Tribological Studies on Coating-Lubricant Combinations in Different Contact Configurations

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Abstract

Diamond-like carbon (DLC) coatings are increasingly being used for both friction reduction and wear protection of machine elements working under boundary lubricated conditions. In this work, the use of DLC coatings for various interfaces of a radial piston hydraulic motor was evaluated. Tribological studies were carried out on different combinations of DLCs and lubricants, using a range of contact configurations. Two types of tetrahedral amorphous carbon (ta-C) DLC coatings (of varying thickness and surface morphology) and seven hydraulic oils (of different API groups and additive packages) were tested. Different tribological test configurations used were steel cylinders against DLC coated steel discs (non-conformal line contact) under reciprocating sliding motion; cast iron blocks against DLC coated steel rings (non-conformal line contact) under unidirectional sliding motion; and cast iron pins against DLC coated steel discs (conformal area contact) under unidirectional sliding motion. As the contact configuration changed, coating characteristics (including roughness and hardness) influenced the tribological performance of the different coating-lubricant combinations tested. The tribological behaviour of the lubricating oils varied according to the contact conditions and the DLC coating surface morphology. Mineral base oils with rust inhibitors or synthetic polyalphaolefins, and synthetic ester base oils gave excellent friction and wear reduction, depending upon the DLC coating roughness and the test setup. Zinc containing oils increased both friction and counter surface wear. These results have shown that the tribological behaviour of ta-C DLC coatings in boundary lubricated conditions is influenced by four factors, i.e., the contact configuration; the lubricant chemistry; the surface morphology of the DLC coating; and the nature of the counter surface.

Keywords: Diamond-like carbon (DLC) coating, conformity, lubrication regimes, running-in, lubricant additives.
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Preface

This project was carried out and completed at Luleå University of Technology with the help of the Division of Machine Elements and Bosch Rexroth (Mellansel, Sweden). The work presented in this thesis was undertaken between 15/01/2015 and 31/08/2015. It was part of the Luleå University of Technology project-based course, ‘Design of lubricated contacts’, from undertaken between 01/09/2014 and 15/12/2014.

This thesis consists of 9 chapters. The first chapter introduces the theory behind tribological studies of coating-lubricant combinations; provides a brief insight to the tribology of hydraulic motor; introduces the fundamentals of lubrication regimes; and also includes a literature review of the research undertaken into tetrahedral amorphous carbon (ta-C DLC) coating’s tribological behaviour. In the second chapter, the aims and objectives of the project are outlined. Chapter 3 and 4 describe the experimental materials, test setups and techniques used. Chapter 5 is divided into two parts, the first of which discusses the characterisation of the two diamond-like carbon (DLC) coatings evaluated, and the second describes the results from each tribotest setup, the profilometer and scanning electron microscopes. Chapter 6, 7 and 8 summarizes the key findings, figure out the conclusions, and outlines the scope of future work respectively. The appendix to this thesis contains the standard experimental procedures used; the friction plots of all tests conducted; tables of the wear scar analysis carried out using a profilometer; and SEM micrographs and EDX analysis of the wear scar on the tested specimens.
# List of abbreviations used

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>a-C</td>
<td>Amorphous carbon</td>
</tr>
<tr>
<td>a-C:H</td>
<td>Amorphous carbon with partial hydrogenation</td>
</tr>
<tr>
<td>ASTM</td>
<td>American Society for Testing and Materials</td>
</tr>
<tr>
<td>AW</td>
<td>Anti-wear</td>
</tr>
<tr>
<td>CETR</td>
<td>Centre for Tribology Research Inc. (now Bruker Nano Inc.)</td>
</tr>
<tr>
<td>CoF</td>
<td>Coefficient of friction</td>
</tr>
<tr>
<td>DLC</td>
<td>Diamond-like carbon</td>
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<tr>
<td>EDX</td>
<td>Energy dispersive X-ray spectroscopy</td>
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<tr>
<td>EP</td>
<td>Extreme pressure</td>
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<td>Fig.</td>
<td>Figure</td>
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<tr>
<td>GMO</td>
<td>Glycerol monooleate</td>
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<tr>
<td>RMS</td>
<td>Root mean squared</td>
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<td>rpm</td>
<td>Rotations per minute</td>
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<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
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<tr>
<td>SRV</td>
<td>Schwingung Reibung Verschleiβ: German, (Oscillating Friction and Wear)</td>
</tr>
<tr>
<td>TDEA</td>
<td>Tallow diethanolamine</td>
</tr>
<tr>
<td>UMT</td>
<td>Universal Materials Tester</td>
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<tr>
<td>Veeco</td>
<td>Organisation for optical profilometer</td>
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<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
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<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>ZDDP</td>
<td>Zinc dialkyldithiophosphate</td>
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<tr>
<td>ZYGO</td>
<td>Organisation for optical metrology</td>
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## List of symbols used

<table>
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<tr>
<th>Symbols</th>
<th>Description</th>
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<tbody>
<tr>
<td>$\alpha$</td>
<td>Angular sliding velocity</td>
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<tr>
<td>b</td>
<td>Contact width</td>
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<tr>
<td>E</td>
<td>Elastic Modulus</td>
</tr>
<tr>
<td>$h_0$</td>
<td>Lubricant film thickness</td>
</tr>
<tr>
<td>g</td>
<td>grams</td>
</tr>
<tr>
<td>GPa</td>
<td>Giga Pascal</td>
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<tr>
<td>L</td>
<td>Length of contact</td>
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<tr>
<td>mins</td>
<td>minutes</td>
</tr>
<tr>
<td>mm</td>
<td>millimetres</td>
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<tr>
<td>mg</td>
<td>milligrams</td>
</tr>
<tr>
<td>MPa</td>
<td>Mega Pascal</td>
</tr>
<tr>
<td>nm</td>
<td>nanometres</td>
</tr>
<tr>
<td>Pa</td>
<td>Mean Pressure</td>
</tr>
<tr>
<td>R</td>
<td>Radius</td>
</tr>
<tr>
<td>Ra</td>
<td>Mean surface roughness</td>
</tr>
<tr>
<td>Rq</td>
<td>Root mean squared surface roughness</td>
</tr>
<tr>
<td>Rv</td>
<td>Depth of valley in a surface profile</td>
</tr>
<tr>
<td>$\mu$m</td>
<td>micrometres</td>
</tr>
<tr>
<td>$\mu$</td>
<td>Friction coefficient</td>
</tr>
<tr>
<td>$\nu$</td>
<td>Poisson's ratio</td>
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<tr>
<td>$V_{\text{sliding}}$</td>
<td>Sliding velocity</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>Normal hertzian stress</td>
</tr>
<tr>
<td>$\tau$</td>
<td>Shear stress</td>
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1. Introduction

When two surfaces move over one another, there is both friction and wear at the interface. To control friction and wear, a lubricating system is sometimes introduced at the interface. The study of friction, wear and lubrication is called Tribology (and the related terms are abbreviated to ‘tribo’). A tribological system is composed of two triboelements (i.e. interacting bodies) and an interfacial medium, which can be either a lubricant or some other medium. The operating conditions play a key role in determining the tribological behaviour of a system. These conditions include temperature, humidity, and load, velocity of motion between interfaces, and the viscosity or shear strength of any interfacial medium present.

1.1 Tribology in hydraulic motors

The function of a hydraulic motor is to convert pressure flow energy into mechanical energy. The mechanical energy in the hydraulic motor is expressed as both torque and rotational motion. The basic working components of a radial piston hydraulic motor are shown in Figure 1.1. This type of motor consists of a rotating cylinder block with a reciprocating piston, and a roller moving on a cam, as a stationary wavy housing. The oil is distributed to the cylinders as they rotate. A hydraulic motor has three main tribological interfaces, as shown in Figure 1.2. These interfaces lie between: 1. the cam and the roller; 2. the roller and the piston; and 3. the piston and the cylinder. This study focuses on the tribological aspects of these interfaces.

The roller-piston interface has conformal area contact. A conformal contact occurs between a convex and a concave surface with small radial clearance between the contact elements. It is characterised by large contact area (journal and sleeve are examples of conformal surfaces). The contact between two nominally flat surfaces may also be considered as conformal. The contact between two convex surfaces can be described as a non-conformal contact (Spur gears and rolling element bearing and inner race are examples of non-conformal surfaces). If the radii of curvature of the convex and concave surfaces are considerably different, it results in a non-conformal contact with smaller contact area [40]. A roller cam interface has non conformal contact at the trough of the cam and conformal contact at crest of the cam (Figure 1.1).

The roller is located over the piston head which undergoes reciprocating sliding motion, along the radial direction of the motor, in the cylinder bore. As the roller moves along the cam, it undergoes a rolling sliding motion at both the roller-piston and roller-cam interfaces.

The working stroke of a hydraulic motor is designed such that it converts the pressure in the working fluid into mechanical torque for rotational motion. As shown in Figure 1.1, during the
working stroke, as the cylinder moves to the crest of the cam, it is at high pressure. The timing is adjusted so that on its return stroke, as the cylinder moves to the trough of the cam surface, it is at low pressure. The tangential force on the piston from the roller (resulting from its motion on the cam), leads to the development of friction between the roller and piston. During the application of heavy loads or variable speeds there is greater sliding than rolling motion at the roller-piston interfaces, resulting in high friction and wear. Under normal operating conditions, the roller and piston are separated from each other by a lubricating oil film, maintained by the lift provided by the pressurized oil from the piston groove. The operating speed above which the hydraulic motor operates in hydrodynamic lubrication, is called the lift-off speed. However, when the motor starts and stops or is running at low speeds, boundary lubrication can occur [1]. In addition, as the piston changes direction with every stroke, the film thickness changes at the piston-cylinder interface, which can also lead to boundary lubrication.

Fig 1.1. A radial piston hydraulic motor and its working [1]

Fig 1.2 Schematics of a radial hydraulic motor with roller-cam (interface 1), roller-piston (interface 2) and piston-cylinder (interface 3).

1.2 Lubrication regimes
For lubricated contacts, the various regimes of lubrication are categorised according to the lubricating film thickness [59 and 60]. Quantitatively, the lubrication film thickness is defined by the lambda ratio ($\lambda$). This is the ratio between the film thickness ($h_0$) and the composite root mean
squared (RMS) roughness (Rq) of surfaces 1 and 2 of the two triboelements being evaluated. This relationship is described in equation 1 from Hamrock and Dawson [29].

\[ \lambda = \frac{h_0}{\sqrt{Rq_1^2 + Rq_2^2}} \]  
(Eq. 1)

When the thickness of the lubricant film between two interacting surfaces is much higher than their mean surface roughness, i.e., when \( \lambda > 3 \), there is hydrodynamic lubrication. In this lubrication regime, wear is minimal. The load applied to the surfaces within the system is supported by the hydrodynamic pressure generated by the lubricating film. When the film thickness is just higher (\( 1 < \lambda < 3 \)) than the mean roughness of the two surfaces, there is a mixed lubrication regime. In this regime, the load is supported both by the lubricating film and the surfaces asperities, which come in contact with each other. However, if the height of the asperities (mean surface roughness) are higher than the thickness of the lubricant film, then the lubrication regime moves from a mixed regime to a boundary lubrication regime (\( \lambda < 1 \)). Under boundary lubrication conditions, the asperities come into contact with each other and support the applied load, leading to a high degree of surface wear. Boundary lubrication usually occurs when the motor starts or stops, as there is an ‘increases’ or ‘decreases’ in velocity, load or viscosity of the working fluid, which changes the film thickness.

The operating parameters of load (P), velocity (v) and viscosity (\( \eta \)) can be quantitatively defined as the lubrication parameter L, as given in equation 2 [2].

\[ L = \frac{\eta v}{P} \]  
(Eq. 2)

The transition into various lubrication regimes as a function of the lubrication parameter can be plotted on a Stribeck curve (an example of which is shown in Figure 1.3). Figure 1.3 shows that increasing the load (P), and reducing both the velocity (v) and viscosity (\( \eta \)) (i.e. increasing the temperature) gives a lower lubrication parameter and boundary lubrication is achieved [59].

Fig 1.3 Stribeck curve showing different lubrication regimes.
1.3 Approaches in friction and wear control

Asperity interactions take place under boundary lubrication conditions, leading to friction and wear. Both the surface morphology of the interacting surfaces and the chemical composition of the lubricant influence the tribological behaviour observed. One way to control friction and wear is to change the surface properties of the triboelements. This can be achieved by surface finishing or hardening, or by applying surface coatings. In addition, the interfacial lubricating medium that forms an intermediate tribolayer, can alter the friction and wear. Adding additives to a lubricant can alter its properties.

The physical properties of surface coatings are key factors in determining the levels of friction and wear observed in a system. Soft coatings, such as molybdenum sulphide and graphite, provide low levels of friction, but they are easily sheared, leading to a high degree of wear. Hard ceramic coatings such as alumina, zirconia, carbides and nitrides of boron and silicon are used for anti-wear purposes.

The coefficient of friction (CoF, \( \mu \)) can be expressed as a relationship between tangential frictional force (\( F \)) and normal load (\( N \)). CoF can also be expressed in terms of shear stress (\( \tau \)) and pressure (\( P \)) acting over an area (\( a \)). These relationships are shown in equation 3 [7].

\[
\mu = \frac{F}{N} = \frac{a \tau}{N} = \frac{\tau}{P}
\]  
(Eq. 3)

For hard and stiff interfaces, the actual contact area between surfaces is small, but the shear stress is high, leading to a high CoF. In contrast, softer interfaces have larger contact areas, leading to a higher CoF. As soft films and coatings give low shear stress values, lower CoFs can be achieved with softer films on hard, stiff substrates. One of the ways to obtain such a system is to coat a substrate with a hard coating, and then use the coated substrate in a lubricated environment. The concept of a coating-lubricant combination is called hybrid lubrication.

The main wear mechanisms in a hybrid lubrication environment are:

- The abrasive effect of hard surface asperities or any trapped debris, which scratch against the surfaces
- The adhesive effect from junctions formed between similar surfaces
- The shearing effect from any material trapped between two surfaces, that goes on to form a tribofilm

Wear volume is volume of the material removed from a body. The wear volume (\( V \)) is calculated from Archard's law given in equation 4, where \( l \) is the sliding distance, \( F \) is the normal load, \( H \) is
the hardness of the softer of the two materials, and $k$ is the wear coefficient. The wear coefficient
is influenced by both the materials used and the wear regime [61]

$$V = \frac{klF}{H}$$  \hspace{1cm} (Eq. 4)

To minimise the wear volume, the coating applied needs to be hard to avoid wear (of both
abrasive and adhesive types). Coatings also need to be strain tolerant and tough to prevent crack
propagation and substrate deformation. This prevents abrasion, which contributes to high
friction and wear, and therefore high wear volume.

1.4 DLC coatings to improve efficiency and durability of machine elements

1.4.1 DLC coatings: types and synthesis

DLC is an amorphous, carbon-based thin film (thickness ranging from fractions of a nanometer
(monolayer) to several micrometers) coating with a high fraction of metastable sp$^3$ hybridised
carbon atoms [7]. Diamond-like carbon (DLC) coatings are an example of hard coatings with high
wear resistance. In addition, tribofilms can form on DLC coatings, leading to improved tribological
performance. Such tribofilms can participate in inter-film or intra-film sliding [5]. As DLC coatings
(films) are hard, intra-film shearing is minimal. However, if the adhesion between a DLC coating
and tribofilm is weak, then shearing can occur at the interface of the tribofilm and DLC coating
(which is known as the inter-film). Intra-film shearing takes place on the surface of the tribofilm
if the adhesive component between the DLC and the tribofilm is too large [6].

DLC coatings are classified into three categories:

1. Hydrogenated and non-hydrogenated
2. Doped (metallic and non-metallic) and un-doped
3. High and low sp$^3$ carbon content

A DLC coating with a high sp$^3$ carbon content is described as a tetrahedral amorphous carbon (ta-C)
coating. It is deposited on a steel substrate using ion or plasma beams. To achieve the maximum
sp$^3$ fraction, these beams have a high ion content at a precise ion energy band of 100 eV [8]. Ion
energies lower than 100 eV lead to the polymerisation of C-H (sp$^3$) bonds, whereas ion energies
greater than 100 eV cause graphitisation of sp$^2$ bonds via the atomic relaxation of implanted
atoms [9]. High ion energy deposition methods, including filtered cathodic vacuum arcs (FCVA),
mass selected ion beam deposition and pulsed laser deposition, have been used to grow ta-C DLC
on different substrates [7].

1.4.2 Mechanical properties of DLC coatings

Both the physical properties and the chemical composition of a DLC coating also influence its
tribological properties. As described by Sheeja et al., both surface roughness and adhesion to the
substrate play important roles in determining the tribological properties of DLC films [12]. Hardness of coating also determines the wear behaviour between the two interacting materials.

Coating film thickness influences the hardness and adhesion strength of DLC films as described by Wei and Yen [13]. In thin film coatings, the addition of an interlayer helps to increase the adhesion strength between the coating and substrate. Often, titanium and chromium are applied to metal substrates as an interlayer. As the overall coating thickness increases, the compressive stress within the coating also increases. This reduces the adhesion between the coating and substrate, thereby diminishing the DLC’s performance. Wei et al. tested the adhesion strength of both thick (thickness in order of micrometers) and thin films (thickness in order of nanometers), using both optical microscopy (observing the peeling degree) and a nano-scratch test. They found that both an increase in film thickness and oxidation impaired film adhesion. Hence carburisation (absorption of carbon) is largely observed in DLC films with a chromium or titanium interlayer [14]. These interlayer decrease the internal stress at the substrate–film interface, and smoothen the difference in lattice parameters between the growing film and substrate thereby improving the adhesion [62].

Analysis using Raman spectroscopy indicates that as the film thickness in thin films increases, both the sp3 fraction and the hardness decreases. Previous studies by Sayer et al. suggest that harder substrates show better adhesion to the substrate [63].

Roughness is another property that greatly influences coating tribology. A surface profilometer can be used to measure a range of roughness parameters, shown in Figure 1.4 b.

Fig 1.4. (a) A sample DLC coated surface, with the horizontal and vertical lines corresponding to the X and Y profile to be measured. (b) The X profile of the sample surface, with the roughness parameters displayed in the top grey box in the right.
The various roughness parameters in Figure 1.4b are defined as:

- **Rq** is the root mean square roughness. Also known as the geometric average roughness, it is the square root of the average of sum of the heights squared of peaks and valleys in a given area.

- **Ra** is the arithmetic roughness average, and is the most commonly measured parameter when analysing surface profiles. It is the average value between the height of peaks and valleys in a given area.

The average values of Rq and Ra for an entire surface area can be calculated by splitting the surface area profile into smaller segments. The values for each segment are added together and an average is taken. The main difference between Ra and Rq, is that Rq amplifies the surface irregularities and Ra averages them. Therefore, an open peak structure has higher Rq than a closed valley structure, even though they might have the same Ra values.

- **Rp** is the height of the highest peak of the profile.

- **Rv** is the height of the lowest valley of the profile.

- **Rt** is the maximum height of the profile (Rp-Rv)

### 1.5 DLC coating-lubricant compatibility

#### 1.5.1 The interactions between coatings and lubricant base oils

Lubricant base oils can be divided into different categories based on a range of criteria [64]:

- Mineral oil, synthetic oil or vegetable oil (based on production process)
- Biodegradable oil or non-biodegradable oil (based on biodegradability)
- Industrial oil, hydraulic oil and automotive oil (based on application)
- American Petroleum Institute (API) groups (based on saturates and sulphur content)

To study the tribological properties of lubricants, it is important to understand their production process and chemical composition. In this thesis the lubricating base oils were classified according to their API groups. API Group I oils, obtained by refining crude oil, are high in aromatics (17%) and sulphur (0.3%). The also contain wax which are long chain organic compounds (lipids) malleable at room temperature. They undergo a solvent extraction refining process, where aromatic components are preferentially removed. The remaining lubricant contains long chain saturates, such as straight, branched and cyclic paraffins, and traces of unsaturated aromatics. To remove unsaturated components, the crude oil undergoes hydrogenation, leaving it with saturates of cyclic (23%) and straight chain (75%) aliphatics.
1. Introduction

API Group II oils are produced by removing high melting point cyclic and long chain aliphatics from crude oil post the processing done for Group I oils. This gives Group II oils improved viscosity indexes, pour points and lower volatilities. By dewaxing Group II oils, API Group III oils are prepared, which have a higher degree of straight chain saturates (86%). Group III oils form the most stable of all mineral-based lubricating oils, in terms of their improved viscosity index and lower volatility [31 and 64].

API Group IV oils are composed of polyalphaolefin (PAO) base stocks. They are synthesized by the catalytic oligomerisation of alphaolefins (alkenes). This gives a wax-free combination of molecules of a predetermined chain length oligomers (In an oligomer there is a limited number of monomers to form a molecular complex). PAOs often have shorter branches on their oligomer backbone; this helps to improve the lubricating properties of the oil. Removing these short branches improves the rheological properties of the oil [32].

Synthetic esters form part of API Group V base stocks. They have saturated or unsaturated alkyl ‘tails’ bound to polar ester head groups. Group V base stocks have high oxidative and thermal stability. Industrial oils, including biodegradable vegetable oils, fall within Group V. Group V oils have a high concentration of polar groups and unsaturated molecules. These functional groups (carboxylic acids and ethers) provide active sites for the reaction and adsorption onto the rubbed surfaces, which improves the base oil’s lubrication properties. The low wear and friction coefficients with these oils, are caused by the low shear strength of lubricant molecules adsorbed onto the metal surfaces, with their polar head groups interacting with the metal, leading to boundary lubrication conditions. High stress levels and temperatures further activate clean areas of the metal surface, which can lead to desorption of the tribolayer [31 and 64].

1.5.2 Effect of additives on friction and wear

Additives are added to base oils to help improve their lubricant properties. The additives that influence the tribological behaviour of lubricants can be classified into three types:

- Anti-wear (AW) additives, e.g. zinc dialkyldithiophosphate (ZDDP)
- Friction modifiers (FM) additives, e.g. molybdenum dithiocarbamate (MoDTC) and glycerol mono-oleate (GMO)
- Extreme pressure (EP) additives, e.g. phosphorous and sulphur

Friction modifiers (FMs) are added to lubricants to reduce friction coefficients in lightly loaded, mixed lubrication regimes. A FM is usually a straight, long chain hydrocarbon, with a terminal polar functional group(s). FMs work by adsorbing onto an interface, forming a protective, cushioning layer. The resultant layer behaves as a cushion, which prevents the direct contact of asperities. On occasion, FMs also form thin, reacted layers, which provide low shear strength. In
1. Introduction

the fluid film lubrication viscosity modifiers (VMs) also help to ‘reduce fiction’. VMs form a continuous, globular layer by reacting with oil components, leading to a shearable tribolayer.

Almost all lubricant additives are designed for ferrous based interfaces, and a majority of these additives are organic friction modifiers. These additives are eco-friendly and biodegradable, and include glyceryl monooleate (GMO), glycerol monooleylether (GME), tallow diethanolamine (TDEA) and oleylamine. These additives contain polar oxygen or nitrogen-containing functional group(s). They have free electron pairs, which have an affinity towards the metal substrate ions devoid of free electrons due to the rubbing action. The polar functional group of the additive binds to the metal substrate, forming a shearable monomolecular film, the presence of which has been confirmed using analytical techniques [35].

In boundary lubrication, as the lubricating conditions become more severe, the interactions between FMs and the surface may fail due to desorption of FMs under the higher applied loads. The resultant severe wear can be prevented by stronger, more durable films. Wear reduction can also be achieved by the addition of AW additives, which form inorganic films on surfaces via tribochemical reactions or chemisorption, resulting in the elimination of organic moieties. An AW film may have a high shear or semi-plastic layer, which can lead to high levels of friction. Therefore, the protection of tribomaterials against wear can sometimes come with the trade-off of high levels of friction [16], demonstrating that additive interactions are not always synergistic.

As a system moves into a boundary lubrication regime with higher loads and greater pressure, there can be high levels of wear and friction. This can be prevented by the addition of extreme pressure (EP) additives, which usually contain sulphur or phosphorous. These additives work by reacting with the surface of rubbed triboelements forming a sacrificial layer of iron sulphide/or iron phosphide and reducing wear and seizure of the contacting surfaces.

Additives such as molybdenum dithiocarbamates (MoDTC) act as friction modifiers by forming low shear, self-lubricating molybdenum disulphide sheets on the substrate [34]. However, MoDTCs generate ash, and are therefore excluded from ashless lubricants.

Zinc dialkyldithiophosphate (ZDDP) acts as an anti-oxidant and anti-wear agent in both engine and transmission oils. ZDDP derived tribofilms are formed on iron-based surfaces in the form of glassy phosphate pads [39]. As explained by Graham et al., these raised pads (about 0.1 nm thick) bear the load between two interfaces and reduce wear by preventing asperity interactions [36].
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1.6 Previous work on the tribological behaviour of ta-C DLC coatings

DLC surfaces are considered to be relatively inert compared to their metallic counterparts. Hydrogenated DLC coatings show excellent friction and wear behaviour in dry and inert atmospheres. Non-hydrogenated (or ta-C DLC) coatings, have shown low friction and wear in lubricated contacts. Based on results obtained from previous work on DLC coatings [24], the tribological behaviour of non-hydrogenated ta-C-type DLC coatings are the focus of the results presented in this thesis.

1.6.1 Interaction between ta-C DLC coatings with lubricant base oils

Vengudusamy et al. investigated the friction properties of DLC-DLC contacts with API Group III oils [37]. Ta-C DLC coatings of varying hardness and surface roughness were tested using a DLC coated ball-on-disc setup. Results showed that ta-C DLC coatings gave a friction coefficient of 0.05 and 0.06 for the soft-rough and hard-smooth coating combinations respectively. Ta-C DLC gave the lowest friction compared to other DLCs tested, including a-C: H type DLC (both doped and undoped). The reduction in boundary friction of the hard and smooth coating was attributed to the surface graphitization, as indicated by the change in sp$_3$ to sp$_2$ ratio, observed by Raman spectroscopy. The soft, rough ta-C DLC demonstrated a greater drop in friction, which was attributed to surface smoothening, evident from reduction in the arithmetic roughness average (Ra) values obtained before and after the test. This reduction of roughness shifted the lubrication regime from boundary to mixed lubrication. The severity in conditions caused due to temperature and load play an important role in the graphitization of the coatings. The soft, rough ta-C DLC coating gave higher ball and disc wear, compared to the hard, smooth ta-C DLC coating, for which no explanation was provided [37].

Substantial research has been carried out in an attempt to explain the friction behaviour of ta-C coatings with polyalphaolefin (PAO) base oils, using various additive concentrations and combinations. Tasdemir et al., tested ta-C DLC coatings in PAO base oils with various additives [17]. The tests were conducted using a pin-on-disc line contact setup at 150 MPa hertzian stress and 80 °C. Using ta-C DLC-coated pins on a steel disc in a PAO lubricated contact, reduced the running-in friction coefficients from 0.11 in a steel/steel contact to 0.08. The DLC/DLC pair and DLC/steel pair gave a low friction coefficient of 0.025 with pure PAO base oil, compared to 0.09 in the reference steel/steel tests, i.e. without DLC coatings [17]. However the stability of friction force with the DLC coatings in the DLC/steel combination in PAO oil was worse compared to the DLC/DLC combination, probably due to the total wearing out of the DLC coatings. When the temperature was decreased from 80 to 50 °C, the friction coefficient of the DLC/steel contact in pure PAO base oil dropped to 0.018, and the friction force showed better stability. This friction coefficient was reported to be the lowest amongst all types of DLC coatings.
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The results observed by Tasdemir et al. was explained by a range of theories: (1) The graphitisation of the upper layer of the ta-C DLC coating due high contact and/or shear stress and the resultant frictional heating resulting in a shearable tribolayer. Using techniques such as Raman spectroscopy and surface reflectometry, the influence of the thickness of such a graphitic layer on the level of friction was measured [42]. (2) Dangling sigma bonds of the ta-C DLC coatings are deactivated by environmental species, such as oxygen and hydrogen, which could reduce the chance of adhesive contact during sliding. This would explain the lower friction coefficient observed in DLC/DLC contacts [51 and 57]. (3) The passivation (shielded from environmental factors such as air and water) of the nascent ta-C DLC surface and the oil interaction after the removal of surface contaminants was suggested by Tasdemir et al. as the cause of low friction coefficients [17]. However the non-polar nature and high stability of PAO prevents it from interacting with ta-C coatings. As a result, the ultra-low friction observed for a DLC coating in a PAO base oil is caused by the DLC itself [43]. Works done by Okubo et al. and Minami et al. provided different results. Tribological tests were undertaken on ta-C DLC/DLC and ta-C DLC/steel-coated cylinder-on-disc contacts using a PAO base oil in a reciprocating setup, under similar conditions to those used by Tasdemir [16 and 44]. High and steady friction coefficients of 0.13 and 0.1 for ta-C DLC/DLC and ta-C DLC/steel contacts were obtained respectively [44]. Kano et al. concluded that the $sp_3/sp_2$ ratio and hydrogen content, rather than any structural transformations, were the main causes for the low friction of DLC coatings [18].

Kalin et al. used synthetic esters, and vegetable & mineral oils to evaluate the effect of both polarity and unsaturation in oils on their tribological behaviour. The polarity increased in order from mineral oils, to (synthetic) saturated esters, to unsaturated esters, with vegetable oils (sunflower oil) having the greatest polarity. These oils were tested in a ball-on-disc setup, coated with a hydrogenated DLC and a silicon interlayer. Saturated esters showed higher friction and wear compared to both unsaturated esters and the vegetable-based oil [33 and 46].

Kano and Martin tested the unidirectional and reciprocating sliding of oleic acid with ta-C DLC coatings. At sliding speeds of 1 mms$^{-1}$ and 50mms$^{-1}$, super-low friction coefficients of 0.05 and 0.005 were measured. In comparison, the friction coefficients of hydrogenated DLC coatings were 0.1 and 0.02 at similar sliding speeds, indicating that the lubrication mechanisms in these two DLCs is different. Ta-C DLCs show better wettability with oleic acid, leading to reducing friction by tribochemical reactions ($-\text{OH}$ termination) on the surfaces of such systems. In contrast, hydrogenated DLC surfaces, alkyl groups terminate generating hydrogen. This causes weak van der Waal’s interaction between surfaces causing low friction [47].
1.6.2 Interactions between ta-C DLC coatings and lubricant additives

Studies by De Barros et al. reported that hydrogenated DLCs gave ultralow friction and wear in PAO base oils with molybdenum dithiocarbamate (MoDTC) and ZDDP additives [34]. When MoDTC interacts with DLC, it forms sulphides and oxides of molybdenum, and ZDDP provides sulphur for the formation of low-shear MoS$_2$ lamellar sheets. The ultralow friction observed in the presence of these additives is due to the high MoS$_2$ to MoO$_3$ ratio [54]. Molybdenum oxides are crystalline solids, which have sharp edges, and damage hydrogenated DLC coatings upon their interaction with them. In contrast, hydrogen-free DLC coatings are unable to form shearable MoS$_2$ layer and exhibit poor lubrication when tested with oils containing MoDTC. Thus hydrogen free ta-C DLCs need ashless lubricants for friction reduction [55].

Both Tasdemir et al. and Kano et al. reported that self-interacting hydrogen free ta-C coatings, combined with glycerol mono-oleylether (GMO) additives and DLC/Steel and DLC/DLC contacts, gave a low friction coefficient of 0.025 [18 and 43]. Smooth and stable friction was observed, probably due to the GMO increasing the durability of the ta-C coatings. Increasing the test temperature 50° C to 110° C or reducing the GMO concentration, further dropped the friction coefficient to 0.016. X-ray Photon Spectroscopy (XPS) analysis of the ta-C worn surface showed C-O and C=O bonds, suggesting that the ta-C surface was hydroxylated during the sliding motion, when in contact with the GMO-containing lubricant. It was hypothesized that the dangling bonds of carbon atoms from the friction activated ta-C coated surface are terminated with hydroxyl (OH) groups. This could then lead to low energy van der Waals interactions between either the two DLC coatings, or the tribofilm monolayer (composed of -OH terminated carbons atoms) and the DLC/steel contacts. Both Tasdemir et al. and Kano et al. suggested that these interactions caused the low friction observed [18 and 43]. Both decreasing the GMO concentration and increasing the test temperature resulted in the PAO base oil acting to further reduce friction [43].

Okubo et al. carried out reciprocating tests using PAO base oils with organic friction modifiers, and observed low friction. The friction coefficient decreased from 0.14 during start up, and steady state CoF of 0.02, 0.036 and 0.04 were measured with GMO, GME and TDEA respectively, due to similar mechanisms, explained by Tasdemir and Kano for GMO in PAO [44].

When ZDDP was added to a PAO base oil with a DLC/steel pair, the friction coefficient increased from 0.08 to 0.085. This was due to a ZDDP-based pad-like tribofilm forming on the steel counter face, which prevented it from coming into contact with the DLC coating and causing its graphitization for friction reduction [17]. There lacks unanimity on the formation of such tribofilm on the DLC coating. Tasdemir et al. observed pad-like films on ta-C coated pins. As explained, this could be due to the transfer of ferrous particles from the counter face to the coating surface during running-in, and the subsequent action of ZDDP on the ferrous particles. Tasdemir
1. Introduction

*et al.* observed that ZDDP pads were not formed on the DLC coated surface when run with the DLC-coated counter surface [19 and 43]. The tribofilms formed when the counter face was also DLC coated, were white and patchy, and could be removed by ultrasonic cleaning [20].

When GMO was added to a ZDDP-based oil, the thickness of the ZDDP tribo film pads generated on the steel surfaces present reduced [21]. The tribochemical reaction between GMO and ZDDP molecules during sliding, or the preferential adsorption of GMO onto the DLC coated surface, prevented ZDDP from forming a tribofilm. Thus GMO and ZDDP do not have any synergistic action [43]. However, in reciprocating tests using DLC/DLC contacts and ZDDP, the addition of organic friction modifiers, such as GME and GMO, decreased the friction coefficient from 0.14 to 0.06 and 0.07 respectively. In contrast, the organic, friction modifier TDEA initiated a drop in the friction coefficient to 0.03 when tested in combination with ZDDP. Further XPS and EDX analysis with AFM (Atomic Force Microscopy) mapping highlighted the formation of a different ZDDP-based tribofilm, compared to the pad-like, thick (100 nm) tribofilm formed with tests run with only ZDDP. The film formed when both TDEA and ZDDP were present, was sulphur-rich, highly viscous and thin (3-4 nm), and caused a further drop in friction compared to the organic friction modifiers. Spikes also reported that GMO prevented the formation of a pad like tribofilm with ZDDP [39 and 60]. The observed wear also increased in organic FMs in the presence of ZDDP, except when TDEA was present [44].

When evaluating the wear of DLC-coated pins, pure PAO base oil gave the highest wear values, followed by PAO with a GMO additive, and a ZDDP additive, with or without a GMO additive [43]. It could be that the monomolecular layer generated by GMO when used alone, prevents asperity interactions, thereby reducing both wear and friction [43]. PAO (in combination with a ZDDP additive) gave the lowest wear value, due to the anti-wear properties of ZDDP. The wear of the pin also depends on the counter face hardness, and was observed to increase from DLC/steel, steel/steel to DLC/DLC in all oils, except for pure PAO where there was delamination of the coating film. The normal wear mechanism observed for DLC/steel contacts was polishing wear in additivated oils [43]. However, the excessive wear of DLC/steel pairs seen in a pure PAO-based lubricant could be due to abrasion from worn steel particles in the oil; oil degradation; or carbon diffusion from the DLC to the counter face, causing tribochemical wear, accelerated by both increasing temperatures and loads [43].

Ultra-low friction was achieved under boundary lubrication conditions when ta-C coatings were run with biodiesel-based lubricants containing esters [22]. The friction behaviour of ta-C coatings was tested using a reciprocating test setup with flat-on-flat and ball-on-disc contacts, at 1.2 GPa for both the contact configuration, using various ball diameters. The coatings were deposited on a 100Cr6 steel disc. A rapeseed methyl ester (RME) based biodiesel was used in varying ratios to
the ester base oil. In the presence of biodiesel and ta-C coating there was a 50% reduction in the friction compared to pure base oil in the ball-on-disc contact configuration. On the other hand the wear of both the ball and disc increased, reducing the contact pressure from the initial value of 1.2 GPa. For the flat on flat contact where the nominal pressure was 10 MPa, ultralow friction results were not repeatable with biodiesel. It was predicted that coating failure observed at high loads and lack of lubrication which could not provide activation to DLC coated surface, caused the intermittent high friction in the flat on flat contact. Simultaneously Oleic acid, Oleic acid with methyl ester, Rapeseed Oil and Biodiesel gave low friction coefficient of 0.03-0.04 and high wear with steel/DLC ball-on-disc test. Biodiesel consists of methyl ester of fatty acid (oleic acid in rapeseed oil) with free fatty acids, glycerol and glycerides (identical to GMO) as impurities. These impurities in biodiesel contribute to the friction and wear reduction in steel/steel contact [45]. They also work by mechanisms where DLC coated surfaces with terminated alcohol/acid functional group gives low shear during sliding. Additionally it was also concluded that test conditions and contact stress could also be influential in tribological behaviour [22]. For example in steel/steel interface friction in linear reciprocating test setup is higher than rotational setup due to asperity interlocking. This behaviour is reversed with DLC/DLC contacts [52].

1.6.3 The effect of surface morphology on ta-C DLC coating tribology

The tribological behaviour of ta-C DLC coatings with various levels of surface roughness (and both with and without surface finishing) were tested in a reciprocating cylinder-on-disc configuration at a hertzian stress of 100 MPa [24]. The results showed that when ta-C DLC coatings were lubricated with a fully formulated oil, a low friction coefficient of about 0.015 was measured. Ta-C DLC coatings with surface finishing gave a steady state friction value of 0.025. In comparison, ta-C DLC coatings without surface finishing gave a lower steady state friction value of 0.016, and required a longer running-in period. The addition of a FM additive (Oleylamine) reduced both the running-in time and wear width in both DLCs with and without surface finishing. However, the steady state friction values increased to 0.04 and 0.036 for DLCs with and without surface finishing respectively. The carbonaceous deposit detected in wear scars in the absence of the Oleylamine additive could have been responsible for the low levels of friction observed [16]. The carbon content of the DLC surfaces decreased after testing with base oil (without the Oleylamine additive), but increased after testing with additivated oil. The carbonaceous deposits may have been from Oleylamine, which decreased the running-in time. Based on roughness data, it was suggested that reducing the surface roughness shifted the lubrication regime from boundary to hydrodynamic, which therefore promoted low levels of friction. Mabuchi et al. found that the wear rate of ta-C DLC coatings under lubricated conditions decreased with increasing surface hardness [23].
The influence of surface modifications on friction in conformal tribopair in different lubrication regimes was studied by Daniel [1]. Results suggested that running-in effectiveness, boundary friction and lift off speed (in transition from boundary to fluid film lubrication) is governed by both surface topography and coating hardness. The harder DLC coatings gave lower boundary friction values, which were unaffected by the running-in. However, in mixed lubrication regimes, DLC coated tribopairs showed a larger drop in friction after running-in compared to uncoated tribopairs. Moving from boundary to mixed lubrication regimes, harder DLCs had more effective running-in and obtained better conformity, thereby resulting in lower friction. The friction coefficient was observed to decrease with smoother surfaces, as these invoke hydrodynamic effects which act to reduce friction [48].

Research into the tribological behaviour of hard and soft DLCs using a stainless steel pin-on-disc test setup, showed that soft DLCs provided lower friction and wear than hard DLC. The influence of test parameters (such as sliding velocity and load) on tribological behaviour depended on the coating type used [50]. At high sliding speeds, there was a greater increase in surface transformation in softer DLC coatings, leading to a more compact transfer layer and lower friction. The counterpart wear rate increased when hard DLC coatings were used. When loads were increased, both hard and soft DLCs displayed higher friction.

The influence of roughness and surface scratches on the wear behaviour of DLC coatings highlights how a rough, scratched DLC surface shows improved durability and tribological behaviour, compared to a smooth DLC coated surface. The scratch induced surface modification breaks the counter body asperity and reduces high, localised contact pressures. This prevents coating degradation and decreases friction with high shear. The troughs on the surface also act as lubricant pockets for improved lubrication [49].

The role of substrate roughness and topographical orientation in the tribological behaviour of sliding DLC/steel dry contacts was elucidated by Kenneth et al. Smoother DLC coatings strengthened surfaces, but rough DLC surfaces had cracks, and showed delamination of asperities at the micro scale. Smooth surfaces also eliminated asperity interlocking, leading to low friction [52]. For hard DLC coatings, the roughness increased the wear rate and switched the wear mechanism from polishing to ploughing. Increasing substrate roughness also increased DLC wear, with chip-flake formation and coating fragmentation [53]. It was concluded that a thinner DLC has less internal deformation and strengthens the surface. DLC coating on a smoother surface has less effects of ploughing friction as smooth substrate increases tension and buckling on the coating. The effects of ploughing friction is significant in increasing friction in rough DLC coating where tribolayer generation is difficult as in dry contact [53].
Surface roughness and hardness also have a major effect on the activation of both lubricants and their additives on surface coatings. A DLC with predefined structure and a rough surface showed a low friction coefficient when lubricated in oil containing MoDTC and ZDDP. The surface roughness and structuring promoted MoS₂ formation by activating the tribofilm derived from the additives MoDTC and ZDDP. The hardest DLC coating with high roughness showed both high friction and high wear. The coating with moderate hardness and high roughness showed the lowest friction, and the friction increased as the roughness was further reduced. Friction increased when softer coatings were used, even with high levels of surface roughness. On investigation of the molybdenum content in the worn DLC surfaces, it was concluded that both high surface roughness and hardness of DLC coatings are influential in additive based tribofilm activation and friction reduction. This is because a concentrated and hard contact in a rough and hard surface energetically promotes tribofilm formation [56].

1.7 Knowledge gaps

Previous research into ta-C DLC coatings contains several knowledge gaps. Studies providing a clear explanation of the interaction mechanisms between base oils and additives were not found for non-hydrogenated ta-C DLCs. There are many lubricants and additives that have not been used in studies of the tribological behaviour of ta-C DLC coatings (including the effect of additive polarity). There has been no clear explanation of how the change in contact configuration, test setup and the counter face triboelement used, affects the friction behaviour of DLC-lubricant interactions. There has been little research into the effect of both surface morphology and surface hardness of ta-C DLC coatings on their tribological behaviour.
2 Objectives of present work

The objectives of the work presented in this thesis are to evaluate the tribological properties of two types of ta-C DLC coatings with different lubricants, with regard to their application in varying interfaces of the hydraulic motor. The optimum ta-C DLC coating lubricant combination for a contact configuration will be sought. Broken down, the aims and objectives include:

1. To verify the previous and current works by repeatability and reproducibility of experiments.
2. To explore the tribological behaviour of ta-C DLC coatings and lubricants, not evaluated in previous studies.
3. To characterise coated and uncoated specimens for surface roughness, hardness and thickness, and to explain their tribological behaviour in light of their surface morphology.
4. To analyse the worn surfaces produced during tests for friction and wear mechanisms with the help of instrumental analysis (SEM-EDX and optical surface profilometer).
5. To evaluate tribological behaviour in varying test setups and contact configurations, thereby simulating different interfaces within a hydraulic motor.
3 Experimental materials and lubricants

3.1 Test specimens for Optimol SRV III tribometer.

Steel cylinders and ta-C DLC coated discs were tested using a Schwingung Reibung Verschleiß (SRV) tribometer. This tribometer was designed by Optimol Instruments Prüftechnik GmbH for analysing fretting and friction wear. The test materials were chosen according to the previous research undertaken within this field [24].

A steel cylinder (high grade 100Cr6 bearing steel also known as AISI 52100 alloy steel; 15 mm diameter, 22 mm length) was used as the upper specimen in the reciprocating type setup in the SRV tribometer. The cylinder had a slightly increasing radius of cross section towards the centre from both ends, hence it formed a convex contact when pressed against a flat surface by its curved surface.

Ta-C DLC coated discs (high grade 100Cr6 bearing steel; 24 mm diameter, 7.9 mm thick) were used as the fixed lower specimen in the SRV tribometer. The discs were coated with two types of DLC coating of varying thickness and surface roughness. The thinner coating with rougher surface was termed as DLC coating B while thicker coating with smoother surface (run-in layer) was termed as DLC coating C as shown in Table 3.1. The steel cylinder was held in the test setup using a cylinder holder, as shown in Fig. 3.1.1. The specimens were characterised, using characterisation techniques mentioned in section 4.1.

![Cylinder holder for the Optimol SRV tribometer cylinder-on-disc setup](image)

**Table 3.1 Characterisation of test specimens for Optimol SRV tribometer.**

<table>
<thead>
<tr>
<th>Specimen type</th>
<th>Coating thickness (µm)</th>
<th>Surface roughness (nm)</th>
<th>Mean hardness (HV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DLC B coated disc</td>
<td>0.5 - 0.7</td>
<td>116.25 ±5</td>
<td>1057Hv50</td>
</tr>
<tr>
<td>DLC C coated disc</td>
<td>1.0 - 1.5</td>
<td>104.96 ±5</td>
<td>1163Hv50</td>
</tr>
<tr>
<td>100Cr6 steel cylinder</td>
<td>−−−−−−</td>
<td>63.22 ±5</td>
<td>869Hv100</td>
</tr>
</tbody>
</table>
3.2 Test Specimens for CETR UMT-2 macro-micro tribometer.

According to the block-on-ring test configuration in the CETR UMT-2 (Centre for Tribology Research now known as Bruker, Universal Materials Tester version 2) tribometer, a rectangular block with cylindrical ring specimens were used.

The block was 9.5 mm in length, 9.5 mm wide and 6.3 mm thick (0.02 mm tolerances) shown in Figure 3.2.1 b. The parallelism of the opposite surfaces was retained at 0.01 mm. The testing surfaces were rectangular, and manufactured with a surface roughness of 0.4 µm. The square faces were held across the pin holder and had a surface roughness of 1.6 µm. The block was made up of grey or laminar cast iron; technically designated as SS-EN-1561-GJL-300. It was manufactured from a cast body of 30 mm diameter with 300 MPa tensile strength.

The ring had an outer diameter, r of 35 mm and an inner diameter, ri of 25.8 mm as shown in Figure 3.2.1 a. The inner faces of the bearing converged so that they could be fixed in the holder of the lower block-on-ring drive of the CETR UMT-2 tribometer. The width, w of the ring was 8.8 mm, with a chamfer of radius, rc of 0.5 mm and 1.5 mm on either end as shown in Figure 3.2.1 a. This gave an effective available wear track width of 6.8 mm. The rings were made up of 100Cr6 high grade bearing steel, and coated with two types of DLC coating (B and C), which varied in their surface roughness and thickness (specified by the manufacturer). The nomenclature of the coatings was set according to previous test specimens (for all tribometers). The block holder for block-on-ring set up is shown in shown in Figure 3.2.1 c. The surface profiles of the cast iron blocks and coated and uncoated steel rings prior to the tests are mentioned in the Figure 3.2.2.

The specimens were characterised, and their properties summarised in Table 3.2

<table>
<thead>
<tr>
<th>Specimen type</th>
<th>Coating thickness (µm)</th>
<th>Surface roughness (nm)</th>
<th>Mean hardness (HV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DLC B coated ring</td>
<td>0.5</td>
<td>350 ± 15</td>
<td>941Hv100</td>
</tr>
<tr>
<td>DLC C coated ring</td>
<td>1.0</td>
<td>201 ± 15</td>
<td>1064Hv100</td>
</tr>
<tr>
<td>Uncoated steel ring</td>
<td>1.0</td>
<td>250 ± 15</td>
<td>848Hv500</td>
</tr>
<tr>
<td>Grey cast iron block</td>
<td>1.0</td>
<td>332 ± 15</td>
<td>297Hv500</td>
</tr>
</tbody>
</table>
3. Experimental materials and lubricants

Fig 3.2.1. (a) Ring dimensions; (b) Block dimensions; & (c) block holder for block-on-ring setup.

Fig 3.2.2. Surface profile of untested specimens with Veeco and ZYGO profilometer. a. Surface profile of cast iron block's rectangular face. b. Surface profile of uncoated ring. c. Surface profile of DLC C coated ring d. Surface profile of DLC B coated ring.
3. Experimental materials and lubricants

3.3 Test Specimens for Phoenix tribology pin-on-disc tribometer.

The Phoenix tribology pin-on-disc tribometer used cylindrical pin and disc specimens. The pins were cylindrical with a 4 mm diameter circular cross section. The edges of the pins were rounded with 0.2 mm radius, resulting in an effective diameter of 3.6 mm. This configuration helped in obtaining the required hertzian stress and ingress of lubricant into the interface. The pin length was 3 mm and protruded 1 mm out of the pin holder, which had a depth of 2 mm as shown in Figure 3.3.1b. The pin holder had a semi-spherical setup, containing a hole to insert the pin. The semi-spherical setup facilitated good alignment of the pin on the disc surface (as shown in Figure 3.3.1c), as it rotated in the cavity of the holder during periods of high shear stress and high levels of vibrations. The pins were polished using the pin holder to a surface roughness of 0.75 µm (0.025 µm tolerance). A 9 µm diamond abrasive slurry “Kemet WX” on a “TEXTMET” cloth was used to polish the pins for 2-3 minutes with Kemet W2 water-based coolant and lubricant. The pin was made up of grey or laminar cast iron (technically designated as SS-EN-1561-GJL-300). It was manufactured from a cast body of 30 mm diameter, and had 300 MPa tensile strength.

The cylindrical disc sample had an outer diameter of 56 mm, and an inner diameter of 20 mm as shown in Figure 3.3.1a. The chamfer on the inner surface enabled insertion of a conical screw to hold the disc in a fixed position, and to avoid any movement or vibration due to eccentricity during rotation. The effective radius available on the disc for tribotesting was 18 mm. The thickness of the disc was 8.15 mm. The substrate was made up of 100Cr6 high grade bearing steel. There were two kinds of ta-C DLC coating used (B and C), which varied in both surface roughness and thickness (specified by manufacturer). The surface profiles of the cast iron pins and coated and uncoated steel disc prior to the tests are mentioned in the Figure 3.3.2.

The specimens were characterised, and their properties are presented in Table 3.3.

Table 3.3. Characterisation of specimens for Phoenix tribology pin-on-disc tribometer.

<table>
<thead>
<tr>
<th>Specimen type</th>
<th>Coating thickness (µm)</th>
<th>Surface roughness (nm)</th>
<th>Mean hardness (HV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DLC B coated disc</td>
<td>0.5</td>
<td>311 ± 15</td>
<td>996Hv100</td>
</tr>
<tr>
<td>DLC C coated disc</td>
<td>1.0</td>
<td>198 ± 15</td>
<td>1238Hv100</td>
</tr>
<tr>
<td>Uncoated steel disc</td>
<td>0.00</td>
<td>125 ± 15</td>
<td>818Hv100</td>
</tr>
<tr>
<td>Cast iron pins</td>
<td>0.00</td>
<td>750 ± 25</td>
<td>375Hv100</td>
</tr>
</tbody>
</table>
Fig 3.3.1. (a) Disc dimensions; (b) pin dimension (set on pin holder); and (c) pin-on-disc setup.

Fig 3.3.2 Surface profile of the untested specimens using a ZYGO profilometer. a. Surface profile of cast iron pin. b. Surface profile of uncoated steel disc. c. Surface profile of DLC B coated disc. d. Surface profile of DLC C coated disc.
3. Experimental materials and lubricants

3.4 Lubricating oil samples

In all of the tribo test configurations used, seven kinds of lubricants were tested. They belonged to different API groups; were sourced from different lubricant manufacturers; and had different additive packages. Table 3.4 describes some of the properties of these lubricants. Both zinc, as well as rust inhibitors (where present), were added by the manufacturers. Lubricant viscosities at 40°C and 100°C were obtained from lubricant data sheets, provided by manufacturers.

Table 3.4. Lubricant characterisation

<table>
<thead>
<tr>
<th>Oil number</th>
<th>API Group</th>
<th>Rust inhibitor present?</th>
<th>Zinc present?</th>
<th>Kinematic viscosity (ASTM D 445) (mm²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>at 40 °C</td>
</tr>
<tr>
<td>1</td>
<td>I</td>
<td>No</td>
<td>No</td>
<td>68</td>
</tr>
<tr>
<td>2</td>
<td>I</td>
<td>No</td>
<td>Yes</td>
<td>71</td>
</tr>
<tr>
<td>3</td>
<td>II</td>
<td>No</td>
<td>No</td>
<td>68</td>
</tr>
<tr>
<td>4</td>
<td>II</td>
<td>Yes</td>
<td>No</td>
<td>68</td>
</tr>
<tr>
<td>5</td>
<td>II</td>
<td>No</td>
<td>No</td>
<td>68</td>
</tr>
<tr>
<td>6</td>
<td>IV</td>
<td>No</td>
<td>No</td>
<td>68</td>
</tr>
<tr>
<td>7</td>
<td>V</td>
<td>Yes</td>
<td>No</td>
<td>46</td>
</tr>
</tbody>
</table>
4 Experimental techniques

4.1 Characterisation of coatings and test specimens

The two kinds of DLC coated specimen specified in section 3 were characterized for their surface roughness, thickness, adhesion, hardness and chemical composition. These properties were analysed using an optical profilometer, a Vickers micro hardness tester and a nano-indenter, as well as scanning electron microscopy (SEM).

4.1.1 Optical profilometer

A Veeco 1100NT profilometer was used to measure the roughness – or profile – of specimens, and provided 3D images of each sample. Using light interference and light scattering, the profilometer detected the profile of the surfaces down to less than 1 nm. Software (Vision32) transformed the data gathered into images. The collected data was plotted into graphs, showing the roughness along both the x and y axes. Figure 4.1 shows an example of the data analysis provided by the software.

![Example of data analysis](image)

**Fig 4.1. Roughness graph and surface image of an unscarred DLC coated surface**

4.1.2 Vickers micro hardness tester

The hardness of DLC coatings was measured using the Vickers indentation test. A test sample was placed in the Vickers micro hardness tester and pressed with a square-base diamond indenter with a pyramid-shaped tip. The Vickers hardness is obtained by calculating the size of the...
4. Experimental techniques

diagonals \(d_1\) and \(d_2\) of the indentation as shown in Figure. 4.2. For the research undertaken for this thesis, applied indentation forces were according to the indentation loads of 50 g, 100 g, 200 g, 500 g, and 1000 g.

![Diagram of Vickers indentation measurement](image)

Fig 4.2. Vickers indentation measurement

Vickers hardness number (HV) gives information on the ductility of a material. When the indenter is applied during the hardness test, it is important to observe whether the indentation creates cracks or a ductile deformation. Low load indentation is preferred for the coating hardness measurement in order to avoid substrate effects (where the hardness values of the coating are affected by the mechanical properties of the substrate). Any cracks created during indentation could be due to the coating and/or the substrate.

For the characterization of a coating’s hardness, the critical force required to penetrate the coating is key. A high loading force tends to exceed the critical limit (above which the coating fails) and brings in the substrate effect. So for thin, hard DLC coatings (in our case DLC B and DLC C) the indentation load should be kept below 100 g. (depth of penetration <1/10 thickness as a rule of thumb for hard coatings) [10].

4.1.3 Nano indenter

Nano-indentation was used to characterize the elastic modulus; the hardness; hardening exponents; creep parameters; and the residual stresses of a test specimen. The test method measures mechanical properties at nano scales. The nano indenter passes a current through a coil located within a circular magnet. This imposes a force on the shaft of the indenter and therefore the test surface, which is directly proportional to the current passing through the coil (Figure. 4.3) [11].

During an instrumented indentation test, both the applied force and the indentation depth of the indenter are measured. Indenters are typically made from diamond, tungsten carbide or sapphire. Their geometries are normally pyramidal with a triangular base (Berkovich indenter), or spherical.
During a testing cycle, linear loading was imposed on the indenter until the maximum force was reached. Thereafter, the indenter was retained in the material so that plasticity or creep effects diminished. The holding time at different indentation force steps should be chosen in such a way that the unloading curve is not overly influenced by the creep of the test specimen [26]. Indentation creep is the change in the depth that occurs at a constant force applied over a long period due to permanent deformation.

Both the elastic modulus and hardness of a sample can be determined from the contact area between the indenter and the specimen (measured using the indenter geometry), and the indentation depth.

The total mechanical work on a sample can be divided into elastic and plastic work. Plastic deformation occurs when the applied load goes beyond the elastic limit of a sample, and permanently deforms it [27]. The characterization of the plastic properties of a coating is normally carried out using a pointed indenter. Elastic deformation occurs due to the stretching of bonds between the atoms when a load is applied. When the load is removed, the specimen returns to its initial shape. The measurement of the elastic properties of a coating is usually undertaken using a spherical indenter. A spherical indenter has a larger radius compared to a pointed indenter, which therefore leads to complete elastic deformation at greater depths. However, due to the larger indentation area generated by a spherical indenter, there is greater uncertainty in the measurement. Sometimes, due to defects in coatings, there can be scatter in the measurements of plastic and elastic deformation.

Fig 4.3. Schematics of Nano indentation machine [58]
4. Experimental techniques

4.1.4 Scanning electron microscope

Scanning electron microscopy (SEM) is a powerful technique, used to observe and analyse the surfaces morphology of sample. A focussed electron beam scans a sample, and instrument detectors detect secondary electrons, back-scattered electrons and photons [28].

An SEM is composed of an evacuated column (minimum pressure equal to $10^{-3}$ Pascals (Pa)), an electron gun, condenser lenses (which narrow the electron beam), deflection coils, a sample chamber, cameras and detectors.

The vacuum in the column is obtained with backing and secondary pumps or, for a higher vacuum, an ionic pump or the ultra-void technique is used. The electron beam is obtained by heating a tungsten filament (which has a negative potential and is terminated by a “pyramid”) at a temperature of 2800 K. An electrode (more negative than the filament) controls the direction of the electron beam. The filament voltage can be varied during EDX analysis (around 0 to 20 keV) depending on the thickness of the sample region to be analysed.

The interaction of the electrons in a SEM with the test specimen results different phenomena as discussed below.

*Back-scattered electrons (BSE)*

Back-scattered electrons (BSE, composed of primary electrons) initially interact with the atomic nuclei and orbital electrons of a sample, and leave the sample with almost the same energy as when they entered it [30]. BSEs are sensitive to the atomic number of the atom: heavier elements will generate more BSEs than lighter elements. Therefore, sample areas that appear brighter during analysis are composed of heavier elements [28].

*Secondary electrons (SE)*

Secondary electrons (SE) are lower in energy compared to BSEs. They are primary electrons that have donated part of their energy to the conduction bands of an electron within a sample. SEs are derived from superficial layers of a sample, making them sensitive to surface changes, and therefore provide information about a sample’s surface topography [28].

*Other phenomena*

When electrons are absorbed into a sample, they can transfer energy to various forms. In addition to BSEs and SEs, Auger electrons, electro-magnetic radiation and X-ray transmission can also be observed.
4. Experimental techniques

4.1.5 Metallographic sample preparation

To observe a DLC coated disc cross section, sample preparation can be divided into the following steps done sequentially in the order of numbering [38]:

1. **Sectioning:** The DLC coated disc was cut into two pieces in the radial direction of the flat surface using an abrasive wheel containing abrasive particles. This produced a disc with a fine surface, and with low levels of deformation to the subsurface layers and coating. The abrasive wheel used was a Buehler B2210 wheel for extra hard ferrous materials (with hardness of about 840 HV).

2. **Mounting:** Phenolic resins were used to mount the specimens in a holder for easier handling. This protected the edges of a specimen, and gave the sample good adhesion to the mount and fit within the resin.

3. **Planar and fine grinding:** Grinding paper containing silicon carbide or alumina particles were used for metals in wet grinding. Grinding papers with 240 to 600 grain size were used for plane grinding, and 1200 grain size paper was used for fine grinding and finishing.

4. **Polishing:** Polishing was undertaken using various textile clothes, on which suspensions of diamond and silicon oxide particles were applied. Pre polishing was done in 3 steps with 9 and 3 µm diamond abrasive slurry "Kemet WX" on "TEXMET" cloths for 2-3 minutes. "Kemet W2" was used as a water-based lubricant. Final polishing was done using a silica suspension of MASTERMET applied to cloths. The sample was then washed and rinsed with soap, followed by methanol.

After preparation was complete, samples were put into plastic boxes, with their cut cross sectional faces facing downwards and submerged in epoxy resin. Once the samples and resin had set, the sample cross sections were analysed in the SEM.

4.2 Tribo testing methods and test configurations

A tribometer is an instrument that measures different tribological properties, such as friction force, wear rate and coefficient of friction. It calculates friction coefficients via a sensor, which detects the friction force compared to a known normal force. Tribometers can be used to simulate the operating conditions of a real-world setup. Tribometers are usually characterised by the triboelements used, and type of motion between these two elements. Different experimental setups can be used to obtain the required relative motion and contact configuration between the two interfaces.

A guide to the standard experimental procedure for all tribometers is given in Appendix A.
4. Experimental techniques

4.2.1 Optimol SRV III type tribometer (ASTM D 6425)
This test configuration had reciprocating sliding motion between two interacting bodies, and the initial contact was non-conformal line contact.

4.2.1.1 Tribometer configuration
In this test method, a cylinder was oscillated at a constant frequency, amplitude and load on a disc under lubricated conditions. The specimen block holding the disc was heated to the desired test temperature. A pair of piezoelectric force transducers enabled in measurement of friction force throughout the test duration. The Optimol SRV tribometer used is shown in Figure 4.4.

4.2.1.2 Test parameters
Test parameters were chosen with consideration given to Xin’s Master’s thesis [24]. The hertzian stresses applied were specified by Bosch Rexroth. A running-in load of 30 N was applied for a period of 30 seconds, and then increased to a steady state load of 48 N for a period of 120 minutes. Thus the total test duration was 120.5 minutes. The test temperature was 50 ºC. The stroke length of the oscillating motion was fixed at 1 mm, with a frequency of 50 Hz. The hertzian contact width 2b was calculated to be 28 µm using equation 5 [4 and 41].

\[
b = \sqrt{\frac{1 - \nu^2}{Ec} \times \frac{8RF}{\pi L}}
\]

Eq. 5

Where Ec is the combined elastic modulus as 100Cr6 steel-steel contact; \(\nu\) is Poisson’s ratio of 100Cr6 steel; R is the radius of cylinder in contact with the disc; L is the length of the contact; and F is the applied load at steady state. By equation 8 in section 4.2.2.2 equation 7 reduces to equation 5 for a steel-steel contact. The hertzian contact stress was calculated to be 100.4 MPa using equation 6 [4 and 41].

\[
\sigma_{\text{Hertzian}} = \frac{2F}{\pi bL}
\]

Eq. 6

Fig 4.4 a. Picture of Optimol SRV III type tribometer (ASTM D 6425) b. Schematics of some working parts of Optimol SRV III type tribometer at Tribolab, LTU.
4.2.2 CETR UMT-2 macro-micro tribometer (ASTM G176)

This tribometer was used in a block-on-ring configuration, with unidirectional sliding motion. The initial contact was non-conformal line contact, which changed to conformal area contact as the test progressed.

4.2.2.1 Tribometer configuration

A block-on-ring configuration was used to simulate the actual contact within a roller-piston interface of a hydraulic motor. The ring was mounted on a lower rotational drive, and the rectangular block was mounted on the mounting block with a slider and suspension by the help of a holder as shown in Figure 4.5. The suspension dampens the shocks and vibrations. A friction load sensor on the slider was used to calculate both the friction and shear forces from the moment or torque applied on the block. A screw in the base of the block-on-ring drive was turned to generate different loads, and the uniformity of these applied loads was monitored using pressure sensitive paper. This paper was also used to check the alignment of the block-on-ring. The pre-test load, approach and retracting velocities of the slider were all set according the tribometer’s handbook [19]. The CETR tribometer in block on ring set-up is shown in Figure 4.5.

Fig 4.5. Schematic of block-on-ring setup of a CETR UMT-2 macro micro tribometer; and a photograph of this instrument at Tribolab, LTU [25].

4.2.2.2 Test parameters

To determine the parameters for the tests on CETR UMT-2 tribometer, a Strubeck curve was plotted (Figure 4.6) for the oils described in Table 3.4. The block-on-disc test setup was run at different rotational speeds at a constant load. The sliding distance was fixed at 396 metres, and the rotational speed and test time duration were set at 20 rpm and 180 minutes respectively. The applied load was increased, and at 100 N and 20 rpm, steady state boundary lubrication was
obtained for all of the oils with a friction coefficient greater than 0.1. The test temperature was maintained at 50 °C.

The hertzian contact width (2b) was calculated to be 131 µm, using equation 7 [4 and 41].

$$b = \sqrt{\frac{1 - v^2}{Ec} \cdot \frac{4RF}{\pi L}}$$  \hspace{1cm} \text{Eq. 7}

Where $v$, is the Poisson's ratio and $Ec$ is is the combined or effective modulus of elasticity calculated from equation 8 [4 and 41].

$$\frac{1 - v^2}{Ec} = \frac{1 - v_1^2}{E_1} + \frac{1 - v_2^2}{E_2}$$  \hspace{1cm} \text{Eq. 8}

Where $E_1$ is 200 GPa for steel and $E_2$ is 122.5 GPa for cast iron. $v_1$ for steel is 0.285 and $v_2$ for cast iron is 0.26 as specified by the supplier.

The hertzian contact stress, $\sigma$ was calculated to be 153.08 MPa for the contact between the block and the ring using equation 6.

Fig 4.6. Stiubeck curve is plotted at various loads and rotational speeds to showcase transition in lubrication regimes for tests using CETR UMT-2 block on ring set up.
4.2.3 Phoenix tribology TE 67 high temperature tribometer

The Phoenix tribometer pin on disc configuration has unidirectional sliding motion between two interacting bodies, and the contact remains conformal area contact throughout the test.

4.2.3.1 Tribometer configuration

In this tribometer, the flat surface of a pin is brought into contact and loaded against the flat surface of a rotating disc. The loading was performed using a pneumatic load actuator, which could handle steady and fluctuating loading up to 1 kN. The friction measurements in done by a force transducer as seen from Figure 4.7a. Prior to the test, both the pneumatic loading system and the friction load cells were calibrated as shown in Figure 4.7b. To control the test temperature, lubrication tests were performed within an enclosure with the disc surrounded by electrical heating resistance elements. The lubricant was constantly pumped onto the contact at a flow rate of 30 mL min⁻¹. Both the contact pressure and temperature were kept constant throughout each test.

4.2.3.2 Test parameters

A steady state load of 1 kN was set for each test, for a hertzian stress of 100MPa on the surface of the given pins. The steady state load was achieved via incremental loading; the load was increased from 100 N via 100N increments at 1 minute intervals, as shown Figure 4.8. The sliding distance used (396 nm) was the same as that used for the block-on-ring configuration in the CETR tester as mentioned in section 4.2.2.2. Taking the sliding distance into account, the sliding velocity, \( v_{\text{sliding}} \) and the testing time were fixed at 0.1 m s⁻¹ and 66 minutes respectively. The time for incremental loading and steady state loading summed up to a total test duration of 75 minutes. The test temperature was maintained at 50 °C. An incremental loading pattern was followed to facilitate smooth load transitions and avoid shock loading at the interfacial contact. The load was increased in 100N increments per minute, from 100 N until a load of 1000N was achieved.

A hertzian stress between for a pin of diameter \( d \) and disc, with an applied load \( F \) was calculated to be 96.17 MPa using Equation 9

\[
\sigma_{\text{Hertzian}} = \frac{4F}{\pi d^2} \quad \text{Eq. 9}
\]

The nominal contact area for a pin was calculated to be 10.179 mm² from equation 10

\[
A_{\text{nominal}} = \frac{\pi d^2}{4} \quad \text{Eq. 10}
\]

The angular sliding velocity for a test track at radius \( r \) from the centre of disc on the pin-on disc set up is given by equation 11
4. Experimental techniques

\[ \alpha_{sliding} = \frac{60v_{sliding}}{2\pi r} \]  

Eq. 11

Taking the pin diameter as the test track width, the annular radius of the disc as the available test track width and the lower RPM limit for motor in pin-on-disc set up at 50 rpm we obtain the possible track radius at 13 mm and 19 mm as shown is Figure 3.3.1a.

Fig 4.7. Photographs at Tribolab, LTU of (a) Phoenix of pin-on-disc tribometer; and (b) and the specific components involved during its calibration.

Fig 4.8. Incremental loading pattern in a pin-on-disc set up
5 Results and discussion

5.1 Characterisation of DLC coated specimens

5.1.1 Surface topography

The results presented in Table 5.1.1 show that coating B was rougher than coating C, probably because thicker coating C had a smoother running-in layer during its manufacturing process. This information was confirmed by the manufacturer (DIARC-Technology Oy). However, the variation in surface roughness between the two coatings was not large. Figure 5.1.1 shows SEM images of the DLC coated specimen, both with and without wear scars.

Table 5.1.1: Surface Roughness of type B and C DLC coated discs from Veeco profilometer

<table>
<thead>
<tr>
<th>DLC type</th>
<th>Surface roughness (sample 1) (nm)</th>
<th>Surface roughness (sample 2) (nm)</th>
<th>Mean surface roughness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coating B</td>
<td>117.96</td>
<td>115.50</td>
<td>116.73</td>
</tr>
<tr>
<td>Coating C</td>
<td>114.52</td>
<td>95.42</td>
<td>104.97</td>
</tr>
</tbody>
</table>

![SEM micrographs](image1.jpg)  ![SEM micrographs](image2.jpg)

Fig 5.1.1 SEM micrographs (140 × magnification) of DLC coated steel (a) without a wear track; and (b) with a wear track.

5.1.2 Coating thickness

Results presented in Table 5.1.5 show that the DLC type C coating was thicker than the type B coating. Coating B was between 0.5 and 0.7 μm thick, and coating C was 1.0 to 1.5 μm thick. The individual coating thickness evaluation are presented in the Figures 5.1.2 and 5.1.3.
5. Results and discussion

Fig 5.1.2. SEM images of cross sections of DLC type B coated samples (a) sample 1 (30000 × magnification); and (b) sample 2 (7500 × magnification).

Table 5.1.2. EDX analysis showing the elemental composition of a cross section of DLC type B coatings (samples 1 and 2).

<table>
<thead>
<tr>
<th></th>
<th>Sample 1</th>
<th></th>
<th>Sample 2</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Element</td>
<td>Weight %</td>
<td>Atomic %</td>
<td>Element</td>
<td>Weight %</td>
</tr>
<tr>
<td>C</td>
<td>69.74</td>
<td>88.51</td>
<td>C</td>
<td>65.32</td>
</tr>
<tr>
<td>O</td>
<td>4.40</td>
<td>4.19</td>
<td>O</td>
<td>7.53</td>
</tr>
<tr>
<td>Si</td>
<td>0.33</td>
<td>0.18</td>
<td>Si</td>
<td>1.07</td>
</tr>
<tr>
<td>Ti</td>
<td>1.62</td>
<td>0.52</td>
<td>Ti</td>
<td>2.00</td>
</tr>
<tr>
<td>Cr</td>
<td>0.38</td>
<td>0.11</td>
<td>Cr</td>
<td>0.38</td>
</tr>
<tr>
<td>Fe</td>
<td>23.07</td>
<td>6.30</td>
<td>Fe</td>
<td>23.54</td>
</tr>
</tbody>
</table>

Fig 5.1.3. SEM images of cross sections of DLC type C coated samples (a) sample 1 (7500 × magnification); and (b) sample 2 (7500 × magnification).
Table 5.1.3. EDX analysis showing the elemental composition of a cross section of DLC type C coatings (samples 1 and 2)

<table>
<thead>
<tr>
<th>Sample 1</th>
<th></th>
<th>Sample 2</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Element</td>
<td>Weight %</td>
<td>Atomic %</td>
<td>Element</td>
</tr>
<tr>
<td>C</td>
<td>68.87</td>
<td>87.31</td>
<td>C</td>
</tr>
<tr>
<td>O</td>
<td>5.72</td>
<td>5.44</td>
<td>O</td>
</tr>
<tr>
<td>Si</td>
<td>0.58</td>
<td>0.32</td>
<td>Si</td>
</tr>
<tr>
<td>Ti</td>
<td>1.71</td>
<td>0.54</td>
<td>Ti</td>
</tr>
<tr>
<td>Cr</td>
<td>0.37</td>
<td>0.11</td>
<td>Cr</td>
</tr>
<tr>
<td>Fe</td>
<td>22.40</td>
<td>6.11</td>
<td>Fe</td>
</tr>
</tbody>
</table>

The presence of carbon in the steel substrate as seen in the EDX analysis in Table 5.1.4 is due to the natural diffusion of carbon from the DLC coating into the substrate.

As we can see from Table 5.1.2 and 5.1.3 carbon, oxygen, iron, chromium, and titanium are the main constituent of the DLC coating and its surrounding substrate. Carbon is the main constituent of the DLC coating. Iron and chromium form part of the substrate. Titanium is used as an interlayer between the coating and substrate. Oxygen and silicon might come from silica or oxidised metal during the cutting of the coated sample for investigation. As shown in Table 5.1.4, Cast iron used for blocks and pins is a grey cast iron which contains carbon, silicon and manganese apart from iron as main component. The 100Cr6 steel substrate below the DLC coating contains chromium, silicon and iron along with carbon as alloy elements, carbon additionally diffused from the DLC coating into the periphery of the coating-substrate interface.

Table 5.1.4. EDX analysis of counter face material (a) cast iron block and pins; and (a) 100Cr6 steel cylinder; also 100Cr6 steel substrate below the DLC coating.

<table>
<thead>
<tr>
<th>Cast iron block or pin sample</th>
<th>100Cr6 steel substrate sample below DLC coating</th>
</tr>
</thead>
<tbody>
<tr>
<td>Element</td>
<td>Weight %</td>
</tr>
<tr>
<td>Fe</td>
<td>95.71</td>
</tr>
<tr>
<td>Si</td>
<td>2.58</td>
</tr>
<tr>
<td>Mn</td>
<td>1.05</td>
</tr>
<tr>
<td>C</td>
<td>0.66</td>
</tr>
</tbody>
</table>
Table 5.1.5. Coating thicknesses of DLC coated discs

<table>
<thead>
<tr>
<th>DLC type</th>
<th>Sample number</th>
<th>Coating thickness (nm)</th>
<th>Mean coating thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coating B</td>
<td>1</td>
<td>685</td>
<td>604</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>523</td>
<td>(Range of 500 to 700 nm)</td>
</tr>
<tr>
<td>Coating C</td>
<td>1</td>
<td>1015</td>
<td>1263</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1510</td>
<td>(Range of 1000 to 1500 nm)</td>
</tr>
</tbody>
</table>

5.1.3 Hardness

5.1.3.1 Micro hardness test

In a Vickers hardness tester to avoid errors, multiple individual readings are taken as repeat units to demonstrate reliability. A load of 500 g was applied to the DLC coated specimen, and the hardness of the coating was measured. The applied load was too high for the coating, and as a result, the indenter pressed through the coating and into the steel substrate. When a load of 1000 g was applied, the coating cracked and broke, meaning that the coating’s hardness could not be measured. So, when a load of 50 g was applied, only the coating was indented, and therefore its effective hardness was successfully measured (Table 5.1.6). After each wear test, the thickness of the DLC coating reduced, leading to a decrease in its effective hardness. Between applied loads of 50 and 500 g, plastic deformation was observed, indicating the ductile behaviour of the coating.

Table 5.1.6: Hardness values of DLC coatings types B and C, and uncoated AISI 52100 steel.

<table>
<thead>
<tr>
<th>Coating type</th>
<th>Individual readings (HV)</th>
<th>Mean hardness (HV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DLC B</td>
<td>1086,1039,1017,1085</td>
<td>1057HV50</td>
</tr>
<tr>
<td>DLC C</td>
<td>1109,1085,1273,1187</td>
<td>1163HV50</td>
</tr>
<tr>
<td>100Cr6 Steel</td>
<td>839, 879,891, 866</td>
<td>869HV100</td>
</tr>
</tbody>
</table>

To collect reliable hardness values, it is important to have a perfect square projected area geometry on the indented area when performing Vickers hardness tests. The micro-hardness values shown in Table 5.1.6 demonstrate the combined hardness values for both the steel substrate and DLC coating. According to the manufacturer (DIARC-Technology Oy), the DLC coating’s intrinsic hardness is 4000HV.
5. Results and discussion

5.1.3.2 Nano-indentation test

Hysteresis curves obtained during nano-indentation tests of DLC type B and C coatings (2 specimens each) with constant loads, are shown in Figure 5.1.4. These curves show that that DLC B coated specimens had mostly greater indentation depths at than the DLC C coated specimens. In addition, the scatter in the plots for DLC B coated specimens is lower than for DLC C specimens. There is a change in the slope of indentation curve for DLC B coated specimens at the indentation depth of coating thickness (700 nm) indicating complete penetration of coating as shown in Figure 5.1.4 a and c. Now as DLC C coated specimens were thicker, they were not completely penetrated through the coating thickness by applied indentation force. The higher indentation of the soft substrate doesn’t come into play for DLC C coating. However DLC B coating being thinner, has substrate indentation at most points, resulting in greater effective indentation than DLC C coating. The higher observed scatter may also result from the greater thickness of DLC C coatings, and the incomplete penetration of indenter into the coating. So additional defects within the bulk of the subsurface of coating gives variable results on indentation. Residual indentation depth of DLC B coated specimens was greater, due to the penetration of the indenter into the substrate causing its plastic deformation.

Fig 5.1.4. Nano Indentation hysteresis curves at constant load for (a) DLC B coating, sample 1 at 350mN load; (b) DLC C coating, sample 1 at 350mN load; (c) DLC B coating, sample 2 at 300mN load; and (d) DLC C coating, sample 2 at 300mN load.
Nano-indentation tests were repeated using increasing loads (0 to 350 mN at different points over the specimen) as shown in Figure 5.1.5. DLC C coated specimens showed greater resistance, with lower indentation depths at individual loads compared to DLC B coated specimens. The residual indentation of DLC B coated specimens was greater, as the DLC B coatings were thinner, and penetration exceeded the indentation depth causing plastic deformation of the substrate. DLC C coatings were thicker, providing greater resistance to penetration at indentation loads which did not exceed the coating thickness. DLC C coatings (both samples 1 and 2) showed more scatter than both DLC B coated specimens. This could be due to the higher coating thickness of the DLC C coated specimens which vary the indentation depth for the coating defects. The surface roughness of DLC coatings, where surface asperities and defects deflect the indenter, particularly at lower indentation loads causing variation in indentation depths.

![Nano Indentation hysteresis curves at increasing load till 350mN for (a) DLC B coating, sample 1; (b) DLC C coating, sample 1; (c) DLC B coating, sample 2; and (d) DLC C coating sample 2.](image)

As B and C coatings are composed of the same material, it may be assumed that they have the same hardness. But as shown in Table 5.1.7 that is not the case. DLC C coated specimen is harder and compared to DLC B coated specimen. This could be explained as the DLC coating material has higher intrinsic hardness than the steel substrate. This results in a higher effective bulk hardness of the DLC C coated specimen which is thicker than DLC B coated specimen.
Table 5.1.7. Hardness results for DLC B and DLCC coated specimens, using both nano-indentation and Vickers micro hardness testing.

<table>
<thead>
<tr>
<th>Coating type</th>
<th>Mean nano-indentation hardness (GPa)</th>
<th>Mean Vickers micro hardness (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DLC B</td>
<td>10.8</td>
<td>10.7</td>
</tr>
<tr>
<td>DLC C</td>
<td>11.3</td>
<td>11.3</td>
</tr>
</tbody>
</table>

5.1.4 Chemical composition of coatings

As seen in both Tables 5.1.8 and 5.1.9 below, the main component of DLC B coating were iron, followed by titanium. Tables 5.1.10 and 5.1.11 show that titanium was the dominant metallic element within the DLC C coating. Worn discs possessed a greater percentage of titanium compared to un-worn discs. When the coating was sufficiently worn, the interface, which contained titanium to improve the adhesion of the coating to the substrate, was more detectable. Additionally in DLC C coating, it was possible to detect carbon, because of its greater thickness compared to DLC B coating. The percentage of iron detected in DLC C coating was also low, because DLC B was laid down as a thin coating, compared to the thicker DLC C coatings.

Table 5.1.8. SEM micrographs (140 × magnification) of a DLC B coated disc (two areas), and EDX analysis at various worn points on the disc for their corresponding EDX spectrum.
5. Results and discussion

Table 5.1.9. SEM micrographs (140 × magnification) of a DLC B coated disc (two areas), and EDX analysis at various non-worn points on the disc for their corresponding EDX spectrum.

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight%</th>
<th>Atomic%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al K</td>
<td>1.99</td>
<td>3.93</td>
</tr>
<tr>
<td>Ti K</td>
<td>12.46</td>
<td>13.81</td>
</tr>
<tr>
<td>Cr K</td>
<td>1.76</td>
<td>1.80</td>
</tr>
<tr>
<td>Fe K</td>
<td>82.11</td>
<td>78.05</td>
</tr>
<tr>
<td>Co K</td>
<td>0.76</td>
<td>0.69</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight%</th>
<th>Atomic%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al K</td>
<td>1.62</td>
<td>3.22</td>
</tr>
<tr>
<td>Ti K</td>
<td>13.05</td>
<td>14.63</td>
</tr>
<tr>
<td>Cr K</td>
<td>1.65</td>
<td>1.70</td>
</tr>
<tr>
<td>Fe K</td>
<td>82.22</td>
<td>79.02</td>
</tr>
<tr>
<td>Co K</td>
<td>0.77</td>
<td>0.70</td>
</tr>
</tbody>
</table>

Table 5.1.10. SEM micrographs (140 × magnification) of a DLC C coated disc (two areas), and EDX analysis at various worn points on the disc for their corresponding EDX spectrum.

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight %</th>
<th>Atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>1.74</td>
<td>3.30</td>
</tr>
<tr>
<td>Ti</td>
<td>10.23</td>
<td>11.38</td>
</tr>
<tr>
<td>Cr</td>
<td>1.35</td>
<td>1.38</td>
</tr>
<tr>
<td>Fe</td>
<td>84.85</td>
<td>80.97</td>
</tr>
<tr>
<td>Co</td>
<td>0.61</td>
<td>0.55</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight %</th>
<th>Atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>0.54</td>
<td>1.07</td>
</tr>
<tr>
<td>Ti</td>
<td>2.96</td>
<td>3.42</td>
</tr>
<tr>
<td>Cr</td>
<td>1.71</td>
<td>1.82</td>
</tr>
<tr>
<td>Fe</td>
<td>93.87</td>
<td>92.84</td>
</tr>
<tr>
<td>Co</td>
<td>0.91</td>
<td>0.86</td>
</tr>
</tbody>
</table>
Table 5.1.11. SEM micrographs (140 × magnification) of a DLC C coated disc (two areas), and EDX analysis at various non-worn points on the disc for their corresponding EDX spectrum.

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight %</th>
<th>Atomic %</th>
<th>Element</th>
<th>Weight %</th>
<th>Atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>55.27</td>
<td>84.68</td>
<td>C</td>
<td>54.72</td>
<td>84.39</td>
</tr>
<tr>
<td>Al</td>
<td>0.51</td>
<td>0.35</td>
<td>Al</td>
<td>0.52</td>
<td>0.36</td>
</tr>
<tr>
<td>Si</td>
<td>0.28</td>
<td>0.18</td>
<td>Si</td>
<td>0.33</td>
<td>0.22</td>
</tr>
<tr>
<td>Ti</td>
<td>5.18</td>
<td>1.99</td>
<td>Ti</td>
<td>4.96</td>
<td>1.92</td>
</tr>
<tr>
<td>V</td>
<td>0.26</td>
<td>0.09</td>
<td>V</td>
<td>0.24</td>
<td>0.09</td>
</tr>
<tr>
<td>Cr</td>
<td>0.79</td>
<td>0.28</td>
<td>Cr</td>
<td>0.69</td>
<td>0.25</td>
</tr>
<tr>
<td>Fe</td>
<td>37.71</td>
<td>12.43</td>
<td>Fe</td>
<td>38.54</td>
<td>12.78</td>
</tr>
</tbody>
</table>

In a wear-tested samples, the percentage of DLC coating elements, such as carbon decreased, with a corresponding increase in steel substrate and counter face elements, such as chromium and iron. This change in composition indicates that during rubbing, the DLC coating (containing carbon) was partially destroyed and there was transfer of material between the coating and the 100Cr6 steel counter face. SEM and EDX of worn and non-worn DLC C coated samples supports this (Tables 5.1.10 and 5.1.11).

The primary difference between DLC B and C coated samples is that the detected iron and titanium content was much greater in the DLC B samples. This is because the electron beam in a SEM during EDX analysis penetrates the thinner coating B than coating C more, detecting more interfacial titanium in DLC B coating as seen from the Table 5.1.9 and 5.1.11. When coatings were completely worn, the interface and the steel substrate remained. This confirmed that both the interface and the intermediate layers were made of titanium. It was confirmed by DIARC-Technology Oy that the amount of titanium used in both the coatings was the same.
5.2 Tribological tests

5.2.1 SRV III type cylinder-on-disc configuration

The coefficient of friction in the first hour of a test using the SRV test setup was usually high and unstable (Figure 5.2.1.1). There was a high running-in time for the DLC coated disc or steel cylinder contact. The higher running-in time could be due to the reciprocating motion of the SRV test configuration, where the orientation of DLC coating asperities and grains in contact with the steel cylinder changes within each stroke of the SRV tribometer. The asperity interlocking in a reciprocating setup also caused unstable running-in boundary friction, as described by Erdemir et al. [3 and 65]. This unstable boundary friction was maintained until the wear was steady, and the wear depth was enough to avoid asperity interaction by accommodating a lubricant film of thickness greater than the mean surface roughness. A steady state was reached during the second hour of the test, with a corresponding drop in the friction coefficient.

The DLC coated discs being harder than the steel cylinder wear out the steel cylinder in contact during running-in. However it should be noted that the difference in hardness between the steel cylinder and the DLC coated steel discs is not very large (1100HV for DLC coated discs (average) compared to 900HV for steel cylinder). Therefore, during running-in, it is also possible that asperities present on the DLC coated surface were deformed by the steel counter face at the given load and temperature, evident from the wear track on the coated disc specimens (section 4.2.1.2). The DLC B coated specimen was slightly rougher than DLC C coated specimens. The wear scar dimensions of both the DLC coated discs and steel cylinders are similar leading to higher conformity between the contact surfaces by the end of the test.

In SRV tests with Oil 1, different friction behaviour was observed with both DLCs (Figure 5.2.1.4 and 5.2.1.5). The harder DLC C coated specimen surface run-in the steel counter surface earlier, giving a low friction coefficient of 0.024. A possible local breakdown of the coating after this caused the friction to increase and stabilise at 0.053. The comparatively softer DLC B coated specimen had a longer running-in time, and reached a lower, steady state friction coefficient of 0.022. The surface roughness of the DLC B coating remained largely unchanged, and due to coating damage, the roughness of the DLC C coating increased only slightly as shown in Figure 5.2.1.3. In Oil 1, the presence of sulphur and unsaturates may have helped to form a shearable layer at the coating-cylinder interface, resulting in the low friction observed in Figure 5.2.1.4.
5. Results and discussion

Fig 5.2.1.1 Mean friction coefficient in first hour of test using a SRV cylinder-on-disc reciprocating setup with various oils as mentioned in Table 3.4.

Fig 5.2.1.2. Mean friction coefficient in second hour of test using a SRV cylinder-on-disc reciprocating setup with various oils as mentioned in Table 3.4.

Fig 5.2.1.3. Mean surface roughness (Ra) in a disc wear scar along the sliding direction (x axis) (before and after the test), for both DLC B and C coatings with oils as mentioned in Table 3.4.
5. Results and discussion

Fig 5.2.1.4. Friction plots for a DLC B coating in various lubricants, using a SRV cylinder-on-disc reciprocating setup with various oils as mentioned in Table 3.4.

Fig 5.2.1.5 Friction plots with DLC C in various lubricants in SRV cylinder-on-disc reciprocating setup with various oils as mentioned in Table 3.4.

Fig 5.2.1.6. Wear Volume of DLC coated discs with various oils as mentioned in Table 3.4.
5. Results and discussion

In Oil 2 (which contained zinc), tests with both the DLC coatings resulted in high friction, which increased steadily from the start of the test. However, DLC C coating displayed lower friction than DLC B coating, until the final 10 minutes of test where DLC C coatings reached a friction coefficient of 0.127, the same as the friction coefficient obtained with DLC B coatings. The high friction observed could be due to the formation of high-shear phosphate or sulphur based tribofilms or pads, as described by Tasdemir et al. [43]. Due to higher surface hardness, DLC C coated specimen run-in the counter face and had lower initial friction compared to DLC B. DLC B coated specimen owing to its higher roughness might have activated formation of sulphur based tribofilm pads causing its higher steady state friction. This followed the role of surface properties in lubricant and its additive activation as mentioned in [56]. Figure 5.2.1.3 shows that the roughness of both the DLC coating remained more or less intact, thus supporting the oil's anti-wear properties.

In Oil 3 (API Group II), lower friction was observed for DLC C coatings than DLC B coatings shortly after running-in. The DLC C coating asperities were smoothed by the counter face, providing a hydrodynamic effect, and a resultant drop in friction. However, the subsequent rise in friction for both the coating (shown in Figure 5.2.1.4 and 5.2.1.5) may be due to the contact being starved of lubricant, or delamination of the coating parts. As a result, the final friction for DLC C was 0.049. In contrast, a value of 0.063 was observed for DLC B, before a sudden rise to 0.078. The coating degradation is evident in Figure 5.2.1.3, from the increase in coating surface roughness after the friction tests with Oil 3.

Oil 4 contained rust inhibitor, which can give the oil, a polar behaviour (due to presence of metallic elements) [15]. When run with both types of DLC coating, Oil 4 gave ultralow friction values. After a short running-in time (shown in Figure 5.2.1.4 and 5.2.1.5), DLC B reached a lower steady state friction coefficient (0.016), compared to DLC C (0.028). The low friction could be attributed to the polar nature of the oil, which may have formed a tribolayer of terminated, polar functional groups on the friction activated DLC coating (mechanisms similar to [43 and 44]). However the higher friction of the DLC C coating may be due to its unstable running-in phase. In addition, the DLC B coated disc was rougher, leading to greater activation of its surface for oil interactions, compared to the DLC C coated disc. The roughness of both DLC coatings was reduced after the test, demonstrating the hydrodynamic effects in friction reduction.

In Oil 5, the harder DLC C coated specimen again showed superior running-in properties, and a low friction coefficient (0.059), which later steadily increased to 0.142 (Figure 5.2.1.4 and 5.2.1.5). The friction of the DLC B coated disc remained high from the start of the test (0.088) and
increased to 0.127 towards the end of the test. This behaviour could not be explained with the current available literature or evidence. However, such results would be expected if the DLC C coated contact was starved of lubricant during the test.

Oil 6 is a synthetic PAO based API Group IV lubricant. In combination with the DLC C coating, it produced a low friction coefficient of 0.029 after steady running-in, which slowly increased to 0.049. The friction coefficient of the DLC B coating remained high from the start of the test, but intermittently dipped to 0.077, and rose to 0.104. The surface roughness of the DLC C coating (compared to the DLC B surface) was unchanged (Figure 5.2.1.3). The surface graphitisation of smoother DLC C coating may have contributed to DLC C’s low friction, as described by Veduguswamy et al. and Tasdemir et al. [37 and 43]. The DLC B coated disc was softer and rougher compared to the DLC C coated disc. It therefore neither effectively run-in the softer steel counter face, nor had surface graphitization, leading to its high friction with Oil 6.

In Oil 7, DLC C produced very low friction of 0.016, despite a jump in friction (to 0.113 as shown in Figure 5.2.1.5) shortly after an otherwise smooth running-in period. Oil 7 is ester-based, so it could have formed a functional group terminated tribo layer, resulting in the low friction observed. The DLC B coating showed high friction from the start of the test, with unstable running-in. For DLC B, a friction coefficient of 0.073 was observed, which increased to 0.104. DLC C’s drop in surface roughness (Figure 5.2.1.3) demonstrates the contribution of hydrodynamic effects in reducing friction.

The wear on DLC C coated discs was mostly lower, compared to DLC B coated discs. DLC C coated discs were harder than DLC B coated discs, therefore DLC C coated discs were more wear resistant. The wear observed in Oils 2 and 4 was minimal. Oil 2 contains zinc, which acts as an anti-wear additive, and helped to reduce the wear on discs with both types of coating. The data suggest that the rust inhibitor in Oil 4 may have also provided a degree of anti-wear protection. DLC C showed low levels of wear in combination with both Oils 1 and 3. The sulphur present in these oils may have acted as an anti-wear agent. When combined with Oils 1, 5 and 7, DLC C showed increased wear that was usual, which may have been due to coating breakdown, leading to fluctuations in friction coefficients, as seen in Figures 5.2.1.5 and 5.2.1.6. The wear profiles of cylinders and both the DLC Coated discs for block on ring tests are shown in Appendix C.1.

A comparison between friction of both DLC B and C is plotted in friction plots in Figure B.1 in Appendix B.
5. Results and discussion

5.2.2 CETR UMT-2 macro-micro block-on-ring configuration

5.2.2.1 SEM-EDX analysis of wear scars on blocks tested with ring specimens

Table 5.1. EDX analysis of worn block test specimens (20 kV filament voltage). The ‘other elements’ described in this table are the ones absent in the cast iron block (i.e. Fe, Si, Mn, C from Table 5.1.4)

<table>
<thead>
<tr>
<th>Lubricant</th>
<th>Other elements in block wear scar, tested with uncoated ring (weight %)</th>
<th>Other elements in block wear scar, tested with DLC B coated ring (weight %)</th>
<th>Other elements in block wear scar, tested with DLC C coated ring (weight %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil 1</td>
<td>S (1.11)</td>
<td>-----</td>
<td>S (0.5)</td>
</tr>
<tr>
<td>Oil 2 (Zn)</td>
<td>Zn (1.4), P (1.3), S (2.1)</td>
<td>Zn (1.4), S (2.6), P (1.3)</td>
<td>S (2.2)</td>
</tr>
<tr>
<td>Oil 3</td>
<td>S (1.11)</td>
<td>S (1.9)</td>
<td>S (0.4)</td>
</tr>
<tr>
<td>Oil 4</td>
<td>S (2.08), P (1.03)</td>
<td>S (0.7), Cu (0.7)</td>
<td>S (1.0)</td>
</tr>
<tr>
<td>Oil 5</td>
<td>P (2.04), S (1.22)</td>
<td>S (1.7)</td>
<td>S (0.3)</td>
</tr>
<tr>
<td>Oil 6</td>
<td>-----</td>
<td>S (0.6)</td>
<td>-----</td>
</tr>
<tr>
<td>Oil 7</td>
<td>-----</td>
<td>-----</td>
<td>Cr (0.5)</td>
</tr>
</tbody>
</table>

It should be noted that in EDX analysis, molybdenum L peaks (Mo++) coincide with the K peaks of sulphur. They have similar EDX/characteristic X-ray energy level. The L shell energy level of Mo is 2.293 keV, and the K shell energy level of sulphur is 2.307 keV. Therefore, it is possible that the peaks initially identified in EDX spectrum as seen in Appendix C.2 as Mo L peaks may actually be sulphur K peaks, since the oils used here are ashless and therefore devoid of Mo. We therefore assume presence of sulphur instead of Mo within the wear scar and tabulate Table 5.1 accordingly. The EDX spectrum can be seen in Appendix C.2.

In sulphur-containing Oil 1 (API Group I), traces of sulphur were identified when the oil was tested with a DLC C coated ring. The sulphur acts an EP additive, and was transferred onto the block-on-ring interface during the test. This formed a protective, sacrificial film of iron sulphide on the surface’s asperities in the wear scar as evident from sulphur detected in Table 5.1.

When the DLC B coated ring was tested in the zinc-containing Oil 2 (API Group I), zinc, sulphur and phosphorus were found in the wear scar of the cast iron block. The weight percentages of zinc (1.4 %), sulphur (2.6 %) and phosphorous (1.3 %), indicate the presence of ZDDP in the oil, which was transferred onto the cast iron counter face in the form of both zinc phosphate and sulphide pads. In this instance, ZDDP acts as an anti-wear additive. In contrast, the wear scar of
the cast iron block run with the DLC C coated ring contained (2.2%) sulphur, rather than zinc, indicating the presence of sulphides, which act as anti-wear and EP additives.

When Oil 3 was combined with the DLC B coated ring, sulphur was found at 1.9 weight percent in the block wear scar. Sulphur content was 0.4 weight percent in tests with DLC C coatings. Higher sulphur content meant better wear protection in severe lubricating condition for DLC B.

In tests run with either Oil 4 or 5 and a DLC coated ring, sulphur peaks were observed at 1% with DLC C and 1.7% with DLC B. Such peaks could also indicate the presence of sulphides. Copper found in Oil 4 could be an anomalous result, or possibly result from the detergents or rust inhibitors based additives (sulphates of copper) used in the Oil 4.

Sulphur, observed when coated rings were tested with Oil 6, could be from the cast iron, or may be an anomalous result. Traces of chromium observed when Oil 7 was tested with DLC C coated rings could be due to material transfer between the 100Cr6 steel ring substrate and the cast iron block.

The sulphur content in blocks run with DLC B coatings appears greater than that those run with DLC C coatings. The varying elemental composition of the wear scars with different types of DLC coated rings could be explained by the difference in lubrication regimes. In the interface between the (comparatively harder) DLC C coated rings and worn block, higher wear and greater conformity was observed with increasing contact area. As a result, the stress within the system was reduced, and overall conditions were milder. In comparison, DLC B coated rings (comparatively softer) showed decreased wear with less conformity, resulting in more severe conditions after running-in. Such behaviour activated sulphur in the oil, which acts as an anti-wear and extreme pressure additive. In addition, the rougher DLC B coated surface may have become more activated, leading to greater activation of the additives in the oils, compared to the smoother surface of DLC C coatings. The EDX results would be explained in the light of friction and wear results in the following sub sections in section 5.2.2.
5. Results and discussion

5.2.2.2  Tests of cast iron blocks with uncoated specimens

Fig 5.2.2.1. Friction coefficients (mean CoF) for Oils 1 - 7 (Table 3.4), tested with uncoated rings, both during running-in (first 5 mins of test) and steady state (final 90 mins of test).

Fig 5.2.2.2. Surface roughness of uncoated ring specimens tested in Oils 1 –7 (mentioned in Table 3.4), after the test. Roughness parameters, Ra: Mean surface roughness; Rq: rms surface roughness; Ra-90 deg: Mean surface roughness perpendicular to the direction of sliding

Fig 5.2.2.3. The wear of cast iron blocks for Oils 1 – 7 (Table 3.4), tested with uncoated rings.
During block-on-ring tests with uncoated specimens, friction coefficients increased slightly after the initial running-in period. In Oil 2, this increase was much greater compared to other oils. This can be explained by considering the contact configuration and surface morphology of the samples. Since the uncoated interface is softer and smoother (see Table 3.2), as the surfaces run-in, the increase in worn contact area is small (from wear data in Figure 5.2.2.3). This maintains the high normal and shear stresses keeping the friction high.

Figure 5.2.2.2 shows that during tests run with different lubricating oils, the surface roughness of the steel rings increased after the test was complete. During running-in, the harder inclusions of manganese oxides or sulphides in cast iron (Table 5.1.4a) (as asperities) ploughed through the asperities on steel, although cast iron is a comparatively softer material. This led to an increase in surface roughness of the uncoated steel ring. Higher surface roughness caused further asperity interlocking under boundary lubrication conditions, increasing the steady state friction coefficient compared to the running-in friction measured during reference tests. This trend in friction coefficient can be seen from the friction plots in Appendix B.2.

The high coefficient of friction in Oil 2 was attributed to the presence of zinc in the oil, which forms zinc sulphide and phosphate pads, as seen from the EDX results in Table 5.1, thereby reducing the shearability of the surface. In Oil 6 (which uses a highly non-polar synthetic base oil), high friction was also observed in the steady state. The polar ester content of Oil 7 was also ineffective in reducing friction. Reference tests with the remainder of the oils showed comparatively lower friction coefficients in the steady state. These low values may be due to the sulphur content of the API Group I and II base mineral oils used in Oils 1 - 5, or the rust inhibitor content of Oil 4, both of which could form a shearable tribolayer of sulphur and phosphorous, as seen in the results of the SEM-EDX analysis (Table 5.1).

Figure 5.2.2.2 shows that the increase in surface roughness was lower for mineral-based oils (Oils 1-5) than for synthetic oils (Oils 6 and 7). This can be explained using the EDX analysis of Table 5.1. The presence of sulphur in mineral base oils facilitated the formation of sulphides on the asperities of the cast iron blocks tested with uncoated specimen. The sulphide layer acted as a protective film, and prevented further ploughing asperity interaction and roughness increase.

The wear of cast iron observed increased, as the roughness of the steel ring increased. However, this additional wear was minimal in order of micro-grams. From Figure 5.2.2.3, it can be seen that Oils 2 and 7 resulted in the highest wear on the blocks tested. This could be due to the formation of phosphate or sulphide pads on cast iron when Oil 2 was used. The polar nature of Oil 7 can also lead to a weak shearable layer which is worn out during the test. The wear with Oil 2 and 7 indicate the tribochemical wear processes in cast iron weight loss.
5. Results and discussion

5.2.2.3 Tests of cast iron blocks with DLC B coated specimens

- Fig 5.2.4. Friction coefficients (mean CoF) for Oils 1-7 (Table 3.4), tested with DLC B coated rings, both during running-in (first 5 mins of test) and steady state (final 90 mins of test).

- Fig 5.2.5. Surface roughness of DLC B coated ring specimens tested in Oils 1–7 (Table 3.4), after the test. Roughness parameters, Ra: Mean surface roughness; Rq: rms surface roughness; Ra-90 deg: Mean surface roughness perpendicular to the direction of sliding.

- Fig 5.2.6. The wear of cast iron blocks for Oils 1–7 (Table 3.4), tested with DLC B coated rings.
Tests undertaken with a block-on-ring setup and DLC B coated specimens, showed a drop in friction coefficients in the steady state, after the running-in period. The friction coefficients initially increased during the running-in period; this can be attributed to the hard and rough surface of the DLC B coated sample. The hard asperities of this surface are likely to have come into contact with the surface of cast iron block, leading to high shear stress at the interface, causing high friction. Simultaneously, as the contact area increased and the worn counter surface became smoother over the progression of the test, leading to more conformal contact. This resulted in hydrodynamic effects, which act to reduce both the normal and shear stress, thereby decreasing the friction coefficients. Due to shallow wear scar, the drop in CoF was small.

A comparison of the steady state friction values of the oils used shows that API Group I oils had the highest friction coefficients, ranging from (highest) Oil 1; Oil 2 (contained zinc); Oil 6 (a synthetic oil); and Oil 7 (ester-based) (lowest). All API Group II oils tested (Oils 3 - 5) produced lower friction coefficients than Group I oils. Group II oils also showed a greater drop in measured friction coefficients from running-in to the steady state, compared to Group I oils. Oil 4 (containing 2% by weight rust inhibitor) gave the lowest friction coefficient. The polyalphaolefin (PAO) based Oil 6 and the ester-based Oil 7, weren’t able to reduce the measured friction, as previously indicated by other authors [43 and 44].

Figure 5.2.2.5 shows that the surface roughness of the DLC B coated rings almost didn’t change after tests with mineral based oils (Oils 1-5), except with Oils 2 and 4, where the coatings showed a decrease in surface roughness. EDX analysis was used to analyse this surface behaviour. Results show that at the start of the test, the hard DLC B and C coating run-in and then wore out the cast iron counter surface (Wear profiles in Appendix C.2). As the test progressed, the cast iron block was rubbed under severe boundary lubrication conditions. This led to the formation of a sulphide layer on the cast iron block's asperities, as shown by EDX analysis of the blocks (Table 5.1). This sulphide layer prevented asperity interactions between the block and the DLC coating. In contrast to the mineral oils, the synthetic oils (Oils 6, 7) are devoid of such additives (i.e. sulphur) that facilitate this surface behaviour. Tests undertaken using Oils 6 and 7 resulted in both smoothening and roughness reduction of the DLC B coated surfaces. During running-in with Oils 6 and 7, the DLC B coating interacted with asperities, unprotected by sulphide layer causing asperity deformations along the direction of sliding. The mean surface roughness (Ra 90°, perpendicular to the direction of sliding), remained the same.

Oil 2 contains zinc, which formed both phosphate and sulphide based tribopads (as seen from EDX analysis in Table 5.1), thus protecting the DLC B coating from wear. These pads also prevented changes to surface roughness of the DLC B coating. The rust inhibitor in Oil 4 prevented
smoothening of DLC B coated rings by possibly forming a shearable tribolayer on the block-ring interface. This layer might have prevented asperity interactions between the DLC B coating and cast iron, and reduced both the friction and overall wear observed.

The wear of DLC B coatings tested with Oil 1 - 7 displayed similar trends with uncoated specimens tested with Oil 1 - 7. Cast iron blocks tested with both DLB B coated and uncoated specimens in Oils 2 and 7, displayed the highest wear, compared to other oils. Sulphur as EP/AW additive in Oil 1 and Oils 3 - 6 helps in forming a protective film to prevent wearing of the block. The zinc in Oil 2, and the polar ester groups within Oil 7, increased the block wear.

5.2.2.4 Tests of cast iron blocks with DLC C Coated Specimen

Fig 5.2.7. Friction coefficients (mean CoF) for Oils 1 - 7 (Table 3.4), tested with DLC C coated rings, both during running-in (first 5 mins of test) and steady state (final 90 mins of test).

Fig 5.2.8. Surface roughness values of DLC C coated ring specimens tested in in Oils 1 – 7 (Table 3.4) after tests. Roughness parameters, Ra: Mean surface roughness; Rq: rms surface roughness; Ra-90 deg: Mean surface roughness perpendicular to the direction of sliding.
5. Results and discussion

The running-in friction coefficients of DLC C coated specimens are higher compared to DLC B and uncoated specimen, but drop to lower steady state values. (Figure 5.2.2.7). The large drop in friction coefficients after running-in is due to the higher hardness of the DLC C coated specimen than DLC B coated and uncoated test specimens. The asperities on the harder DLC C coated specimen (as compared to DLC B coated specimen), caused greater shear during running-in face (explained in Theory section 1.3), more deformation and wear on the block's counter. Figure 5.2.2.13 and wear profiles from C.2 shows that after the running-in, a wider wear scar (compared to those found in DLC B coated samples) caused the contact to become larger and more conformal, and hence reduced the normal stress. The real contact area (contact area at the micro or asperity level) also increased due to the smoother interface. As a result, hydrodynamic effects came into effect, and reduced the shear stress in the steady state, causing a further drop in friction.

The trend in friction coefficients for Oils 1 – 7 tested with DLC C coated specimens is similar to tests performed using uncoated specimens. The synthetic, hydrocarbon-based Oil 6; the ester-based Oil 7; the API Group I-based Oil 1, and the zinc-containing Oil 2, all gave the highest steady state friction values. The polar, ester-based Oil 7, and the PAO-containing Oil 6 weren't able to greatly reduce friction, as previously suggested in the literature [43, 44 and 47]. The API Group II Oils 3, 4 and 5 gave the lowest friction coefficients. Among these three oils, Oil 4 (which contained a rust inhibitor) provided the lowest friction values.

Figure 5.2.2.8 shows that roughness parameters increased after the tests. This could be due to the removal of the soft and smooth running-in layer from the surface of the DLC C coating. Black particles in the oils after the tests provided evidence for this conclusion. A decrease in Rq was followed by an increase in Ra (Ra-90°) perpendicular to the sliding direction indication a more distributed roughness on the x-y plane. The increase in roughness was lowest when Oils 2 and 7 were used. Oil 2 contained zinc, which formed a tribofilm (in the form of pads) on the cast iron.
block surface, and prevented severe asperity interactions and subsequent wear. Oil 7 contained polar-ester functionalities, which can form polar functional group terminated tribofilms, which also act to reduce wear [43, 44 and 47].

The wear of DLC C coated samples is shown in Figure 5.2.2.9. The wear observed was high compared to other DLC B coated and uncoated specimens. DLC C coated specimens are harder than DLC B coated specimens, and the roughness of the coated rings increased during the test. The hard asperities of the DLC C coating interacted frequently with the cast iron block under severe operating conditions, which resulted in wearing of the block. The wear of the DLC coated samples was highest in Oils 2 and 7. As the roughness of the coated rings perpendicular to direction of sliding increases the frequency of asperity interaction across the wear track increases which aids to the wearing out of the cast iron block tested with these oils. Oil 4 resulted in both the lowest friction values, as well as the lowest wear levels. Here as well the possible effect of tribofilm formed in DLC interface by rust inhibitor in Oil 4 could be mentioned for both its friction and wear reduction properties.

5. Results and discussion

5.2.2.5 Comparative analysis of tribological test results

For friction plots for block on ring test with uncoated and both DLC B and DLC C coated specimen, Figures B.2, B.3 and B.4 in Appendix B can be referred respectively.

The wear profiles of blocks for block on ring tests are shown in Appendix C.2.

![Coefficient of friction graph](image)

Fig 5.2.2.10. Running-in friction coefficients for uncoated, DLC B and C coated ring specimens, over the first five minutes of the test, performed in Oils 1 – 7 (Table 3.4).
5. Results and discussion

Fig 5.2.2.11. Steady state friction coefficients for uncoated, DLC B and C coated ring specimens, over the final 90 minutes (1.5 – 3 hours) of the test, performed in Oils 1 - 7 (Table 3.4).

The running-in friction coefficients of DLC C coated rings were greater than for both uncoated and DLC B coated rings. At the beginning of each test cycle in both uncoated and coated systems there were higher levels of asperity interactions. In DLC C coated rings, harder asperities (compared to those of DLC B coated rings) interacted with the counter face, resulting in higher friction coefficients and greater wear of the cast iron blocks. This result demonstrates the influence of coated specimen’s effective hardness (due to coating thickness) and surface morphology on measured friction coefficients, and is similar to the findings published by Daniel [1 and 48]. His demonstrated that a shift in the lubrication regime from boundary to hydrodynamic caused a reduction in friction coefficients for DLC coatings in the steady state.

The steady state friction coefficients for DLC C coating were lower than for DLC B coatings. This may be due to the high running-in friction values of DLC C coatings, which led to activation of the DLC C surface for oil interactions to take place. In addition, after running-in, the wear scar of the DLC C counter face was wider and deeper than the DLC B wear scar (refer Figure 5.2.2.13 and Appendix C.2 for wear profiles). Hence, there was greater conformity between the ring and the cast iron block with DLC C surfaces. This led to a reduction in both the contact pressure and friction coefficients, as hydrodynamic effects came into effect.
5. Results and discussion

Fig 5.2.12. Weight loss of cast iron blocks, when tested with DLC B and DLC C coated ring specimens, in Oil 1 – 7 (Table 3.4).

Fig 5.2.13. Wear volume of cast iron blocks, when tested with DLC B and DLC C coated ring specimens, in Oil 1 – 7 (Table 3.4).

The weight loss (effective wear) of the cast iron block when run with DLC B coated rings was lower (5 to 7 times) than when run with DLC C coated rings. DLC C coated ring specimens are harder than DLC B coated ring specimens, therefore DLC coated rings caused more abrasion to the test pins. The wear scar depth and width, and hence the wear volume, of cast iron blocks run with DLC C coated rings was 5 to 7 times higher than that of DLC B coated rings, as shown in Figure 5.2.2.13.
5. Results and discussion

5.2.3 Phoenix tribometer pin-on-disc configuration

5.2.3.1 SEM-EDX analysis of pins tested with disc specimens

Table 5.2. EDX analysis of worn pin test specimens (15 kV filament voltage). The ‘other elements’ described in this table are the ones absent in the cast iron block (i.e. Fe, Si, Mn, C from Table 5.1.4)

<table>
<thead>
<tr>
<th>Lubricant</th>
<th>Other Elements in worn pin surface tested with uncoated disc (weight %)</th>
<th>Other Elements in worn pin surface tested with DLC B coated disc (weight %)</th>
<th>Other Elements in worn pin surface tested with DLC C coated disc (weight %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil 1</td>
<td>S(1.98)</td>
<td>S(0.99)</td>
<td>S(0.35)</td>
</tr>
<tr>
<td>Oil 2 (Zn)</td>
<td>Zn++(2.84), S(4.32)</td>
<td>Zn++(2.68), S(5.63)</td>
<td>Zn++(2.51), S(4.24)</td>
</tr>
<tr>
<td>Oil 3</td>
<td>S(0.57)</td>
<td>S(0.72)</td>
<td>S(0.74)</td>
</tr>
<tr>
<td>Oil 4</td>
<td>S(1.02)</td>
<td>S(0.58)</td>
<td>S(2.28)</td>
</tr>
<tr>
<td>Oil 5</td>
<td>S(1.64)</td>
<td>-----</td>
<td>S(0.49)</td>
</tr>
<tr>
<td>Oil 6</td>
<td>S(1.71), P(1.11)</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>Oil 7</td>
<td>P(1.07)</td>
<td>Ca(0.58)</td>
<td>C(25.06), O(4.76)</td>
</tr>
</tbody>
</table>

Taking the explanation from section 5.2.2.1, we assume presence of sulphur instead of Mo (from the Mo L peaks in EDX spectrum in Appendix C.3) within the disc wear scar and worn pin surface, Table 5.2. The EDX spectrum can be seen in Appendix C.3

When uncoated discs were tested, sulphur was found in all of the formulated oils used, except Oil 7 (which contains a biodegradable synthetic ester). The sulphur could be from the oil or the cast iron block. On the worn surface of the pin, sulphur may have been present as sulphides of manganese or iron. These sulphides may have acted as protective, shearable films, and helped to reduce friction or wear at the pin and disc interface. When Oil 2 (which contains zinc) was tested, zinc was detected at the worn pin surface.

After testing worn pin surfaces with DLC B coated discs, sulphur was detected in Oil 1. In worn pin surfaces run with Oil 2 and DLC B, 2.68 weight percent of zinc, and 5.63 weight percent of sulphur was detected. These indicate the presence of sulphides, which act as AW and EP additives. Furthermore in worn pin surfaces tested with Oils 3 and 4, traces of sulphur were also detected.
Worn pin surfaces were tested with DLC C coated discs, and traces of sulphur were detected in all API Group I and II mineral base oils (Oils 1 - 5). Sulphides formed a sacrificial layers on the asperities of the pin, when it experienced high shear stress. When Oil 2 was tested with a DLC C coated disc, zinc (2.51 weight %) was detected. In this case, zinc acted as an anti-wear additive. In worn pin surfaces tested with Oil 7 and DLC C, carbon and oxygen were detected. This shows that there was oxidation of metal of pin surface, and that asperities present on the surface of the pin interacted with the coated disc surface. As a result those regions of the pin in contact with substrate have deeper wear tracks on the worn surface. For wear profiles of pins and discs (both DLC coated and uncoated), Figures in Appendix C.3 can be referred.

5.2.3.2 Test of cast iron pins with uncoated specimens

![Friction coefficient graph]

Fig 5.2.3.1. Steady state friction coefficients of uncoated specimens: reference pin on disc tests, with Oil 1 – 7 (Table 3.4).

![Mean Surface Roughness graph]

Fig 5.2.3.2. Surface roughness (Ra) of pins and uncoated discs before and after pin on disc test with Oil 1 – 7 (Table 3.4).
5. Results and discussion

Reference tests performed using a pin-on-disc test rig with uncoated steel discs, showed high friction coefficients in all oils, similar to that described in the literature [24, 43 and 46] for steel on steel contacts. However, friction coefficients (below 0.1) were obtained with API Group II oils, Oil 4 being the lowest at 0.084 as seen in Figure 5.2.3.1.

A high friction coefficient of 0.11 was obtained in tests with Oil 6 (synthetic PAO base oil) and Oil 7 (synthetic ester base oil), which is similar to the findings of Tasdemir *et al.* and Kalin *et al.* [43 and 46]. Apparently the long chain oligomers and esters of Oils 6 and 7 respectively were ineffective in forming any physically adsorbed layers on the interface between the cast iron pins and uncoated steel disc. The friction coefficients in tests using Oils 1 and 2 (API Group I oils) were also high (0.117 and 0.116 respectively) which could be due to the presence of a large quantity of aromatic, unsaturated and cyclic paraffins, usually found in API Group I oils. These paraffins were unable to form any molecular tribolayer on the cast iron counter face, and therefore did not help to reduce friction. In addition, as evident from wear profiles in Appendix C.3 the pad-like tribofilm formed by Oil 2 on the cast iron counter face, increased the friction coefficient due to the film’s high shear strength. API Group II oils contain no aromatics or unsaturated cyclic compounds to hinder the formation of a tribolayer. It is possible that short chain paraffins present, easily formed a physisorbed layer, which helped to reduce friction. In Oil 4, the rust inhibitor further strengthened the shearable layer formed, and helped to reduce friction to the lowest value amongst all the reference tests.

The friction results of the reference test done with uncoated disc specimens can be explained using the roughness analysis of the pins and disc presented in Figure 5.2.3.2. The surface of each cast iron pin underwent smoothening during the pin on disc test, due to deformation of surface asperities of the pin. These effects led to a reduction of the pins’ surface roughness. In comparison, the roughness of the uncoated steel disc increased during the period of the test. This could be due
to the presence of hard manganese oxide inclusions (as asperities) on the surface of the pins, acting as abrasives bodies (as seen from EDX of cast iron Table 5.1.4 a). There is a correlation between the surface roughness of the pins and disc at the end of each test, and the friction measured. API Group II oils (Oils 3, 4 and 5), which gave lower friction coefficients, showed higher surface roughness reduction for pins, while the disc surface roughness remained almost unchanged. Hence, the high friction was due to the increased effective roughness values of the surfaces, leading to greater asperity interactions.

SEM-EDX analysis shows the presence of protective tribofilm pads on the surface of pin and disc specimens run with Oil 2 (Table 5.2). These anti-wear protective pads experienced high shear, and increased friction (as explained in [43]). Sulphides were detected on the surfaces of pins run in Oil 1. Oil 1 is low grade, and therefore oil ran-in the steel surface, which increased its roughness. Despite the presence of shearable sulphides and a smooth pin counter face, friction values in Oil 1 were high. Tests run in Group II oils indicated the presence of sulphur, which formed shearable sulphide layer, thus supporting the low friction values measured. The presence of phosphorus, on the pin surface in Oils 6 and 7 (Table 5.2) may have been as a result of phosphate pads formed, which may have prevented surface activation and action of esters based functional groups, and led to high friction. For friction plots, Figure B.5 in Appendix B can be referred.

In conclusion, the wear of the pins run on the uncoated steel discs was minimal in order of micrograms. Pin wear trend is similar to friction trend for pin on disc test with uncoated samples. Both API Group I oils and synthetic oils (Oil 6 and 7) resulted in the highest pin surface wear levels. For wear profile, Figures C.31-C.3.21 in Appendix C.3 can be referred.

5.2.3.3 Test cast iron pins with DLC B coated specimens

Fig 5.2.3.4. Steady state friction coefficients of for DLC B coated disc specimens in pin-on disc-test with Oil 1-7 (Table 3.4).
5. Results and discussion

Fig 5.2.3.5. Surface roughness (Ra) of pins and DLC B coated disc specimens after pin on disc tests with Oil 1 – 7 (Table 3.4).

Fig 5.2.3.6. Weight loss of pins when tested with DLC B coated disc specimens in pin on disc test with Oil 1 – 7 (Table 3.4).

The DLC B coated discs resulted in a large drop in friction coefficients, compared to uncoated surfaces. When DLC B coated discs were tested using a pin-on-disc test rig, Oils 5, 6 and 7 demonstrated the lowest friction coefficients.

High friction coefficients were obtained in tests with API Group I oils (Oils 1 and 2), which could be due to the inability of these oils to activate the DLC B coating [56]. In addition, it is possible that sulphur and unsaturated paraffins in Oil 1 formed a shearable tribolayer (evident from the presence of sulphur in EDX analysis of the worn pin surfaces Table 5.2). Figure 5.2.3.5 shows a decrease in roughness of both the pins and disc specimens after each test, which would reduce asperity interactions. This would result in a shift into a mixed lubrication regime, thereby reducing the friction of the system. The high friction observed in tests using Oil 2 is likely due to the presence of zinc in this oil. As evident from EDX analysis, the zinc and sulphur in this oil...
formed tribofilm pads. The anti-wear behaviour of these pads is shown by the low degree of wear of the DLC B coated disc, and a minor drop in its surface roughness. The increase in friction observed was due to the interaction between DLC B asperities and these tribofilm pads.

Friction levels in API Group II oils (Oils 3 - 5) were lower than those in Group I oils. In Group II oils, DLC B coated discs displayed ultra-low friction, in agreement with results published by other authors for friction in hard and rough coating with mineral oils [37]. In tests with Group II oils, pins showed a large decrease in surface roughness. Also the EDX analysis of the pins run with Oil 3 demonstrated the presence of sulphur. In this oil, the roughness of the DLC B coated disc was high, and remained relatively unchanged during the test. Less smoothening of the asperities was observed in Group II oils, and as a result, friction was lower than in API Group I oils tested (see Figure 5.2.3.5).

Friction values in tests with Oil 4 were low due to the presence of the polar rust inhibitor. This may have activated the DLC B coating, and created a tribolayer. Such a layer would further smoothen the DLC B coating’s asperities, providing a possible explanation for the reduction in friction observed.

EDX results of Oil 5 with a DLC B coated disc, show that no tribolayer was formed. Hence, there is direct coating to counter face interaction which leads to roughness reduction and smoothening of asperities of both the tribo elements as shown in Figure 5.2.3.5. This resulted in the introduction of hydrodynamic effects, which caused a large decrease in friction compared to the tests with other Group II Oils.

When DLC B coated disc was tested with Oil 6 (API Group IV), the friction coefficient value reached to 0.022, in agreement with results published by Tasdemir et al. [43]. This low friction has been attributed to a range of causes, including the graphitisation of the DLC B coating surface, or activation of the coated surface during running-in [43]. The high surface roughness of the DLC B coating may have led to this activation during interaction with Oil 6 (suggested by [56]).

Low friction was measured during tests with Oil 7 (containing polar, ester functionalities). The surface profile analysis of both the disc and DLC B coated pin shows that the Ra values of both of these elements dropped during the test, resulting in a decrease in the friction coefficient. Ester-containing lubricants may attach their polar functional groups to friction-activated, dangling bonds of the DLC B surface, thus forming a shearable tribolayer. This provides an additional explanation for the drop in friction observed during this test.

In pin on disc tests conducted with DLC B coated specimens, quicker running-in and greater smoothening of both the pin counter face and the DLC B coated disc was observed, compared to
tests with uncoated discs. The reduction in effective surface roughness shift the lubrication regime from boundary to mixed lubrication and brings in hydrodynamic effects in friction reduction. For friction plots, Figures B.6 in Appendix B can be referred.

The weight loss of the cast irons pins was measured (Figure 5.2.3.6). The weight change of the DLC B coated discs was small and contained a high degree of error. The cast iron pins lost the most weight in tests run with Oils 2 and 5 (2.56 mg and 0.59 mg respectively). The smallest weight loss was recorded in tests conducted with Oils 1, 3 and 6 (0.38 mg, 0.25 mg, and 0.35 mg respectively). High pin weight losses also corresponded with low friction coefficients.

5.2.3.4 Test cast iron pins with DLC C coated specimens

![Friction coefficient graph](image)

Fig 5.2.3.7. Steady state friction coefficients of for DLC C coated disc specimens in pin on disc test with Oil 1 – 7 (Table 3.4).

![Roughness graph](image)

Fig 5.2.3.8. Surface roughness (Ra) of pins and DLC C coated discs specimens after pin on disc test with Oil 1 – 7 (Table 3.4).
Tests performed with DLC C coated specimens resulted in a lower friction coefficient compared to tests undertaken with uncoated specimens. However, DLC C coatings are thicker and smoother than DLC B coatings, which led to different friction behaviour between these two coatings. For friction plots, Figure B.7 in Appendix B can be referred.

Friction values of tests run with Oil 1 (API Group I) were obtained around 0.03 (Figure 5.2.3.7). The smoother DLC C coating (compared to the DLC B coating) created less severe conditions, which did not facilitate the activation of the sulphur, found in Group I oils. Therefore, sulphur was unable to form a sacrificial layer, which on DLC B surfaces, acted to reduce asperity interactions. Oil 1 resulted in smoothening of the DLC C coated surface, which reduced friction.

In tests conducted with Oil 2 (which contains zinc), a tribofilm consisting of zinc and sulphur pads formed, resulting in wearing of the pin surface, as seen during EDX analysis. As a result of the smooth pin surface and smooth DLC C coating (compared to DLC B coatings), the asperities of the DLC C surface came in contact with the high shear pads, generating high friction.

Low friction coefficients were measured in tests undertaken with Oil 3 (API Group II). EDX analysis highlighted the presence of sulphur on the worn pin surface, as well as a reduction in its surface roughness (Figure 5.2.3.8). These effects can combine to give a shearable smooth interface of the pin and disc and cause low friction. However in spite of a smoother pin surface after the pin on disc test (Figure 5.2.3.8), the friction coefficient obtained for DLC C coated specimen tested with Oil 4 and Oil 5 were 0.047 and 0.04 respectively (Figure 5.2.3.7). The smooth surfaces did not activate the coating, or lubrication Oil 4 and 5 to form a tribolayer but acted to reduce the severity of the test conditions to reduce the friction.
The smoother surfaces on pin and disc (Fig 5.2.3.8) were not fully activated when tested with Oils 6 and 7. Therefore, neither graphitisation, nor friction activation (both leading to the production of a tribofilm), appear to have taken place. Despite the smoothening of the pin and disc surface, the friction remained high in the synthetic base Oils 6 and 7 (0.057 and 0.047 respectively) compared to Oil 1, 3 and 5.

The cast iron pins demonstrated the highest weight loss when tested with Oils 2, 6 and 7 (4.37 mg, 6.21 mg and 5.6 mg respectively), and the smallest loss with Oils 1, 4, 3 and 5 (1.27 mg, 2.4 mg, 1.8 mg and 1.75 mg respectively). DLC C surfaces are particularly smooth, compared to DLC B surfaces. Hence the load was distributed over a larger number of asperity summits. It is thus possible that tests conducted using the DLC C coated surfaces generated milder test conditions, which were incapable of activating any anti-wear agents within the oils, and therefore protective tribofilms were not formed. As the test track radius increased, the wear of the pins also increased (Figure 5.2.3.9 and Appendix C.3), and this led to scatter in the pin weight loss results. This is because in a wear track, the sliding velocity within the pin increases along the diameter perpendicular to the direction of sliding (sliding velocity = angular velocity X track radius). As the wear track radius increases, it leads to higher gradient in sliding velocity and sliding distance across the flat cross section and causes higher wear. So different wear mass is obtained for different radius of wear tracks. The wear profiles are shown in the Appendix C.3

5.2.3.5  Comparative analysis of tribological test results

![Friction coefficient graph](image)

Fig 5.2.3.10. Steady state friction coefficients of uncoated, and both DLC B and DLC C coated disc specimens in pin on disc test with Oil 1 – 7 (Table 3.4).
Friction coefficients measured during pin-on-disc tests with uncoated, and both DLC B and DLC B coated discs, were compared (Figure 5.2.3.10). These show that coated discs produced lower friction coefficients compared to uncoated discs. For most oils (except Oils 1 and 3), DLC B coated discs gave lower friction coefficients than DLC C coated discs. As DLC B has a rougher surface (smaller real contact area results in a concentrated contact), it generated harsher test conditions, as any load was distributed over a smaller (real) contact area. This might cause the coating to become activated (to a greater degree than DLC C), thus activating the lubricants’ additives (also mentioned in [56]). DLC C is thicker and smoother than DLC B, so loads were spread over a greater (real) contact area. In addition, the greater degree of effective hardness of DLC C coated specimen (compared to DLC B coated specimens) makes it more difficult to shear (mentioned in section 1.3). As a result, DLC C generated more frictional force during the test.

Both Oils 1 and 3 fail to follow the trends identified in Figure 5.2.3.10. These mineral oils contain sulphur, as well as cyclic and unsaturated paraffins. These components may have prevented the smoothening of the rough DLC B coating asperities, by creating a sacrificial (protective) sulphur coating on the pins, (EDX analysis, Table 5.2). This prevents direct asperity interaction and may have led to a smaller reduction in the surface roughness of the pin and DLC B coated disc. Hence due to a higher effective roughness the lubrication regime is predominantly in boundary lubrication and hydrodynamic effects in not significant in DLC B coated disc as in DLC C coated disc with Oil 1 and 3. This gives higher friction in DLC B coated disc tested with Oil 1 and 3.

![Graph showing weight loss of pins tested with both DLC B and DLC C coated disc specimens in pin on disc test with Oil 1 – 7 (Table 3.4).]
During pin-on-disc tests, both the roughness and hardness of the disc (Coated and uncoated) affected the wear of cast iron pins. Figure 5.2.3.11 shows that DLC B coated discs wore the pins’ counter surfaces less than DLC C coated discs. As DLC B coated specimens are softer, they may not have worn the counter surface as much as the harder DLC C coated specimens. Oil 2 formed zinc, sulphur and phosphorous based tribofilm pads on the cast iron pins. These hard, pad-like films interacted with the asperities of the DLC coatings, and wore out the cast iron pin. The major wear mechanism observed during pin-on-disc tests was abrasive wear.

DLC B coatings are rougher than DLC coatings, meaning that they have smaller (real) contact area and interacted more frequently, at high contact and shear stress with the cast iron counter face, causing more rapid wear. In addition, higher surface roughness caused greater activation of the counter face, and therefore the rapid reaction of iron and zinc with sulphur from the Oil 2 (also supported by [56]). Phosphate and sulphur based tribofilm pads also formed at the activated surface. This is evident from the higher zinc and sulphur content on pins rubbed with DLC B coated disc than DLC C coated disc (Table 5.2). The harder DLC coated specimens then wears out the counter face with a sacrificial layer easily than wearing out the counter surface alone. This tribo chemical wear mechanism is more predominant with DLC B coated disc than DLC C coated disc. However, abrasive wear mechanism is also prevalent in the system and as explained by Archard wear equation (4) the harder DLC C coated specimen wears out the pin counter face more than DLC B coating by abrasion. So the wear mechanism is both abrasive and tribo chemical. The combination of both mechanisms lead to the lower difference in pin wear with both DLCs with Oil 2 compared to other Oils.
6 Summary of work

In this thesis work, ta-C type of DLC coatings were characterised and investigated for their tribological performance in different contact configurations. This was done by testing the tribology of the coatings in three different tribo test setups.

DLC coatings named as DLC B and DLC C were investigated, and their thickness, hardness, composition, adhesion and surface topography were measured, which provided information to facilitate tribological analysis. Seven oils of different grades, additive packages and makes were used in these tests. Other variables tested included the relative motion between the tribological elements, contact conditions and the counter face material. Overall, 42 different test conditions were produced.

The triboelements within the Schwingung Reibung Verschleiß (SRV) test were steel, and DLC coated steel. These elements were rubbed under lubricated conditions using a reciprocating sliding motion with non-conformal line contacts. The difference in hardness between the tribo elements was small. Hence both the tribo elements including the DLC coating had measurable wear. The DLC C coated specimens were hard and smooth, and gave low friction values in most of the oils tested. Tests done with DLC C coated specimens reached a steady state friction value faster after running-in, compared to the tests done with softer and rougher DLC B coated specimens. However, during tests with Oils 1, 4 and 5, there was coating damage and/or spallation, and the contact conditions varied from the required DLC/steel contact conditions. This led to fluctuations in the friction values measured, either during or after running-in. A degraded coating couldn’t give a steady state friction and the friction coefficients later increased in these oils. The fluctuations and unsteady friction could also be explained from the light of oil starvation in the contact as many tests did not have significant running-in after which there was a steady increase in friction.

Block-on-ring tests were undertaken in well-lubricated conditions in a unidirectional sliding motion setup, with a cast iron counter surface. Stable and sufficient running-in was observed in all the tests. The smoother DLC C coated specimens showed greater running-in friction values, but lower steady state friction values. The trend in friction coefficient with varying Oils 1 - 7 was similar with both DLC B and C coated and uncoated specimens. Oil 4 gave the lowest friction coefficient with all specimens tested. Oils 1, 6 and 7 only showed a small drop in friction. Proper alignment of the block on the ring was key to avoiding fluctuations in test results.

Pin-on-disc set in unidirectional sliding motion had conformal area contact with DLC coated steel disc and cast iron pins as tribo elements. However, the results obtained were different from the
CETR UMT-2 block on ring and Optimol SRV cylinder on disc tests. In pin on disc test set up with conformal area contact, the surface roughness of the coated specimen played a major role in friction determination. This roughness effect was coupled with effects from the lubricants’ chemistry, as some of the oils reduced measured friction by activating the interface, forming a tribofilm with particularly with rougher DLC B coated specimens. Triboelements underwent greater surface roughness reduction when tested with Oils 4, 5, 6 and 7. This reduction in roughness resulted in hydrodynamic effects, and therefore decreased friction values, as previously described by other authors [1, 37 and 48]. Oils 1 and 3 had a mineral base oil, and were therefore unable to activate the rough DLC B surface to form sacrificial sulphur-based films on the pin counter face, which would have prevented asperity smoothening. The rougher DLC C coating underwent higher surface roughness reduction during its running-in with Oils 1 and 3, giving lower friction with Oils 1 and 3. Oil 2 on the other hand contained zinc, which lead to formation of high shear zinc based tribofilm responsible for high friction observed in most contact configurations with both coated and uncoated specimens.

Hence, in a conformal area contact configuration the mechanism of friction reduction with smoother and thicker DLC C coated specimen can be attributed to hydrodynamics effect, while with rougher and softer DLC B coated specimen, the friction reduction mechanism can be attributed to both hydrodynamic effects and surface activation of DLC coating with lubricant interaction and tribofilm formation.
7 Conclusions

Two types of ta-C DLC coated specimens were used for the tribological tests. They were characterised using various instrumental techniques for their surface and mechanical properties. The ta-C DLC coated specimens were found to have a coating thickness of 0.5 µm and 1µm. The thicker DLC coating was provided with smoother layer by surface finishing and the thinner DLC coating was devoid of any such layer, making it rougher. The thinner and rougher DLC coating was named as DLC B and the thicker and smoother DLC coating was named as DLC C. Both the DLCS has same intrinsic hardness. However depending on their coating thickness, they gave different effective hardness when coated on 100Cr6 steel substrate of the given specimen. The thicker DLC coating C gave a higher effective hardness to the coated specimen compared to the thinner DLC coating B. Both the DLC coatings were adhered to their substrate using titanium in the interface and intermediate layers of the coating.

In tribological tests with cast iron, both the DLC B and C coated specimens showed negligible surface wear. The thicker DLC coating C was always more wear resistant, and wore the counter face more than the thinner DLC coating B. This was because abrasive wear was the dominant wear mechanism, which was influenced by the DLC coated specimen hardness. This followed from “Archard” wear equation (Equation 4) where DLC C coated specimen being the harder coating was more wear resistant. However there was also evidence of tribochemical wear which was influenced by coating roughness. The rougher DLC B coating upon interaction with lubricant and its additives activated formation of a sacrificial tribolayer on the counter face which wore the counter face faster during the tribological testing than the smoother DLC C coating. Oil 2, due to the presence of zinc based AW additive, imparted the greatest wear resistance to both DLC coatings when these were rubbed with a comparatively hard steel counter face (an abrasive wear mechanism). However, Oil 2 resulted in the greatest counter face wear, as tribofilms formed by this oil accelerated the wearing process (both abrasive and tribochemical wear mechanism). Oils 6 and 7 also contributed to a high degree of counter face wear, indicating that they did not display anti-wear behaviour for the counter face. Oil 4 showed low wear in all tribo test configurations and lowest with line contact setups of Optimol SRV and CETR UMT-2. This result indicates that the rust inhibitor present in Oil 4 not only formed a friction-reducing tribofilm, but also provided anti-wear properties to the interface of DLC coating and counter face. It can be concluded that the wear of the counter face specimen tested with a DLC coating depends on the hardness of the DLC coated specimen (influenced by the coating thickness) and the anti-wear behaviour of the tribofilm formed by the interaction of counter face and coating with the lubricant (influenced by the coating roughness).
Both the coating characteristics and the contact conditions influenced the friction. For non-conformal line contact where the severity of contact conditions decreases with the test duration (increasing wear scar dimensions), the hardness of the coated specimen (coating thickness) plays a vital role in determining the running-in and steady state friction. In both the cylinder-on-disc, and block-on-ring setups, the configuration moved from non-conformal to conformal contact as the test progressed. Both the thickness and roughness of the DLC coating B and C determined the running-in and conformity of the contact later in the test. A more conformal contact reduced test severity by introducing hydrodynamic effects, thereby decreasing friction. In cylinder-on-disc configurations, the steel counter face was hard and smooth, but softer than the both the DLC coatings. The hard DLC wore out the steel counter face rapidly, leading to superior interface conformity and therefore led to lower friction values. In block-on-ring configurations, the thicker DLC coating C led to greater wearing of the relatively soft cast iron block counter face. This led to superior conformity with the thicker DLC C coated specimens, (also smoother) giving low friction values compared to DLC B coated specimens. In a pin-on-disc setup as the normal stress (load) is uniformly distributed over large area contact, coating surface roughness plays a vital role in determining the friction force (shear stress). In conformal contacts, surface smoothening led to hydrodynamic effects, which helped to reduce friction. High surface roughness activated lubricating oil additives, when present during running-in leading to tribofilm formation. As a result, the rougher and thinner DLC B coatings were smoothened to a greater degree than the smoother and thicker DLC C coatings. Hence the rougher DLC coatings resulted in lower friction values in conformal contact configurations. So the friction behaviour at a given tribological interface of a contact configuration is heavily influenced by the surface properties of DLC coatings.

The tribofilm assisting in friction and wear reduction was always formed on the soft, ferrous-based counter face. Most oils of the oils tested (and their additives) were more likely to react with the iron surface, rather than the comparatively inert DLC surface. However the lubricant and its additives may activate the DLC surface to aid in friction reduction depending on the contact and operating (test) conditions. Mineral Oil 4 (which contains a rust inhibitor) played a vital role in reducing friction in non-conformal contacts with thicker DLC C coatings (both in SRV and CETR UMT-2 test set up). The rust inhibitor in Oil 4 is not activated by rough DLC coating in a conformal contact as much as by initial running-in and severe conditions in non-conformal contact. However, synthetic oils containing polyalphaolefins and ester functionalities (Oil 6 and 7) were more successful at reducing friction in conformal contacts. The severity of test conditions within non-conformal contacts was insufficient to activate DLC coatings, and to facilitate the formation of a physisorbed tribolayer with Oils 6 and 7, to reduce friction. Oil 4 gave the lowest friction results in reference tests with uncoated test specimens, irrespective of the contact configuration,
whereas Oils 6 and 7 gave high friction values in the similar configurations. This supports the ability Oil 4 with rust inhibitor and inability of synthetic oils in friction reduction in ferrous (steel-cast iron) contacts. Also, Oil 2 resulted in high friction with both DLCs, irrespective of the contact configuration. Oil 2 contains zinc, which acted as an anti-wear additive, but also led to high levels of friction (caused by the formation of high shear strength tribofilm pads [43]) and counter face wear. Thus the activation of lubricant additives upon interaction with DLC coated surface for tribofilm formation (friction and wear reduction) depends on the operating and contact conditions.

Hence for obtaining lower friction in a given contact configuration the following conclusions could be followed. In non-conformal contacts both with triboelements of steel specimen and DLC coated specimen (hardness difference of 200HV) and with triboelements of cast iron specimen and DLC coated specimen (hardness difference of 700HV), the thicker and smoother DLC coating gave lower friction values when tested with the soft counter face. As we moved into conformal contact of triboelements of cast iron specimen and DLC coated specimen (hardness difference of 700HV), the rougher and thinner DLC coating gave lower friction when tested with the soft counter face. In all of the contact configuration hydrodynamic effects (caused by both surface smoothening and conformity) and possible tribofilm formation played a major role in friction reduction. Each test setup used could be related to a given tribological interface within a hydraulic motor. Within a hydraulic motor, it would be viable to coat the roller (Figure 1.2) with the type of DLC coating and use a hydraulic oil, chosen such that the combination gives lower friction in the required contact configuration. A motor's cam ring is usually made of 100Cr6 steel, and piston from cast iron. The SRV test setup could be related to the cam-roller interface, as a non-conformal line contact interface. The results of both the block-on-ring, and pin-on-disc test setup could be related to the piston-roller interface, as a conformal line contact, undergoing both rotational and reciprocating sliding motion. The piston-cylinder is another interface which undergoes reciprocating sliding motion with conformal area contact, can also be considered for such correlations. Thus, the tribological behaviour of ta-C DLC coatings under lubricated conditions is influenced by the contact configuration, the lubricant chemistry, and the surface properties of the DLC coating and nature of its counter face.
8  **Suggestions for future work**

Further investigations could be undertaken to determine the friction mechanisms in the systems tested. The role of lubricant chemistry in reducing friction with changing contact configurations could be studied in greater detail using new lubricant combinations. The mechanisms of surface graphitisation and tribofilm formation in ta-C type DLC coatings could be validated by studying the bond structure \( (\text{sp}^2/\text{sp}^3 \text{ ratio}) \) on the coated surface after the test using advance instrumental techniques. For example, instrumental investigation of the DLC surfaces post-test could be undertaken using techniques of Surface reflectometry, Raman spectroscopy and X-Ray Diffraction (XRD). The results could be used to validate the mechanism in which graphitisation leads to friction reduction. Elemental analysis could be used to precisely quantify the amount of a tribofilm formed on the counter face. This would explain the potential of each oil and DLC coating to form a tribofilm. Oils should be analysed both before and after each test, to measure any change in chemical composition, and therefore the additives used up during friction reduction. The presence of any surface tribofilms and worn particles within the oils could be evaluated using SEM micrographs at high magnification and EDX analysis. The SEM micrographs at high magnification on worn surface profile could also be used to provide further information on the dominant wear mechanism in each test.
9 References


9. References


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9. References


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Appendix

A. Experimental procedures

Standard experimental procedures for all tests were followed:

1. Specimens were cleaned (10–15 minutes) using an ultrasonic cleaner with industrial benzine as non-polar solvents, and acetone as polar solvents. Cleaning was performed both before and after testing.
2. The hardness of each specimen was characterised using the Vickers Micro Indentation test, and these results were verified using Nano Indentation testing.
3. The cross section of DLC B and DLC C coated specimens was measured using a scanning electron microscope, to determine coating thickness.
4. The surface roughness of all specimens was measured using a surface profilometer, both before and after testing. The surface roughness of the worn profile on the DLC Coating is taken either along or perpendicular to the direction of sliding (or both as per requirement for analysis of test results).
5. To monitor any weight loss or gain, specimens were weighed using a digital balance both before and after testing.
6. The tribometers used (Optimol SRV, CETR UMT-2, Phoenix Pin-on-disc) was calibrated (friction and normal load) and the test parameters and operating conditions were set. Tests were conducted using the specified configurations.
7. Wear morphology of counter faces and coated discs were observed using a Veeco/Zygo surface profilometer, and their surface roughness parameters were calculated.
8. Scar dimensions and wear volumes were measured using a ‘stitching operation’ in Veeco and/or Zygo profilometer.
9. Wear profiles were observed using scanning electron microscopy.
10. EDX analysis was conducted to analyse tribofilms and/or transfer layers formed.
B. Friction plots

Fig. B.1. Coefficient of friction plots of tests with SRV cylinder on disc setup with disc specimens of DLC coating type B and type C with (a) Oil 1; (b) Oil 2; (c) Oil 3; (d) Oil 4; (e) Oil 5; (f) Oil 6 and; (g) Oil 7 (Table 3.1 and Table 3.4)
Fig. B.2. Coefficient of friction plots of repeatability tests with CETR UMT-2 block on ring setup with uncoated specimens 100Cr6 steel in (a) Oil 1; (b) Oil 2; (c) Oil 3; (d) Oil 4; (e) Oil 5; (f) Oil 6 and; (g) Oil 7 (Table 3.2 and Table 3.4)
Fig. B.3. Coefficient of friction plots of repeatability tests with CETR UMT-2 block on ring setup with DLC B coated ring specimens with (a) Oil 1; (b) Oil 2; (c) Oil 3; (d) Oil 4; (e) Oil 5; (f) Oil 6 and; (g) Oil 7 (Table 3.2 and Table 3.4)
Fig. B.4. Coefficient of friction plots of repeatability tests with CETR UMT-2 block on ring setup with DLC C coated ring specimens with (a) Oil 1; (b) Oil 2; (c) Oil 3; (d) Oil 4; (e) Oil 5; (f) Oil 6 and; (g) Oil 7 (Table 3.2 and Table 3.4)
Fig. B.5. Coefficient of friction plots of repeatability tests with Phoenix pin on disc setup with uncoated disc specimens with (a) Oil 1; (b) Oil 2; (c) Oil 3; (d) Oil 4; (e) Oil 5; (f) Oil 6 and; (g) Oil 7 (Table 3.3 and Table 3.4)
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Fig. B.6. Coefficient of friction plots of repeatability tests with Phoenix pin on disc setup with DLC B coated disc specimens with (a) Oil 1; (b) Oil 2; (c) Oil 3; (d) Oil 4; (e) Oil 5; (f) Oil 6 and; (g) Oil 7 (Table 3.3 and Table 3.4)
Fig. B.7. Coefficient of friction plots of repeatability tests with Phoenix pin on disc setup with DLC C coated disc specimens with (a) Oil 1; (b) Oil 2; (c) Oil 3; (d) Oil 4; (e) Oil 5; (f) Oil 6 and; (g) Oil 7 (Table 3.3 and Table 3.4)
C. Wear profile analysis

C.1. For tests with Schwingung Reibung Verschleiβ type tribometer.

Figures C.1.1 – C.1.14 describe the wear scar profiles of DLC coated discs and cylinders after tribological tests using the Schwingung Reibung Verschleiβ (SRV) reciprocating tribometer. The tribometer’s circular cylinder creates a wear scar of varying length, width and depth on the coated disc. The scar length was measured using a stitching operation in the (ZYGO) profilometer. The sub figures have been labelled on top of the figure with letters ‘a’ and ‘b’.

Fig C.1.1. Wear profiles by ZYGO profilometer at 100x for SRV test with Oil 1 of (a) DLC B coated disc and (b) 100Cr6 steel cylinder.

Fig C.1.2. Wear profiles by ZYGO profilometer at 100x for SRV test with Oil 2 of (a) DLC B coated disc and (b) 100Cr6 steel cylinder.
Fig C.1.3. Wear profiles by ZYGO profilometer at 100X for SRV test with Oil 3 of (a) DLC B coated disc and (b) 100Cr6 steel cylinder.

Fig C.1.4. Wear profiles by ZYGO profilometer at 100X for SRV test with Oil 4 of (a) DLC B coated disc and (b) 100Cr6 steel cylinder.

Fig C.1.5. Wear profiles by ZYGO profilometer at 100X for SRV test with Oil 5 of (a) DLC B coated disc and (b) 100Cr6 steel cylinder.
Fig C.1.6. Wear profiles by ZYGO profilometer at $100^X$ for SRV test with Oil 6 of (a) DLC B coated disc and (b) 100Cr6 steel cylinder.

Fig C.1.7. Wear profiles by ZYGO profilometer at $100^X$ for SRV test with Oil 7 of (a) DLC B coated disc and (b) 100Cr6 steel cylinder.

Fig C.1.8. Wear profiles by ZYGO profilometer at $100^X$ for SRV test with Oil 1 of (a) DLC C coated disc and (b) 100Cr6 steel cylinder.
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Fig C.1.9. Wear profiles by ZYGO profilometer at 100X for SRV test with Oil 2 of (a) DLC C coated disc and (b) 100Cr6 steel cylinder.

Fig C.1.10. Wear profiles by ZYGO profilometer at 100X for SRV test with Oil 3 of (a) DLC C coated disc and (b) 100Cr6 steel cylinder.

Fig C.1.11. Wear profiles by ZYGO profilometer at 100X for SRV test with Oil 4 of (a) DLC C coated disc and (b) 100Cr6 steel cylinder.
Fig C.1.12. Wear profiles by ZYGO profilometer at 100X for SRV test with Oil 5 of (a) DLC C coated disc and (b) 100Cr6 steel cylinder.

Fig C.1.13. Wear profiles by ZYGO profilometer at 100X for SRV test with Oil 6 of (a) DLC C coated disc and (b) 100Cr6 steel cylinder.

Fig C.1.14. Wear profiles by ZYGO profilometer at 100X for SRV test with Oil 7 of (a) DLC C coated disc and (b) 100Cr6 steel cylinder.
C.2. For tests with CTR UMT-2 Macro-micro Tribometer.

The wear scar of the cast iron blocks used in the block on ring test configuration in the CTR tribometer have been shown in the figures C.2.1–C.2.21. The EDX spectrum of the wear scar region has also been shown for tests done with both DLC B and C coated rings. The rings, both coated and uncoated were worn out throughout the surface and are not shown here for their wear profile. ZYGO profilometer has also been used for visualisation of worn surface of block. The sub figures have been labelled on their top or left with letters ‘a’, ‘b’ and ‘c’ accordingly.

![Fig C.2.1](image1.png)

**Fig C.2.1.** Wear profile of cast iron blocks tested by CTR UMT-2 with uncoated ring in Oil 1 by (a) SEM at 150x and (b) ZYGO profilometer at 2.75x

![Fig C.2.2](image2.png)

**Fig C.2.2.** Wear profile of cast iron blocks tested by CTR UMT-2 with uncoated ring in Oil 2 by (a) SEM at 150x and (b) ZYGO profilometer at 2.75x.
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Fig C.2.3. Wear profile of cast iron blocks tested by CETR UMT-2 with uncoated ring in Oil 3 by (a) SEM at 150X and (b) ZYGO profilometer at 2.75X.

Fig C.2.4. Wear profile of cast iron blocks tested by CETR UMT-2 with uncoated ring in Oil 4 by (a) SEM at 150X and (b) ZYGO profilometer at 2.75X.

Fig C.2.5. Wear profile of cast iron blocks tested by CETR UMT-2 with uncoated ring in Oil 5 by (a) SEM at 150X and (b) ZYGO profilometer at 2.75X.
Fig C.2.6. Wear profile of cast iron blocks tested by CETR UMT-2 with uncoated ring in Oil 6 by (a) SEM at 150x and (b) ZYGO profilometer at 2.75x.

Fig C.2.7. Wear profile of cast iron block tested by CETR UMT-2 with uncoated ring in Oil 7 by (a) SEM at 150x and (b) ZYGO profilometer at 2.75x.
Fig C.2.8. Wear profile of cast iron block tested by CETR UMT-2 with DLC B coated ring in Oil 1 by (a) SEM at 50x; (b) ZYGO profilometer at 2.75x and (c) EDX spectrum of (a).

Fig C.2.9. Wear profile of cast iron block tested by CETR UMT-2 with DLC B coated ring in Oil 2 by (a) SEM at 50x; (b) ZYGO profilometer at 2.75x and (c) EDX spectrum of (a).
Fig C.2.10. Wear profile of cast iron block tested by CETR UMT-2 with DLC B coated ring in Oil 3 by (a) SEM at 50X; (b) ZYGO profilometer at 2.75X and (c) EDX spectrum of (a).

Fig C.2.11. Wear profile of cast iron block tested by CETR UMT-2 with DLC B coated ring in Oil 4 by (a) SEM at 50X; (b) ZYGO profilometer at 2.75X and (c) EDX spectrum of (a).
Fig C.2.12. Wear profile of cast iron block tested by CETR UMT-2 with DLC B coated ring in Oil 5 by (a) SEM at 50X; (b) ZYGO profilometer at 2.75X and (c) EDX spectrum of (a).

Fig C.2.13. Wear profile of cast iron block tested by CETR UMT-2 with DLC B coated ring in Oil 6 by (a) SEM at 50X; (b) ZYGO profilometer at 2.75X and (c) EDX spectrum of (a).
Fig C.2.14. Wear profile of cast iron block tested by CETR UMT-2 with DLC B coated ring in Oil 7 by (a) SEM at 50X; (b) ZYGO profilometer at 2.75X and (c) EDX spectrum of (a).

Fig C.2.15. Wear profile of cast iron block tested by CETR UMT-2 with DLC C coated ring in Oil 1 by (a) SEM at 50X; (b) ZYGO profilometer at 2.75X and (c) EDX spectrum of (a).
Fig C.2.16. Wear profile of cast iron block tested by CETR UMT-2 with DLC C coated ring in Oil 2 by (a) SEM at 50X; (b) ZYGO profilometer at 2.75X and (c) EDX spectrum of (a).

Fig C.2.17. Wear profile of cast iron block tested by CETR UMT-2 with DLC C coated ring in Oil 3 by (a) SEM at 50X; (b) ZYGO profilometer at 2.75X and (c) EDX spectrum of (a).
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Fig C.2.18. Wear profile of cast iron block tested by CETR UMT-2 with DLC C coated ring in Oil 4 by (a) SEM at 50X; (b) ZYGO profilometer at 2.75X and (c) EDX spectrum of (a).

Fig C.2.19. Wear profile of cast iron block tested by CETR UMT-2 with DLC C coated ring in Oil 5 by (a) SEM at 50X; (b) ZYGO profilometer at 2.75X and (c) EDX spectrum of (a).
Fig C.2.20. Wear profile of cast iron block tested by CETR UMT-2 with DLC C coated ring in Oil 6 by (a) SEM at 50×; (b) ZYGO profilometer at 2.75× and (c) EDX spectrum of (a).

Fig C.2.21. Wear profile of cast iron block tested by CETR UMT-2 with DLC C coated ring in Oil 7 by (a) SEM at 50×; (b) ZYGO profilometer at 2.75× and (c) EDX spectrum of (a).
C.3. For tests with Phenix Tribology Pin on Disc Tribometer.

The worn surface of the cast iron pin and both uncoated and coated (DLC B and C) disc used in the pin on disc test configuration in the CETR tribometer have been shown with the help of SEM and ZYGO profilometer in the figures C.3.1 – C.3.21. The EDX spectrum of the wear scar region has also been shown for tests done with both uncoated and coated (DLC B and C coated) disc. The sub figures have been labelled on their top or left with letters ‘a’, ‘b’, ‘c’, ‘d’ & ‘e’ accordingly.

Fig C.3.1. Wear profiles of pin on disc test with uncoated disc in Oil 1 for (a) uncoated disc with SEM at 100X; (b) cast iron pin with SEM at 50X; (c) cast iron pin with ZYGO profilometer at 2.75X; (d) EDX spectrum of (a) and (e) EDX ‘spectrum of (b).
Fig C.3.2. Wear profile of pin on disc test with uncoated disc in Oil 2 for (a) uncoated disc with SEM at 100X; (b) cast iron pin with SEM at 50X; (c) cast iron pin with ZYGO profilometer at 2.75X; (d) EDX spectrum of (a) and (e) EDX spectrum of (b).
Fig C.3.3. Wear profiles of pin on disc test with uncoated disc in Oil 3 for (a) uncoated disc with SEM at 100X; (b) cast iron pin with SEM at 50X; (c) cast iron pin with ZYGO profilometer at 2.75X; (d) EDX spectrum of (a) and (e) EDX spectrum of (b).
Fig C.3.4. Wear profiles of pin on disc test with uncoated disc in Oil 4 for (a) uncoated disc with SEM at 100×; (b) cast iron pin with SEM at 50×; (c) cast iron pin with ZYGO profilometer at 2.75×; (d) EDX spectrum of (a) and (e) EDX spectrum of (b).
Fig C.3.5. Wear profiles of pin on disc test with uncoated disc in Oil 5 for (a) uncoated disc with SEM at 100x; (b) cast iron pin with SEM at 50x; (c) cast iron pin with ZYGO profilometer at 2.75x; (d) EDX spectrum of (a) and (e) EDX spectrum of (b).
Fig C.3.6. Wear profiles of pin on disc test with uncoated disc in Oil 6 for (a) uncoated disc with SEM at 100X; (b) cast iron pin with SEM at 50X; (c) cast iron pin with ZYGO profilometer at 2.75X; (d) EDX spectrum of (a) and (e) EDX spectrum of (b).
Fig C.3.7. Wear profiles of pin on disc test with uncoated disc in Oil 7 for (a) uncoated disc with SEM at 100X; (b) cast iron pin with SEM at 50X; (c) cast iron pin with ZYGO profilometer at 2.75X; (d) EDX spectrum of (a) and (e) EDX spectrum of (b).
Fig C.3.8. Wear profiles of pin on disc test with DLC B coated disc in Oil 1 for (a) DLC B coated disc with SEM at 120×; (b) cast iron pin with SEM at 50×; (c) cast iron pin with ZYGO profilometer at 2.75×; (d) EDX spectrum of (a) and (e) EDX spectrum of (b).
Fig C.3.9. Wear profiles of pin on disc test with DLC B coated disc in Oil 2 for (a) DLC B coated disc with SEM at 100x; (b) cast iron pin with SEM at 50x; (c) cast iron pin with ZYGO profilometer at 2.75x; (d) EDX spectrum of (a) and (e) EDX spectrum of (b).
Fig C.3.10. Wear profiles of pin on disc test with DLC B coated disc in Oil 3 for (a) DLC B coated disc with SEM at 190X; (b) cast iron pin with SEM at 50X; (c) cast iron pin with ZYGO profilometer at 2.75X; (d) EDX spectrum of (a) and (e) EDX spectrum of (b).
Fig C.3.11. Wear profiles of Pin on disc test with DLC B coated disc in Oil 4 for (a) DLC B coated disc with SEM at 100X; (b) cast iron pin with SEM at 50X; (c) cast iron pin with ZYGO profilometer at 2.75X; (d) EDX spectrum of (a) and (e) EDX spectrum of (b).
Fig C.3.12. Wear profiles of pin on disc test with DLC B coated disc in Oil 5 for (a) DLC B coated disc with SEM at 100×; (b) cast iron pin with SEM at 50×; (c) cast iron pin with ZYGO profilometer at 2.75×; (d) EDX spectrum of (a) and (e) EDX spectrum of (b).
Fig C.3.13. Wear profiles of pin on disc test with DLC B coated disc in Oil 6 for (a) DLC B coated disc with SEM at 100x; (b) cast iron pin with SEM at 50x; (c) cast iron pin with ZYGO profilometer at 2.75x; (d) EDX spectrum of (a) and (e) EDX spectrum of (b).
Fig C.3.14. Wear profiles of pin on disc test with DLC B coated disc in Oil 7 for (a) DLC B coated disc with SEM at 100X; (b) cast iron pin with SEM at 50X; (c) cast iron pin with ZYGO profilometer at 2.75X; (d) EDX spectrum of (a) and (e) EDX spectrum of (b).
Fig C.3.15. Wear profiles of pin on disc test with DLC C coated disc in Oil 1 for (a) DLC C coated disc with SEM at 100×; (b) cast iron pin with SEM at 50×; (c) cast iron pin with ZYGO profilometer at 2.75×; (d) EDX spectrum of (a) and (e) EDX spectrum of (b).
Fig C.3.16. Wear profiles of pin on disc test with DLC C coated disc in Oil 2 for (a) DLC C coated disc with SEM at 100X; (b) cast iron pin with SEM at 50X; (c) cast iron pin with ZYGO profilometer at 2.75X; (d) EDX spectrum of (a) and (e) EDX spectrum of (b).
Fig C.3.17. Wear profiles of pin on disc test with DLC C coated disc in Oil 3 for (a) DLC C coated disc with SEM at 100X; (b) cast iron pin with SEM at 50X; (c) cast iron pin with ZYGO profilometer at 2.75X; (d) EDX spectrum of (a) and (e) EDX spectrum of (b).
Fig C.3.18. Wear profiles of pin on disc test with DLC C coated disc in Oil 4 for (a) DLC C coated disc with SEM at 100X; (b) cast iron pin with SEM at 50X; (c) cast iron pin with ZYGO profilometer at 2.75X; (d) EDX spectrum of (a) and (e) EDX spectrum of (b).
Fig C.3.19. Wear profiles of pin on disc test with DLC C coated disc in Oil 5 for (a) DLC C coated disc with SEM at 100X; (b) cast iron pin with SEM at 50X; (c) cast iron pin with ZYGO profilometer at 2.75X; (d) EDX spectrum of (a) and (e) EDX spectrum of (b).
Fig C.3.20. Wear profiles of pin on disc test with DLC C coated disc in Oil 6 for (a) DLC C coated disc with SEM at 100×; (b) cast iron pin with SEM at 50×; (c) cast iron pin with ZYGO profilometer at 2.75×; (d) EDX spectrum of (a) and (e) EDX spectrum of (b).
Fig C.3.21. Wear profiles of pin on disc test with DLC C coated disc in Oil 7 for (a) DLC C coated disc with SEM at 100×; (b) cast iron pin with SEM at 50×; (c) cast iron pin with ZYGO profilometer at 2.75×; (d) EDX spectrum of (a) and (e) EDX spectrum of (b).