EFFECT OF SURFACE TRANSFORMATION AND TRANSFER LAYER ON FRICTION OF CARBONACEOUS HARD COATINGS

by

Nor Azimmi Bin Masripan

A thesis submitted in partial fulfillment for the degree of Doctor of Engineering

in the DEPARTMENT OF MECHANICAL SCIENCE AND ENGINEERING GRADUATE SCHOOL OF ENGINEERING

2013
NAGOYA UNIVERSITY

EFFECT OF SURFACE TRANSFORMATION AND TRANSFER LAYER ON FRICTION OF CARBONACEOUS HARD COATINGS

by

Nor Azmni Bin Masripan

A thesis submitted in partial fulfillment for the degree of Doctor of Engineering

in the DEPARTMENT OF MECHANICAL SCIENCE AND ENGINEERING GRADUATE SCHOOL OF ENGINEERING

2013
In this thesis, we present the effect of surface transformation and transfer layer on the friction of carbonaceous hard coatings. Carbonaceous hard coatings have been used in recent years as coatings for tribological components; especially for vehicles, in order to reduce friction and wear, which consequently increases the lifespan and working efficiently of components. Carbonaceous hard coatings are used in many industrial applications, due to their excellent tribological properties of low friction, high wear resistance, and chemical inertness. Another essential advantage of carbonaceous hard coatings is that it provides a low friction coefficient; either under dry conditions or boundary lubrication in oil. This particular advantage has attracted more research to understand the tribological behaviour of carbonaceous hard coatings, as a guideline for future usage. Consequently, we performed two experiments; one in dry and the other in oil conditions. In the first experiment, we investigated the effect of the transfer layer on the ultra-low friction of CNx coating under blowing dry Ar. Meanwhile, the second experiment investigated the effect of the transformed layer, in terms of their thickness and hardness on friction under boundary lubrication, in additive-free mineral-based oil.
In a dry condition, CNx coating can provide a low friction coefficient of 0.003 under blowing Ar, in an ambient environment, with help from the formation of a transfer layer at the sliding interface. Following the friction test, an ex-situ observation showed that the transfer layer could be found easily on the counter part’s surface. Therefore, we think that an in-situ observation is needed to observe the formation of the transfer layer that influences the friction behaviour under a dry condition. However, no reports exist about an in-situ observation of the formation of a transfer layer during friction testing in a dry condition. We have developed a new experimental apparatus, based on a ball-on-disc tribometer. We used a transparent sapphire hemisphere ball (α-Al₂O₃) as a counterpart against a CNx coated disc for friction testing. With help of an optical microscope and a CCD camera, images of the formation of a transfer layer can be recorded through the transparent sapphire hemisphere ball during the friction test.

The friction test’s results show that the friction coefficient under blowing Ar, decreases from 0.18 to a steady state value of 0.003. An in-situ observation showed that the friction coefficient decreased rapidly, as the transfer layer started to generate at the contact interface. As the thickness of the transfer layer increased to 500 nm, the friction coefficient had a constant value at 0.003. Meanwhile, an ex-situ observation was performed using Raman analysis of the transfer layer, and found the transfer layer structure to be similar to graphite. The results showed that the formation of a graphite-like transfer layer from the CNx coating played an essential role in the low friction mechanism of CNx.

In the other experiment, we performed a friction test of a DLC coated sliding bearing (SUJ2) against an S55C disc under boundary lubrication conditions, in an additive-free mineral-based oil. Since the low friction mechanism under this condition was still unclear, we tried to investigate the low friction mechanism from a different point of view i.e., through the thickness and hardness of the transformed layer through an ex-situ observation. The thickness of the transformed layer was measured on wear track of DLC’s coating using reflectance spectroscopy, and the hardness of the transformed layer was calculated using the depth of a scratch test, using Atomic Force Spectroscopy (AFM).

We prepared three types of DLC, which we named DLC1, DLC2, and DLC3, with different hardness's of 47.1, 11.8, and 6 GPa, respectively. The tribological properties of DLCs were investigated using a pin-on-disc tribometer, and friction tests were performed under boundary lubrication conditions, in an additive-free
mineral-based oil, at different oil temperatures of 24, 80, 120 and 160°C. The experiment’s results showed that DLC1 provided the lowest friction coefficient and wear rate of 0.03 and in the order of $10^{-11} mm^3/Nm$, respectively. The transformed layer was found at the topmost surface of DLC coating after the friction test. The pressure-induced graphitization was responsible for the DLCs structure changing from $sp^3$ into $sp^2$. The pressure-induced graphitization, which was confirmed by Raman analysis, showed that the value of $I_D/I_G$ increased with increasing oil temperatures.

Reflectance spectroscopy was used to measured the thickness of transformed layer after friction test. In this work, we did find that the friction decreased by increasing the ratio of the thickness of the transformed layer, $t$ and the deviation of roughness, $\sigma^*$. It was found that, the friction coefficient decreased significantly when the $t/\sigma^*$ value higher than 1.

We performed an AFM scratch test to determine the nano characteristics of the transformed layer in terms of its hardness. We found that the hardness of the transformed layer decreased significantly at oil temperatures above 80°C, compared to the hardness of the as-deposited DLC.

The empirical-based friction model map, which presents the thickness and hardness of the transformed layer, correlated to friction coefficient data in a graphical manner, was able to provide us with information of how the thickness and hardness of the transformed layer influenced the friction’s behaviour. The combination of a thick transformed layer (more than 100 nm) and a moderate hardness of the transformed layer (2.8-4.3 GPa) can provide low friction. This combination avoids direct contact between the mating surfaces and the hard bulk DLC. Therefore, the mating surface can slide smoothly on the low shear strength of the transformed layer, without touching the hard bulk DLC.
Acknowledgements

First and foremost I would like to express my heartfelt gratitude to my advisor Professor Noritsugu Umehara. It has been an honor to be his Ph.D. student. He has taught me, both consciously and unconsciously, how good experimental tribology is done. I could not have asked for better role models, each inspirational, supportive, and patient.

I would also like to thank my examiners, Professor Kenji Fukuzawa, Professor Nagahiro Saito, and Associate Professor Hiroyuki Kousaka, who provided encouraging and constructive feedback. I am very grateful for their thoughtful and detailed comments.

This work was collaborate with DAIDO Metal Co. Ltd, and I would like to thank to Mr. Shigeru Inami, Mr. Koji Zushi and Mr. Mashahito Fujita for their generous support.

I owe a debt of gratitude to Associate Professor Dr. Hiroyuki Kousaka, Assistant Professor Dr. Takayuki Tokoroyama, Dr. Yosuke Tsukiyama and Mr. Shinko Senda for their involvement and support in different aspects of my research project, as well as the various group meetings that expanded my understanding.

I owe a special thanks to my research partner, Mr. Kenji Ohara, Mr. Yuki Miyahira, Mr. Hidenori Nishimura and all members from the Advanced Materials and Manufacturings for their invaluable help during laboratory works. I am very happy to be a part of the Umehara Laboratory.

Special thanks to Malaysian government and Universiti Teknikal Malaysia Melaka (UTeM) for financial support under Skim Latihan Akademik Bumiputera (SLAB), without it, my study at Nagoya University, Japan would have not been possible.

I owe a lot to my parents, Masripan Bin Abu and Rokeyah Binti Yasman, who loved me at every stage of my life. There is no enough words to thank for your sacrifice to make my life meaningful.

I am very much indebted to my family, my wife Norazah Binti Amir, daughters Alifah Ilyana and Alifah Raschika, and son Alif Hakim, who supported me in every possible way to see the completion of this work. I love you all so much.
I also thank my friends especially Dr. Mohd. Fadzli Bin Abdollah for providing support and friendship that I needed.

Above all, I owe it all to Almighty ALLAH S.W.T for granting me the wisdom, health and strength to complete my works.
Contents

Abstract i

Acknowledgements iv

List of Figures ix

List of Tables xiii

1 Introduction 1
  1.1 Introduction to tribology 1
  1.2 Industrial needs of hard coating 2
  1.3 Carbon coatings 7
    1.3.1 Diamond-like carbon (DLC) 8
    1.3.2 Carbon nitride (CNx) 11
    1.3.3 Friction mechanism of carbon coatings 11
  1.4 Purpose of this study 14
  1.5 Outline of dissertation 17

2 Effect of transfer layer on ultra low friction of CNx coating under blowing dry Ar 18
  2.1 Introduction 18
  2.2 Experimental procedure 20
    2.2.1 Test specimen 20
    2.2.2 Friction test 20
    2.2.3 Estimation of the thickness of transfer layer 21
    2.2.4 Raman and AES analyses 22
  2.3 Results and discussion 23
    2.3.1 Effect of the thickness of transfer layer on friction coefficient 23
    2.3.2 Effect of area of transfer layer and contact pressure on friction coefficient 27
    2.3.3 Phase transition of CNx coating at sliding contact interfaces 29
    2.3.4 Ex-observation of wear track with Optical microscope (OM), Raman spectroscopy and Auger Electron Spectroscopy (AES) 31
3 Hardness effect of DLC on tribological properties for sliding bearing under boundary lubrication condition in additive-free mineral-based oil

3.1 Introduction ................................................. 38
3.2 Experimental details ........................................ 39
3.3 Results and discussion .................................... 43
  3.3.1 Correlation between results with Raman spectroscopy and spectroscopic ellipsometry .......... 43
  3.3.2 Hardness .................................................. 48
3.4 Friction and wear behaviors .............................. 50
3.5 Conclusions .................................................. 54

4 Effect of thickness of transformed layer on friction behaviour

4.1 Introduction .................................................. 55
4.2 Experimental method and procedure ........................ 58
  4.2.1 Test specimens and friction test ....................... 58
4.3 Spectroscopic reflectometry ................................ 59
4.4 Results ...................................................... 63
  4.4.1 The effect of oil temperature on the reflectance intensity .......... 63
  4.4.2 The effects of contact pressure and sliding distance on the reflectance intensity ............. 65
  4.4.3 The effects of friction conditions on the thickness of the transformed DLC layer using spectroscopic reflectometry .......... 67
    4.4.3.1 The effect of oil temperature on the thickness of the transformed DLC layer using spectroscopic reflectometry .......... 67
    4.4.3.2 The effects of contact pressure on the thickness of the transformed DLC layer using spectroscopic reflectometry .......... 68
    4.4.3.3 The effects of sliding distance on the transformed layer thickness of DLC with spectroscopic reflectometry .......... 69
  4.4.4 The effects of the friction condition on the surface roughness of the DLC coatings using spectroscopic reflectometry .......... 70
    4.4.4.1 The effects of oil temperature on the surface roughness of the DLC coatings using spectroscopic reflectometry .......... 70
    4.4.4.2 The effects of the contact pressure on the surface roughness of the DLC coatings using spectroscopic reflectometry .......... 71
    4.4.4.3 The effects of sliding distance on the surface roughness of the DLC coatings using spectroscopic reflectometry .......... 72
5 Characteristics of transformed layer of DLC after friction test under boundary lubrication in additive-free mineral-based oil

5.1 Introduction ............................................................................. 77

5.2 Experimental details .............................................................. 79
  5.2.1 Friction test and Raman analysis ....................................... 79
  5.2.2 Scratch test ...................................................................... 79

5.3 Results and discussion ............................................................ 82
  5.3.1 Raman spectroscopy results ............................................. 82
  5.3.2 Dependence of scratch depth on oil test temperature .... 83
  5.3.3 Scratch hardness of transformed layer ......................... 85
  5.3.4 Dependence of friction coefficient on the scratch hardness of the transformed layer ......................................... 86

5.4 Conclusion .............................................................................. 90

6 Conclusion ................................................................................ 91

References .................................................................................. 94

Publication lists ........................................................................... 105

International Conference ............................................................ 106
List of Figures

1.1 Possible improvements based on Stribeck diagram by DLC coating application. .................................................. 3
1.2 Cycles to failure for combination of steel-steel. DLC-DLC and DLC-steel under boundary lubrication condition. .......... 4
1.3 Components that can be coated with DLC for use in an automotive engine. ......................................................... 5
1.4 sp², sp³ and sp¹ hybridised bonding. .................................................. 7
1.5 Ternary phase diagram for various DLC films with respect to their sp², sp³ and hydrogen contents. .......................... 8
1.6 Outline of dissertation. .................................................. 17

2.1 Test rig based on pin-on-disk method. Combination of optical microscope and CCD camera were used to observe the in-situ frictional behavior CNx coated disk against Sapphire hemisphere. ....... 21
2.2 Schematic illustration of relationship between transfer layer and Newton’s ring during sliding test for estimation of transfer layer thickness. (a) Initial state and (b) during sliding with the formation of transfer layer. .................................................. 22
2.3 (a) The frictional behavior of CNx coating against Sapphire hemisphere as a function of sliding cycles and (b) Transfer layer thickness as a function of sliding cycles. .................................................. 23
2.4 Microscopic images of Newton’s ring and real contact area for estimation of transfer layer thickness and mean Hertzian’s contact pressure respectively. .................................................. 25
2.5 (a) Sudden increase of friction coefficient during sliding between CNx coatings against Sapphire hemisphere as a function of sliding cycles (b) Images of transfer layer and Newton’s ring. ................. 26
2.6 Relation between mean Hertzian’s contact pressure and friction coefficient as a function of sliding cycles. ................. 28
2.7 Relation between estimated mean Hertzian’s constant pressure and transfer layer thickness as a function of sliding cycles. .................................................. 29
2.8 Calculated transition temperature of CNx coating as a function of Hertzian’s contact pressure referring to Clapeyron law. .................................................. 30
2.9 a) SEM observation of wear track and debris on CNx coating disk after sliding test. (b) Microscopic image of transfer layer on the sapphire hemisphere after sliding test. .................................................. 31
List of Figures

2.10 Raman spectra of (a) as-deposited (b) wear track on CNx coating (c) transfer layer on sapphire hemisphere and (d) wear debris on CNx coating. 33
2.11 AES analysis for Ar, C, N and O content on CNx coating (a) as-deposited, (b) wear track and (c) wear debris. 33
2.12 Relation between the thickness of transfer layer and contact pressure to friction coefficient. 34
2.13 Microscopic and AFM images of transfer layer on sapphire hemisphere. 35
2.14 In-situ observation of relative humidity and oxygen content at sliding contact interface under blowing Ar. 36
3.1 Schematic illustration of the pin-on-disk type tribometer. 40
3.2 Schematic diagram of roller on disk friction test. 40
3.3 Raman spectroscopy of as-deposited DLC coatings before and after friction tests under different temperatures for (a) DLC1, (b) DLC2 and (c) DLC3. 45
3.4 Intensity of D peak of DLC obtained by Raman spectroscopy as a function of oil temperature. 46
3.5 IP/I_G ratio of DLC obtained by Raman spectroscopy as a function of oil temperature. 46
3.6 Thickness of the transformed layer after sliding in oil detected on wear track using spectroscopic ellipsometry as a function of oil temperature. 47
3.7 Correlation between intensity of D peaks and the thickness of transformed layer. 47
3.8 The hardness of DLC1, DLC2 and DLC3. 48
3.9 Load-displacement curves of different DLC by nanoindenter. 49
3.10 Friction coefficient of DLC as a function of oil temperature. 50
3.11 Correlation between friction coefficient and hardness of DLC. 51
3.12 Specific wear rate of DLC as a function of oil temperature. 52
3.13 Relation between specific wear rate and inverse hardness of DLC. 52
4.1 Schematic illustration of the reflectance spectrometry measurement for analysing the wear track on pin. 58
4.2 The cross-sectional image of the DLC1 coating cut by FIB and elemental analysis using EDS/SEM. 59
4.3 Reflectance intensity spectrum of the friction scar on the DLC1 coating after sliding. 60
4.4 Penetration depth for each wavelength of light and the corresponding thickness of the DLC coating. 61
4.5 Reflectance intensity spectrum of the friction scar on the DLC2 coating after sliding. 61
4.6 Penetration depth of each wavelength of light through the coating. 62
4.7 Reflectance intensity spectrum of the friction scar in the DLC1 coating after sliding under various contact pressures. 63
4.8 Reflectance intensity spectrum of the friction scar in the DLC2 coating after sliding under various contact pressures. 64
4.9 Reflectance intensity spectrum of the friction scar in the DLC3 coating after sliding under various contact pressures. 64
4.10 Reflectance intensity spectrum of the friction scar in the DLC1 coating after sliding under various contact pressures. 65
4.11 Reflectance intensity spectrum of the friction scar in the DLC1 coating after sliding under various sliding distances. 66
4.12 Effect of oil temperature on the thickness of the transformed layer and friction coefficient of various DLC coatings after sliding in the based oil. 67
4.13 Effect of contact pressure on the thickness of the transformed layer, t, and friction coefficient, μ, of the DLC1 coating after sliding in the mineral-based oil at a temperature of 25°C. 68
4.14 Effect of sliding distance on the thickness of the transformed layer, t, and the friction coefficient, μ, of the DLC1 coating after sliding in the mineral-based oil with a temperature of 25°C. 69
4.15 Effect of oil temperature on the deviation of the roughness height, σ ∗, and friction coefficient, μ, of various DLC coatings after sliding in the mineral-based oil. 70
4.16 Effect of contact pressure on the deviation of the roughness height, σ ∗, and the friction coefficient, μ, of the DLC1 coating after sliding in the mineral-based oil with a temperature of 25°C. 71
4.17 Effect of sliding distance on the deviation of the roughness height, σ ∗, and friction coefficient, μ, of the DLC1 coatings after sliding in the mineral-based oil with a temperature of 80°C. 72
4.18 Relation between transformed layer thickness, t, and friction coefficient, μ. 73
4.19 Relation between the deviation of the roughness height, σ ∗, and friction coefficient, μ. 74
4.20 The effect of t/σ ∗ on the friction coefficient of various DLC coatings after sliding in the mineral-based oil. 75

5.1 Schematic diagram of scan and nanoscratch test area at worn surface of DLC coating after friction test. 80
5.2 Schematic diagram of nano-scratch area a) top-view b) side-view. 81
5.3 I_D/I_G ratios by Raman spectroscopy on wear track for each DLC as a function of oil temperature. 82
5.4 a) Surface topography after scratch hardness test b) cross-section profile of A-A and wear depth at different oil test temperatures. 83
5.5 Scratch depth as a function of oil temperature for DLC1, DLC2 and DLC3. 85
5.6 Scratch hardness as a function of oil temperature for DLC1, DLC2 and DLC3. 86
5.7 Friction coefficient as a function of hardness of transformed layer for DLC1, DLC2 and DLC3. 87
5.8 Friction coefficient as a function of transformed layer thickness. . . 87
5.9 Friction coefficient map as a function of the thickness and hardness of the transformed layer. . . . . . . . . . . . . . . . . . . . . . . . . . . . 89
5.10 Friction model regarding the combination of thickness and hardness of the transformed layer. (a) LH-TkTL and LH-TnTL. (b) MH-TnTL and MH-TnTL. (c) MH-TkTL. . . . . . . . . . . . . . . 89
List of Tables

1.1 Guideline for coating selection ................................................. 6
1.2 Mechanical properties of various carbon films employing different
deposition methods ................................................................. 10
1.3 Mechanical properties of CNx films by different deposited method .... 11
3.1 Properties of as-deposited DLC coated sliding bearing and disk .... 39
Chapter 1

Introduction

1.1 Introduction to tribology

The word tribology is a combination between *tribo*, “rub” in classic Greek, and *-logy*, “knowledge of”. Widely used as an engineering term since 1966, it is a new discipline in the field of mechanical engineering and materials science correlating to the study of friction, lubrication, and wear [1]. The problem posed by friction when moving heavy objects using the sliding method has challenged mankind for a thousand years. During early tribology history, the Egyptians first used water, and later natural oils as lubricants to reduce friction at the sliding interface in order to move massive stones over great distances for the construction of pyramids. A breakthrough in tribology technology occurred with the introduction of a rolling part such as a wheel and bearing to further reduce friction.

Friction and wear are basic problems in the tribology system due to abrasion on the contact surface of two moving parts leading to a reduction in the lifespan of the tribology component. Friction is defined as a tangential force against the sliding motion of a body in an opposite direction. Wear is the result from the friction process where the greater the friction, the higher the wear. Therefore, in the tribology system, it is essential to separate two relative moving contact surfaces in order to minimize friction and wear. The focus of this study is the application of a liquid as a lubricant at the contact interface.

The demand for tribological technology increased in tandem with industrial growth and this led to the need for a better understanding of its aspects in various areas.
Chapter 1. Introduction

The role of tribology became more significant of late when researches acknowledged the looming problem of an energy crisis in the not too distant future. As such, the onus is on tribologists to increase knowledge in this area and come up with an efficient system that does not lose too much energy to the forces of friction.

1.2 Industrial needs of hard coating

It has been reported that friction, lubrication, and wear have a significant influence on the efficiency and lifespan of mechanical components employed in industries. In the long run, this influence plays a deciding role in the economic development of a nation. The report emphasized that viewing tribology from a scientific and technological perspective is crucial in order to avoid major economic losses [2]. The concern here is not only related to the economy, but also to the environment, as machinery and vehicles with high efficiency will significantly reduce CO₂ emission. It has been acknowledged that the major source of rising CO₂ emission can be traced to cars and trucks [3]. This environmental problem continues to escalate with the increasing demand for transportation which leads to a heightening of the greenhouse effect. Studies revealed that when it comes to transportation, passenger cars are responsible for 45% of total energy use and emissions [4]. The most fundamental part of a car system is the internal combustion engine which converts chemical energy into mechanical energy. The potential energy is generated by the internal combustion engine during the process of fuel burning. This energy is then converted into mechanical power which moves the car. However, part of the energy is diverted towards overcoming the adherent friction in the car system. Friction in the engine and transmission system contributes to about 17% of total energy losses in areas such as the piston assembly, the valve train, and the bearings and seals as reported in [5].

Friction behavior is dependent on whether the lubrication involved is boundary lubrication, mixed lubrication or hydrodynamic lubrication as illustrated by the recognized “Stribeck-curve” shown in Figure 1.1 [6]. However, tribological engine components will experience all three kinds of lubrication conditions because the speed of the engine is constantly changing during driving. Of the three, the one that matters most in the “Stribeck-curve” is boundary lubrication because of its potential for high friction and wear. Boundary lubrication occurs during starts, stops, shock-loads, direction changes, and when the vehicle is moving at a slow
Chapter 1. Introduction

Figure 1.1: Possible improvements based on Stribeck diagram by DLC coating application.[6]

to intermediate speed. This can be attributed to the almost complete absence of an oil film between two contact surfaces. The topmost surfaces fully contact each other and the sliding or rolling motion results in high friction. High friction leads to high fuel consumption because the system needs more power to overcome the resistance. At the same time, high friction also causes the component to undergo more wear which culminates in a reduction of its lifespan.

Figure 1.2 shows the number of cycles to failure for material combinations employed for a friction test under boundary lubrication conditions [7]. The combination of DLC-steel displays a significantly longer lifespan of the component compared to a steel-steel and DLC-DLC combination. This result indicates that hard coating can improve the tribological properties of a component in terms of friction coefficient and wear as depicted in Figure 1.1. Tribologists are challenged to come up with a suitable coating material that can improve tribological behavior in terms of low friction and high wear resistance under specific conditions.

Industrial applications that involve tribological components include internal combustion engines for automobiles, material processing, gas turbine engines, rail transportation etc. The coating material selected for a particular application depends on the device and its operating conditions as well as the required performance and lifespan of the component [8]. Some examples on the use of coating
technology for increasing the tribological performance of internal combustion engines for automotive applications are shown in Figure 1.3 [9]. Tribological components will experience different contact conditions depending on their application. These conditions include contact stress at normal load, sliding abrasion, impact, surface fatigue, fretting and chemical dissolution. Table 1.1 shows the guideline for coating selection which depends on dominating contact conditions [10].
Chapter 1. *Introduction*

**FIGURE 1.3:** Components that can be coated with DLC for use in an automotive engine. [9]
Table 1.1: Guideline for coating selection.\cite{10}

<table>
<thead>
<tr>
<th>Contact type</th>
<th>Dominating contact condition</th>
<th>Required surface properties</th>
<th>Recommended coatings</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sliding</td>
<td>Low friction sliding</td>
<td>Low shear strength at surface to layer</td>
<td>DLC, MoS₂, diamond</td>
</tr>
<tr>
<td></td>
<td>Mild wear</td>
<td>Good load support</td>
<td>TiN, TiAlN, TiC, Al₂O₃, CrN</td>
</tr>
<tr>
<td>Abrasion</td>
<td>(a) Third-particle indentations</td>
<td>(a) Good-microtoughness and load support</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(b) Two-body ploughing</td>
<td></td>
</tr>
<tr>
<td>Impact</td>
<td>Concentrated impacting stress wave</td>
<td>Good macrotoughness</td>
<td>Multilayer</td>
</tr>
<tr>
<td></td>
<td>Abrasive wear</td>
<td>Good elasticity</td>
<td></td>
</tr>
<tr>
<td>Fatigue</td>
<td>Continuous large stress waves</td>
<td>Good macrotoughness, Good load support</td>
<td>TiN, DLC Multilayer</td>
</tr>
<tr>
<td>Fretting</td>
<td>High-frequency large stress wave, Wear debris in contact continuously</td>
<td>Good elasticity, Low shear strength surface layer, Not producing hard wear debris</td>
<td>MoS₂, Cu-Ni-In, Multilayer</td>
</tr>
<tr>
<td>Chemical dissolution</td>
<td>High temperature</td>
<td>Non-soluble, Thermally conductive</td>
<td>TiN, TiAlN, TiC, WC, CrAlN, DLC, diamond</td>
</tr>
<tr>
<td>Lubricated sliding</td>
<td>Coating giving load support for lubricant film and acting as emergency layer</td>
<td>Interaction with lubricant additives, Texturing to support lubricant prevalence</td>
<td>DLC, TiN, TiC, CrN</td>
</tr>
</tbody>
</table>
1.3 Carbon coatings

Carbon is a unique material which can provide high hardness and good thermal conductivity in the form of a diamond, as well as softness and high lubricity in the form of graphite. Carbon exists in many forms in carbon-based allotropes. These forms include white carbon (ceraphite), nanotubes, buckyballs, other fullerenes, carbon-carbon composites, glassy carbons, and carbon nanofibres. Diamond-like carbon (DLC), carbon nitride, and boron nitride are a few examples of thin coating technology in which carbon, widely used in engineering technology, is the key element. Carbon is the preferred choice due to its outstanding tribological properties which contribute towards the reduction of friction and wear.

Carbon coatings can have different mechanical properties because they consist of sp\(^3\), sp\(^2\) and sp\(^1\) as shown in Figure 1.4 [11]. These combinations can provide a great variety of crystalline and disordered structures. A diamond consists of a sp\(^3\) configuration where four carbon atoms bond with each other to build a tetrahedral structure which in turn makes a strong σ bond to an adjacent atom. These structures provide high mechanical hardness, chemical and electrochemical inertness, and a wide band gap. In the sp\(^2\) configuration, as in graphite, the three of four valence electrons enter trigonally directed sp\(^2\) orbitals. These form σ bond in a plane. The fourth electron of the sp\(^2\) atom enters a π orbital which lies normal to the σ bonding plane [11]. Graphite has a strong intra-layer σ bonding and a weak Van der Waals bonding between its layers [12]. As these layers can be separated and slide easily, the resulting friction is low [13, 14]. In the sp\(^1\) configuration, two of the four valence electrons enter σ, each forming an σ bond directed along the ±x-axis, and the other two electrons enter π orbitals in the y and z directions [11].

![Figure 1.4: sp\(^3\), sp\(^2\) and sp\(^1\) hybridised bonding.][11]
1.3.1 Diamond-like carbon (DLC)

DLCs are commonly used as a hard coating in many industrial applications due to their excellent tribological properties of low friction, high wear resistance, and chemical inertness.

Ferrari and Robertson studied the different types of DLCs using spectroscopic techniques to define their structure and chemical content. Figure 1.5 shows the ternary phase diagram by dividing various DLCs into different regions based on the fraction of sp\(^3\) or sp\(^2\) and hydrogen content [15].

Generally, the mechanical and tribological properties of DLCs depend on the sp\(^3\)/sp\(^2\) ratio. However, the additional dopant material such as silicon, hydrogen, and metal/carbide, can also contribute different tribological properties to the DLC coating. Examples of diamond-like carbon are hydrogen-free amorphous carbon (a-C), hydrogenated GLC (a-C: H), tetrahedral amorphous carbon (ta-C) and hydrogenated tetrahedral amorphous carbon (ta-C: H). The other types of DLC which contain the dopant elements silicon and metal/carbide will be termed Si-DLC and Me-DLC respectively. Hydrogenated DLC coatings are generally soft with low internal stress. Thus, with good adhesion, it is possible to apply thicker film on the substrate [16]. However, hydrogen-free DLC coatings have a high degree of hardness and consequently high internal stress. As such, it is difficult to
deposit thicker hydrogen-free DLC. Generally, the thickness of hydrogen-free DLC is limited to 1 µm [11].

There are two types of deposition techniques commonly used for deposition of DLC coatings and these are Plasma Vapour Deposition (PVD) and Chemical Vapour Deposition (CVD). The PVD procedure involves atomistic deposition processes, in which material is vaporized from a solid or liquid state in the form of atoms or molecules, and then transported in the form of a vapour through a vacuum or a low pressure gaseous (or plasma) environment to the substrate where it condenses. Typically, PVD processes are used to deposit films with thickness in the range of a few nanometres to thousands of nanometres. Typical PVD deposition rates are 10-100 Å (1-10 nanometers) per second [17]. There are several types of PVD coating techniques such as vacuum evaporation, sputter deposition (in a plasma environment or in a vacuum), ion plating and Ion Beam Assisted Deposition (IBAD).

Thermal Chemical Vapour Deposition (CVD) is the deposition of atoms or molecules by substantial temperature reduction or decomposition of a chemical vapour precursor which contains the material to be deposited. Deposition at a low temperature is facilitated by the introduction of plasmas into CVD reactors. The plasmas are typically generated by radio-frequency (rf) techniques and the process is called plasma-enhanced CVD (PE-CVD) [17].