PIIA PALOKUNNAS
DIAMOND-LIKE CARBON COATING IN TRIBOLOGICAL APPLI-
CATIONS

Bachelor's thesis

ABSTRACT

PIIA PALOKUNNAS: Diamond-like carbon coating in tribological applications
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This thesis is a literary study of diamond-like carbon coatings, their properties, deposition methods and performance in tribological applications. In applications the focus is on bearings and gears as they contribute to major part of wear and friction production in gearboxes. Gears and bearings suffer from surface failures which cause reliability issues. The DLC coatings are studied to improve resistance against wear, pitting and scuffing. Some coating suppliers are presented to give insight of the industrial coatings that are available.

The aim of thesis is to give basic understanding of DLC coatings. Some studies are presents as an example of DLC coatings which are used in laboratory tests to enhance properties of the components. The tribological performance of the DLC depends on multiple factors, for example, load, lubrication condition, coating type and counterface material. The DLC shows improved lifetime under certain parameters but more tests with specific conditions are needed because comprehensive conclusions cannot be made solely based on this thesis.

PREFACE

This bachelor's thesis is written for Department of Materials Science in Tampere University of Technology.

I would like to thank professor Arto Lehtovaara and professor Pasi Peura from Department of Materials Science for examining the thesis and for giving valuable comments and suggestions. In addition, I would like to thank Kaisu Soivio from Moventas Gears Oy for introducing me to the topic and for giving me inspiration for the thesis.

Finally, I am especially grateful to my loved ones for their encouragement and support during the writing process.

Tampere, 10.12.2018

Piia Palokunnas

CONTENTS

LIST OF FIGURES

LIST OF SYMBOLS AND ABBREVIATIONS

DLC	Diamond-like carbon
a-C	Amorphous carbon
ta-C	Tetrahedral amorphous carbon
a-C:H	Hydrogenated amorphous carbon
ta-C:H	Hydrogenated tetrahedral amorphous carbon
UHV	Ultra-high vacuum
EP	Extreme pressure, additive in oil
AW	Anti-wear, additive in oil
PVD	Physical vapor deposition
PECVD	Plasma enhanced chemical vapor deposition
DC	Direct current
RF	Radio frequency
MSP	Micro shot peening
PAO	Polyalphaolefin

1. INTRODUCTION

The interest towards diamond coatings has emerged during recent years due to the increasing demands by manufacturing industries. Machine systems are facing demands for longer lifecycle and pressure to increase energy efficiency. Industrial use of tribological components is often limited by wear and failure of the surface. To enhance the durability on the component they can be coated. The coating also enhances the energy efficiency by reducing friction that causes energy loss.

This thesis covers principles of the diamond-like carbon coating and how it can be used in tribological applications, mainly in journal bearings and gears. The goal of the coating is to add wear resistance and to minimize friction in the surface area. For example, the journal bearings are most likely to break during start up and shut down when they experience higher loads than during running period.

True diamond offers great mechanical, chemical and tribological properties, but it is difficult to manufacture. Diamond-like carbon coatings have similar properties, but it is easier to deposit. The properties of DLC can be altered by changing the composition, doping elements and hybridization ratio of the carbon. The differences in the composition defines the most suitable applications for the coating type.

2. BASICS OF DIAMOND-LIKE CARBON COAT-INGS

Diamond-like carbon coatings have excellent wear resistance, high hardness and good tribological qualities and they are chemically inert. These properties make them suitable for various tribological applications.

2.1 Types of DLC coatings

DLC-coating can be roughly categorized into three different categories based on their chemical composition: non-doped, doped and hybrid DLCs. These main categories as well as their subcategories are presented in Figure 1.
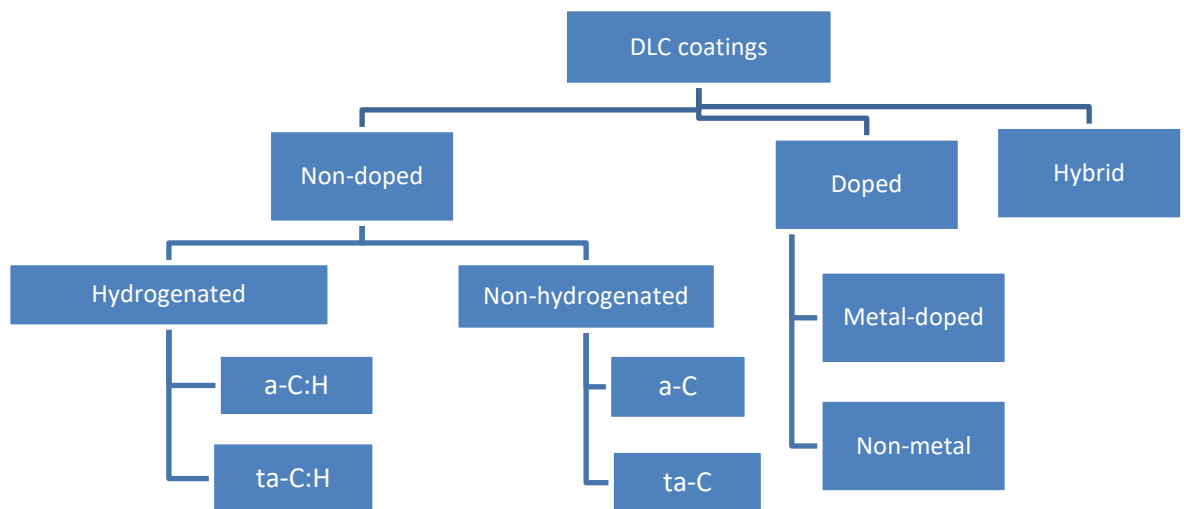
Figure 1. *Classification of DLC coatings [1].*

 In non-doped DLCs, carbon atoms bonds with hydrogen or another carbon atom and the structure is free from other elements. Non-doped coatings can be divided into subclasses based on hydrogen content. These subclasses are hydrogenated and nonhydrogenated DLC coatings. Hydrogenated DLC coatings consist of amorphous DLC (a-C:H) and tetrahedral amorphous DLC (ta-C:H). Nonhydrogenated DLC coatings consist of hydrogen-free amorphous DLC (a-C) and tetrahedral amorphous DLC (ta-C). [2]

Ternary phase diagram of amorphous carbon is seen in the Figure 2. It shows the relation how nonhydrogenated and hydrogenated DLC is formed when amounts of sp^2, sp^3 and hydrogen are mixed.
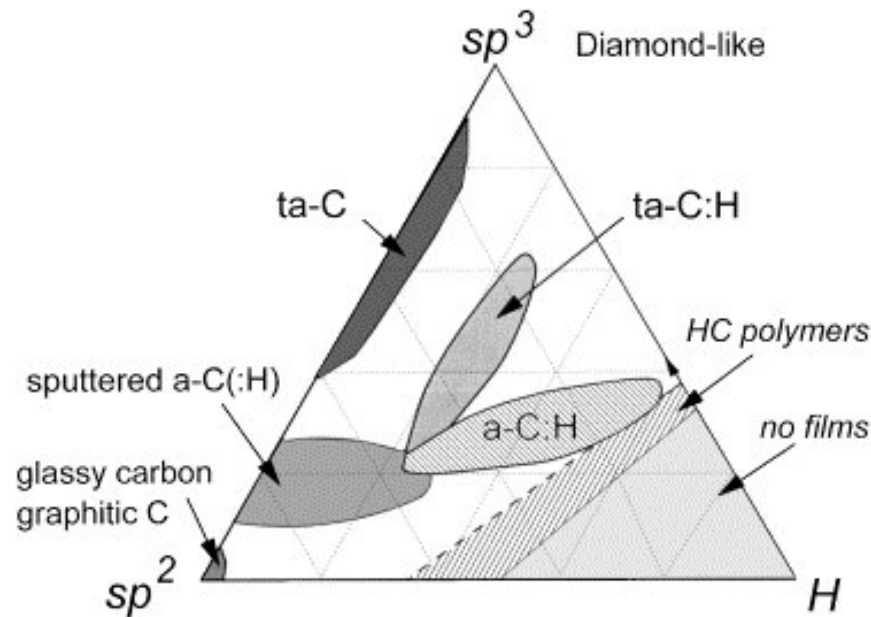
Figure 2. *Ternary phase diagram of amorphous carbon [3].*

In doped DLC coatings, metal or non-metal atoms can be added to the coating to increase reactivity with lubricant additives. With metal-doped coatings, chromium, titanium, molybdenum or tungsten can be used to achieve reactivity and to create tribochemical films. What it comes to non-metals elements, nitrogen, silicon or fluorine can be used. Hybrid DLC coating consist of thin multilayered DLCs, made with usually both doped and non-doped coatings. This type of DLC coatings have beneficial properties from both coating types.

2.2 Deposition methods

Difficulty with true diamond coating is a need for high deposition temperature, specific substrate and surface finishing after deposition. Diamond-like carbon offers same mechanical, optical and thermal properties as true diamond but with lower, near room temperature deposition and with various substrates. [4]

DLC is a collective term for wide range of amorphous carbon coatings. The properties depend on the fraction of tetrahedral-bonded atoms, hydrogen content, doping elements and interlayers, all of which need to be taking into consideration when choosing the deposition method. The most common deposition methods are PVD (physical vapor deposition) and PECVD (plasma enhanced chemical vapor deposition). The conventional CVD requires high temperature tolerance from the substrate material, so it has limitations in industrial use. In a physical process, a beam of carbon or hydrocarbon ions are impacted on the surface of the substrate. This impact induces sp^3 bonding in a physical way. On the contrary, in a CVD method, the sp^3 bonding stabilizes by the chemical process. [3, 5]

The basic idea of PVD process is to vaporize solid or liquid coating material and to guide it through a vacuum or partial vacuum to the target surface that needs to be coated. When manufacturing DLC film, solid carbon source or hydrocarbon gas, such as methane or acetylene, is used. The growth rate obtained by using solid carbon source are significantly lower compared the gaseous source. The vacuum is maintained between the range of 10^{-1} and 10^{-5} Pa. The target is charged with negative potential to attract vaporized ions or atoms. The PVD process can be divided into subclasses based on the way the plasma is created and what is the source of the heating. Examples of these subclasses include ion beam deposition, arc vapor deposition and sputter deposition. [6, 7]

2.2.1   Ion beam deposition

In the ion bean deposition, the needed carbon ions can be produced from graphite cathode by plasma sputtering or from hydrocarbon gas, such as methane, by ionizing the gas in a plasma. The ions are then removed from the plasma by a bias voltage. The ions are accelerated in the high vacuum chamber so that the energy of the ion beam is typically between 100-1000 eV. The carbon ions are then directed to the substrate and thin film is formed. The advantage of this method is good control over the film thickness, uniformity and great adhesion to the substrate. [3]

The ion beam can be filtered in order to produce precisely selected ions and to control their energy. This method is called mass selected ion beam method and is mainly used for laboratory scale. Graphitic target is used to produce carbon ions with similar ion energies. The ions are accelerated through a magnetic filter that selects desirable carbon ions and filters out neutral particles. The beam is directed to the substrate to form ta-C coating. This method gives good control over the composition of the film, but the deposition is expensive, and the deposition rate is low. [3]

2.2.2   Cathodic arc vapor deposition

In cathodic arc vapor deposition two electrodes are placed closely and a high current between 60-120 A is passed through them to create an electric arc. The arc discharge is then focused on the cathode target material, for example graphite, and ionized plasma is generated. The plasma consists of the ions that are needed for the coating. The substrate is charged with negative bias voltage and the ions from the plasma start to move towards the substrate material at supersonic speed. When the ions collide with the substrate, a thin film is formed. The density of the film depends on the velocity of the particles. Higher temperature of the substrate and slower deposition rate leads to denser coating. Both the cathode and the anode are kept in a vacuum chamber at a pressure of 10^{-1} Pa. [6]

The difficulty with cathodic arc deposition is that macroparticles, such as droplets or debris particles from cathode surface may be ejected if the arc discharge is placed at the same spot for too long. The macroparticles have poor adhesion to the surface and can

degrade properties of the coating. The prevention methods include lowering the substrate temperature, increasing cathode-substrate distance and reducing the current level. If the macroparticles still occur, they can be filtered out by magnetic fields that separate droplets from the coating flux. High percentages of ta-C can be achieved with filtered arc deposition. Reactive gases can also be introduced to the evaporation process in order to form compound coatings. [6]

2.2.3   Sputter deposition

In sputter deposition method, a target material is bombarded with energetic ions. The argon gas is introduced to the vacuum chamber and it is ionized by plasma between the target and the substrate. The Ar^+ ions and electrons are formed. The target is a cathode and the substrate is an anode in this arrangement. When producing DLC films, the target material is typically graphite and direct current (DC) or radio frequency (RF) is used. The argon ions are attracted to negatively charged target materials and they release atoms from the target material as a result of the collision. These atoms move to the substrate, forming a thin film layer by layer. In this method, the deposition rate is low and high temperatures can be reached because the plasma is situated close to the target. [3, 6, 8]

Deposition configuration can be altered to modify the results. In a magnetron sputtering, a magnetic field is used to circulate electrons around the target, resulting denser plasma and higher deposition rate. The down side is nonuniform thickness of the coating. In a reactive sputtering, a process is performed with a gaseous phase. The reactive gas reacts chemically with the sputtered particles before coating the substrate. Metal containing DLC (Me-DLC) is commonly manufactures by using acetylene as reactive gas and transition metal or metal carbide as a target material. The a-C:H can be produced by using methane or hydrogen as a reactive gas in Ar plasma environment. The ion bombardment helps the formation of sp^3 bonds in the film. This is utilized in ion beam sputtering. The argon ions are used to bombard the graphitic target which create a flux of carbon. The second beam of argon is focused on the growing film, helping the sp^3 bonding and densifying the film. It is also known as ion plating or ion beam assisted deposition. [3, 6, 8]

2.2.4   Pulsed laser deposition

Pulsed laser deposition is PVD method. A short and very intense energy pulses of the laser is used to vaporize coating material. The formed plasma expands in the surrounding vacuum towards the substrate and forms a thin coating. The ion energy is similar than in cathodic arc method and mass selected ion beam method, so the produced ta-C films are similar than from those methods.

The properties of the film depend on varies deposition parameters that include chamber pressure, energy of the particles, laser pulse frequency and target material. The pulsed laser deposition can produce non-hydrogenated films with high purity and sp^3 hybridized

carbon. To achieve these high concentrations of sp^3 carbon, fully ionized plasma and highly energetic particles of the plasma are needed. The pulse duration of the laser determines the velocity of the ions and ionization grade, which contribute the properties of the film. Also, the pressure of the background gas influences the ablated particles. At higher pressure, the portion of sp^2 hybridization in the film increases because the particles scatter and lose their kinetic energy. [9]

2.2.5 PECVD

Plasma enhanced chemical vapor deposition (PECVD) is a modification of chemical vapor deposition method since chemical reactions occur in the gas mixture after the plasma is created. The advantage of the PECVD over typical CVD is that PECVD can be performed in lower temperatures because the substrate does not need to be heated. This makes PECVD suitable for thermally sensitive substrates. Plasma is used to replace heat as an energy source. Widely used method for plasma generation is electric discharge in gaseous phase between two electrodes but radio frequency or microwave sources can also be used. The electrons from the plasma collide with hydrocarbon particles and form a thin film on the substrate. Energy is delivered on the surface of the substrate to enhance the properties and the structure of the film by particle migration and nucleation. PECVD is useful when coating geometrically challenging objects as the film distributes uniformly. [10, 11]

The gas used in PECVD affects the properties of the a-C:H coating. Different hydrocarbon gases have different hydrogen contents. For mechanical applications, hardness of the coating is important. As the increasing hydrogen content hardness decreases, so hydrogen-carbon ratio of the gas is minimized. For this reason, acetylene is preferred for hard coatings. Also, the ionization energy dictates the growth rate of the film. The growth rate increases exponentially with the decreasing ionization energy. [3]

2.3 Mechanical properties

Graphite and diamond are allotropies of carbon, as both are made solely out of carbon, but the way their carbon atoms are bonded in space is different. This results in different properties, such as hardness, strength and durability of those materials [12]. DLC coatings have similar properties from both of these allotropies, which makes them suitable for various tribological applications.

DLC coatings are chemically inert, optically transparent and semiconducting films with high mechanical hardness and low friction coefficient. From these properties, the most important ones from the point of view of tribology, are low friction coefficient and high mechanical hardness. Mechanical properties depend on the ratio of sp^3/sp^2 hybridized covalent bonded carbon. Sp^1 orbital hybridized atoms are also known as acetylene-like bonded structure. Similarly, sp^2 is called graphite-like and sp^3 diamond-like bond. [13]

In graphite, carbon atoms are bonded with trigonal sp^2 bonds so that they form a graphene sheet. In that structure, that is seen in the Figure 3, carbon atoms form a planar hexagonal lattice. Graphite also has π orbitals that connects horizontally adjacent graphene sheets. Graphite is soft material and graphite sheets can easily slip past one another since sheets are only joined by weak van der Walls bonds. [14]

Contrary to graphite, diamond has more desirable mechanical properties for wear resistant coating, such as high atomic density, hardness and Young's modulus. This is due the four sp^3 covalent bonds that connects each carbon atom to their nearest neighbor. The structure of the diamond is seen in the Figure 3. The bonding results diamond to be tetrahedrally coordinated so it has high bond energy in all directions. [14]
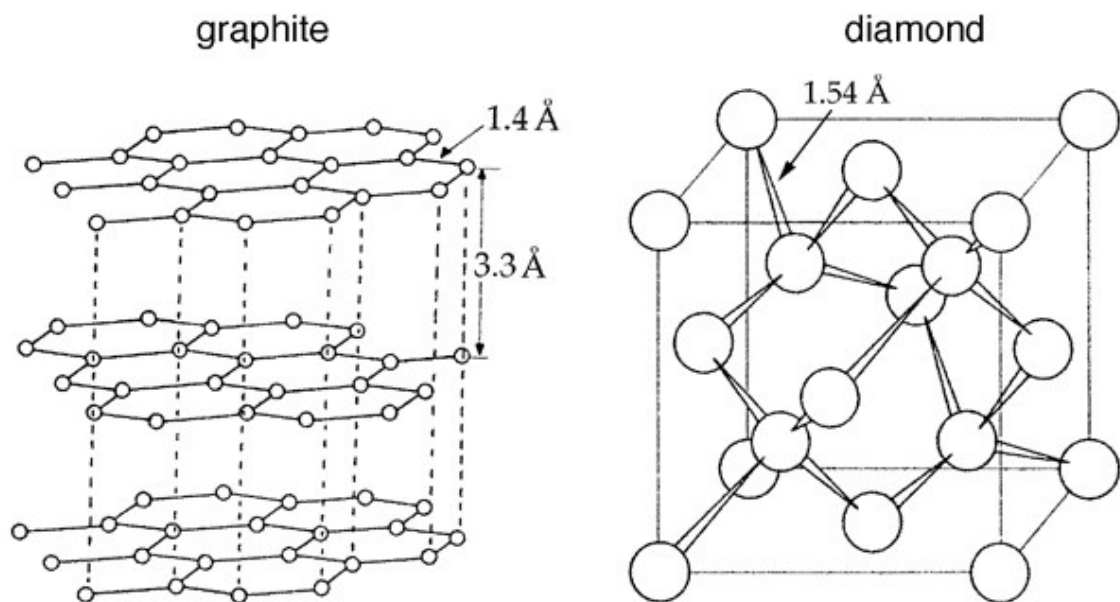
Figure 3. *Structure of the graphite and diamond is presented [15].*

Physical properties of DLC coatings are determined by the ratio of sp^3/sp^2 bonds and hydrogen content. DLC film consists of sp^3 bonded matrix which has sp^2 bonded carbon clusters in it [16]. Most of the DLC films are amorphous by nature, meaning that they have highly disarranged network of sp^3 and sp^2 bonded carbon atoms [17].

Even though diamond possess extreme mechanical properties, such as high density and hardness, it is problematic as a coating material for its high growth temperature. In DLC coating both diamond and graphite properties are combined. High growth temperature of the diamond is overcome in DLC as it has room temperature deposition method. DLC is also smooth on the surface because of its amorphous nature. [17]

Differences in structure leads to different hardness and elastic modulus for different types of DLC coatings. Hardness-Young's modulus (H/E) ratio for DLC is unusually high (0.08-0.2) compared to steels and ceramics. This means that DLC has relatively high tolerance for strain. The variety of values can be seen on Table 1.

Table 1.   *Hardness and Young's modulus values for different DLC types [18].*

	a-C	a-C:H	ta-C	ta-C:H
Hardness (GPa)	12–18	7–30	28–65	28–60
Elastic modulus (GPa)	160–190	60–210	210–650	175–290
H/E ratio	0.08–0.1	0.1–0.16	0.1–0.2	0.16–0.21

Although DLC coatings have extensive advantages, they also have few difficulties what it comes to mechanical toughness and compressive strength associated with thin films. Fortunately, DLC is amorphous and therefore it can be alloyed with metal or other elements to solve some of these problems. [17]

2.4   Tribological performance

Generally, materials with high stiffness and hardness have also high wear resistance. As tribology is a study of friction, lubrication and wear, these properties are desirable for coatings in tribological applications. Friction can be seen as result of three phenomena: abrasion, shearing and adhesion. Material properties determine which of these phenomena is controlling mechanism of friction. As mechanical properties vary greatly depending on which type of DLC is in question, as noted in Chapter 2.3, so does the predominant mechanism. [18]

DLC is different to other solid lubricants because of the lubrication mechanism is distinctive. For example, lubricity provided by graphite is due to shear deformation of sliding planes. As the DLC is amorphous, it cannot undergo this type of bulk shear. Instead of shearing planes, DLC films shear through an interface between the counterface material and the DLC itself. In here, a transfer layer can be formed to reduce the friction coefficient. [17]

Tribological performance of DLC coatings depend on several factors that can be categorized internal and external factors. Internal factors include hydrogen content, configuration of carbon atoms etc. External factors consist of sliding speed, type of motion and applied load.

Tetrahedral amorphous ta-C has the highest sp^3 hybridized carbon-carbon bonds of all DLC coatings. Sp^3 fraction of carbon bond is important because hardness, smoothness, density and Young's modulus correlates directly with the fraction in ta-C. [17]

External factors such as sliding speed and applied load have different influence in friction coefficient depending on which type of DLC coating is used. The ta-C is denser, harder and it is more stable as results of its sp^3 bonded structure whereas a-C:H has softer, less dense nature. The a-C:H film is therefore prone to sliding wear. When comparing ta-C and a-C:H it was noticed that the ta-C has higher wear resistance than the a-C:H film but also higher friction coefficient. The ta-C has more stable friction coefficient over wide

range of normal loads and sliding speeds. Typical value of friction coefficient for ta-C against steel is between 0.14-0.19. The friction increased to 0.23 when a high load and sliding speed is applied. This might be caused by increased temperature in the contact surface which resulted in decline in humidity. Contrary to the ta-C film, the friction coefficient of a-C:H against steel decreases when sliding speed and normal load is increased. The low friction behavior is due the graphitization process that occurs in high loads and high velocity. The graphitic carbon is formed on wear debris as the hydrogen atoms are released from sp^3 structure because of increase of temperature and contact frequency. The high loading conditions contribute to the shear deformation and graphite formation of the low-hydrogen DLC structure. Graphitization also occurs on ta-C films, but it requires more energy. The ta-C has highly sp^3 bonded, hydrogen-free structure so the shear deformation and the graphitic transformation has higher energy demand than the a-C:H films. [2]

2.4.1 Effect of humidity

Humidity of the atmosphere influences tribological behaviors of DLC coatings. Especially with ta-C, which lacks hydrogen in the structure, it is important that there is humidity in the air when coating is used in sliding conditions. The friction coefficient reaches higher values in dry sliding conditions. The ta-C can be doped with hydrogen during deposition process. Test results show that the more hydrogen content in the film is increased, the lower values of friction coefficient is achieved. Hydrogen from the coating itself is important especially in dry condition. Hydrogen is naturally present in the a-C:H film and it has therefor low friction performance in dry conditions.

Hydrogen plays a vital part of lubricity behavior. Depending on concentration and the origin of the hydrogen around the sliding counterfaces, friction can increase suddenly from a superlow friction regime (of 10^{-2}) to up to 0.6 or stabilize in the same millirange when tested in ultra-high vacuum chamber (UHV). The low steady-state friction is achieved in highly hydrogenated (40 at%) films and is due to weak van der Waals interactions between sliding surfaces. Hydrogen atoms passivate the dangling ponds, resulting the formation of C-H bonds, which is seen in the Figure 4. When these types of bonds are on the both sides of sliding planes, they interact with only weak binging energy of 0.08 eV, resulting low friction. These ultra-low friction regimes are achieved usually only in vacuum or inert atmospheres. [19, 20]

	Van der Waals interaction	$\pi-\pi^*$ interaction
Schematic representation of atomic interaction during sliding		
	High flexibility	Low flexibility
Binding energy	0.08 eV	0.4–0.8 eV

Figure 4. *Representation of the sliding behavior of highly hydrogenated DLC and low-hydrogen DLC films [19].*

If the hydrogen content is significantly lower than 40 at%, the superlow lubrication regime cannot be sustained for long in vacuum atmosphere. When only carbon atoms are interacting with each other at the sliding interface, higher binding energies of 0.4-0.8 eV are present due to stronger interactions between π-π -interaction. This is seen in the Figure 4. The superlow friction, that is experienced momentarily, is caused by diffusion of the hydrogen from the interstitials of the bulk matrix to the sliding surfaces. The friction coefficient rises significantly when the hydrogen reservoirs in the carbon network structure are used. The shift from low to high friction can be postponed with temperature and addition of hydrogen in the atmosphere. With moderate temperatures, hydrogen's diffusion can be increased and therefore longer period with low friction can be achieved. Superlow friction state can be maintained for low-hydrogen films if molecular hydrogen is present in the atmosphere. When tested in UHV conditions with high hydrogen pressure (10 hPa), similar superlow friction behavior is achieved for low-hydrogen film than for hydrogenated film. [19, 20]

On the other hand, high humidity interferes with the van der Waals forces in the a-C:H, resulting the contact layer to become oxidized/hydrated. Since the contact layer is prevented from forming, the friction increases. [3] Luckily, adding silicon to the a-C:H structure helps to sustain the low friction performance from low to high humidity conditions. Silicon forms a silica-sol together with water vapor that aids the sliding abilities. [21]

2.4.2 Temperature dependency

When the a-C:H film with hydrogen content of 34 at% is tested in UHV chamber, it is noticed that at elevated temperatures (150 C°) superlow friction regime is prolonged considerably. This results friction coefficient to be much lower (<0.005) than at the room temperature. The results correspond with the thermally aided diffusion of the hydrogen atoms at elevated temperatures from the matrix of the film towards sliding interface. It is observed overall that initially friction coefficient reaches the superlow values faster at

elevated temperatures. This is regardless of the pressure and the atmosphere (UHV, Ar, H_2). Faster hydrogen release from the structure might also cause higher wear rate. [19]

3. USAGE IN APPLICATIONS

The extensive studies and versatile properties have created multiple applications for DLC. Nowadays the DLC coatings are used in multiple industries, from mechanical components to orthopedic and dental biomedical implants and electronics. The wear and corrosion resistance are utilized in magnetic storage devises, razor blades and fuel injection systems for cars. The self-lubricating character is useful in applications where tradition liquid lubrication cannot be used, such as food and textile processing industry and space technology applications. The lubricating effect is useful also in more tradition power transmitting field, such as in gears and bearings. [1, 22]

In power transmitting applications, energy has to be transferred from one component to another. This results in rolling or sliding contacting surfaces, which create friction. In industrial applications, these components usually operate under lubricated conditions. However, if the lubrication fails, whether it is due the start-up period or due high applied load or pressure, DLC coating can be useful for its self-lubricating properties and high hardness. [1]

The gears and bearings experience high loads and they require high functional reliability. This study focuses on the possibility of applying DLC coatings in tribological components in order to better their performance. Reliability problems in tribological applications, for example in gears and bearings, are often concentrated on near the surface. These problems include wear, pitting and scuffing. [23]

Micropitting is a form of surface contact fatigue where repeated contact stress causes surface cracks and detachment of material. Initiation of micro-pits is strongly controlled by contact pressure, lubrication conditions, roughness of contact surfaces and the boundary-contact friction. Propagation of the pits is resulted from speed and slide-to-roll ratio. Micropitting can escalade to macropitting as surface cracks propagate into larger pits. The increased surface roughness causes increase in localized stress which then leads to fatigue failure of the component. [24-26]

Scuffing refers to rubbing behavior of two contacting surfaces [27]. It is caused by lubrication failure when the lubricating film is breaking down, often after rise in operating temperature. Scuffing causes local damage to the surface by solid-state welding as the metal transfers from surface to another. For example, for gears, this means that asperities on flank surfaces contact, weld together and tear apart. This solid-state welding results a scratch-like surface. [26, 28]

3.1 Tribological applications

From the point of view of tribological applications, wear resistance and lubrication of DLC coatings are crucial. As DLC coatings can be divided into "soft" and "hard" coatings, they perform differently in different applications. "Soft" coatings can include soft metals or graphite and can therefor act as a solid lubricant and have low friction coefficient. "Hard" coatings are composed of hard ceramics (carbides, nitrides etc.) and they offer increased durability and good protection against wear. The threshold value of hardness for "soft" and "hard" coatings is around 10 GPa which is in line with hardness value of widely used structural metals. Also, threshold value for friction, 0.3 between solid lubricant and wear-resistant coatings, is roughly the same value than most metals. [17]

Most of the engine component are manufactured from metal. DLC is suitable coating material for coating metal because DLC has higher hardness and Young's modulus than most metals. This makes DLC coating a useful protective layer for substrate.

For the long service life of the applications, the strong adhesion of the coating to the substrate is important. To enhance this adhesion, interlayers are deposited on the substrate prior the actual coating. In addition to adhesion, the interlayer also distributes the loads more evenly to the substrate. The most common interlayers are made with chromium, but tungsten (W), titanium nitride (TiN) and chromium nitride (CrN) are also used. [1]

Most commercially available DLC coatings have difficulty what it comes to compressive residual stresses and the adhesion failures induced by that. Multilayer structures of other coating types have proven to have beneficial impact on reducing residual stress, so a study was conducted to study this effect also on DLC. In the study conducted by Lin et al. [29], it was found that multilayer DLC coating consisting of both soft and hard layers improves wear resistance at high contact stresses. The M2 steel was first coated with chromium metal layer and after that with a Cr/C transition layer to enhance adhesion. The soft and hard layers of DLC, each of them 30 nm thick, were then deposited with magnetron sputtering technique on top of transition layer, resulting a coating of total thickness of 600 nm. Total of five different consistencies of DLC were tested: soft, hard and then coatings with 30 %, 50 % and 70 % of hard layers. The coatings were tested in dry sliding conditions on ball-on-disc tribometer with counterpart of WC-6 % Co ball. The hardness of the hard layer was 36 GPa and hardness of the soft layer was 14 GPa. The multilayered and hard coatings showed improved wear resistance with soft-top layer when tested with 20 N load. The study showed that adding 50 nm soft-layer on top, the wear volume of the run-in period of the test decreased 70 %. For example, when loaded with 40 N, the hard coating without soft layer could not stand the load and fractured after seconds, but when the soft-top layer is added to the hard coating, it sustains the load and on top of that it shows the lowest wear volume. This can also be seen in the friction coefficient - without a soft-top layer the friction stays longer high, between 0.5 and 0.15 before reaching steady-state of 0.1. This can be noted in the Figure 5a. Correspondingly, the lower wear

rate and the lower friction coefficient during run-in period can be seen in the Figure 5b, when the soft-top layer is added.
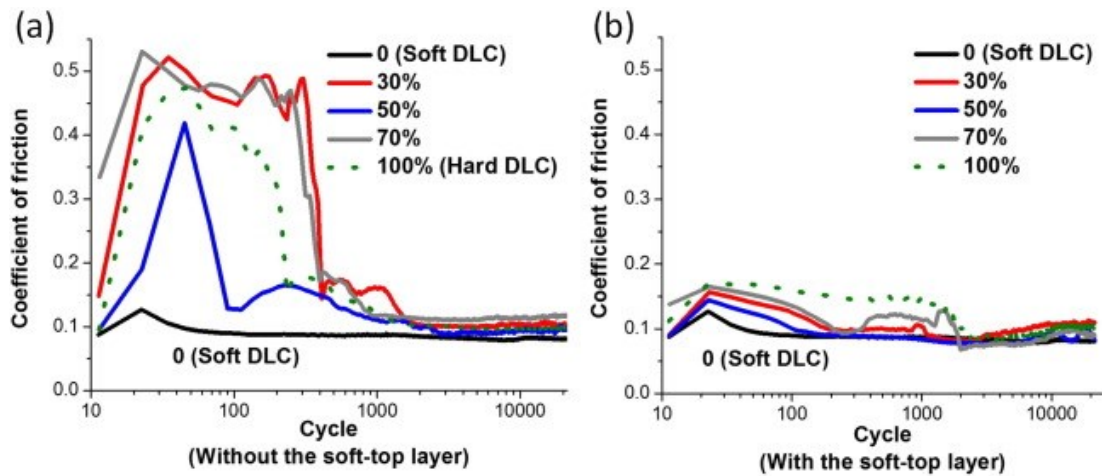

Figure 5. *Friction coefficient and wear cycles a) without the added soft-top layer and b) with the additional soft-top layer in the tribotest when the load is 20 N (2.5 GPa) [29].*

The best wear result at extreme stress of 80 N (4 GPa) was achieved with multilayered coating consisting of 50 % hard layers because of its low residual stress and its relative high hardness values. The extreme stress on 80 N led the hard coating and 30 % hard multilayered coating with soft top fail during test, before reaching 10 677 cycles and at the same stress level the hard coating without soft layer was worn out directly. This shows how versatile combinations multilayering different coatings can produce. [29]

3.1.1 Gear wheels

The high pressure and desire to minimize dimensions of the gears can lead to change in lubricating conditions. When the conditions change from full film lubrication to boundary lubrication, severe adhesive wear and pitting can occur. The wear rate can be reduced by depositing low friction coating that decreases the risk of adhesive wear. In the case of full lubrication, Gåhling et al. [30] state that the low friction coating has only minimal effect.

Xiao et al. compared three different coating types for heavy-duty and high speed gears and analyzed the wear mechanism. The coatings were TiN, WC/C and DLC (a-C) and the substrate was AISI 52100 steel. The study was performed with four-ball test method under lubricated sliding conditions. The study found no significant difference in friction coefficients of the coated and uncoated balls. At the stable state the friction varied between 0.067 (DLC) and 0.085 (TiN). The oil film in the test system may have prevented mechanical contact between balls. [31]

The wear behavior of the coatings was also observed in this study. The TiN coating experienced clear wear scars caused by oxidation and peeling wear. Oxidation wear and

small craters were also seen in WC/C coating. During high contact pressure (5.40 GPa) test, deposition defect micro-holes connected into larger flake-like particles which led to oxidation pitting. What it comes to DLC coating, it remained unharmed after the test, although small craters, transfer layers and patched peeling were detected. In conclusion, they found that WC/C and DLC coatings had excellent performance under thermal load and high contact pressure and these qualities improved with decreasing lubrication. Therefore, these coatings are adequate for demanding gear applications. [31]

DLC coating is also tested against pitting. In the study carried out by Fujii et al., a tungsten carbide doped DLC (WC/C) coating was tested in a spur gear test under lubricated conditions. Three gears were tested, an uncoated one and two WC/C coated, one of which was conventional WC/C coating and the other one had a 1 μm CrN interlayer. The gear matrix was carburized and quenched chromium molybdenum steel (JIS SCM415). Under maximum Hertzian stress of 1700 MPa, the conventional WC/C coating has longer fatigue life than uncoated gear. When stress is increased to 1900 MPa, their fatigue lives are similar, due the peeling of the coating. Peeling occurred also for interlayered coating, which led to shorter or equal fatigue life with uncoated gear. Peeling occurred mainly on lower part of the tooth, the dedendum flank. After the peeling of the coating, wear penetrated to matrix and pitting occurred on the tooth flank, leading to the decrease in surface durability. [32]

Both tungsten doped (WC/C) and the a-C coating perform well under high pressure. These studies also show that if the WC/C coating remains undamaged, it can offer longer lifetime against wear for gear than uncoated version. The interlayer between the steel and coating did not offer significant advantage over peeling. Once the peeling of the coating occurs, the wear rate is similar than uncoated gear. [32]

Additionally, boron carbide (B_4C) and molybdenum disulfide (MoS_2) have been used for coating gears [28]. In a study conducted by Ylimaz et al., a MoS_2 coating and DLC (ta-C) coating on case-carburized 16MnCr5 steel were tested in dry lubrication conditions for gear applications. The surface coatings have possibility of improving wear resistance in tribological contacts. The results of this study show that coating does improve wear resistance compared to uncoated sample with dry lubrication, but the wear rate was still higher than in lubricated conditions. The lifetime of MoS_2 was longer than of ta-C coated surface. Also, the friction coefficient was slightly lower for MoS_2 (0.100) than for ta-C (0.153). When coatings were tested with mineral oil with EP additive, the friction coefficient is distinctly lower than in dry lubricated conditions, even with tribological coatings. This study concludes that coatings increase tribological performance under dry lubrication, however the operation in dry conditions without coating is not reliable. Adding a small amount of oil can be enough for lubrication of moderately- to high-loaded gearboxes but the heat management remains a problem for the system. [33]

The loss of lubrication in normally lubricated systems can have severe impact on the wear of the surface. Murakawa et al. executed a gear performance test in loss-of-lubrication conditions after the test machine had experienced brief full lubrication. A case hardened, carburized steel (JIS G4105 SCM415) gears were grinded and some of them micro shot peened (MSP) after the grinding. The shot peening was performed to eliminate possible problems caused by the grinding trace and to increase the adhesion of the coating. The DLC coating that was used consisted multilayered structure of alternating layers of WC and hydrogenated amorphous carbon (ME-C:H). Four types of gears were prepared for the test: an uncoated ground gear, WC/C coated gears, gears with MSP pretreatment and finally gears with both the MSP pretreatment and WC/C coating. [34]

The tested gear pair was first submerged into the oil lubricant and run for full load for 60 seconds before the lubricant was drained out of the gearbox so that the loss-of-lubrication condition was achieved. The gears were checked every 30 minutes of operation for their condition. If the noise level exceeded 90 dB, vibration level reached 3 G, or the gear face showed notable wear scar or scuffing, the gear's lifetime was considered to have ended. Otherwise, the test was continued until 10^7 integrated revolutions were reached. The test showed that WC/C coated gears lasted two to three times longer than the uncoated gears. The MSP pretreatment had no significant difference in the lifetime of the uncoated gears. [34]

The MSP pretreatment alone cannot prolong the lifetime but combined with the WC/C coating, a significant increase in the lifetime was observed. The gear pair that was micro shot peened and then coated with DLC endured severe loading condition and reached the fatigue limit of 10^7 cycles, whereas only WC/C coated gear did not last that long. In other words, WC/C coating is better option for loss-of-lubrication conditions than uncoated gear, but MSP pretreatment enhances the lifetime even further. [34]

3.1.2 Journal bearings

In sliding contact bearing, known as journal or plain bearing, the sliding takes place between fixed and moving element of the bearing. The clearance between those two parts is usually filled with lubricant. For hydrodynamic bearings, seen in the Figure 6, fluid, liquid or gas lubricants without any external pressure create the separation of the sliding surfaces. The pressure that is required to support the journal inside the bearing is induced by wedging action.
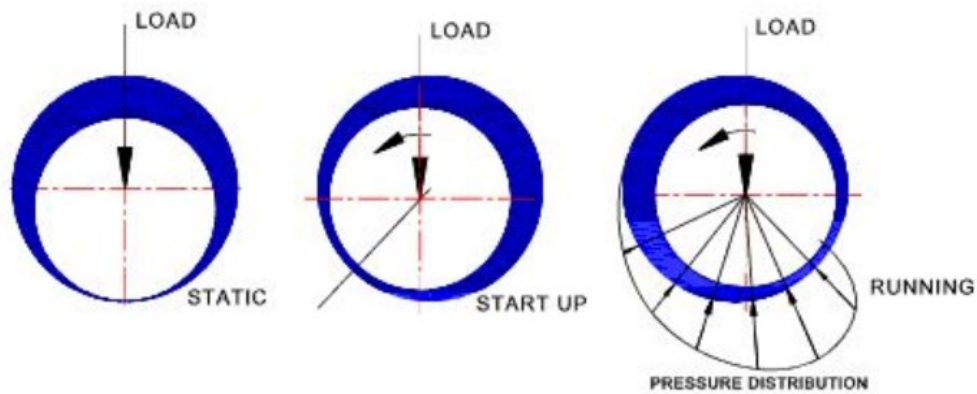
Figure 6. Hydrodynamic lubrication of the journal bearing [38].

At the start, the shaft is statically laying on the bearing and for uncoated parts, metal-metal contact is present. When the shaft starts to move from the rest, the boundary lubrication becomes relevant. The boundary lubrication is typical when full fluid condition cannot be achieved, usually at the beginning and at the end of the sliding, at low speeds, or at high loads. [38]

Journal bearings experience boundary lubrication regime during startup and shutdown. This metal-metal contact is possible due to slow rotational speed that prevents sufficient oil film formation. During these startup and shutdown periods the bearing is most likely to be damaged [35]. This type of damage can be postponed by using hard DLC coating. The DLC shows little beneficial affects during fully oil lubricated tribological contacts but during mixed and boundary lubrication DLC and WC/C multilayer DLC coatings can reduce friction considerably. [22]

Boundary lubricated friction and wear test were performed on a multilayer WC-doped hydrogenated DLC coating against hardened ball-bearing steel (AISI 52100). Coating thickness was about 2 μm, hardness of the coating was 1200 HV, whereas hardness of the steel was 850 HV. Steel ball bearing was 10 mm of diameter and the maximum Hertzian pressure was in the range of 1.0–3.0 GPa. It was noted that coating material was transformed from the W-DLC coating to the uncoated steel ball when reciprocating sliding was tested in pure PAO or PAO with low extra-pressure (EP) and anti-wear (AW) additive concentrations. A WC-type of transfer-layer was formed to steel counterface and no reaction products were found in W-DLC coating. This transfer-layer causes the friction coefficient to be lower compared to steel/steel contact. Sulfur-based EP additives reacts with the transferred tungsten and they form WS_2-containing tribofilms and enabling low friction behavior. Lowest friction coefficient of about 0.1 was obtained with EP concentrations of 2.5 % and 5 %, which also gave smoothest sliding from the beginning until 6×10^6 cycles. Reduction and increase of the EP additive concentration, increased friction coefficient and had more unstable friction behavior. [39]

Hydrogen-free ta-C shows improved wear resistance and low friction performance compared to a-C:H due to higher hardness and better tribofilm formation in lubricated conditions [40]. On the other hand, the high hardness and the improved wear resistance of the ta-C films is complicated phenomenon. As the coating itself shows low wear, the counterpart has higher wear rate in comparison to a-C:H. This might indicate that steel counterpart could wear prematurely when in contact with ta-C. Hauert states that ta-C coatings are mainly used in applications that do not have same surfaces continuously sliding with each other, as the tribofilm would not occur in these circumstances [22].

Some results also show promising effect when soft and lubricating DLC coating is used to protect component from micropitting. A study tested four different coating pairs to evaluate tribological performance in mixed sliding and rolling conditions usual for bearings in wind turbine drive train. The coating was soft, highly hydrogenated DLC film. The test was performed in a micropitting rig (MPR) which was lubricated with PAO base oil, with normal load of 430 N and maximum Hertzian contact pressure of 1.79 GPa. For the test rig, rollers and rings were prepared from AISI 52100 steel. The parts were deposited with 50 nm thick chromium interlayer and 1μm thick DLC film. The tested pairs were uncoated/uncoated pair, DLC roller with uncoated rings, uncoated roller with DLC rings and both the roller and the rings coated with DLC. The study discovered that the uncoated steel/steel pair failed after 32 million cycles while the tests that had at least one surface coated with DLC lasted for 100 million cycles without serious failures. [23]

When sliding against steel in ambient conditions, the a-C:H coating has an ability to form transfer layer on the metal surface that protects the metal from further wear. When hard ta-C is sliding on metal, the formation of the transfer layer is delayed. If the transfer layer is not an important issue, ta-C film can show lower wear of the coating than a-C:H film. Hauert states that in full oil film lubricated conditions, DLC coatings do not show beneficial influence. Nevertheless, when the lubrication conditions change to mixed and boundary lubrication, DLC and tungsten containing DLC can reduce friction significantly. [22]

Amorphous hydrogenated carbon film (a-C:H), similar film with titanium surface layer (a-C:H(Ti)) and non-hydrogenated a-C film were tested in dry and oil lubricated conditions. The purpose was to study the effect of tribological performance of DLC coating in boundary lubricated conditions. To improve the adhesion of the coating to the substrate, a TiC intermediate layer was deposited on the substrate. For the a-C films, thin Ti intermediate layers was deposited to improve adhesion. The test was carried out with reciprocating pin-on-disc test where polished, AISI 52100 steel ball with 10 mm diameter was used as a pin. The normal load was 10 N. The oils used in the test were low viscosity mineral based oil without additives, other than oxidation inhibitor (Oil 1) and mineral based oil with higher viscosity and limited EP-additive concentration (Oil 2). [36]

In the Figure 7 can be seen that all the coatings showed low friction coefficient in dry conditions compared to uncoated disc. With the a-C and a-C:H coatings, the mineral oil lubrication decreased the friction slightly. The lowest friction value (0.08) with the mineral oil with EP additive oil was reached with the a-C. This suggest that hydrogen-free coating can benefit from EP additives. For the a-C:H(Ti), the lowest values were reached in dry conditions and the friction increased slightly with the addition of the oils. [36]
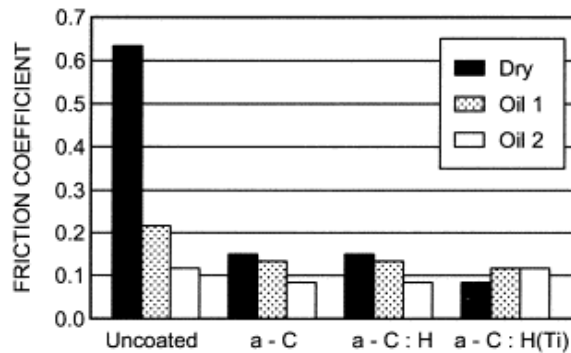

Figure 7. *The coefficient of friction at steady-state for different DLC coatings at the end of the sliding test [36].*

To demonstrate the wear rate of the coatings, un uncoated steel disc was tested for comparison. In the Figure 8 can be seen that the steel pin suffers from intensive wear in dry sliding condition against uncoated steel disc. In dry sliding conditions, the wear rate of the a-C film was very low, in the range of 0.05×10^{-6} mm^3/Nm and in both lubricated condition no wear was detected. On the other hand, the steel pin suffered from relatively high wear rates in unlubricated and mineral oil (Oil 1) lubricated conditions, but with EP additive oil (Oil 2) the wear was reduced. [36]

The wear rate of the disc with the a-C:H was higher, in the range of 0.41×10^{-6} mm^3/Nm in dry conditions. With the mineral base oil (Oil 1) only minimal wear, in the range of 0.07×10^{-6} mm^3/Nm, was detected but the steel pin suffered intensive wear. No wear of the coating and only a little wear of the pin occurred during mineral oil with EP additives (Oil 2). The a-C:H(Ti) coating showed decreasing wear behavior with oil lubrication. The wear of the pin remained at low rate in all conditions. [36]
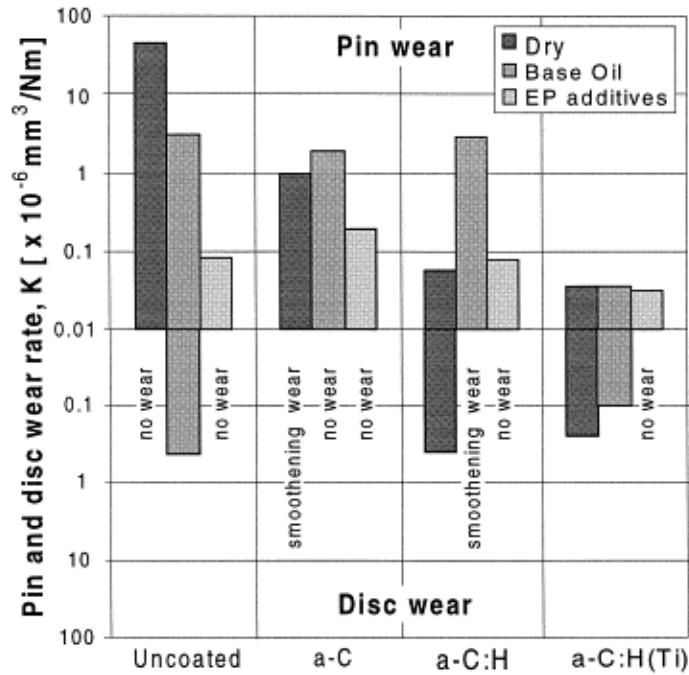
Figure 8. *The wear rates of the steel pin and the uncoated and DLC coated discs under normal force of 10 N in dry and oil lubricated conditions [36].*

Typically, a protecting tribolayer forms on the pin surface in dry sliding with the a-C and a-C:H coatings. With oil lubrication, the beneficial tribolayer did not form. This is seen in lower friction coefficient of a-C:H(Ti) in dry conditions compared to uncoated disc in oil lubrication. Also, the wear rate of the pin was higher in lubricated test conditions (Oil 1). The EP additives in Oil 2 decreased pin wear in all the coatings because chemical reactions formed a boundary lubrication film. Both coefficient of friction and wear of the counterface are affected by the oil lubrication so the additive content and the lubricant type needs to be considered. [36]

When the DLC coatings is in contact with the same coating instead of steel surface, the tribological behavior changes. Tasdemir et al. studied the tribological behavior of self-mated DLC/DLC contact under boundary lubrication in synthetic oil. The coatings were ta-C, a-C:H, silicon doped a-C:H(Si) and chromium doped a-C:H(Cr). Each of them was deposited on SUJ2 bearing steel disc (22.5 mm diameter) and pin (cylindrical, 5 mm diameter). The test load was 5 N, corresponding to 150 MPa Hertzian contact pressure and the test lasted for 1 hour and 10700 cycles. A synthetic polyalpha-olefin (PAO4) base oil was used and the test disc/pin system was fully immersed. [37]

The friction coefficients of the self-mated DLC contacts as a function of sliding cycles are seen in the Figure 9. The running-in time was the longest for ta-C but when the friction reached steady-state, the coefficient was the lowest, in the range of 0.025. The highest friction coefficient was shown for a-C:H(Si), reaching the steady-state at 0.1. The friction values for a-C:H and a-C:H(Cr) were around 0.06. [37]
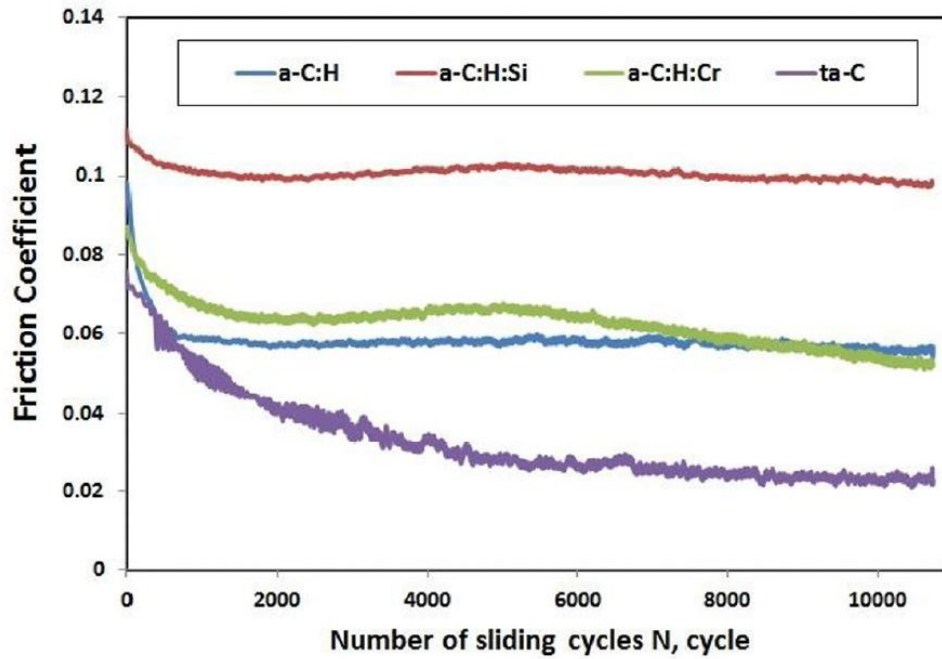
Figure 9. *Coefficient of friction for self-mated DLC coatings in synthetic oil lubrication [37].*

The wear of the DLC coated discs was so minimal that the wear scars were hardly noticeable. For that reason, the wear rates are only presented for the pins. In the Figure 10 the wear rates of the coated pins are presented. The a-C:H coating experienced the highest wear. The second highest wear was detected for ta-C, despite its lowest friction coefficient. The chromium-doped a-C:H(Cr) film showed lowest wear, although the coefficient of friction was similar with a-C:H film. Silicon-doped a-C:H(Si) resulted in better wear resistance than a-C:H, while the friction coefficient was the highest. [37]
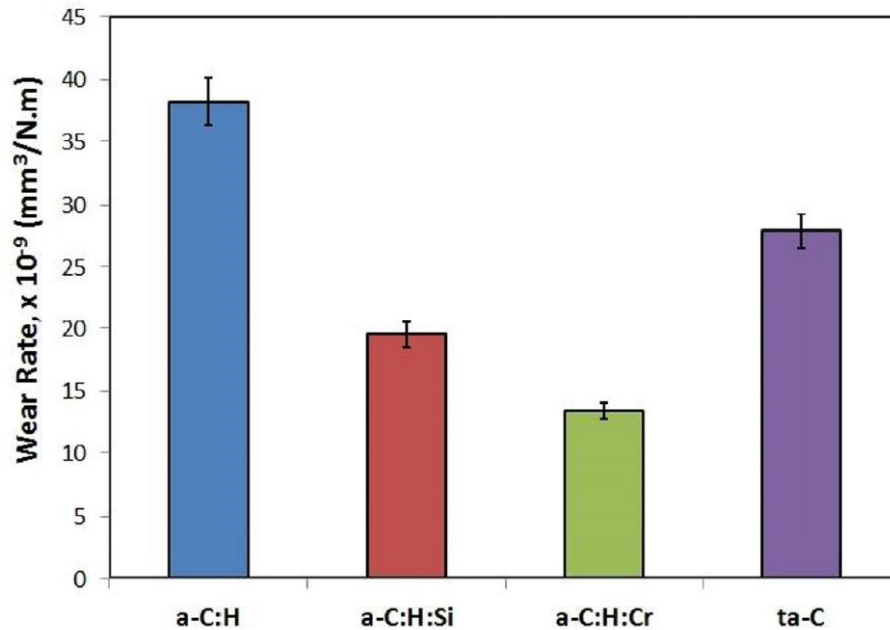
Figure 10. *Wear rate of the self-mated DLC coated pins after base oil lubricated test [37].*

These results show that the dopant elements strongly influence the tribological properties of the DLC coating in oil lubricated conditions. This study considers that the graphitization can be linked to the reduced friction of the a-C:H coating, but for other DLC coatings, hydrogen content, sp^3 hybridization and deposition methods could have stronger influence. [37]

A a-C:H film with 40 % hydrogen content was tested against AISI 52100 hemispherical bearing steel pin in a UHV conditions. It was noted that when a normal load of 3 N was applied to 8 mm radius of pin, it induced 550 MPa Hertzian contact pressure. The friction coefficient for sliding speed of 0.5 mm/s is about 2.7 x10^{-3}. However, the exact value is very difficult to measure due to extremely low friction force. [17]

3.2 Alternative coatings for tribological applications

For sliding applications soft coating such as manganese phosphate, copper and silver can be used as a sacrificial layer. They offer protection against micropitting and scuffing during start-up period. Instead of DLC in high-wear applications, boron carbide can protect from wear and scuffing. [28] High hardness leads to indirect lubrication as the coefficient of friction can be higher, but the coating still prevents seizure and protects from wear. Some examples include oxides, nitrides and borides.

Titanium nitride (TiN) is hard coating type that can be produced as thin film. TiN has high hardness, wear and corrosion resistance and chemical inertness [41]. It forms a dense, typically 3 μm thick coating that can be deposited with PVD. TiN can be doped

with metals to enhance the properties. For example, titanium carbo-nitride (TiCN) and titanium aluminum nitride (TiAlN) can be used. TiAlN has high temperature tolerance, around 800 °C whereas TiN tolerates 500 °C. [42, 43]

Boron nitride (BN) has two crystalline forms, a cubic and a hexagonal form. In a cubic form boron nitride is second hardest material after diamond and is used as a grinding media or a coating for metal-cutting tools. Hexagonal boron nitride on the other hand is soft and used a solid lubricant or lubricating additive. The lamellar structure enables co-efficient of friction in air to be around 0.2–0.3. Boron nitride is also corrosion resistive and it can be used in high temperatures up to 1000 °C before oxidative degradation. Boron nitride has been used as a dispersive additive in oils. These powder particles reduce wear of bearing steels even in small quantities when steels slide against each other. [44]

Boron carbide (B_4C) is used as a tribological coating due to its very high hardness, low density and high melting point. B_4C can be deposited with either PVD or CVD. Boron carbide can reduce adhesive wear, add lubricity and heat resistance of the component. Coefficient of friction for industrial scale boron carbide is less than 0.4 and hardness reaches 4500 HV. Typical coating thickness is typically 1–3 μm. Boron carbide coating has shown signs of polishing bearing and gear steel surfaces without severe wear. [45, 46] Boron carbide reduces wear when sliding against steel surface in oil lubricated conditions [47].

Molybdenum disulfate (MoS_2) is widely used as a solid lubricant in tribological applications. It has a crystalline lamellar structure, similar to graphite. The friction reduction properties originate from weak van der Waals forces between the sheets. The molybdenum atoms are strongly bonded to sulfur atoms within the sheet but the interactions between the planes are weak. This enables easy sliding of the planes. MoS_2 has also good load carrying capacity perpendicular to sliding direction due to compressive strength of the film. The low friction coefficient and good wear properties remain also in high-temperature and vacuum conditions. [42, 48]

4. COATING SUPPLIERS

4.1 DIARC Technology Oy

DIARC Technology Oy is Finnish surface engineering company that specializes in thin film coatings which improve durability and performance of tools and components. DIARC was founded in 1993 and is located in Espoo, Finland. All of their coatings are deposited below 100 °C by filtered cathodic arc plasma accelerator deposition (FCAPAD). In February 2018 DIARC was acquired by Oerlikon Balzers, one of the leading companies of surface technologies in the world. [49]

The coating types of DIARC include ta-C DLC film, dense metal nitride and oxide coatings and functional surfaces made of carbon and metal nanocomposite films. For bearings and gears, the most interesting coatings seems to be low friction ta-C DLC coatings DIARC Miclub and Dialub. Miclub is design to perform in boundary lubricated conditions, to reduce friction and to improve functionality of the lubricants. Dialub reduces wear and friction in high temperatures and is suitable for conditions with limited lubrication. Both coatings have hardness values between 4000–5500 HV and their maximum service temperature is 500–550 °C. [50]

4.2 IHI Ionbond AG

IHI Ionbond AG offers coating equipment and low friction, wear protective thin film coatings deposited by PVD, CVD or PACVD methods. The coatings are used to improve functionality, durability and efficiency of the components and tools. Ionbond has operation centers in 17 countries in Europe, Asia and North America and over 1100 employees worldwide. [51]

Ionbond has a wide coating portfolio serving various industrial fields, including cutting, forming and molding tools, medical and decorative field and components for aerospace, power generation, transportation and oil and gas production. As an example of mechanical component coatings, the Tribobond series consists of chromium doped hydrogenated and non-hydrogenated DLC (Cr + a-C:H, Cr + a-C, Cr + ta-C) coatings, chromium nitride (CrN) coatings and titanium nitride (TiN) coatings. The friction coefficient for DLC coatings against steel is generally 0.1 and the micro hardness varies between 1000 – 4000 HV, depending on the coating type. [52]

4.3 Teer Coatings Ltd.

Teer Coatings Ltd. produces PVD coatings and coating machines and it is part of Miba Coating Group. Teer Coatings offer low friction, solid lubricant coatings, such as

MoS_2/metal coating and DLC films, as well as hard, wear resistant coatings including TiN, CrN and CrAlTiN coatings.[53]

The DLC coatings are named Graphit-iC coating and Dymon-iC coating. Both experience low wear rate and fiction coefficient. Graphit-iC is non-hydrogenated carbon-chromium multilayer DLC coating (a-C) deposited at 300 °C to thickness of 2-4 μm. The typical coefficient of friction for it is 0.08 and hardness is 1500 HV. Dymon-iC is hydrogenated DLC (a-C:H) deposited at 250 °C to thickness of 2-4 μm. Its coefficient of friction is 0.15 and hardness 1600 HV. [54, 55] Both of them were tested in oil lubricated condition by Stallard and Teer. In oil environment and sliding motion, the coefficient of friction was 0.1 for Dymon-iC and Graphit-iC, and both reduced wear of the counterface compared to CrN coating. [56]

5. CONCLUSIONS

DLC coatings offer great options for friction reduction and improved wear resistance. The hard and self-lubricating surface of DLC has found applications in multiple industrial fields. For gear applications, the wear behavior of the coating may be a more important factor than low friction coefficient when the gear is operating mostly under lubricated conditions. For journal bearings, fluctuating running conditions can benefit from self-lubricating properties of the DLC. This shows the wide range of applications that can benefit from DLC coatings.

The researches presented in this thesis are mostly performed in dry sliding conditions and in laboratory scale. Some studies are carried out in oil lubricated conditions and although they appear to have promising results for wear and friction reduction, the tribological performance is a complex phenomenon. Because the tribological performance of the DLC depends on various factors, including load, motion type, counterface material and lubricant composition, the test parameters play important role in the research result.

The application conditions determine the most suited DLC type. Softer DLC have only minimal effect in wear reduction if the contact surfaces are fully lubricated. On the other hand, the hard a-C type DLC performs well in lubricated, high contact pressure conditions, reducing wear significantly. Multilayering the a-C:H coating with tungsten carbide also increases wear lifetime up to three times longer than uncoated surface in loss-of-lubrication conditions. The hard DLC coatings, such as a-C and ta-C, experience low wear rate of the coating but can increase the wear of uncoated counterpart. Both the a-C:H and the ta-C coatings in self-mated sliding contacts have low coefficient of friction and wear rate in lubricated conditions, so coating both surfaces should be considered to protect gearbox components.

As the traditional lubricants are optimized for steel surfaces, the reactions between the lubricant and the DLC coating can differ. For further study, the influence of the commercial lubricants to wear and friction behavior of the specific DLC coated component should be studied. This is especially important when designing DLC coatings for commercial use. Specified tests are recommended to ensure optimal functionality in operating conditions. An interesting topic is the compatibility with the oil additives and the self-mated DLC coatings. For example, in boundary lubricated conditions the ta-C or chromium doped a-C:H have performed well in a previous study. The future tests could confirm the suitability of these coatings with the substrate material, additives, load conditions etc. In a conclusion, the DLC coatings are versatile and improve lifetime and reliability of tribological applications.

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