more running in time to form tribofilms [173,194]. On the other hand, Kalin et al reported higher chemical reactivity of Ti-DLC than W-DLC
and H-DLC when tested in EP + mineral oil combination. The phosphorous and sulphur (P/S) ratio measured was much higher (12.8) whereas for W-DLC P/S value is 1.2 [194]. They proposed that the higher reactivity of Ti is related to titanium oxidation state (TiO$_2$). Titania is more reactive which acts as a bonding site for EP additives. They mentioned that the TiO$_2$ is formed inside the coating by Ti doping and could also form due to higher frictional temperature.

In a recent study, Fouts et al tested W-DLC and Ti-DLC coatings with mineral oil, Aryl Zinc dialkyl dithiophosphate, molybdenum dithiocarbamate (MoDTC), and FF gear oil. These tests were conducted in a reciprocating sliding contact. Results similar to the study were observed with both the coatings. W-DLC showed better performance in mineral oil and poor behavior in FF commercial gear oil whereas Ti-DLC behavior was vice versa. The authors proposed that a hydrogen abstraction mechanism might be responsible for their different behaviors in the presence of additives. According to this mechanism, all the W and Ti in the coating is not in the form of carbides and there is free W and Ti present in the carbon matrix. Free Ti would create stronger bonds with hydrogen than W. The stronger bond formation with Ti suppresses the hydrogen abstraction from the coating and therefore inhibits coating graphitization. W on the other hand is weakly bonded to the hydrogen does not inhibit hydrogen abstraction that destabilizes the random covalent network of DLC. The destabilized network collapses to from a graphitic layer which results in high wear in W-DLC coatings [195].

These results show that the effectiveness of additives depends on the nature of the chemical interaction between the coating and steel. The differences in the coating + additive interaction can be attributed to several factors including metal and non-metal
doping, hydrogen content, and lubricant formulation. The type of chemical species of
lubricant additives may react differently with coating composition.

In the base oil, W-DLC acted synergistically to enhance the coating life while in
FF gear oil the life was lower accompanied by wear. Steel failure mechanisms were quite
different, in base oil it failed due to pitting and in FF gear oil both micropitting and wear
occurred. Ti appears to be acting more synergistically with fully formulated oils containing
ZDDP and MoDTC. The thick tribo film formation on the Ti-DLC surface with formulated
oils facilitates improved fatigue performance. This study can guide a selection and
development of optimized or appropriate coating for fatigue applications.

8.5 Conclusions

In the present work, rings and roller specimens were fatigue life tested and failure
mechanisms of Ti-DLC and W-DLC coated systems lubricated with PAO4 oil and fully
formulated commercial gear oil were studied. The following conclusions can be made

- A combination of W-DLC with PAO4 oil and Ti-DLC with FF commercial gear
  oil outperformed all the other material + oil combinations.
- W-DLC and Ti-DLC reached 100 million cycles without any significant damage
  on the roller surface with the base oil and FF gear oil.
- The performance of the W-DLC and Ti-DLC is linked with the lubricant additive
  interaction and the metal dopants in the DLC coatings.
CHAPTER IX
CONCLUSIONS

9.1 Solid Film Lubrication

The coating characterization on Ti-MoS$_2$ showed improved mechanical properties and dense incoherent microstructure with Ti addition into the MoS$_2$ matrix. Ti is in solid solution with MoS$_2$ as no precipitates and multilayers of Ti was observed even with 16 at.% Ti. Friction and wear measurements under sliding contact showed environment and temperature dependence. Microstructure analysis revealed the reorientation of MoS$_2$ basal planes turning parallel to the direction of sliding which is a contributing factor for the low friction and wear. Raman analysis complimented HRTEM results by revealing crystalline peaks inside the wear scar while outside the scar film was completely amorphous. Atom probe tomography (APT) results also confirmed amorphous structure with Ti atoms uniformly distributed in the MoS$_2$ matrix.

Rolling contact experiments performed for the first time to quantify the useful life of Ti-MoS$_2$ films in vacuum and humid air. The vacuum performance complimented the performance in humid environment in ball on rod experiments. However in humid environment tests failed due the onset of adhesive wear after coating depletion while in vacuum onset of pitting was responsible for failure.
Bearing test showed different failure mechanisms when either raceways or balls were coated compared to both raceways and ball coated. The results demonstrated that the Ti doping do not have adverse effect on the MoS$_2$ performance in vacuum while it significantly improved the useful life in humid atmospheres. The excellent performance of Ti-MoS$_2$ films is believed to arise from their dense structure, featureless morphology and amount of Ti doping in the MoS$_2$ microstructure.

The investigation on the Sb$_2$O$_3$/Au-MoS$_2$ composite films was performed after sputtering from a target composed of 82% MoS$_2$, 11% Sb$_2$O$_3$ and 7% Au composition. Microstructure of the films was amorphous with columnar porosity and contain Au nanoparticle uniformly distributed in an amorphous MoS$_2$-Sb$_2$O$_3$ matrix. Friction and wear behavior under sliding contact showed load dependence which has been attributed to the shear driven reorientation of [002] MoS$_2$ basal planes that align along the sliding direction. The shear driven reorientation was confirmed by TEM examination which showed Au agglomeration and long range order of crystalline planes of MoS$_2$ near the top surface inside the wear track. The basal plane oriented material on the counterface and inside the wear track account for low friction and wear.

Rolling contact experiments on thrust bearing also showed contact stress dependence where torque increased with load unlike sliding experiments where friction decreased with increased load. The different behaviors are related to the pronounced ordering of MoS$_2$ basal planes under sliding contact than they are in rolling contact. Raman analysis verified that this mechanism where it revealed pronounced Raman features of crystalline MoS$_2$ in sliding wear track than in the rolling contact.
Bearing tests on both Ti-MoS$_2$ and Sb$_2$O$_3$/Au-MoS$_2$ films demonstrated that the amount of material (solid lubricant) present in the contact directly correlates to the useful life of bearings. For bearings to be used in vacuum coating only rolling elements would be sufficient to increase the coating life while in humid atmospheres both rolling elements and raceways should be coated. Solid lubricant function in rolling contact appeared to be different from the sliding contact. Rolling contact experiments measurements are in agreement with the Amontons’ law whereas the sliding contact experiments showed opposite results. This research study on MoS$_2$ based solid lubricants conclude that there is no direct co-relation between the sliding and rolling contact performance.

9.1.1 Outlook

Lubrication of mechanical moving assemblies in space systems is challenging. The system encounters harsh environments, temperature differentials and transient operating conditions. Solid lubricants such as molybdenum disulphide (MoS$_2$) have been used to protect contacting surfaces from failure. MoS$_2$ based coatings are the current standards for space applications such as satellites. However, there is continuous research to improve the useful life, by doping MoS$_2$ with metals and oxides, use of exotic architectures, and novel coating designs.

It is expected that the demand for environmentally robust and adaptable solid lubricants to mitigate friction and wear will continue to grow for space applications. There are several contributing factors. The need for longer life and the requirement to go more complex motion profiles are pushing extreme lubricants to their limits. The decreasing size
of components (miniaturization) further pushing the envelope of solid lubricants to offer the prospect of operation in a low lubrication regime.

On the contrary, the reliability of space mission depend upon the reliability of tribological components such as bearing, slip rings, and gears. After launch, these components become inaccessible and therefore cannot be repaired or replenished. Moreover these solid lubricants have finite lifetimes which can jeopardize the successful completion of the mission. Hence, there is need to develop more robust films to withstand the vibrations of the launch and thermal extremes, radiations and vacuum in the outer environment.

Furthermore, there is continuous increase in the space exploration programs around the world to explore the possibility of existence of life on other planets, to increase the reach to farther planets and to start a tourist shuttles to moon. Developing countries like China and India vastly expanded their research on space exploration including satellites for monitoring, sensing and spying. These programs demands increase in reliability and smoother operation due to increasing more sophisticated systems for current and future needs. Therefore, there is a stronger need to optimize existing films and develop new films by incorporating novel designs and new materials to increase long term durability since solid lubricants cannot be replenished. Moreover, existent research methods are insufficient to simulate the outer space and it is hard to determine the precise tribological behavior. New systems should be developed with the use of new technologies which can simulate the outer space to close proximity.
9.2 Fluid Film Lubrication

H-DLC coatings investigated in combination with PAO4 base oil showed significant improvement in the fatigue life as compared to the untreated samples. The uncoated specimens failed after 32 million cycles whereas after coating no failure was observed and tests were terminated after 100 million cycles. The improvement in fatigue life was related to the coating mechanical properties and the ability of the coating to form a tribofilm by combining with lubricant hydrocarbons. Experimental results showed that the H-DLC coatings can provide sufficient delay to the onset of surface initiated fatigue even when only one side of the contacting components is coated. The material transfer from the coated to the uncoated counter-face facilitates the tribofilm formation on the untreated surface to prevent the initiation of surface contact fatigue. In addition to tribofilm formation, low friction coefficient of H-DLC reduces the magnitude of shear stresses which are associated with the formation of surface initiated fatigue. The improvement in fatigue life after coating with H-DLC can be beneficial for tribological components which encounter severe rolling/sliding motions. In particular, wind turbine drive train components that suffer from high slide to roll ratios due to extreme operating conditions may achieve reliable and cost-effective operation with the application of H-DLC coating.

The fully formulated gear oil (FF gear oil) and base oil interaction studied on the uncoated, Ti-DLC coated and W-DLC coated gear steel revealed significant differences in their tribological performance under sliding/rolling contact. In PAO4 oil, Steel material pair failed due to the formation of macro-pits whereas in FF gear oil large amount of wear was observed. Ti-DLC and W-DLC performance was inversely correlated when tested in base oil and FF gear oil. W-DLC outperformed Ti-DLC in base oil while in FF oil the
performance was vice-versa. The performance of coatings in FF oil was linked to the chemical reactivity of dopant metals to form a thick stable tribofilm on the surface. Ti appears to be more reactive than W to form a tribofilm on the surface. This study can guide a selection and development of optimized or appropriate coatings for fatigue applications.

9.2.1 Outlook

Tribology components are being continuously exposed to demanding operating conditions in several applications including internal combustion engines and wind turbines for power generation. The extreme operating conditions result in several types of tribological failures related to fatigue, wear, scuffing, pitting etc. These failures have generated the need to evaluate variety of surface engineering and lubrication techniques to ensure safe reliable operation.

The rising of fuel costs and stricter guidelines to reduce air pollution have led manufacturers to develop fuel efficient engines. In addition, parasitic losses account for a significant reduction in fuel economy. It is estimated that energy losses due to friction in transmission and engines estimated to be around 28% of total fuel energy consumed. Hence to reduce energy losses, increase fuel economy, to meet demanding operational conditions, stringent emission controls and to increase the durability of components new methods are required that can potentially increase the fuel economy. Road transportation being the largest means of transportation, which is expected to grow in the near future demands significant improvements in the durability of tribological components and increase in fuel economy.

Wind turbines operate in a unique environment, which considerably influences the reliability of drive train components such as gears and bearings. Gears and bearings are
one of the major contributing factors to wind turbine O&M costs. In consideration of the major failures in drive train components, there is need to evaluate novel coatings and new lubricant chemistries to improve reliability and decrease in O&M costs. According to wind energy market technology report by the US Department of Energy, wind energy is the fastest growing renewable energy source. The increased demand towards use of renewable resources emphasizes the installation of new wind power plants to increase the power generation capacity. In 2011, wind energy comprised of 32% of US electric generating power capacity [196]. The wind power generating capacity is further expected to grow at fast pace that places considerable emphasis on the reliable operation of wind turbine drive train system. The reliability issues and challenges linked to gear bearing and gears may be addressed by the use of novel surface engineering and lubrication formulations.

Final Remarks

The papers based on this research are either published/submitted or in preparation. The papers published or submitted form the research are presented in their original form or may contain few changes and overlaps with different chapters.
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Hetzian contact Stress calculation

When two non-conforming bodies come in contact, initially they touch at a point. When load is applied these bodies deform at the point of contact and they touch over an area which is finite though small compared to the size of bodies. For example, in gears, bearings, seals and cam the contact areas are small and resultant pressures are very high. Hertz developed a theory and model to calculate the contact stresses between the flat and spherical surface. The shape of the contact area depends on the curvature of the contacting bodies.

By convention, convex surfaces possess positive curvature and concave surfaces have negative curvature. So, if the center of curvature lies between the solids then the curvature is positive, if it lies outside the solid then the curvature is negative. This is required while defining the parameter called reduced radius of curvature.
Consider two elastic bodies’ one sphere and other flat. Since the center of curvature lies in the body the curvature is positive.

The reduced radius of curvature is calculated by

\[
\frac{1}{R'} = \frac{1}{R_x} + \frac{1}{R_y} = \frac{1}{R_{ax}} + \frac{1}{R_{inx}} + \frac{1}{R_{ay}} + \frac{1}{R_{bxy}}
\]

where \(R\) is radius of curvature, \(x\) and \(y\) are the significant dimensions of the body, \(a\) is body 1 and \(b\) is body 2.

Since flat surface has an infinite radii of curvature, therefore \(R_{bx} = R_{by} = \infty\)

And the reduced radius of curvature then becomes:
\[
\frac{1}{R'} = \frac{1}{R_x} + \frac{1}{R_y} = \frac{1}{R_{ax}} + \frac{1}{R_{ay}}
\]

The pressure acting on on the second body is equal to that on the body 1, so the reduced elastic modulus is calculated by

\[
\frac{1}{E'} = \frac{1}{2} \left[ \frac{1 - \mu_A^2}{E_a} + \frac{1 - \mu_B^2}{E_b} \right]
\]

where \(\mu\) is a Poisson’s ratio and \(E\) is elastic modulus

Contact area dimensions are calculated from the following formula

\[
a = \left( \frac{3WR'}{E'} \right)^{\frac{1}{3}}
\]

Maximum and average contact stress acting:

\[
P_{\text{max.}} = \frac{3W}{2\pi a^2}
\]

\[
P_{\text{avg.}} = \frac{W}{\pi a^2}
\]

Maximum deflection

\[
\delta = \left( \frac{W^2}{E'^2 R'} \right)^{\frac{1}{3}}
\]

Maximum shear stress
\[ \tau_{\text{max.}} = \frac{1}{3} P_{\text{max.}}. \]

**Lubricant Film Thickness Calculation**

In a lubricated contact, the contact surfaces are separated by the lubricating film.

\[
\frac{h_o}{R'} = 2.69 \times \left( \frac{U \eta_o}{E' R'} \right)^{0.67} \times (\alpha E')^{0.53} \times W \left( \frac{W}{E' R'^2} \right)^{-0.067} (1 - 0.61 e^{-0.73K})
\]

(4)

Where \( h_o \) is the minimum film thickness (m)

\( U \) is the entraining surface velocity (m/s) which is the average velocity of body 1 and body 2

\( \eta \) the viscosity at atmospheric pressure of the lubricant (Pas)

\( E' \) is the reduced young’s modulus (Pa)

\( R' \) is the reduced radius of curvature (m)

\( \alpha \) is the pressure-viscosity coefficient (m²/N)

\( W \) is the contact load, N

\( K \) is the ellipticity parameter i.e. \( K = a/b \) where \( a \) is the semi-axis of the contact ellipse in the transverse direction (m) and \( b \) is the semi-axis in the direction of motion (m)

Ellipticity parameter is calculated by:
\[ K = 1.0339 \left( \frac{R_x}{R_y} \right)^{0.636} \]

where \( R_x \) and \( R_y \) is the reduced radius of curvature in the x and y directions. Usually, for line contacts \( K = \infty \) and for point contact \( K = 1 \). For elasto-hydrodynamic film thickness equations are applicable for \( K \) between 0.1 and \( \infty \).

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